

Metal organic framework MIL-101(Cr) for dehydration reactions

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Abstract. Porous chromium terephthalate MIL-101 (Cr-MIL-101) has been prepared by direct method under hydrothermal conditions and characterized using X-ray diffraction, N₂ sorption, TGA and FT-IR. The nitrogen adsorption–desorption isotherm shows that the Cr-MIL-101 possesses BET specific surface area of 2563 m²/g. Catalytic performance of Cr-MIL-101 in the dehydration of 1,4-butanediol and 1-phenylethanol is assessed under vapour phase conditions in the temperature range of 513–533 K and time on stream (TOS) at 513 K. Cr-MIL-101 demonstrates superior catalytic activity with conversion of 95% of 1-phenylethanol. Moreover, high surface area and nanocages with coordinated unsaturated sites of Cr-MIL-101 have allowed us to attain higher dehydrated products selectivity than Cr-supported activated carbon (Cr/AC), amberlyst-15 and HZSM-5 catalysts.

Keywords. Cr-MIL-101; 1,4-butanediol; 1-phenylethanol; dehydration reaction

1. Introduction

Porous metal organic frameworks (MOFs) are of significant interest both in academics and industry due to their coordination structure, diverse topologies and potential applications in gas storage, separation, catalysis and drug delivery.¹ MOFs possess unique two or three dimensional structures formed by the self-assembly of metal ions or metal clusters (the connectors) are bridged with polytopic organic ligands as linkers, which allows the design of specific nanometer-scale framework geometries with pore structures. In particular, the coordinated unsaturated sites in MOFs play an important role in catalysis as metals or cations are Lewis acidic centres and the organic linkers or anions are Lewis-basic centres. Although, MOFs are currently of great interest in many research areas, catalytic applications of these materials have not been explored much. Recently, the heterometallic [Cu(II)/Fe(II)]-coordinated polymer has been reported for catalytic reactions; however, the catalyst dissolved partially in the employed reaction conditions. Among many other MOFs with one and two-dimensional structures, the porous chromium(III) terephthalate, Cr-MIL-101 has a rigid zeolite crystal structure with two types of quasi-spherical cages limited by 12 pentagonal faces for the smaller and 16 faces

(12 pentagonal and 4 hexagonal) and pore diameter is close to 29 and 34 Å. In Cr-MIL-101, two coordinated unsaturated sites in trimeric Cr(III) octahedral cluster are formed after heating two water molecules at 423 K in air, which act as Lewis acidic site or catalytic active site in organic transformation reactions.^{2–4} In recent years, synthesis of fine, specialty chemicals and their derivatives have rapidly garnered tremendous interest as these products provide access to various synthetic intermediates. In particular, tetrahydrofuran (THF) has been used as a one of the important solvents in organic reactions, as precursor for polyurethane, elastic fibres; however, traditionally it is synthesized from maleic anhydride and its derivatives by hydrogenation over bimetallic Pd-Re-based catalysts.^{5–7} Moreover, La₂O₃, Nd₂O₃, ZrO₂, ZSM-5, Y-Zeolite, mordenite, ferrierite, amorphous silica and γ -alumina have been employed as catalysts for the preparation of THF from 1,4-butanediol by cyclodehydration; but, the yields were less than 70%.^{8,9} On the other hand, dehydration of 1-phenylethanol is one of the industrial important reactions to obtain styrene, which is one of the raw materials for polymers, and plastics.^{10,11} Dehydration reaction in gas phase has been carried out over solid acid catalysts such as silica gel, alumina, alkali alumina, aluminum silicates and H-type synthetic zeolites and metal oxide catalysts such as titanium, thorium or aluminum oxide.^{12–15} Chromium-based catalysts were used for the transformation of alkyl aromatic to aromatic ketones

