

Advances on Transition Metal Oxides Catalysts for Formaldehyde Oxidation: A

Review

Abubakar Yusuf ^{a, b}, Colin Snape ^c, Jun He ^{a, b *}, Honghui Xu ^d, Chaojie Liu ^{a, e}, Ming Zhao ^{f *}, George Zheng Chen ^{a, c, e}, Bencan Tang ^a, Chengjun Wang ^g, Jiawei Wang ^h, Sailesh N. Behera ⁱ

^a *Research Group of Natural Resources and Environment, Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo, PR China*

^b *International Doctoral Innovation Centre, The University of Nottingham Ningbo China, Ningbo, PR China*

^c *Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

^d *Zhejiang Meteorological Science Institute, Hangzhou, PR China*

^e *Centre for Sustainable Energy Technologies, Faculty of Science and Engineering, The University of Nottingham Ningbo China*

^f *School of Environment, Tsinghua University, Beijing 100084, China*

^g *College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, PR China*

^h *Aston Institute of Materials Research, Aston University, Birmingham, B4 7ET, UK*

ⁱ *Department of Civil Engineering, Shiv Nadar University, Greater Noida, U.P., India*

Correspondence:

Dr Jun He, email: jun.he@nottingham.edu.cn;

Dr Ming Zhao, email: ming.zhao@tsinghua.edu.cn

1 **Abstract**

2 This review highlights recent advances in the development of transition metal based catalysts for
3 formaldehyde oxidation, particularly the enhancement of their catalytic activity for low
4 temperature oxidation. Various factors that enhance low temperature activity are reviewed, such
5 as morphology and tunnel structures, synthesis methods, specific surface area, amount and type of
6 active surface oxygen species, oxidation state and density of active sites are discussed. In addition,
7 catalyst immobilization for practical air purification, reaction mechanism of formaldehyde
8 oxidation and the reaction parameters affecting the overall efficiency of the reaction are also
9 reviewed.

10 **Keywords:** formaldehyde, transition metal oxides, catalysts, oxidation

11 **1. Introduction**

12 Formaldehyde (HCHO) is one of the main sources of hazardous indoor air pollution. Furniture and
13 building materials such as composite wood, particle board, vinyl coverings and adhesives are some
14 of the major indoor sources of HCHO emissions (1,2). A comprehensive review of both the indoor
15 and outdoor sources of HCHO and its concentrations in various indoor environments can be found
16 in the work of Salthammer et al. (3). Exposure to HCHO may cause adverse health effects on
17 humans such as irritation to eyes, nose and throat, headache, fatigue, edema, severe allergic
18 reaction and dermatitis (4,5). In 2006, the International Agency for Research on Cancer (IARC)
19 under the World Health Organization (WHO) classified HCHO as a carcinogen to humans. There
20 are sufficient evidences to ascertain that it causes nasopharyngeal cancer and there are also strong
21 indications that it may also cause sinonasal cancer and leukemia over long term exposure (6). As
22 such there are various international guidelines and recommended thresholds for indoor air HCHO
23 concentrations, a summary of which can be found in the review of Salthammer et al. (3). The WHO
24 proposes a short term HCHO exposure limit (30 minutes) of 0.1 mg/m^3 for the avoidance of
25 sensory irritation and a long term exposure limit of 0.2 mg/m^3 for protection against long term
26 health effects (7). Thus, the effective removal of HCHO from indoor air is imperative to improving
27 indoor air quality and safeguarding human health.

28 Various techniques for HCHO removal have been investigated and reported in the literature,
29 including adsorption (8-12), photo-catalytic oxidation (13-17) and catalytic oxidation (thermal and
30 non-thermal). The effectiveness of physical adsorption of HCHO on adsorbents such as activated
31 carbon (AC) is constrained by the material's maximum adsorption capacity, relative humidity
32 (RH) or moisture deactivation and also by the environmental risk when desorption occurs during
33 regeneration (18,19). Photo-catalytic oxidation using ultraviolet light on the other hand may lead

34 to the generation of toxic by-products (20). Catalytic oxidation is able to achieve complete
35 conversion of HCHO to H₂O and CO₂ without the formation of harmful by-products or secondary
36 pollutants (21). This could even be achieved at room temperature especially with noble metal
37 catalysts (22-26), thus making it the most promising HCHO removal technique (18).

38 Noble metal-based catalysts: Pt, Au, Pd, Rh, Ru and Ag supported on conventional materials such
39 as TiO₂, SiO₂, Al₂O₃ and zeolites (27-35); single transition metals (36-47) and transition metal-
40 based composites (48-51) exhibit excellent HCHO oxidation activities at temperatures lower than
41 100°C and even at room temperature. Comprehensive reviews on noble metal catalysts for HCHO
42 oxidation have been conducted (4, 25), whilst here a summary of some of the noble metal catalysts
43 and their reaction conditions are presented in Table 1. However, the industrial applications of noble
44 metal catalysts are restricted by their high costs, limited resources and poor thermal stabilities (53).
45 Hence recent research efforts have been focused on the development of relatively cheap materials
46 for low temperature HCHO catalytic oxidation (54-56). More abundant and cost effective metal
47 oxides especially those of the transition metals, including single transition metals and transition
48 metal based composites are shown to be active for HCHO oxidation. However their relatively low
49 activity compared to noble metals catalysts has motivated effort for further improvement.
50 Therefore, the development of highly active and cost effective catalysts for HCHO oxidation is
51 still a major challenge for practical application.

52 A number of review papers have been published on HCHO removal. Pei and Zhang (52) reviewed
53 chemisorption method and catalytic oxidation of HCHO majorly on noble metal catalysts. The
54 photo-catalytic oxidation of HCHO using TiO₂ as a photo-catalyst both in aqueous and gaseous
55 mediums and the effects of different light sources and photoreactors have also been reviewed in a
56 short article (57). More recently, Bai et al. (4) reviewed the catalysts for HCHO oxidation with a

57 major focus on the factors affecting the activity of noble metal catalysts. From the literature review,
58 it can be seen that significant progress has been made on improving the activity of transition metal
59 based catalysts and their immobilization for practical application since 2000. However, to the best
60 of our knowledge, the development of transition metal based catalysts for HCHO degradation has
61 not been reviewed in any detail so far. Therefore, we consider this review fills a key gap for this
62 active area of heterogeneous catalysis.

63 This review focuses exclusively and extensively on recent developments over the past one and half
64 decade towards enhancing the activity of transition metal catalysts for low temperature HCHO
65 oxidation, considering their cost reduction potential, activity and stability. Various factors that
66 enhance their catalytic activities are discussed, including preparation methods, morphology and
67 structure, specific surface area, concentration of surface active oxygen species, oxygen mobility
68 and metal active sites. The influence of reaction parameters such as relative humidity, HCHO
69 concentration and space velocity are also reviewed. The reaction mechanisms of HCHO oxidation
70 on transition metal oxides and their immobilization on suitable substrate materials for application
71 in air purification are also elaborated and finally areas for further investigations to achieve higher
72 activities at low temperatures are proposed.

73 **2. Transition metal based catalysts and their performances**

74 As mentioned earlier, recent research efforts have been focused on the utilization and efficiency
75 improvement of transition metal based catalysts for low temperature oxidation of HCHO.
76 Transition metal oxides are relatively cheap, abundant and have also been presented to be active
77 for HCHO oxidation at low temperatures (21,67,68). Different terminologies such as HCHO
78 removal, conversion, degradation and elimination are used in the literature to refer to the efficiency
79 of HCHO oxidation. Hereinafter, efficiency of HCHO oxidation is referred to as conversion where

80 oxidation efficiency was reported as a function of CO₂ generation/concentration in the effluent
81 stream and as removal where efficiency was reported based on residual HCHO concentration in
82 the effluent gas stream (see footnotes of Table 1&2).

83 Some conventional transition metal-based catalysts have been reported to show good catalytic
84 activities for HCHO oxidation. Sekine (2) first demonstrated the catalytic oxidation of HCHO over
85 metal oxide catalysts. Of the investigated catalysts: CoO, MnO₂, TiO₂, CeO₂ and Mn₃O₄, MnO₂
86 was described to exhibit the highest catalytic activity. Metal oxides in the conventional bulk form
87 possess low catalytic activity for HCHO oxidation owing to inferior surface properties (69). On
88 the contrary, specially synthesized nanostructured transition metal catalysts of similar
89 compositions to their bulk counterparts exhibit improved morphologies and surface properties and
90 hence higher activities for HCHO oxidation (21,70). As such, current investigations on transition
91 metal-based catalysts are focused on improving and developing materials with enhanced
92 morphologies and structures. The structure of these catalysts and their morphologies improve their
93 activity through the improvement of parameters (discussed in Section 4) such as specific surface
94 area, high surface reducibility, porosity, active surface species, active lattice and surface
95 adsorbed oxygen species and tunnel size and structure (54,55). Transition metal-based catalysts
96 for HCHO oxidation found in the literature could basically be classified as single/mono-metal and
97 composite metal oxides. A summary of both group of catalysts and their activities and conditions
98 of reaction are respectively presented in Table 2 and 3.

99 2.1 Single transition metal based catalysts

100 2.1.1 Manganese oxide based catalysts

101 Manganese oxide is the most widely explored transition metal catalyst for HCHO oxidation owing
102 to its high catalytic activity, thermal stability, existence in various crystal morphologies such as α -

103 , β -, γ - and δ - MnO_x (71) and several tunnel assemblies (1D tunnels, layered structures such as
104 birnessite and buserite and 3D spinel tunnel structures) (72). Chen et al. (55) studied the
105 influence of tunnel structures of various manganese oxide catalysts (pyrolusite, cryptomelane and
106 todorokite) on HCHO oxidation. Cryptomelane displayed the highest activity with 100% HCHO
107 conversion at 140°C, 400 ppm HCHO concentration, and a space velocity of 18,000 mL/g·h, while
108 20 and 40% conversions were attained by pyrolusite and todorokite, respectively, under similar
109 reaction conditions. Tunnel size and structure were shown to be the determinant factors affecting
110 activity other than factors such as specific surface area, degree of crystallinity, surface reducibility
111 and average oxidation states of the catalysts. Similarly, Zhang et al. (19) attributed the high HCHO
112 catalytic activity of δ - MnO_2 to its interlayer and tunnel structures which help in expediting
113 adsorption and diffusion to and from the catalyst's active sites. These results indicate that activity
114 is closely related to morphological and structural properties of the catalyst.

115 Tian et al. (54) investigated the impact of synthesis temperature on birnessite type manganese
116 oxide catalysts. A general trend of catalytic activity rise was observed with increasing synthesis
117 temperature from 80 to 120°C. The catalyst synthesized at 120°C exhibited the highest activity
118 with a HCHO conversion of 100% at 100°C. This observed high activity was attributed to higher
119 surface reducibility, specific surface area, crystallinity and porosity compared to other catalysts
120 synthesized at different temperatures. Wang et al. (73) studied the effect of H_2O molecules on the
121 activity of birnessite manganese for HCHO oxidation at room temperature and indicated that
122 activity depends on the amount of both adsorbed H_2O molecules and interlayer hydroxyl and H_2O
123 molecules present in the catalyst. Interestingly, as the drying temperature increases from 30 to
124 500°C, so does the specific surface area, but activity dramatically decrease as displayed in Figure
125 1(a) due to the reduction in water content. This result indicates that the activity of birnessite is

126 more a function of the interlayer H₂O molecule content than specific surface area. The presence of
127 H₂O molecules enhances adsorption of HCHO molecules on the surface, conversion and
128 desorption of intermediates from the catalyst's surface.

129 Furthermore, the effect of manganese vacancy (V_{Mn}) on the activity of birnessite-type MnO₂ was
130 studied (74). Their results indicate that the presence of V_{Mn} improves the content of the surface
131 adsorbed oxygen containing species facilitated by the presence of interlayer K⁺, which helps in
132 charge imbalance compensation caused by the created vacancy. The effect of surface pores created
133 by the modification of birnessite-MnO₂ with nitric acid and tetra-ammonium hydroxide on HCHO
134 oxidation was also investigated (75). The created defects as proposed by the authors served as sites
135 for activation of molecular oxygen and H₂O, hence resulting in the increased density of active
136 surface oxygen species and activity of the modified catalyst.

137 Tian et al. (56) also examined the effect of synthesis reaction temperature on the catalytic activities
138 of various cryptomelane manganese octahedral molecular sieve K-OMS-2 catalysts. The K-OMS-
139 2 nanoparticle catalyst prepared at room temperature exhibited a higher catalytic activity compared
140 to K-OMS-2 nanorod structured catalyst prepared at 100°C. The former attained 64% HCHO
141 conversion at the reaction temperature of 100°C was due to the existence of a higher proportion of
142 pore channels compared to the 10% accomplished by the latter under the same reaction conditions.
143 Tian et al. (36) studied the relationship between textural properties and catalytic activity of the
144 cryptomelane manganese oxide catalyst, and showed that a resultant increase in textural properties
145 (specific surface area and pore volume) as a result of synthesis temperature increment from 15 to
146 70°C led to a dramatic improvement in catalytic activity.

147 Three dimensional mesoporous MnO₂ (3D MnO₂) catalysts prepared via nanocasting route using
148 KIT-6 hard template, which retain the mesoporous properties of the template were shown to be
149 promising for HCHO oxidation (76). The mesoporous structure, high specific surface area and
150 large number of surface active Mn⁴⁺ ions enhanced its high activity compared to the corresponding
151 α -MnO₂ and β -MnO₂ nanorod catalysts. Complete HCHO oxidation to H₂O and CO₂ was
152 accomplished at 130°C with 3D MnO₂ while same conversion was achieved at 140°C and 180°C
153 respectively with α -MnO₂ and β -MnO₂ under similar reaction conditions. This indicates that
154 activity is closely related to morphological structures of the catalyst. The catalytic activities of α ,
155 β , γ and δ phase structures of MnO₂ were also investigated (19). The following order of activity
156 for complete HCHO oxidation was established: δ - > α - > γ - > β - MnO₂. Complete HCHO oxidation
157 was attained at 80°C on δ -MnO₂. Its high activity was suggested to be a function of its abundant
158 concentration of lattice oxygen species (see section 4.3 for further discussion on the roles active
159 surface oxygen species) and 2D layered structure, the latter of which enables easy adsorption and
160 diffusion of HCHO.

161 Chen et al. (21) prepared mesoporous hollow and honeycomb structured K_xMnO₂ nanospheres.
162 The former displayed higher activity of up to 100% HCHO removal at 80°C, while the latter
163 attained similar removal efficiency at 100°C under similar reaction conditions. Catalytic activity
164 of hollow structured K_xMnO₂ nanospheres was attributed to its porosity and the ability to retain
165 HCHO in its pores for a longer period compared to honeycomb structured catalyst. Zhou et al. (77)
166 examined the catalytic activity of various structures of Mn and the following order of decreasing
167 activity was established at reaction temperature below 120°C: cryptomelane Mn₂O > birnessite
168 Mn₂O > ramsdellite Mn₂O > monoclinic MnOOH. However, birnessite turns out to exhibit better
169 activity for complete HCHO oxidation at higher temperature, achieving 100% removal at 140°C

170 while cryptomelane at 160°C under similar conditions. This was possibly a result of weakened
171 HCHO adsorption on cryptomelane at lower temperature as suggested by the authors.

172 *2.1.2 Cobalt oxide based catalysts*

173 Cobalt oxide is another important transition metal-based oxide that has recently been attracting
174 attention for low temperature VOC catalytic applications. Similar to MnO_x , Co_3O_4 also exhibit
175 various morphologies which include nano-fibers (78), nano-sheets, nano-cubes, nano-rods (79)
176 and the morphologies influence its catalytic activity through the exposure of catalytically active
177 surface sites (70). The activity of Nano-, 2D- and 3D- Co_3O_4 structures for complete HCHO
178 oxidation was compared and the following order of reactivity was established: 3D- Co_3O_4 > 2D-
179 Co_3O_4 > nano- Co_3O_4 (70). The superior activities of 3D and 2D- Co_3O_4 was ascribed to their
180 mesoporous channel structure which enables easy diffusion of reactants to undergo reaction on the
181 active surface compared to the non-porous nano- Co_3O_4 ; in addition, the best performance of 3D-
182 Co_3O_4 was closely related to its abundant surface adsorbed oxygen species, large specific surface
183 area and exposed active Co^{3+} species on the (2 2 0) crystal face. Similarly, Ma et al. (51) indicated
184 that 2D- Co_3O_4 composed mainly of active Co^{3+} species on the (1 1 0) facet was able to achieve
185 20.3% HCHO oxidation at room temperature.

186 Fan et al. (67) investigated the effect of precipitants on the activity of Co_3O_4 catalysts. The catalysts
187 synthesized using carbonates and bicarbonates displayed better textural properties and superior
188 catalytic activities. The catalyst produced from KHCO_3 reached 100% HCHO conversion at 90°C,
189 compared to 120°C and 130°C for those prepared from KOH and $\text{NH}_3\cdot\text{H}_2\text{O}$, respectively.
190 Recently, Wu et al. (78) described the utilization of porous Co_3O_4 nanofibers prepared by spiral
191 electrospinning and controlled calcination (500°C) as highly active catalysts for HCHO oxidation.
192 Complete oxidation was accomplished at 98°C under a space velocity of 30,000 mL/g·h and it was

193 shown to be highly stable for up to 160 hrs. Its activity was attributed to its high specific surface
194 area and large pore volume which provided more active sites for the reaction.

195 Despite the reported influence of morphological structure on the activity of Co_3O_4 based catalysts,
196 very few structures have been exploited for HCHO oxidation. There is therefore the need for
197 further work to investigate other structures such as nano-sheets, nano-cubes, nano-rods and the
198 extent to which they can influence other properties such as specific surface area, porosity and
199 exposure of active metal sites and active oxygen species for improved low temperature HCHO
200 oxidation.

201 *2.1.3 Other metal oxides*

202 Beside manganese and cobalt based catalysts, other metal oxides have been investigated in the
203 literature. Xia et al. (69) synthesized 3D ordered rhombohedra Cr_2O_3 using assisted ultrasound
204 nanocasting in the presence of 3D mesoporous silica (KIT-6) as template. The catalyst attained up
205 to 90% HCHO conversion at 117°C . The ultrasound assisted synthesis played a major role in
206 improving the characteristics and activity of the catalyst compared to similar catalysts synthesized
207 in the absence of ultrasound. Huang et al. (80) first recounted the use of bifunctional Eu-doped
208 CeO_2 with both thermal- and photo-catalytic oxidation capabilities for HCHO oxidation. Doping
209 Eu onto CeO_2 dramatically enhanced its HCHO oxidation activity and complete oxidation
210 temperature was reduced from 310°C on pure CeO_2 to 120°C on 4% Eu doped CeO_2 . Catalytic
211 activity was promoted through oxygen vacancy creation on the surface of CeO_2 , greater redox
212 ability, more abundant surface active Ce^{3+} and enhanced surface reaction. The created defects
213 provide more sites for oxygen activation hence providing more active surface oxygen species for
214 reaction. In addition, the catalysts exhibited an outstanding stability of up to 100 hrs on stream
215 without any sign of deactivation. Similarly, Zeng et al. (81) demonstrated that hydrogenation

216 treatment of TiO₂ and C-TiO₂ improved their activity through the creation of more surface oxygen
217 vacancy and surface hydroxyl groups. The untreated catalysts virtually displayed no activity for
218 HCHO oxidation in a static chamber reaction after 4 hrs at room temperature in the absence of
219 light illumination, while the treated catalysts including H-TiO₂ and H-C-TiO₂ were able to
220 respectively attain 53% and 57% removal under similar reaction conditions.

221 In general, manganese and cobalt based catalysts were demonstrated to be active compared to other
222 transition metals catalysts for HCHO oxidation. However, not much work has been done on other
223 transition metals. In order to explore their full potentiality as viable catalysts, further work is
224 needed to explore their utilization for low temperature HCHO oxidation. In addition, more work
225 is required to explore surface oxygen vacancy or defects creation using various dopants to improve
226 oxygen activation ability of metal oxide catalysts, to enrich active surface oxygen concentration
227 for enhanced low temperature reaction.

228 2.2 Transition metal-based composites/mixed oxides

229 Transition metal-based composites have been widely applied in the control of pollutants such as
230 CO (83,84) and ammonia (85). Composite catalysts for HCHO oxidation have also been
231 investigated and reported in the literature. These catalysts are generated by co-synthesis of two
232 transition metals oxides or the addition of other metal oxides either by co-precipitation (48,86) or
233 by other synthesis methods such as nanocasting (51). Composite catalysts were shown to exhibit
234 superior catalytic activities compared to the corresponding single materials synthesized using
235 similar procedure. This is due to synergistic or promotional influence of improved oxidation
236 capabilities either through higher surface oxygen mobility, creation of more oxygen vacancies
237 (48,86) or enhancing charge transport during redox cycles (87). To improve oxygen vacancy
238 formation in a composite catalysts and reduce the energy requirement for such, it was suggested

239 that the dopant should possess weaker M-O bonds; have larger radius and possess lower
240 electronegativity (88). Various composites such as $\text{MnO}_x\text{-CeO}_2$ (48,86), $\text{Co}_3\text{O}_4\text{-CeO}_2$ (51), $\text{MnO}_2\text{-}$
241 Fe_2O_3 (89), CuO-MnO_2 (51,89), $\text{MnO}_x\text{-SnO}_2$ (90), $\text{Co}_3\text{O}_4\text{-ZrO}_2$ (91) and Co-Mn oxide (68) have
242 been studied for HCHO oxidation.

243 2.2.1 $\text{MnO}_x\text{-CeO}_2$ composites

244 The composites of Mn and Ce oxides were shown to be active for HCHO oxidation owing to the
245 synergistic effect of Mn high activity and O_2 storage capacity of ceria. In addition, the composites
246 aid in attaining higher oxidation states for Mn (83,92) which is vital for HCHO oxidation (87).
247 Formation of solid solution between Mn and Ce is also critical to achieving synergistic influence
248 through O_2 transfer mechanism (48,86). Solid solution was shown to be attained in the Mn-Ce
249 molar ratio ($\text{Mn}/(\text{Mn} + \text{Ce})$) range of 0.3 to 0.5, with 0.5 molar ratio being the optimum
250 composition (48,86,93) and the solubility limit for the substitution of Ce ions by Mn ions in the
251 composite (53).

252 Tang et al. (86) indicated that the manifestation of synergy in $\text{MnO}_x\text{-CeO}_2$ solid solution
253 composite, which enables the composite to attain complete HCHO conversion at lower
254 temperature (100°C) compared to pure MnO_x and CeO_2 . The synergy was attained through a series
255 of redox cycles ($\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$) involving the activation of molecular oxygen by Ce
256 and its transfer to Mn. The optimum calcination temperature for solid solution stability was shown
257 to be 550°C , above which activity decreased owing to phase segregation. In another investigation,
258 Tang et al. (48) further highlighted that above Mn-Ce molar ratio of 0.5, MnO_x crystallizes out of
259 the solid solution, with a consequent drastic reduction in catalytic activity, which is in conformity
260 with the findings of Li et al. (93). However, higher total decomposition temperature of 270°C was
261 reported by Li et al. (93) for $\text{Mn}_{0.5}\text{Ce}_{0.5}\text{O}_2$. Nonetheless, the catalysts were able to totally oxidize

262 HCHO at room temperature in the presence of 506 ppm ozone (O_3) in the feed stream. The ozone
263 molecules enhance the reaction by dissociating on the catalyst's surface and providing enough
264 atomic oxygen species to drive the reaction (93).

265 Quiroz et al. (53) studied the impact of acid treatment over MnO_x - CeO_2 composite for HCHO
266 oxidation. Their results indicated that the treatment had no pronounced effect on the textural and
267 redox properties of the composites within the solubility limit of Mn (Mn molar ratio ≤ 0.5) in
268 CeO_2 . However, at higher Mn molar ratio (0.7 and 1) when MnO_2 began to crystallize out of the
269 solid solution, significant improvement in catalytic activity was observed owing to the increased
270 specific surface area and higher oxidation state of surface Mn. It is important to mention that while
271 textural properties of the solid solution were not altered by the acid treatment, the oxygen transfer
272 ability of CeO_2 was significantly hampered by the formation of $Ce(SO_4)_2$ resulting into a drastic
273 reduction in activity. Therefore, acid treatment has positive effects on pure MnO_2 and an inhibitive
274 effect on the synergy of the solid solution composites. The modification of birnessite-structured
275 MnO_2 with ceria for HCHO oxidation was also reported in the literature (94). The incorporation
276 of cerium ions inhibited the growth of MnO_2 crystals leading to particle size reduction and increase
277 in specific surface area, as the amount of doped ceria increases. The doping led to the increase in
278 the amount of oxygen vacancies and the rate of molecular oxygen activation into surface adsorbed
279 oxygen species (O_2^- , O^- or terminal hydroxyl (OH) group (74)). The catalyst with the highest ratio
280 of surface adsorbed oxygen to lattice oxygen exhibited the best catalytic performance. At higher
281 ceria doping (Ce - MnO_2 , molar ratio 5:10), the birnessite structure collapsed leading to decrease in
282 catalytic activity.

283 Tang et al. (48) further demonstrated that impregnating Pt on MnO_x - CeO_2 composite significantly
284 improved its activity by attaining 100% HCHO conversion at room temperature as shown in Table

285 1. It is noteworthy to mention that the formed composite (Pt/MnO_x-CeO₂) was prone to
286 deactivation with increasing HCHO concentration. Its activity dropped from 100% conversion at
287 30 ppm to 54% in the presence of 580 ppm HCHO at room temperature as shown in Figure 2.
288 Meanwhile the same authors (86) showed that MnO_x-CeO₂ composite was stable for complete
289 HCHO oxidation over 48 hrs without any sign of deactivation at similar concentration (580 ppm).
290 It should however be noted that the latter experiment was conducted at 100°C and the high
291 temperature could aid the decomposition of intermediate species while the former was conducted
292 at room temperature. This indicates that Pt might be prone to deactivation by HCHO at higher
293 concentration, which needs to be investigated further.

294 2.2.2 Co₃O₄-CeO₂ composites

295 Ma et al. (51) investigated the oxidation of HCHO at room temperature on 2D-Co₃O₄-CeO₂
296 composites. They discovered that no synergy or activity improvement was realized by the formed
297 2D-Co₃O₄-CeO₂ composites and that 2D-Co₃O₄ was more active than the composites with
298 respective HCHO conversions of 13.2% and 20.3% at room temperature. It should however be
299 noted that no solid solution formation was observed in the 2D-Co₃O₄-CeO₂ composites, which is
300 a phenomenon reportedly required for achieving synergy through ceria O₂ transfer mechanism
301 (48,86). The incorporation of Au in the composite (2D-Au/Co₃O₄-CeO₂) improved the composite's
302 activity to 50% conversion at room temperature (Table 1) by promoting desorption of surface
303 active oxygen species (51). Liu et al. (50) presented the evidence of solid solution formation in 3D
304 ordered macroporous (3DOM) CeO₂-Co₃O₄ catalysts with low loading of Co₃O₄. However, the
305 3D-CeO₂-Co₃O₄ catalysts with various Ce-Co molar ratios were shown to possess low catalytic
306 activities. Loading Au particles (3 wt. %) on the composites distinctively improved their catalytic
307 activities, and in fact all the Au supported composites were able to completely convert HCHO into

308 CO₂ and H₂O below 65°C. The composites (3D Au/CeO₂-Co₃O₄), with lower Co content in CeO₂-
309 Co₃O₄ in the region solid solution, presented better activity in this study. When higher Co molar
310 ratios was employed, segregation between CeO₂ and Co₃O₄ occurred, which led to weaker
311 interaction and thus reduced the activity of the Au/CeO₂-Co₃O₄ catalysts.