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and acids in homogenous medium; however, excess usage of chromium catalyst has adverse effect on environment due to toxic nature of chromium.¹⁶ Therefore, in recent years, considerable attention has been paid to development of chromium-based heterogeneous catalysts for wide variety of organic transformation such as oxidation of aromatic, dehydrogenation, epo-oxidation of olefins and allylic oxidation reactions.^{17–20} To the best of our knowledge, there are no reports available on dehydration of 1,4-butanediol and 1-phenylethanol reactions over Cr-MIL-101 catalyst. In the present study, cyclodehydration of 1,4-butanediol and dehydration of 1-phenylethanol over Cr-MIL-101 and 35 wt% Cr/AC catalysts have been studied. In addition, effect of temperature and time on stream (TOS) on product selectivity and conversion are systematically investigated.

2. Experimental

2.1 Preparation of chromium terephthalate (Cr-MIL-101)

Cr-MIL-101 was prepared by the hydrothermal reaction of 1,4-benzene dicarboxylic acid (1 mmol) with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mmol), hydrofluoric acid (1 mmol), and H_2O (265 mmol) at 493 K for 8 h. After cooling, unreacted carboxylic acid is removed by solvothermal method at 353 K for 24 h using 95% ethanol and 1M NH_4F solution at 343 K for 24 h.

2.2 Preparation of 35 wt% Cr/AC

Activated carbon (M/S Norit, with surface area $\sim 1000 \text{ m}^2 \text{ g}^{-1}$) has been purified by a sequential treatment with conc. HNO_3 , NH_3 solution and distilled water followed by drying at 383 K for 10 h.²¹ Later, 35 wt% Cr/AC was prepared by impregnation of aqueous solution of chromium nitrate nonahydrate on activated carbon. The resultant material was dried at 383 K followed by calcination at 823 K in presence of nitrogen for 5 h.

2.3 Characterizations

Structural order of the prepared materials were determined using Rigaku Ultima-IV Powder X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) analysis of the samples was performed with Perkin Elmer Spectrum GX FT-IR spectrometer using KBr discs, in the range of $4000\text{--}400 \text{ cm}^{-1}$. Nitrogen adsorption–desorption isotherms were determined by the Quantachrome Quadrasorb-SI at 77 K. Prior to measurement,

the samples were degassed at 423 K to remove guest water molecules. Specific surface area was calculated using the Brunauer–Emmet–Teller (BET) method in the P/P_0 range of 0.05–0.3. Average pore size determined from the isotherm and total pore volume is taken by a single point method at $P/P_0 = 0.99$. Thermogravimetric analysis was used to determine the thermal stability of materials on TGA Q500A analyser with heating rate of $10^\circ\text{C}/\text{min}$ in argon flow.

2.4 Catalyst activity

The catalytic activity study was carried over Cr-MIL-101 and 35 wt% Cr/AC catalysts for dehydration of 1,4-butanediol and 1-phenylethanol in the temperature ranges of 513–533 K and 498–523 K in a fixed bed reactor. The products were collected in ice cold trap and analysed by HP 6890 series gas chromatography having flame ionization detector, using OVI-101 capillary column (0.32 i.d 30 m length and $0.25 \mu\text{m}$ film thickness). The obtained products are further confirmed by Shimadzu GCMS-QP 5050A on ZB-Wax capillary column (30 m length, 0.53 mm id and $0.25 \mu\text{m}$ film thickness).

3. Results and discussion

The powder X-ray diffraction patterns of chromium terephthalate (Cr-MIL-101) shown in figure 1, indicate well-resolved diffraction reflection of (022), (113), (115), (228) and (357) corresponding to cubic structure.²² Intensity of the used catalyst increases due to deposition of unreacted reactants on the catalyst surface from the reaction mixture, which confirms that