312 *2.2.3 Co-Mn oxides Composites*

313 The composites of Co and Mn oxides were also studied and shown to be more active than the
314 individual pure oxides for HCHO complete oxidation (95). Favorable synergy was obtained due
315 to the abundant surface adsorbed oxygen species generated by the oxygen vacancies created in the
316 Co-Mn oxides solid solution. Textural and redox properties were also shown to be affected by the
317 synthesis method employed. Co-precipitation synthesis produced a more active catalyst with
318 higher specific surface area, higher relative content of surface adsorbed oxygen species and surface
319 active manganese (Mn⁴⁺) that completely oxidized HCHO at 75°C compared to 100°C over that
320 synthesized using sol-gel method.

321 Wang et al. (68) further studied the efficiency of the cycling “storage-oxidation” process for
322 HCHO oxidation using 3D ordered mesoporous Co-Mn oxides composite (3D-Co-Mn)
323 synthesized using KIT-6 template and that of Co-Mn oxides composite synthesized using co-
324 precipitation. During the storage process, the catalysts were first exposed to a feed stream of O₂
325 and HCHO; subsequently, the stored HCHO was oxidized in a flow of O₂ at elevated temperature
326 to evaluate its activity. The 3D-Co-Mn oxides composite was shown to have superior storage
327 capacity of up to 0.8 mmol/g-catalyst and HCHO complete oxidation temperature of 70°C,
328 compared to the storage capacity of 0.428 mmol/g-catalyst and HCHO complete oxidation
329 temperature of 75°C respectively achieved by co-precipitated Co-Mn oxides composite. The

330 excellent activity of 3D-Co-Mn oxides composite was attributed to its larger specific surface area
331 and ordered mesoporous structure. Lu et al. (96) studied HCHO oxidation over $\text{MnO}_x\text{-Co}_3\text{O}_4\text{-CeO}_2$
332 composites and found out that the incorporation of MnO_x into $\text{Co}_3\text{O}_4\text{-CeO}_2$ greatly improved its
333 textural properties and the amount of available surface active oxygen species, resulting in an
334 improvement in catalytic activity.

335 *2.2.3 Other Composites*

336 Other composites such as $\text{MnO}_x\text{-SnO}_2$ (90) and zirconia supported cobalt oxide catalysts (91) have
337 been reported in the literature. Wen et al. (90) showed that the redox properties of $\text{MnO}_x\text{-SnO}_2$,
338 which were in turn influenced by the preparation method, played a crucial role in determining its
339 activity. Their experimental results highlighted that higher oxidation states of Mn were more active
340 in HCHO oxidation. The dominant oxidation state of Mn in the composite synthesized using redox
341 co-precipitation was Mn^{4+} while Mn^{3+} was the main state in the co-precipitated composite, which
342 accounted for the difference in their activities as shown in Table 3. This is in agreement with other
343 reported literatures for the active state of Mn for HCHO oxidation (76,86). Lu et al. (87)
344 investigated the catalytic performance of graphene- MnO_2 (G-Mn) hybrid for complete oxidation
345 of HCHO. The G-Mn hybrid catalyst achieved complete HCHO conversion at 65°C , compared to
346 140°C for pure MnO_2 and the completely inactive graphene (G) nanosheets. The hybrid system
347 exposed more Mn^{4+} active sites, enhanced charge transport during Mn redox cycle and offered a
348 larger amount of surface HYDROXYL species which eased HCHO oxidation and improved
349 activity.

350 **3. Catalyst immobilization on porous materials for practical HCHO oxidation**

351 For practical applications, deployment of powdered form materials especially nanosized, gives rise
352 to engineering challenges such as dust contamination and nanoparticle leaching in flue gas streams

353 (82). Therefore, catalysts immobilization on porous materials with low air pressure drop is
354 considered viable for air purification processes. A variety of porous materials with low air
355 resistance including polyethylene terephthalate (PET) (18), polyester particulate filter (97) and
356 porous cellulose fiber (82) have been used as supporting materials for immobilizing nanoparticle
357 catalysts for HCHO oxidation. A summary of the activity of these immobilized catalysts is
358 presented in Table 4. Wang et al. (18) reported the in-situ coating of δ -MnO_x nanosheet on the
359 surface of PET first through surface reaction followed by in-situ deposition. The formed composite
360 which is light with low air resistance and high specific surface area, proved highly active and stable
361 for low concentration HCHO (0.6 mg/m³) oxidation at room temperature for 10 hrs. Sidheswaran
362 et al. (97) supported Mn based catalyst with 84% nsutite, 2% cryptomelane and 13% manjiroite
363 composition on the surface of a thin polyester particulate filter for heating ventilation and air
364 conditioning (HVAC) and evaluated its performance for HCHO oxidation. Experimental results
365 indicated that stable single pass HCHO oxidation with over 80% removal efficiency at room
366 temperature was achieved continuously for 35 days for both high and low face velocities close to
367 typical building air ventilation systems.

368 Zhou et al. (82) likewise demonstrated an in situ deposition of MnO₂ nanosheets on cellulose fiber
369 composite (8.86 wt.% MnO₂/cellulose fiber) and showed that even though birnessite powder is
370 slightly more active than the composite (100% and 99.1% at 140°C, respectively), the composite
371 is about 19 times more active in terms of HCHO removal per mg of MnO₂. However, the observed
372 difference could supposedly be attributed to the removal/adsorption capacity of cellulose fiber and
373 not necessarily HCHO conversion as CO₂ generation and catalytic activity of the cellulose fiber
374 were not monitored in the experiment. Li et al. (98) and Dai et al. (71) respectively utilized AC for
375 immobilizing birnessite-MnO₂. In both cases, HCHO was completely converted into CO₂ in a

376 static reaction chamber. However, the conversion patterns in the individual experiments were such
377 that the concentration of HCHO sharply dropped in the first 60 mins with little corresponding CO₂
378 generation, possibly indicating that the molecules were actually adsorbed onto the surface of AC.
379 The adsorbed molecules were consequently and slowly converted into CO₂ over 6 hrs (98) and 9
380 hrs on birnessite-MnO₂/AC (71) respectively as shown in Figure 3(a&b). Similar patterns were
381 observed over unsupported birnessite as shown in Figure 1(b) (73). In contrast, simultaneous
382 HCHO conversion and CO₂ generation were observed over modified birnessite with manganese
383 vacancies and up to 81.7% conversion was attained in the first one hour of the static experiment
384 (74). This indicates that the HCHO is instantaneously converted into CO₂, as opposed to the AC
385 supported birnessite (71,98) in which the HCHO is adsorbed onto the AC and subsequently
386 converted over time. Few immobilized transition metal-based catalysts for HCHO oxidation have
387 been reported as presented in Table 4; therefore, further investigations are required to evaluate
388 more effective substrate materials for immobilization and to understand their interactions with the
389 catalysts and effectiveness for practical application in air purification process. In addition, these
390 materials need to be tested under indoor conditions in air purifiers or HVAC systems and evaluate
391 the effect of conditions such as particle leaching, dust contamination, relative humidity and
392 temperature variation, on the effectiveness and stability of these materials.

393 **4. Influence of catalyst based factors on HCHO oxidation efficiency**

394 The effectiveness of HCHO oxidation process is majorly related to the activity/reactivity of the
395 catalyst deployed and other reaction parameters such as temperature, concentration, space velocity,
396 catalyst mass and relative humidity. Catalytic activity is in turn influenced by a number of
397 physicochemical properties which include structure and morphology, preparation or synthesis
398 method, degree of crystallinity, surface reducibility, specific surface area, amount of active oxygen

399 species and active metal sites (54). A combination of these properties is decisive for high catalytic
400 activity and for an effective HCHO oxidation at low reaction temperature.

401 4.1 Influence of synthesis methods and conditions on textural properties, morphology and
402 activity

403 Several conventional preparation methods can be used to synthesize catalysts for HCHO oxidation
404 including sol-gel method (56), precipitation and co-precipitation (86,97). Recent researches have
405 mainly focused on improving and modifying catalysts preparation methods to enhance their
406 performance and catalytic activities through the utilization of synthesis techniques such as
407 hydrothermal synthesis (77), electrospinning (78), electrodeposition (80) and hard template
408 nanocasting (70,76). Synthesis methods and reaction conditions are able to tailor catalysts' textural
409 and surface properties, structures and morphologies (as shown in Figure 4 (77)) and hence
410 influence their catalytic activity (36,54) as shown in. For instance, the utilization of ultrasound
411 assisted nanocasting of 3D-Cr₂O₃ using KIT-6 as template helps in enhancing the penetration of
412 precursor materials into the mesoporous structure of KIT-6, which proved efficient in improving
413 its specific surface area, pore volume and mesoporosity compared to 3D-Cr₂O₃ synthesized
414 without the aid of ultrasound (69). Zhang et al. (19) highlighted that by varying reaction conditions
415 in a hydrothermal synthesis, various crystal structures of MnO₂ including: α - and δ -MnO₂; β - and
416 γ -MnO₂, with entirely different properties can respectively be produced from the same starting
417 materials.

418 Reaction temperatures in hydrothermal synthesis have tremendous effects on morphology and
419 structural evolution of structured manganese catalysts. Tian et al. (54) highlighted that the reaction
420 temperature greatly affects the crystallinity, surface reducibility, specific surface area and activity
421 of birnessite structured manganese oxide catalysts. At low synthesis temperature of 80°C, poorly

422 crystalline birnessites were produced, whilst the birnessites were transformed into well-crystalline
423 structures when reaction temperature was increased to 100°C, thereby increasing its activity.
424 However, higher temperature (140°C) led to decomposition of the birnessite structure as a result
425 of excessive reduction of Mn⁷⁺ by benzyl alcohol during the synthesis. Zhou et al. (77) also
426 observed that birnessites structure obtained at 120°C synthesis temperature transformed into
427 monoclinic MnOOH at 150°C and eventually collapsed into 1D MnOOH nanorods at 180°C as
428 shown in Figure 4. Similarly, a correlation between synthesis temperature and catalyst's
429 morphology for cryptomelane-type manganese octahedral molecular sieve (K-OMS-2) was
430 reported by Tian et al. (56). The morphologies of the K-OMS-2 catalysts changed from
431 nanoparticles at room temperature to nanorods at reaction temperatures of 80-100°C and to
432 nanowires at 120°C.

433 Tian et al. (36) reported that essential properties of cyptomelane catalyst such as morphology,
434 crystallinity, specific surface area and pore structure could be tailored by manipulating the
435 hydrothermal synthesis temperature. Increasing synthesis temperature distinctively raised the
436 crystallinity and textural properties of the catalyst. However, too high temperatures diminished
437 crystallinity and this is in agreement with the findings of Tian et al. (54) for birnessite manganese
438 catalysts. Textural properties such as specific surface area and pore volume were also shown to
439 vary with the synthesis temperature. An increase in the synthesis temperature led to a dramatic
440 improvement in textural properties: specific surface area and pore volume increased from 68 m²/g
441 and 0.2 cm³/g at synthesis temperature of 15°C, to 206 m²/g and 0.3 cm³/g at 70°C, respectively.
442 Such an improvement in textural properties in turn led to enhancement in catalytic activity.

443 Calcination temperature was also demonstrated to be very critical for catalysts structural stability
444 and activity. Wang et al. (73) indicated that between 30 and 300°C only a little change was

445 observed in the sizes of birnessite nanospheres and that the structure was prevented from
446 collapsing by interlayer K^+ and H_2O molecules present. However, when the calcination
447 temperature reached up to $500^\circ C$, the layered structure of birnessite completely collapsed and
448 transformed into cryptomelane with a 2×2 tunnel structure due to the loss of interlayer H_2O
449 molecules. The calcination temperature of composite MnO_x-CeO_2 prepared using modified co-
450 precipitation was shown to greatly influence its catalytic activity for HCHO oxidation (86). As the
451 temperature rises from $300-500^\circ C$, the relative amount of surface active Mn^{4+} and lattice oxygen
452 also rises, however at higher temperature ($700^\circ C$) both the activity and the relative amount of
453 lattice oxygen dramatically decreased due to phase segregation evident by the appearance of MnO_2
454 crystals in the otherwise solid solution composite. Likewise, Wu et al. (78) indicated that high
455 calcination temperatures ($600-800^\circ C$) led to the decrease in the activity of Co_3O_4 nanofibers as a
456 result of aggregation growth and collapse of the catalyst's mesoporous structure.

457 The utilization of templates and surfactants in catalysts synthesis for HCHO oxidation is also
458 attracting attention. When templates are deployed in catalyst preparation, the catalyst's structures
459 and morphology could easily be manipulated to enhance their catalytic activities (56,76) and
460 replicate the characteristics of the template materials used. While Shi et al. (95) demonstrated that
461 Co-Mn oxides composites prepared using co-precipitation method were far more active than those
462 prepared using sol-gel method, the same group (68) further disclosed that 3D mesoporous Co-Mn
463 oxides synthesized using KIT-6 hard template possessed superior activity owing to their better
464 textural properties. Similarly, the synthesis of 3D- Cr_2O_3 (69), 3D- Co_3O_4 (70) and 3D- MnO_2 (76)
465 have been demonstrated using KIT-6 molecular sieve hard template for HCHO oxidation. The
466 presence of the template improved the mesoporous structure and specific surface area and exposes
467 more active sites thereby enhancing catalytic activity. Other mesoporous structures including 2D-

468 MnO_2 (99) and 2D- Co_3O_4 (51,70) have been prepared using SBA-15 hard templates, which turned
469 out to be more active than the corresponding non-porous materials but less active than their 3D-
470 counterparts. Furthermore, Tian et al. (56) highlighted that highly active nanoparticle
471 cryptomelane (K-OMS-2) catalyst could be synthesized at room temperature with the aid of
472 cetyltrimethylammonium bromide (CTAB) surfactants without necessarily the use of high reaction
473 temperature as earlier reported (36).

474 Acidity of the reaction medium and the type of acid deployed in controlling the pH have significant
475 effects on the morphology of manganese based catalysts. Chen et al. (21) showed that mesoporous
476 hollow and honeycomb K_xMnO_2 nanospheres with varying properties and activities could be
477 produced by varying the ratio of KMnO_4 and oleic acid during the synthesis process. Zhou et al.
478 (77) revealed that introducing H_2SO_4 (decreasing the pH) into a reaction medium that would
479 otherwise produce birnessite structured manganese led to the production of cryptomelane
480 structured manganese. However, the type of anions present in the acid is also critical in
481 determining the resultant morphology under similar conditions. While the addition of H_2SO_4 led
482 to cryptomelane structure, addition of H_3PO_4 and HNO_3 produced birnessite and ramsdellite
483 structured manganese, respectively as shown in Figure 4. This shows that different anions play
484 dissimilar roles in channeling the mechanism of crystal formation towards a particular
485 morphology.

486 4.2 Influence of catalyst's morphology on activity

487 Catalysts' morphology and structure play an important role in promoting catalytic activities.
488 Control over the morphological structure of catalysts is able to influence other properties such as
489 pore size, specific surface area and the exposure of available surface active sites. The activity of
490 manganese oxide catalysts with square tunnel structures (pyrolusite, cryptomelane and todorokite)

491 is majorly affected by their tunnel sizes (55). Similarly the available surface active sites depend on
492 the nature of the catalysts. 3D- MnO_2 catalyst have more exposed Mn^{4+} on its crystal lattice plane
493 thereby improving its activity compared to the one-dimensional $\alpha\text{-MnO}_2$ and $\beta\text{-MnO}_2$ nanorod
494 materials (76).

495 Chen et al. (55) investigated the effect of MnO_x tunnel structure on the active oxidation of HCHO
496 as shown in Figure 5. Three types of Mn tunnel structures were investigated including pyrolusite
497 with tunnel structure of ca. $0.23 \times 0.23 \text{ nm}^2$, cryptomelane consisting of double edge sharing MnO_6
498 octahedral with tunnel diameter of ca. $0.46 \times 0.46 \text{ nm}^2$ and todorokite composed of triple chains
499 edge-sharing MnO_6 with tunnel of ca. $0.69 \times 0.69 \text{ nm}^2$. Experimental results indicated that
500 cryptomelane had the highest catalytic activity achieving 100% HCHO conversion at 140°C .
501 Cryptomelane possesses an effective tunnel diameter close to HCHO's dynamic diameter (0.234
502 nm) thereby allowing better adsorption and higher catalytic activity (55). Yu et al. (41) indicated
503 that the micropore channel structure of nest- and urchin-like MnO_2 improved their catalytic activity
504 by allowing better adsorption of HCHO compared to that of cocoon-like MnO_2 without mesopores
505 present despite having higher specific surface area.

506 Tian et al. (54) also highlighted that the presence of smaller catalytic pore sizes could extend the
507 residence of HCHO molecules in the catalyst's pores thereby improve its oxidation efficiency.
508 Correspondingly, the work of Tian et al. (56) underscored that the pore structures of nanoparticle
509 K-OMS-2 were readily accessible to HCHO molecules, enhancing higher adsorption and better
510 activity compared to K-OMS-2 nanorods with similar specific surface areas. Zhang et al. (19)
511 further highlighted that the 2D layered tunnel structure of $\delta\text{-MnO}_2$ enhanced its activity through
512 facilitating the adsorption and desorption of HCHO to active sites compared to other structures ($\alpha\text{-}$
513 $\beta\text{-}$ and $\gamma\text{-MnO}_2$). In another research, Chen et al. (21) stressed that catalyst's activity depends

514 more on its porosity and nanoplatelets crystal size than specific surface area. Mesoporous hollow
515 K_xMnO_2 nanospheres, which have smaller nanoplatelets size and specific surface area twice less
516 than those of its corresponding mesoporous honeycomb structure, achieved higher activity in
517 HCHO oxidation.

518 Wang et al. (73) showed that the structure of birnessite is such that it contains HYDROXYL groups
519 and H_2O molecules at the interlayer surface. The presence of these molecules greatly improved its
520 catalytic activity for HCHO removal even at room temperature. After the removal of both the
521 hydroxyl groups and H_2O molecules at high temperature, the birnessite structure collapsed and the
522 catalyst lost its high activity. Likewise, Sidheswaran et al. (97) indicated that the existence of H_2O
523 molecules in interstitial voids of MnO_2 based catalysts with varying composition of nsutite,
524 cryptomelane and pyrolusite contributed to its higher catalytic activity compared to 99% pyrolusite
525 catalyst which has smaller tunnel structure and lower H_2O molecules content in its interstitial
526 voids.

527 4.3 Roles of active surface oxygen in HCHO oxidation

528 It is reported in the literature that surface oxygen species either in the form of surface adsorbed
529 oxygen species (O_2^- , O^- or terminal hydroxyl (OH) group (74)) and lattice oxygen are critical to
530 the effectiveness of the catalytic oxidation of HCHO and other intermediates into CO_2 and H_2O
531 (51,67,95). However, there is a discrepancy regarding the respective roles of each type of oxygen
532 specie for HCHO oxidation over transition metal based catalysts. For example, Zhang et al. (19)
533 stipulated that since HCHO oxidation was shown to conform to Mars van Krevelen mechanism,
534 abundant lattice oxygen on the catalyst surface will lead to higher catalytic activity. They further
535 showed that the catalytic activities of four MnO_2 catalysts (α , β , γ and δ - MnO_2) are closely linked
536 to their respective amount of surface lattice oxygen (relative to surface adsorbed oxygen species)

537 and the following order of activity was established: δ - > α - > β - > γ - MnO_2 . Similarly, Tang et al.
538 (86) indicated that the catalytic activity trend of MnO_x - CeO_2 composite catalysts synthesized using
539 various methods, followed the trend of their relative lattice oxygen content. Those richer in lattice
540 oxygen relative to surface adsorbed oxygen presented better activity.

541 On the other hand, surface adsorbed oxygen species were shown to be directly involved in the
542 activation of HCHO and its subsequent oxidation into CO_2 and H_2O (74,75). It was shown that the
543 activity of layered birnesite- MnO_2 catalysts with surface pits corresponds to the relative amount
544 of surface adsorbed oxygen species on the catalysts (75). The surface pits acts as vacancies for
545 activation of molecular oxygen and or H_2O into surface adsorbed oxygen and the higher the
546 relative amount of these species the better the catalytic activity. Wang et al. (94) contended that
547 while surface adsorbed oxygen species participates in the oxidation reaction of HCHO, lattice
548 oxygen species enhance their formation through its complex interaction with oxygen vacancy and
549 molecular oxygen. Huang et al. (80) reported that the enhancement of the relative amount of
550 surface adsorbed active oxygen species was achieved through the creation of surface defects by
551 doping Eu on CeO_2 . The created oxygen vacancies served as sites for oxygen activation into active
552 superoxide (O^{2-}) species which could partake in surface reaction, hence enhancing the
553 concentration of surface adsorbed oxygen and the catalyst's activity. Similarly, surface defects
554 created on birnesite- MnO_2 catalysts served as pits for activation of molecular oxygen and H_2O into
555 surface active oxygen species, hence increasing the surface density of these species leading to
556 higher catalytic activity (74,75). Ma et al. (51) also underscored the role of surface adsorbed
557 oxygen (O^{2-} , O^\cdot) in HCHO oxidation over cobalt based catalysts. They showed that catalytic
558 activity is closely associated to the ease with which active surface oxygen desorb from catalysts
559 surface. They further demonstrated that catalytic activity can be improved by increasing the ease

560 with which surface active oxygen desorb from catalyst's surface through the incorporation of Au
561 nanoparticles into $\text{Co}_3\text{O}_4\text{-CeO}_2$ composite. Likewise, it was demonstrated that 3D- MnO_2 with
562 abundant concentration of surface adsorbed oxygen species which easily desorb from the catalyst
563 at lower temperature exhibited better catalytic activity compared to 2D- MnO_2 with lower surface
564 adsorbed oxygen species concentration and nano- Co_3O_4 with virtually no active oxygen species
565 (O^{2-} , O^-) present (70).

566 In addition, Lu et al. (87) indicated that surface adsorbed oxygen species (hydroxyl group) and not
567 lattice oxygen are responsible for the high activity of graphene- MnO_2 hybrid catalyst for HCHO
568 oxidation. They further pointed out that the abundant relative amount of surface adsorbed hydroxyl
569 group on the catalyst did not only improve its catalytic activity but also simplified HCHO
570 conversion pathway by direct hydroxyl ion oxidation of formate species to CO_2 without the
571 formation of CO intermediates. It was also shown that surface adsorbed hydroxyl groups were
572 directly involved in the room temperature oxidation of HCHO on the surface of birnessite, which
573 led to the formation of formates and carbonates (73). Similarly, Wang et al. (18) showed that the
574 high amount of surface adsorbed oxygen in the form of hydroxyl species were responsible for the
575 high HCHO oxidation activity of $\delta\text{-MnO}_2/\text{PET}$ at room temperature. Similarly, Fan et al. (67)
576 underscored that hydroxyl species on the surface of Co_3O_4 are the key active surface oxygen
577 required for the formation of dioxymethylene (DOM) species and their subsequent conversion to
578 formate species in HCHO oxidation process.

579 4.4 Influence of reducibility and active metal sites on catalysts surface

580 The surface reducibility of catalysts plays an important role in determining their catalytic activity.
581 It indicates the amount of reactive species on the catalyst's surface and their onset reaction
582 temperatures (54). It could also indicate catalyst's oxygen mobility, which might cause more

583 oxygen adsorption and further excitement to active oxygen species which participate in the
584 oxidation reaction (19). Tian et al. (54) indicated a correlation between reduction temperature and
585 catalytic activity for birnessite manganese based catalysts. The established trend disclosed that the
586 lower the catalyst's reduction temperature (higher surface reducibility), the higher its HCHO
587 oxidative activity and vice-versa. Tang et al. (86) presented that owing to solid solution formation,
588 $\text{MnO}_x\text{-CeO}_2$ catalysts possessed higher surface reducibility and better catalytic activity compared
589 to pure MnO_x and CeO_2 . Furthermore, the catalysts' activity reduced as surface reducibility
590 decreased (high reduction temperature) with increasing calcination temperature because of phase
591 segregation. Xia et al. (69) also indicated that chromia catalysts with the highest reducibility
592 possessed the best HCHO catalytic activity. Similar trends was also reported for HCHO oxidation
593 over Co_3O_4 catalysts (67).

594 The active sites present on catalyst's surface are critical and key for determining activity. The
595 higher the concentration or availability of exposed active metal sites on catalyst's surface, the
596 better its HCHO oxidative activity. Bai et al. (70) presented that Co^{3+} ions are the surface active
597 state and sites of 3D- Co_3O_4 for HCHO oxidation. The (220) crystal plane of the catalyst is
598 majorly composed of Co^{3+} against the Co^{2+} present on the (111) crystal plane of nano- Co_3O_4 ,
599 thereby making it more active and achieving complete HCHO oxidation at lower temperature.
600 Similarly, Ma et al. (51) demonstrated that the (110) facet of 2D- Co_3O_4 which is mainly composed
601 of Co^{3+} is the key active facet for effective HCHO oxidation. High activity for HCHO oxidation
602 by 3D- MnO_2 was attributed to the presence of high content of Mn^{4+} active sites on the exposed
603 (110) crystal plane surface (76). These exposed ions provided sufficient sites upon which the actual
604 oxidation reaction takes place, thereby improving its activity. It was also shown that Mn^{4+} is the
605 active state and site for HCHO oxidation for $\text{MnO}_x\text{-CeO}_2$ based composite and the catalyst with

606 the highest amount of Mn^{4+} possessed the best activity (48,86,87). Zhang et al. (19) also
607 highlighted that amongst their investigated catalysts (α , β , γ and δ - MnO_2), those with the highest
608 content of Mn^{4+} displayed the best HCHO catalytic activity. Improving the electrochemical
609 properties of catalysts was proven to enhance their catalytic activities. Lu et al. (87) established
610 that the charge transport ability and interfacial electron transfer of MnO_2 during $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox
611 cycle can be enhanced by incorporating graphene into MnO_2 (G-Mn hybrid), which was revealed
612 to improve the electrical conductivity of MnO_2 and decrease electron transfer resistance. In
613 addition, it offered high specific surface area and 2D plane structure for increased exposure of
614 metal surface active sites (100).

615 4.5 Influence of specific surface area on HCHO catalytic activity

616 Catalysts' specific surface area is an important parameter affecting HCHO catalytic oxidative.
617 High specific surface area could enhance adsorption of HCHO molecules onto the catalyst's
618 surface and help in exposing more surface active sites, improving surface lattice defect and oxygen
619 vacancy, thereby leading to abundant surface active oxygen species (70,78), which is a key
620 requirement for oxidation reactions. A correlation between catalyst's surface and activity was
621 established by Wu et al. (78) for Co_3O_4 nanofibers. Activity increase was observed with increasing
622 specific surface area and pore volume as the calcination temperature increased from room
623 temperature to 500°C , above which a decline in activity was observed due to the destruction of the
624 mesopores and the consequent decrease in specific surface area at higher temperatures. Tian et al.
625 (36) also demonstrated that higher specific surface area greatly enhanced catalytic activity for
626 HCHO oxidation. Nanoparticle cryptomelane catalyst, with specific surface area as high as 206
627 m^2/g and smaller uniform mesopores exhibited higher catalytic activity than the corresponding
628 nanorod cryptomelane catalyst with a specific surface area of $68 \text{ m}^2/\text{g}$. The high specific surface

629 area and small nanoparticle sizes improved cryptomelane activity by increasing the available
630 surface active sites and more accessible pore channels for adsorption and desorption of HCHO
631 molecules and reaction products respectively (36). Sekine (2) showed that fine MnO₂ catalysts
632 with higher specific surface area (163 m²/g) achieved higher HCHO oxidation compared to MnO₂
633 catalysts with a specific surface area of 61 m²/g. Similarly, Tian et al. (54) also reported that
634 birnessite structured manganese catalysts having higher specific surface area exhibited better
635 catalytic activities compared to those with lower specific surface areas.

636 However, high specific surface area does not always translate into superior catalytic activities in
637 HCHO oxidation reactions. The activity of birnessite-type MnO₂ was shown to be independent on
638 the catalysts' specific surface area trend (74) but on the relative content of surface adsorbed oxygen
639 species and the manganese oxidation state. The catalyst with the highest manganese vacancy had
640 the lowest specific surface area but exhibited the best catalytic activity. Shi et al. (95) also
641 demonstrated that the activity trend of Co-Mn oxides composite with varying Co/Mn molar ratios
642 did not follow their specific surface area trend, and in fact the catalysts with the smallest specific
643 surface area exhibited the best catalytic activity. Complete oxidation of HCHO was achieved at
644 75°C on Co-Mn oxides (molar ratio: 3/1) with specific surface area of 92 m²/g while only 64%
645 conversion was attained on Co-Mn oxides (molar ratio: 2/1) with specific surface area of 172 m²/g
646 at the same reaction temperature. The higher activity of Co-Mn (3/1) oxides was a result of increase
647 in the relative amount of surface adsorbed oxygen species realized from the creation of solid
648 solution by the incorporation of Mn into the lattice structure of Co₃O₄. Fan et al. (67) also showed
649 that Co₃O₄ catalysts with high surface content of K⁺, CO₃²⁻ and Co³⁺ exhibited better activity
650 despite having relatively smaller specific surface area.

651 **5. Effect of reaction conditions on HCHO oxidation efficiency**

652 Reaction parameters for HCHO oxidation process such as temperature, relative humidity,
653 reactants' space velocity and HCHO concentration play great roles in ensuring the overall
654 effectiveness of the oxidation reaction. These parameters need to be optimized especially reaction
655 temperature considering the potential application of the process (no harmful by-products
656 generation), in order to realize practically effective HCHO oxidation.

657 5.1 Reaction temperature and time

658 Reaction temperature is critical in HCHO oxidation, and generally the efficiency of HCHO
659 oxidation over catalyst improves with increasing temperature even though some highly active
660 catalysts are able to achieve complete oxidation at room temperature. Most of the reported
661 transition metal based catalysts attained complete HCHO oxidation at temperatures above 100°C
662 (21,36,55,67,73,82) with very few below 100 °C (19,21,73,87,95,98). Figure 6 presents the
663 conversion/removal efficiency of HCHO as a function of reaction temperatures over different
664 catalysts. However, it does not provide a basis for comparison due to the differences in the initial
665 HCHO concentration and feed flow rate employed in various experiments. This makes it difficult
666 to evaluate the specific reaction rates (equation 1) (74) of variously reported catalysts for rational
667 comparison. For static systems, experiments are normally conducted at room temperature; in
668 which case HCHO oxidation becomes a function of time in addition to other factors catalyst based
669 factors discussed earlier (section 4). Figure 7 presents HCHO removal efficiency over various
670 catalysts as a function of reaction time. It can be seen in Figure 7 that long reaction time is required
671 to achieve complete HCHO removal in static system. For proper comparison, other factors such as
672 initial HCHO concentration and the mass of catalyst used should be taken into account.

673 In view of these, more investigations are required to improve the activity of transition metal based
674 catalysts at low temperature in order to compete with noble metal based catalysts which could
675 successfully oxidize HCHO even at room temperature (48,101).

676
$$\text{specific reaction rates } \left(\frac{\mu\text{mol}}{\text{m}^2 \cdot \text{min}} \right) = \frac{C_{\text{HCHO}} \div 22.4 \times F \times \eta}{S_{\text{BET}} \times m} \dots\dots\dots (1)$$

677 Where C_{HCHO} is the inlet HCHO concentration (ppm), F is the flow rate (ml/min), η is the
678 percentage HCHO conversion (CO_2 generation), S_{BET} catalysts specific surface area and m is the
679 catalyst mass.

680 5.2 Relative humidity

681 Relative humidity (RH) at moderate levels influences the efficiency of HCHO oxidation, however
682 at higher RH competitive adsorption of H_2O molecules tend to block the catalyst's active surface
683 hence impinging activity. RH also helps in replenishing the supply of surface active hydroxyl
684 groups which are consumed during HCHO oxidation, via the reaction of H_2O vapor and surface
685 active oxygen (O_2^- , O^-) (73,102). Wang et al. (18) noted that in the presence of 50% RH, H_2O
686 vapor react with surface active oxygen to generate enough surface hydroxyl groups to sustain
687 HCHO oxidation reaction at RT. H_2O vapor also helps in carbonates desorption from the catalyst's
688 surface via competitive adsorption, thereby enabling recovery of catalytic activity (73). Wang et
689 al. (73) indicated that RH in the range of 33% to 65% enhanced HCHO removal on birnessite
690 structured manganese at room temperature. However at higher RH (92%), catalytic activity was
691 impacted owing to competitive adsorption of H_2O molecules on the catalyst's surface. Similar
692 effects were observed with MnO_2/PET (18): at 0% RH significant deactivation was observed due
693 to the formation of formate species on the catalyst's surface; however at higher RH (50%), the
694 catalyst remained active and stable while activity significantly dropped when the RH was further

695 raised to 80% due to competitive adsorption of H₂O molecules. This conforms to the findings of
696 Sidheswaran et al. (97).

697 5.3 Feed flow rate and feed concentration

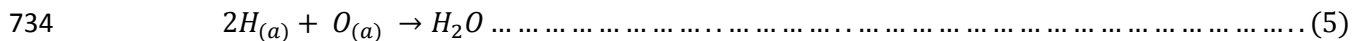
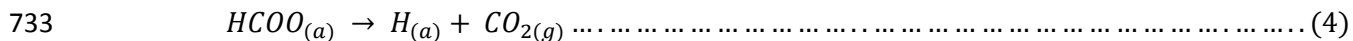
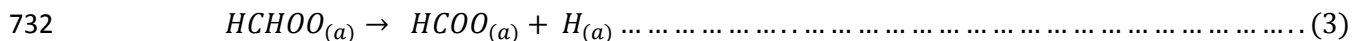
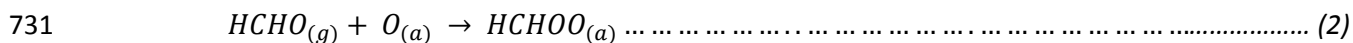
698 The significance of feed (reactants) flow rate in terms of gas hourly space velocity (GHSV) on
699 catalytic oxidation of HCHO was also reported in the literature. GHSV can improve the efficiency
700 of a fixed bed reaction system in two ways; at higher velocity, it will help to a certain extent in
701 enhancing external mass transfer while at a lower velocity it increases the residence time of
702 reactants in the reactor (52). It was however reported that the efficiency of HCHO oxidation
703 reactions decreases with increasing space velocity (39,69,70,101) and vice-versa. In view of
704 these, it could be insinuated that external mass transfer has little or no limitation on the efficiency
705 of HCHO oxidation reaction, although an experimental evaluation on external mass transfer effect
706 would be required.

707 In addition, HCHO feed concentration is another significant parameter for HCHO oxidation
708 process. HCHO oxidation efficiency tends to decrease with an increase in the feed concentration.
709 Chuang et al. (28) demonstrated that an increase in HCHO feed concentration led to a decrease in
710 conversion at the same reaction temperature. Likewise, Tang et al. (48) reported that catalytic
711 activity decreased with rise in HCHO feed concentration from 30 to 580 ppm and that the catalysts
712 were more active and stable at lower concentration. Correspondingly, Li et al. (98) pointed out that
713 MnO₂/AC completely lost its activity when exposed to 5 mg/m³ HCHO feed concentration in 32
714 hrs, compared to its sustained HCHO oxidation efficiency of up to 70% for 80 hrs under a HCHO
715 feed concentration of 0.5 mg/m³.

716 **6. Reaction mechanism of catalytic oxidation of HCHO**

717 Understanding the reaction mechanism of HCHO oxidation over transition metal based catalysts
718 is vital for the development of catalysts with high efficiency, low cost and good stability. Different
719 catalysts for HCHO oxidation may exhibit varying reaction mechanisms because different
720 intermediate species could be formed with various active oxygen species and surface active sites
721 (4). Oxidation reaction of HCHO over some transition metals based catalysts were shown to
722 conform to Mars-van Krevelen mechanism (18,19,97). In this mechanism, reaction proceeds via a
723 two-stage redox reaction with an assumption of constant surface oxygen. The catalyst's surface is
724 first oxidized by gas phase molecular oxygen to form surface adsorbed oxygen species which
725 subsequently reduces the pollutant (52).

726 Sekine (2) proposed that HCHO oxidation on metal oxides catalysts proceeds first by adsorption
727 on the catalyst's surface followed by decomposition through the formation of formate
728 intermediates on the surface, then the intermediates are subsequently decomposed to H₂O and CO₂
729 as presented in equations (2-5) where *g* and *a* indicate gaseous phase and adsorbed species,
730 respectively.



735 Tang et al. (86) indicated the oxidation of HCHO over MnO_x-CeO₂ catalyst was attained through
736 the effective transfer of oxygen species from CeO₂ oxygen reservoir to MnO₂ active state. This
737 synergy is achieved through the effective activation of feed molecular oxygen and the transfer of

738 the activated oxygen to replace the released active oxygen species from MnO_2 which participated
739 in HCHO oxidation through a series of redox cycles involving $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ (48,86)
740 as shown in Figure 8.

741 Wang et al. (73) proposed three-step mechanism for HCHO oxidation on birnessite structured
742 manganese catalyst at room temperature as presented in Figure 9. The reaction first proceeds
743 through H-bond between HCHO molecules and birnessite bonded H_2O molecules. The adsorbed
744 molecules are then oxidized to formate and carbonates by structural hydroxyl species.
745 Subsequently, the consumed hydroxyl ions are replaced through the reaction between surface
746 active oxygen and H_2O molecules. An oxygen vacancy is then formed on the site of the consumed
747 surface active oxygen species, which further acts as a site for molecular oxygen activation to active
748 species for continuous reaction (74). Wang et al. (68) reported that only hydrocarbonate species
749 were observed on the surface of 3D-Co-Mn catalysts with no obvious formation of formate species,
750 probably due to the fast conversion rate of formate to hydrocarbonates on the catalyst's surface as
751 suggested by the authors. The hydrocarbonate species were totally decomposed at 70°C as reported
752 by Shi et al. (95) for Co-Mn.

753 Shi et al. (95) indicated that the mechanism of HCHO oxidation over Co-Mn oxides proceeds via
754 the formation of DOM and formate species as intermediates. During adsorption process, HCHO is
755 immediately converted to DOM as no HCHO molecules were observed on the catalyst surface at
756 room temperature. The active DOM species react with surface adsorbed oxygen species to form
757 formate species and part of them are further oxidized to hydrocarbonates. At higher temperature
758 (50°C), further oxidation of formate and degradation of hydrocarbonate species occur. At the
759 complete oxidation temperature of HCHO (75°C), only adsorbed H_2O molecules were observed,
760 indicating complete oxidation of all the intermediate species. Hence, formate oxidation and

761 hydrocarbonate decomposition are considered as the rate-limiting steps for HCHO oxidation over
762 Co-Mn oxides catalyst.

763 A reaction mechanism for 2D ordered mesoporous Co_3O_4 , $\text{Au}/\text{Co}_3\text{O}_4$ and $\text{Au}/\text{Co}_3\text{O}_4\text{-CeO}_2$ at room
764 temperature had been proposed by Ma et al. (51) as depicted in Figure 10. In this mechanism,
765 formate species are first generated by the nucleophilic attack on the C-H in HCHO by surface
766 active oxygen on the (110) facet of Co_3O_4 (with Co^{3+} as the active state). The formate species are
767 further oxidized to bicarbonates by surface active oxygen species. Carbonic acid species are then
768 generated by the reaction of the bicarbonates and H^+ , which are subsequently decomposed to CO_2 .
769 In contrast, Fan et al. (67) indicated that hydroxyl groups were responsible for the immediate
770 oxidation of HCHO on the surface of Co_3O_4 and that DOM and formate species were observed as
771 the intermediates during the adsorption of HCHO on the catalyst's surface as previously reported
772 (95). However, the behavior of the catalysts at elevated temperature in the presence of O_2 was
773 influenced by the existence of K^+ ions on the catalyst's surface. In the presence of K^+ ions, DOM
774 species generated during the adsorption process are converted to formate species and formate
775 oxidation to bicarbonates becomes the key reaction step. It was proposed that hydroxyl groups
776 were generated from surface hydrolysis of K_2CO_3 and got consumed during the reaction. The
777 consumed hydroxyl groups were replenished by the H_2O molecules generated thus K_2CO_3 surface
778 hydrolysis was sustained and the reaction was accelerated. On the other hand, in the absence of
779 K_2CO_3 at elevated temperature (80°C) only few DOM species could be converted to formate
780 species due to the lack of hydroxyl groups on the surface of Co_3O_4 , thus formate decomposition to
781 carbonates and bicarbonates became the key reaction step at $\geq 80^\circ\text{C}$. Here it could be observed
782 that the existence of K^+ on the surface of Co_3O_4 changed the reaction path from formate
783 decomposition to formate oxidation and continued supply of surface hydroxyl group necessary for

784 the oxidation reaction was sustained by K_2CO_3 surface hydrolysis thus promoting HCHO
785 oxidation. Similar promotion effects of K^+ was observed for Ag/ Co_3O_4 (46), Na^+ for ceramic
786 honeycombs (103) and Na^+ for Pd/ TiO_2 (59).

787 Lu et al. (87) proposed a reaction pathway for HCHO over graphene- MnO_2 hybrid catalysts. In
788 this mechanism, HCHO is first oxidized to form formate intermediates while molecular oxygen is
789 activated and transferred to active Mn sites through Mn^{4+}/Mn^{3+} redox cycle. Graphene being an
790 electrical conductor reduces electron transfer resistance and enhances the rate of charge transfer
791 between Mn^{4+} and Mn^{3+} , thereby improving the overall efficiency of the process. Thereafter, due
792 to the abundant amount of surface hydroxyl groups on the hybrid catalyst, formate species were
793 directly converted to CO_2 and H_2O , while the consumed hydroxyl ions were regenerated by the
794 produced H_2O molecules as reported by other authors (67).

795 The reaction mechanism of HCHO catalytic oxidation is intricate and varies with the type and
796 amount of surface active oxygen or hydroxyl species present. But generally, formate species are
797 key intermediates present on almost all transition metal based catalysts. Other species such as
798 DOM and hydrocarbonates are also reported as intermediates for HCHO oxidation. However, the
799 reported pathways for HCHO decomposition varied in the literature. In some mechanisms DOM
800 species are first generated followed by their conversion to formate intermediates, which are
801 subsequently oxidized to hydrocarbonates and finally CO_2 and H_2O molecules are generated by
802 hydrocarbonate decomposition. In other mechanisms, no DOM species are observed and formates
803 are directly oxidized to CO_2 and H_2O especially in the presence of high amount of surface hydroxyl
804 groups (67,87). The reaction mechanism of transition metal based catalysts for HCHO oxidation
805 is minimally reported in the literature. This prompts the need for further elaborate investigation
806 into the mechanism on various active transition metals especially as it relates to the surface

807 properties of these catalysts, and the specific role of hydroxyl and oxygen species and the
808 promotional effects of alkali metals (Na^+ , K^+) on the overall efficiency of the reaction. This will
809 provide more information and offer the basis for the design of yet more active and cost-effective
810 catalysts for practical application.

811 **7. Conclusions and outlook**

812 Formaldehyde is one of the most harmful indoor air pollutants as it has adverse effects on human
813 health due to its toxicity and carcinogenicity. Techniques such as adsorption, photo-catalytic
814 oxidation and catalytic oxidation have been used in HCHO removal. Adsorption removal is limited
815 by the adsorption capacity of the adsorbents deployed and the hazard of HCHO desorption during
816 regeneration while photo-catalytic oxidation produces hazardous by-products. Catalytic oxidation
817 offsets these drawbacks and can achieve complete conversion of HCHO into CO_2 and H_2O
818 molecules without the formation of hazardous by-products.

819 Noble metal based catalysts exhibit excellent low and even room temperature HCHO oxidation
820 capabilities but their practical application is restricted by their cost and availability. Recent
821 investigations focus on the use of relatively cheap and abundant transition metals oxides and
822 improving their low temperature performance. More attention has mainly been focused on the
823 improvement and exploitation of various structures and morphologies of manganese oxide
824 catalysts due to its high activity yet with little attention on other transition metal catalysts. As such,
825 more investigation needs to be done on the improvement of morphological structures, textural and
826 redox properties of these materials.

827 For practical air purification application in air purifiers or building HVAC systems, substrate
828 materials with low air resistance and pressure drop are required to immobilize catalysts to avoid

829 dust contamination and catalysts leaching into treated air stream. However, only a few substrate
830 materials have been reported in the literature and hence the need for further evaluation of more
831 materials to understand their interactions with the catalysts and effect on activity for pragmatic air
832 purification process. In addition to the development of these materials, they need to be tested under
833 real indoor environmental conditions in air purifiers to evaluate the effects of system conditions
834 such as face velocity, dust particle contamination and particle leaching on the efficiency and
835 stability of the catalysts.

836 No single property is decisive for catalytic performance of transition metal oxides for complete
837 oxidation of HCHO but a combination of several factors which include specific surface area, metal
838 oxidation state, adsorbed and surface oxygen species, structure and morphology of the catalyst.
839 Improvement of the morphological structures of transition metal based catalysts relative to their
840 conventional bulk counterparts enhances their catalytic activity through improvement of specific
841 surface area, mesoporosity and exposure of surface active metals and oxygen species. The tunnel
842 structure of catalysts enhances the rate of adsorption of HCHO onto the active sites for
843 decomposition and the rate of product desorption from the sites to make them available for the
844 next molecules. This is particularly promoted when the catalyst's effective diameter is close to the
845 dynamic diameter of HCHO (55). Oxidation state of metals in the catalyst is also vital for
846 determining activity and higher oxidation states seem to be more active; Mn^{4+} in the case of
847 manganese and Co^{3+} in the case of cobalt were identified to be the most active states for HCHO
848 activation. Several methods have been proposed for improving the oxidation state of metal oxides
849 which include modified synthesis, controlling calcination temperature and the relative molar ratio
850 of component elements, to maintain solid solution stability in the case of composite catalysts (86).

851 The use of hard template materials has been proven effective in providing the plane structure for
852 improved exposure of more surface active sites and enhanced access to these sites.

853 Active surface oxygen and hydroxyl species directly participate in oxidizing HCHO molecules
854 and all other intermediate species into CO₂ and H₂O. The higher the concentration of these active
855 materials on the catalyst's surface the better its HCHO oxidative activity. The availability of
856 surface active oxygen species and the rate of molecular oxygen activation could be enhanced by
857 the formation of surface vacancy using dopants and formation of solid solution composites with
858 oxygen carrier materials. Recently reported works (80,81) indicated that creating oxygen surface
859 vacancy using dopants increases the activation rate of molecular oxygen to more active and
860 reactive oxygen species thereby providing more abundant oxygen species for HCHO oxidation.
861 However not much has been reported on surface vacancy creation and surface modification using
862 dopants on transition metal based catalyst for HCHO oxidation, thereby prompting the need for
863 further exploration. The use of oxygen carrier materials for composite formation on the other hand
864 improves the transfer rate of active oxygen from the rich oxygen sources of the carrier to the active
865 metal sites in a complete redox cycle. The formation of solid solution within the solubility limit of
866 the composite is critical to achieving synergistic effects either through oxygen transfer or oxygen
867 vacancy creation, above which phase segregation occurs and synergy is lost. Most of the reported
868 composites in the literature for HCHO oxidation focus on the use of CeO₂ as composite material
869 with little or no attention to other oxygen carriers.

870 Furthermore, enhancing the electrical conductivity of catalyst through the formation of hybrids or
871 composites with electrically conducting materials such as graphene (87) was shown to greatly
872 improve catalytic activity at low temperature. The hybrid system exposed more Mn⁴⁺ active sites,
873 enhanced charge transport during Mn redox cycle and offered higher content of surface hydroxyl

874 species, which eases HCHO oxidation and improves the catalyst's activity at low temperature.
875 However, very few studies have been reported for catalyst's electrical conductivity enhancement
876 using conductor materials for HCHO oxidation. Hence further investigation into the influence of
877 dopants and other conductor materials on the activity of transition metals based catalysts for
878 improved low temperature HCHO oxidation will be desirable. In addition to catalytic properties,
879 reaction parameters such as reaction temperature, relative humidity, space velocity and HCHO
880 feed concentration also affect the overall efficiency of HCHO oxidation. Relative humidity at
881 moderate levels helps in enhancing the availability of surface active hydroxyl groups via the
882 reaction of H₂O vapor and surface active oxygen but becomes detrimental at higher levels.

883 The reaction mechanism of HCHO is complex and depends on the type of catalysts, the oxidation
884 state and amount of active metals and the nature of surface active oxygen (adsorbed and or lattice)
885 present. Although further research is required to ascertain the respective role of each in HCHO
886 oxidation. Only a few mechanisms were reported for transition metal catalysts, as such further
887 investigation is required into the reaction mechanism especially as it relates to the catalyst's surface
888 properties and the role of surface active oxygen or hydroxyl species. But generally, formate
889 species, DOM and hydrocarbonates are the identified intermediates for HCHO oxidation on
890 transition metal based catalysts. However, the reported pathways for HCHO decomposition varied
891 in the literature. In some mechanisms DOM species are first generated followed by DOM
892 conversion to formate intermediates, which are subsequently oxidized to hydrocarbonates and
893 finally CO₂ and H₂O molecules are generated by hydrocarbonate decomposition. In other
894 mechanisms, no DOM species are observed and formates are directly oxidized to CO₂ and H₂O
895 molecules without the formation of hydrocarbonates especially in the presence of high amount of
896 surface hydroxyl groups.

897 **Acronyms**

898	1D	One Dimensional
899	2D	Two Dimensional
900	3D	Three Dimensional
901	3DOM	Three Dimensional Ordered Macroporous
902	AC	Activated Carbon
903	CTAB	Cetyltrimethylammonium Bromide
904	DOM	Dioxymethylene
905	GHSV	Gas Hourly Space Velocity
906	HCHO	Formaldehyde
907	HVAC	Heating Ventilation and Air Conditioning
908	IARC	International Agency for Research on Cancer
909	KIT-6	Korea Advanced Institute of Science and Technology-6
910	K-OMS-2	Potassium-Octahedral Molecular Seive-2
911	PET	Polyethylene Terephthalate
912	R	Specific Reaction Rate
913	Redox	Reduction-Oxidation
914	RH	Relative humidity
915	SBA-15	Santa Barbara Amorphous-15
916	TOF	Turnover Frequency
917	VOC	Volatile Organic Compounds
918	WHO	World Health Organization

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927 **References**

- 928 (1) Maddalena, R.; Russell, M.; Sullivan, D.P.; Apte, M.G. Formaldehyde and Other Volatile
929 Organic Chemical Emissions in Four FEMA Temporary Housing Units. *Environ. Sci. Technol.*
930 **2009**, *43* (15), 5626-5632.
931
- 932 (2) Sekine, Y. Oxidative decomposition of formaldehyde by metal oxides at room temperature.
933 *Atmos. Environ.* **2002**, *36* (35), 5543-5547.
934
- 935 (3) Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the Indoor Environment. *Chem. Rev.*
936 **2010**, *110* (4), 2536-2572.
937
- 938 (4) Bai, B.; Qiao, Q.; Li, J.; Hao, J. Progress in research on catalysts for catalytic oxidation of
939 formaldehyde. *Chin. J. Catal.* **2016**, *37* (1), 102-122.
940
- 941 (5) Sekine, Y.; Nishimura, A. Removal of formaldehyde from indoor air by passive type air-cleaning
942 materials. *Atmos. Environ.* **2001**, *35* (11), 2001-2007.
943
- 944 (6) International Agency for Cancer Research (IACR) working group on the identification of
945 Carcinogenic Risks to Humans. *Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol.*
946 WHO; Lyon France, 2006; volume 88.
947
- 948 (7) World Health Organization. *WHO guidelines for indoor air quality: selected pollutants*; WHO:
949 Copenhagen, 2010.
950
- 951 (8) Le, Y.; Guo, D.; Cheng, B.; Yu, J. Bio-template-assisted synthesis of hierarchically hollow SiO₂
952 microtubes and their enhanced formaldehyde adsorption performance. *Appl. Surf. Sci.* **2013**, *274*,
953 110-116.
954
- 955 (9) Chen, D.; Qu, Z.; Sun, Y.; Wang, Y. Adsorption-desorption behavior of gaseous formaldehyde
956 on different porous Al₂O₃ materials. *Colloids Surf., A* **2014**, *441* 433-440.
957
- 958 (10) Ma, C.; Li, X.; Zhu, T. Removal of low-concentration formaldehyde in air by adsorption on
959 activated carbon modified by hexamethylene diamine. *Carbon* **2011**, *49* (8), 2873-2875.
960
- 961 (11) Rezaee, A.; Rangkooy, H.; Jonidi-Jafari, A.; Khavanin, A. Surface modification of bone char for
962 removal of formaldehyde from air. *Appl. Surf. Sci.* **2013**, *286*, 235-239.
963
- 964 (12) Lu, Y.; Wang, D.; Ma, C.; Yang, H. The effect of activated carbon adsorption on the
965 photocatalytic removal of formaldehyde. *Build. Environ.* **2010**, *45* (3), 615-621.
966
- 967 (13) Tong, H.; Zhao, L.; Li, D.; Zhang, X. N, Fe and WO₃ modified TiO₂ for degradation of
968 formaldehyde. *J. Alloys Compd.* **2011**, *509* (22), 6408-6413.
969
- 970 (14) Fu, P.; Zhang, P.; Li, J. Photocatalytic degradation of low concentration formaldehyde and
971 simultaneous elimination of ozone by-product using palladium modified TiO₂ films under UV
972 254+ 185nm irradiation. *Appl. Catal., B* **2011**, *105* (1), 220-228.
973
- 974 (15) Liang, W.; Li, J.; Jin, Y. Photo-catalytic degradation of gaseous formaldehyde by TiO₂/UV,
975 Ag/TiO₂/UV and Ce/TiO₂/UV. *Build. Environ.* **2012**, *51*, 345.-350

- 976 (16) Ghosh, J.P.; Sui, R.; Langford, C.H.; Achari, G.; Berlinguette, C.P. A comparison of several
977 nanoscale photocatalysts in the degradation of a common pollutant using LEDs and conventional
978 UV light. *Water Res.* **2009**, *43* (18), 4499-4506.
979
- 980 (17) Shie, J.L.; Lee, C.H.; Chiou, C.S.; Chang, C.T.; Chang, C.C.; Chang, C.Y. Photodegradation
981 kinetics of formaldehyde using light sources of UVA, UVC and UVLED in the presence of
982 composed silver titanium oxide photocatalyst. *J. Hazard. Mater.* **2008**, *155* (1), 164-172.
983
- 984 (18) Wang, J.; Yunus, R.; Li, J.; Li, P.; Zhang, P.; Kim, J. In situ synthesis of manganese oxides on
985 polyester fiber for formaldehyde decomposition at room temperature. *Appl. Surf. Sci.* **2015**, *357*,
986 787-794.
987
- 988 (19) Zhang, J.; Li, Y.; Wang, L.; Zhang, C.; He, H. Catalytic oxidation of formaldehyde over
989 manganese oxides with different crystal structures. *Catal. Sci. Technol.* **2015**, *5* (4), 2305-2313.
990
- 991 (20) Luengas, A.; Barona, A.; Hort, C.; Gallastegui, G.; Platel, V.; Elias, A. A review of indoor air
992 treatment technologies. *Rev. Environ. Sci. Bio/Technol.* **2015**, *14* (3), 499-522.
993
- 994 (21) Chen, H.; He, J.; Zhang, C.; He, H. Self-assembly of novel mesoporous manganese oxide
995 nanostructures and their application in oxidative decomposition of formaldehyde. *J. Phys. Chem.*
996 *C* **2007**, *111* (49), 18033-18038.
997
- 998 (22) Zhang, C.; He, H. A comparative study of TiO₂ supported noble metal catalysts for the oxidation
999 of formaldehyde at room temperature. *Catal. Today* **2007**, *126* (3), 345-350.
1000
- 1001 (23) Zhang, C.; Liu, F.; Zhai, Y.; Ariga, H.; Yi, N.; Liu, Y.; Asakura, K.; Flytzani - Stephanopoulos,
1002 M.; He, H. Alkali- Metal- Promoted Pt/TiO₂ Opens a More Efficient Pathway to Formaldehyde
1003 Oxidation at Ambient Temperatures. *Angew. Chem., Int. Ed.* **2012**, *51* (38), 9628-9632.
1004
- 1005 (24) Huang, H.; Leung, D.Y. Complete elimination of indoor formaldehyde over supported Pt
1006 catalysts with extremely low Pt content at ambient temperature. *J. Catal.* **2011**, *280* (1), 60-67.
1007
- 1008 (25) Kim, S.S.; Park, K.H.; Hong, S.C. A study on HCHO oxidation characteristics at room
1009 temperature using a Pt/TiO₂ catalyst. *Appl. Catal., A* **2011**, *398* (1), 96-103.
1010
- 1011 (26) Yan, Z.; Xu, Z.; Yu, J.; Jaroniec, M. Enhanced formaldehyde oxidation on CeO₂/AlOOH-
1012 supported Pt catalyst at room temperature. *Appl. Catal., B* **2016**, *199*, 458-465.
1013
- 1014 (27) Nie, L.; Jianguo, Y.; Xinyang, L.; Bei, C.; Gang, L.; Mietek, J. Enhanced performance of NaOH-
1015 modified Pt/TiO₂ toward room temperature selective oxidation of formaldehyde. *Environ. Sci.*
1016 *Technol.* **2013**, *47* (6), 2777-2783.
1017
- 1018 (28) Chuang, K.T.; Zhou, B.; Tong, S. Kinetics and Mechanism of Catalytic Oxidation of
1019 Formaldehyde over Hydrophobic Catalysts. *Ind. Eng. Chem. Res.* **1994**, *33* (7), 1680-1686.
1020
- 1021 (29) An, N.; Zhang, W.; Yuan, X.; Pan, B.; Liu, G.; Jia, M.; Yan, W.; Zhang, W. Catalytic oxidation
1022 of formaldehyde over different silica supported platinum catalysts. *Chem. Eng. J. (Amsterdam,*
1023 *Neth.)* **2013**, *215*, 1-6.
1024

- 1025 (30) Peng, J.; Wang, S. Performance and characterization of supported metal catalysts for complete
1026 oxidation of formaldehyde at low temperatures. *Appl. Catal., B* **2007**, *73* (3), 282.
1027
- 1028 (31) Park, S.J.; Bae, I.; Nam, I.S.; Cho, B.K.; Jung, S.M.; Lee, J.H. Oxidation of formaldehyde over
1029 Pd/Beta catalyst. *Chem. Eng. J. (Amsterdam, Neth.)* **2012**, *195*, 392-402.
1030
- 1031 (32) de la Peña O'Shea, V. A.; Alvarex-Galvan, M.C; Fierro, J.L.; Arias, P. L. Influence of feed
1032 composition on the activity of Mn and PdMn/Al₂O₃ catalysts for combustion of
1033 formaldehyde/methanol. *Appl. Catal., B* **2005**, *57* (3), 191-199.
1034
- 1035 (33) Huang, H.; Leung, D.Y. Complete Oxidation of Formaldehyde at Room Temperature Using TiO₂
1036 Supported Metallic Pd Nanoparticles. *ACS Catal.* **2011**, *1* (4), 348-354.
1037
- 1038 (34) Mao, C.F.; Vannice, M. A. Formaldehyde Oxidation Over Ag Catalysts. *J. Catal.* **1995**, *154* (2),
1039 230-244.
1040
- 1041 (35) Qu, Z.; Shen, S.; Chen, D.; Wang, Y. Highly active Ag/SBA-15 catalyst using post-grafting
1042 method for formaldehyde oxidation. *J. Mol. Catal. A: Chem.* **2012**, *356*, 171-177.
1043
- 1044 (36) Tian, H.; He, J.; Liu, L.; Wang, D. Effects of textural parameters and noble metal loading on the
1045 catalytic activity of cryptomelane-type manganese oxides for formaldehyde oxidation. *Ceram.*
1046 *Int.* **2013**, *129* (1), 315-321.
1047
- 1048 (37) Li, H. F.; Zhang, N.; Chen, P.; Luo, M. F.; Lu, J. Q. High surface area Au/CeO₂ catalysts for low
1049 temperature formaldehyde oxidation. *Appl. Catal., B* **2011**, *110*, 279-285.
1050
- 1051 (38) Imamura, S.; Uchihori, D.; Utani, K.; Ito, T. Oxidative decomposition of formaldehyde on silver-
1052 cerium composite oxide catalyst *Catal. Lett.* **1994**, *24* (3-4), 377-384.
1053
- 1054 (39) An, N.; Yu, Q.; Liu, G.; Li, S.; Jia, M.; Zhang, W. Complete oxidation of formaldehyde at
1055 ambient temperature over supported Pt/Fe₂O₃ catalysts prepared by colloid-deposition method. *J.*
1056 *Hazard. Mater.* **2011**, *186* (2), 1392-1397.
1057
- 1058 (40) Shen, Y.; Yang, X.; Wang, Y.; Zhang, Y.; Zhu, H.; Gao, L.; Jia, M. The states of gold species in
1059 CeO₂ supported gold catalyst for formaldehyde oxidation. *Appl. Catal., B* **2008**, *79* (2), 142-148.
1060
- 1061 (41) Yu, X.; He, J.; Wang, D.; Hu, Y.; Tian, H.; He, Z. Facile Controlled Synthesis of Pt/MnO₂
1062 Nanostructured Catalysts and Their Catalytic Performance for Oxidative Decomposition of
1063 Formaldehyde. *J. Phys. Chem. C* **2011**, *116* (1), 851-860.
1064
- 1065 (42) Hu, P.; Amghouz, Z.; Huang, Z.; Xu, F.; Chen, Y.; Tang, X. Surface-Confined Atomic Silver
1066 Centers Catalyzing Formaldehyde Oxidation. *Environ. Sci. Technol.* **2015**, *49* (4), 2384-2390.
1067
- 1068 (43) Bai, B.; Qiao, Q.; Arandiyani, H.; Li, J.; Hao, J. Three-Dimensional Ordered Mesoporous MnO₂-
1069 Supported Ag Nanoparticles for Catalytic Removal of Formaldehyde. *Environ. Sci. Technol.*
1070 **2016**, *50* (5), 2635-2640.
1071
- 1072 (44) Zhang, J.; Jin, Y.; Li, C.; Shen, Y.; Han, L.; Hu, Z.; Di, X.; Liu, Z. Creation of three-
1073 dimensionally ordered macroporous Au/CeO₂ catalysts with controlled pore sizes and their
1074 enhanced catalytic performance for formaldehyde oxidation. *Appl. Catal., B* **2009**, *91* (1), 11-20.

- 1075 (45) Wang, R.; Li, J. OMS-2 Catalysts For Formaldehyde Oxidation: Effects of Ce And Pt on
1076 Structure And Performance of the Catalysts. *Catal. Lett.* **2009**, *131* (3-4), 500-505.
1077
- 1078 (46) Bai, B.; Li, J. Positive Effects of K⁺ Ions on Three-Dimensional Mesoporous Ag/Co₃O₄ Catalyst
1079 For HCHO Oxidation. *ACS Catal.* **2014**, *4* (8), 2753-2762.
1080
- 1081 (47) Ma, L.; Wang, D.; Li, J.; Bai, B.; Fu, L.; Li, Y. Ag/CeO₂ nanospheres: Efficient catalysts for
1082 formaldehyde oxidation. *Appl. Catal., B* **2014**, *148*, 36-43.
1083
- 1084 (48) Tang, X.; Chen, J.; Huang, X.; Xu, Y.; Shen, W. Pt/MnO_x-CeO₂ catalysts for the complete
1085 oxidation of formaldehyde at ambient temperature. *Appl. Catal., B* **2008**, *81* (1), 115-121.
1086
- 1087 (49) Tang, X.; Chen, J.; Li, Y.; Li, Y.; Xu, Y.; Shen, W. Complete oxidation of formaldehyde over
1088 Ag/MnO_x-CeO₂ catalysts. *Chem. Eng. J. (Amsterdam, Neth.)* **2006**, *118* (1), 119-125.
1089
- 1090 (50) Liu, B.; Liu, Y.; Li, C.; Hu, W.; Jing, P.; Wang, Q.; Zhang, J. Three-dimensionally ordered
1091 macroporous Au/CeO₂-Co₃O₄ catalysts with nanoporous walls for enhanced catalytic oxidation of
1092 formaldehyde. *Appl. Catal., B* **2012**, *127*, 47-58.
1093
- 1094 (51) Ma, C.; Wang, D.; Xue, W.; Dou, B.; Wang, H.; Hao, Z. Investigation of Formaldehyde
1095 Oxidation over Co₃O₄-CeO₂ and Au/Co₃O₄-CeO₂ Catalysts at Room Temperature: Effective
1096 Removal and Determination of Reaction Mechanism. *Environ. Sci. Technol.* **2011**, *45* (8), 3628-
1097 3634.
1098
- 1099 (52) Pei, J.; Zhang, J.S. Critical review of catalytic oxidization and chemisorption methods for indoor
1100 formaldehyde removal. *HVACR Res.* **2011**, *17* (4), 476-503.
1101
- 1102 (53) Quiroz, J.; Giraudon, J.M.; Gervasini, A.; Dujardin, C.; Lancelot, C.; Trentesaux, M.; Lamonier,
1103 J.F. Total Oxidation of Formaldehyde over MnO_x-CeO₂ Catalysts: The Effect of Acid Treatment.
1104 *ACS Catal.* **2015**, *5* (4), 2260-2269.
1105
- 1106 (54) Tian, H.; He, J.; Liu, L.; Wang, D.; Hao, Z.; Ma, C. Highly active manganese oxide catalysts for
1107 low-temperature oxidation of formaldehyde. *Microporous Mesoporous Mater.* **2012**, *151*, 397-
1108 402.
1109
- 1110 (55) Chen, T.; Dou, H.; Li, X.; Tang, X.; Li, J.; Hao, J. Tunnel structure effect of manganese oxides in
1111 complete oxidation of formaldehyde. *Microporous Mesoporous Mater.* **2009**, *122* (1), 270-274.
1112
- 1113 (56) Tian, H.; He, J.; Zhang, X.; Zhou, L.; Wang, D. Facile synthesis of porous manganese oxide K-
1114 OMS-2 materials and their catalytic activity for formaldehyde oxidation. *Microporous*
1115 *Mesoporous Mater.* **2011**, *138* (1), 118-122.
1116
- 1117 (57) Tasbihi, M.; Bendyna, J. K.; Notten, P. H. A Short Review on Photocatalytic Degradation of
1118 Formaldehyde. *J. Nanosci. Nanotechnol.* **2015**, *15* (9), 6386-6396.
1119
- 1120 (58) Chen, B.B.; Shi, C.; Crocker, M.; Wang, Y.; Zhu, A.M. Catalytic removal of formaldehyde at
1121 room temperature over supported gold catalysts. *Appl. Catal., B* **2013**, *132*, 245-255.
1122
- 1123 (59) Zhang, C.; Li, Y.; Wang, Y.; He, H. Sodium-Promoted Pd/TiO₂ for Catalytic Oxidation of
1124 Formaldehyde at Ambient Temperature. *Environ. Sci. Technol.* **2014**, *48* (10), 5816-5822.

- 1125 (60) Xu, Z.; Yu, J.; Jaroniec, M. Efficient catalytic removal of formaldehyde at room temperature
 1126 using AlOOH nanoflakes with deposited Pt. *Appl. Catal., B* **2015**, *163*, 306-312.
 1127
- 1128 (61) Li, D.; Yang, G.; Li, P.; Wang, J.; Zhang, P. Promotion of Formaldehyde Oxidation over Ag
 1129 Catalyst by Fe Doped MnO_x Support at Room Temperature. *Catal. Today* **2016**, *277*, 257-265.
 1130
- 1131 (62) Zhang, Y.; Shen, Y.; Yang, X.; Sheng, S.; Wang, T.; Adebajo, M. F.; Zhu, H. Gold catalysts
 1132 supported on the mesoporous nanoparticles composited of zirconia and silicate for oxidation of
 1133 formaldehyde. *J. Mol. Catal. A: Chem.* **2010**, *316*, 100-105.
 1134
- 1135 (63) Li, C., Shen, Y.; Jia, M.; Sheng, S.; Adebajo, M. O.; Zhu, H. Catalytic combustion of
 1136 formaldehyde on gold/iron-oxide catalysts. *Catal. Commun.* **2008**, *9* (3), 355-361.
 1137
- 1138 (64) Xu, Q.; Lei, W.; Li, X.; Qi, X.; Yu, J.; Liu, G.; Wang, J.; Zhang, P. Efficient Removal of
 1139 Formaldehyde by Nanosized Gold on Well-Defined CeO₂ Nanorods at Room Temperature.
 1140 *Environ. Sci. Technol.* **2014**, *48* (16), 9702-9708.
 1141
- 1142 (65) Chen, H.; Tang, M.; Rui, Z.; Ji, H. MnO₂ Promoted TiO₂ Nanotube Array Supported Pt Catalyst
 1143 for Formaldehyde Oxidation with Enhanced Efficiency. *Ind. Eng. Chem. Res.* **2015**, *54* (36),
 1144 8900-8907.
 1145
- 1146 (66) Chen, Y.; He, J.; Tian, H.; Wang, D.; Yang, Q. Enhanced formaldehyde oxidation on Pt/MnO₂
 1147 catalysts modified with alkali metal salts. *J. Colloid Interface Sci.* **2014**, *428*, 1-7.
 1148
- 1149 (67) Fan, Z.; Zhang, Z.; Fang, W.; Yao, X.; Zou, G.; Shangguan, W. Low-temperature catalytic
 1150 oxidation of formaldehyde over Co₃O₄ catalysts prepared using various precipitants. *Chin. J.*
 1151 *Catal.* **2016**, *37* (6), 947-954.
 1152
- 1153 (68) Wang, Y.; Zhu, A.; Chen, B.; Crocker, M.; Shi, C. Three-dimensional ordered mesoporous Co-
 1154 Mn oxide: A highly active catalyst for "storage-oxidation" cycling for the removal of
 1155 formaldehyde. *Catal. Commun.* **2013**, *36*, 52.
 1156
- 1157 (69) Xia, Y.; Dai, H.; Zhang, L.; Deng, J.; He, H.; Au, C.T. Ultrasound-assisted nanocasting
 1158 fabrication and excellent catalytic performance of three-dimensionally ordered mesoporous
 1159 chromia for the combustion of formaldehyde, acetone and methanol. *Appl. Catal., B* **2010**, *100*
 1160 (1), 229-237.
 1161
- 1162 (70) Bai, B.; Arandiyani, H.; Li, J. Comparison of the performance for oxidation of formaldehyde on
 1163 nano-Co₃O₄, 2D-Co₃O₄, and 3D-Co₃O₄ catalysts. *Appl. Catal., B* **2013**, *142*, 677-683.
 1164
- 1165 (71) Dai, Z.; Yu, X.; Huang, C.; Li, M.; Su, J.; Guo, Y.; Xu, H.; Ke, Q. Nanocrystalline MnO₂ on an
 1166 activated carbon fiber for catalytic formaldehyde removal. *RSC Adv.* **2016**, *6* (99), 97022-97029.
 1167
- 1168 (72) Feng, Q.; Kanoh, H.; Ooi, K. Manganese oxide porous crystals. *J. Mater. Chem.* **1999**, *9* (2), 319-
 1169 333.
 1170
- 1171 (73) Wang, J.; Zhang, P.; Li, J.; Jiang, C.; Yunus, R.; Kim, J. Room-Temperature Oxidation of
 1172 Formaldehyde by Layered Manganese Oxide: Effect of Water. *Environ. Sci. Technol.* **2015**, *49*
 1173 (20), 12372-12379.

- 1174 (74) Wang, J.; Li, J.; Jiang, C.; Zhou, P.; Zhang, P.; Yu, J. The effect of manganese vacancy in
1175 birnessite-type MnO₂ on room-temperature oxidation of formaldehyde in air. *Appl. Catal., B*
1176 **2017**, *204*, 147-155.
1177
- 1178 (75) Wang, J.; Zhang, G.; Zhang, P. Layered birnessite-type MnO₂ with surface pits for enhanced
1179 catalytic formaldehyde oxidation activity. *J. Mater. Chem. A* **2017**, *5* (12), 5719.
1180
- 1181 (76) Bai, B.; Qiao, Q.; Li, J.; Hao, J. Synthesis of three dimensional ordered mesoporous MnO₂ and
1182 its catalytic performance in formaldehyde oxidation. *Chin. J. Catal.* **2016**, *37*, 27-31.
1183
- 1184 (77) Zhou, L.; Zhang, J.; He, J.; Hu, Y.; Tian, H. Control over the morphology and structure of
1185 manganese oxide by tuning reaction conditions and catalytic performance for formaldehyde
1186 oxidation. *Mater. Res. Bull.* **2011**, *46* (10), 1714-1722.
1187
- 1188 (78) Wu, Y.; Ma, M.; Zhang, B.; Gao, Y.; Lu, W.; Guo, Y. Controlled synthesis of porous Co₃O₄
1189 nanofibers by spiral electrospinning and their application for formaldehyde oxidation. *RSC Adv.*
1190 **2016**, *6*, 102127-102133.
1191
- 1192 (79) Zeng, L.; Li, K.; Huang, F.; Zhu, X.; Li, H. Effects of Co₃O₄ nanocatalyst morphology on CO
1193 oxidation: Synthesis process map and catalytic activity. *Chin. J. Catal.* **2016**, *37*, 908-922.
1194
- 1195 (80) Huang, Y.; Long, B.; Tang, M.; Rui, Z.; Balogun, M.S.; Tong, Y.; Ji, H. Bifunctional catalytic
1196 material: An ultrastable and high-performance surface defect CeO₂ nanosheets for formaldehyde
1197 thermal oxidation and photocatalytic oxidation. *Appl. Catal., B* **2016**, *181*, 779-787.
1198
- 1199 (81) Zeng, L.; Song, W.; Li, M.; Zeng, D.; Xie, C. Catalytic oxidation of formaldehyde on surface of
1200 H TiO₂/H C TiO₂ without light illumination at room temperature. *Appl. Catal., B* **2014**, *147*,
1201 490-498.
1202
- 1203 (82) Zhou, L.; He, J.; Zhang, J.; He, Z.; Hu, Y.; Zhang, C.; He, H. Facile In-Situ Synthesis of
1204 Manganese Dioxide Nanosheets on Cellulose Fibers and their Application in Oxidative
1205 Decomposition of Formaldehyde. *J. Phys. Chem. C* **2011**, *15* (34), 16873-16878.
1206
- 1207 (83) Imamura, S.; Shono, M.; Okamoto, N.; Hamada, A.; Ishida, S. Effect of cerium on the mobility of
1208 oxygen on manganese oxides. *Appl. Catal., A* **1996**, *142* (2), 279-288.
1209
- 1210 (84) Luo, M. F.; Ma, J. M.; Lu, J. Q.; Song, Y. P.; Wang, Y.J. High-surface area CuO–CeO₂ catalysts
1211 prepared by a surfactant-templated method for low-temperature CO oxidation. *J. Catal.* **2007**, *246*
1212 (1), 52-59.
1213
- 1214 (85) Ding, Z.Y.; Li, L.; Wade, D.; Gloyna, E.F. Supercritical water oxidation of NH₃ over a
1215 MnO₂/CeO₂ catalyst *Ind. Eng. Chem. Res.* **1998**, *37* (5), 1707-1716.
1216
- 1217 (86) Tang, X.; Li, Y.; Huang, X.; Xu, Y.; Zhu, H.; Wang, J.; Shen, W. MnO_x–CeO₂ mixed oxide
1218 catalysts for complete oxidation of formaldehyde: effect of preparation method and calcination
1219 temperature. *Appl. Catal., B* **2006**, *62* (3), 265-273.
1220
- 1221 (87) Lu, L.; Tian, H.; He, J.; Yang, Q. Graphene–MnO₂ Hybrid Nanostructure as a New Catalyst for
1222 Formaldehyde Oxidation. *J. Phys. Chem. C* **2016**, *120* (41), 23660-23668.
1223

- 1224 (88) Lou, Y.; Cao, X.-M.; Lan, J.; Wang, L.; Dai, Q.; Guo, Y.; Ma, J.; Zhao, Z.; Guo, Y.; Hu, P.; Lu,
1225 G. Ultralow-temperature CO oxidation on an In₂O₃-Co₃O₄ catalyst: a strategy to tune CO
1226 adsorption strength and oxygen activation simultaneously. *Chem. Commun. (Cambridge, U.K.)*
1227 **2014**, 50 (52), 6835-6838.
1228
- 1229 (89) Wang, Z.; Pei, J.; Zhang, J. Catalytic oxidization of indoor formaldehyde at room temperature–
1230 Effect of operation conditions. *Build. Environ.* **2013**, 65, 49-57.
1231
- 1232 (90) Wen, Y.; Tang, X.; Li, J.; Hao, J.; Wei, L.; Tang, X. Impact of synthesis method on catalytic
1233 performance of MnO_x-SnO₂ for controlling formaldehyde emission. *Catal. Commun.* **2009**, 10
1234 (8), 1157-1160.
1235
- 1236 (91) Bai, L.; Wyrwalski, F.; Lamonier, J.F.; Khodakov, A.Y.; Monflier, E.; Ponchel, A. Effects of β-
1237 cyclodextrin introduction to zirconia supported-cobalt oxide catalysts: From molecule-ion
1238 associations to complete oxidation of formaldehyde. *Appl. Catal., B* **2013**, 138, 381-390.
1239
- 1240 (92) Xuesong, L.; Jiqing, L.; Kun, Q.; Huang, W; Mengfei, L. A comparative study of formaldehyde
1241 and carbon monoxide complete oxidation on MnO_x-CeO₂ catalysts. *J. Rare Earths* **2009**, 27 (3),
1242 418-424.
1243
- 1244 (93) Li, J.W.; Pan, K.L.; Yu, S.J.; Yan, S.Y.; Chang, M.B. Removal of formaldehyde over Mn_xCe_{1-x}
1245 O₂ catalysts: Thermal catalytic oxidation versus ozone catalytic oxidation *J. Environ. Sci.* **2014**,
1246 26, 2546-2553.
1247
- 1248 (94) Zhu, L.; Wang, J.; Rong, S.; Wang, H.; Zhang, P. Cerium modified birnessite-type MnO₂ for
1249 gaseous formaldehyde oxidation at low temperature. *Appl. Catal., B* **2017**, 211, 212-221.
1250
- 1251 (95) Shi, C.; Wang, Y.; Zhu, A.; Chen, B.; Au, C. Mn_xCo_{3-x}O₄ solid solution as high-efficient
1252 catalysts for low-temperature oxidation of formaldehyde. *Catal. Commun.* **2012**, 28, 18-22.
1253
- 1254 (96) Lu, S.; Li, K.; Huang, F.; Chen, C.; Sun, B. Efficient MnO_x-Co₃O₄-CeO₂ catalysts for
1255 formaldehyde elimination. *Appl. Surf. Sci.* **2017**, 400, 277-282.
1256
- 1257 (97) Sidheswaran, M. A.; Destailhats, H.; Sullivan, D. P.; Larsen, J.; Fisk, W. J. Quantitative room-
1258 temperature mineralization of airborne formaldehyde using manganese oxide catalysts. *Appl.*
1259 *Catal., B* **2011**, 107 (1), 34-41.
1260
- 1261 (98) Li, J., Zhang, P., Wang, J. and Wang, M. Birnessite-Type Manganese Oxide on Granular
1262 Activated Carbon for Formaldehyde Removal at Room Temperature. *J. Phys. Chem. C* **2016**, 120
1263 (42), 24121-24129.
1264
- 1265 (99) Bai, B.; Li, J; Hao, J. 1D-MnO₂, 2D-MnO₂ and 3D-MnO₂ for low-temperature oxidation of
1266 ethanol. *Appl. Catal., B* **2015**, 164, 241-250.
1267
- 1268 (100) Sun, Y.; Zhang, W.; Li, D.; Gao, L.; Hou, C.; Zhang, Y.; Liu, Y. Facile synthesis of
1269 MnO₂/rGO/Ni composite foam with excellent pseudocapacitive behavior for supercapacitors. *J.*
1270 *Alloys Compd.* **2015**, 649, 579-584.
1271
- 1272 (101) Zhang, C.; He, H.; Tanaka, K.I. Catalytic performance and mechanism of a Pt/TiO₂ catalyst for
1273 the oxidation of formaldehyde at room temperature. *Appl. Catal., B* **2006**, 65 (1), 37-43.
1274

- 1275 (102) Chen, B.B.; Zhu, X. B.; Crocker, M.; Wang, Y.; Shi, C. FeO x-supported gold catalysts for
1276 catalytic removal of formaldehyde at room temperature. *Appl. Catal., B* **2014**, *154*, 73-81.
1277
- 1278 (103) Yu, J.; Li, X.; Xu, Z.; Xiao, W. NaOH-Modified Ceramic Honeycomb with Enhanced
1279 Formaldehyde Adsorption and Removal Performance. *Environ. Sci. Technol.* **2013**, *47* (17),
1280 9928-9933.