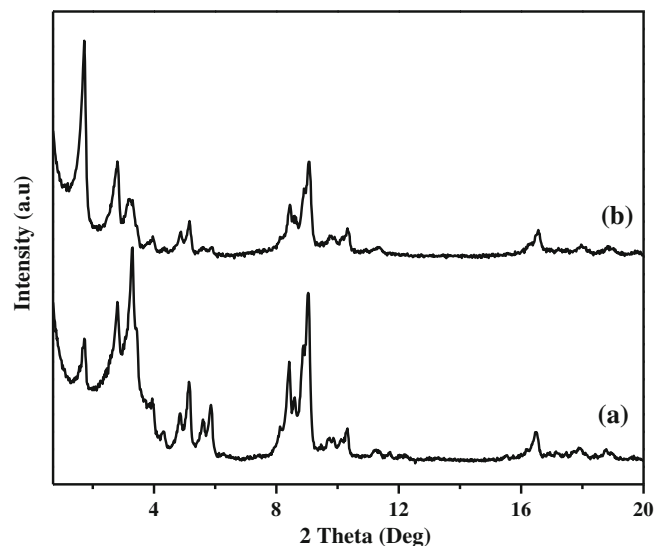


Figure 1. XRD patterns of Cr-MIL-101 (a) fresh and (b) used catalysts.

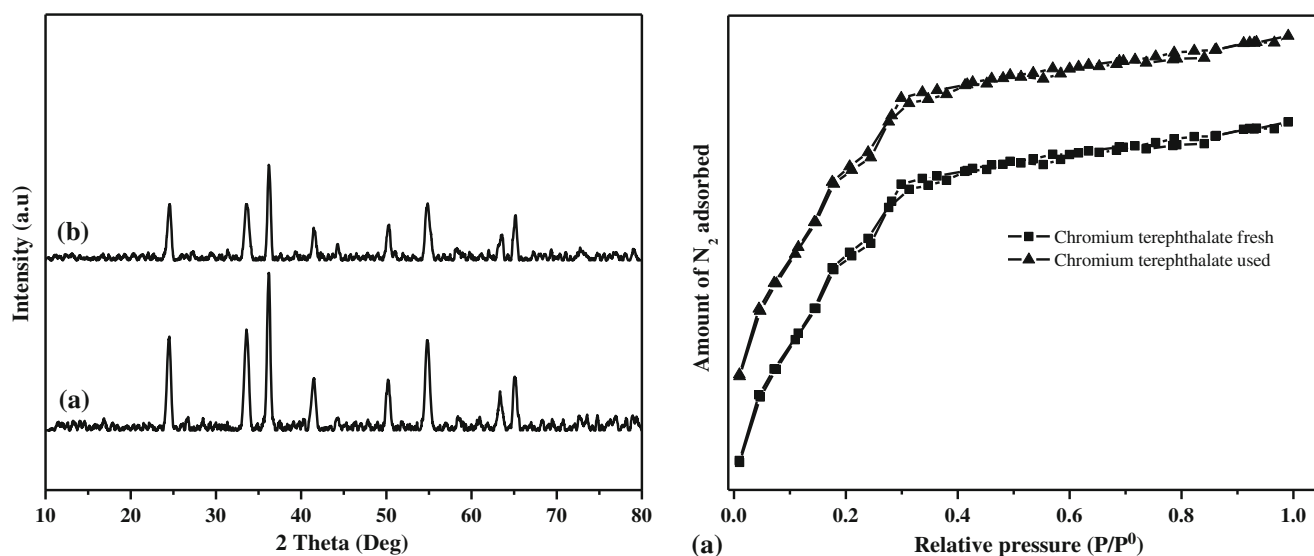


Figure 2. XRD pattern of 35 wt% Cr/AC (a) fresh and (b) used catalysts.

the structural order was intact after the reaction.²³ The diffraction pattern in figure 2 shows reflections that match well with rhombohedral chromium oxide (CAS No: 85-0730). There is no change in the crystallinity of used catalyst of 35 wt% Cr/AC (figure 2b). Textural properties of Cr-MIL-101, activated carbon (AC), 35 wt% Cr/AC of fresh and used catalysts obtained from nitrogen adsorption–desorption isotherm are summarized in table 1. The specific surface area and pore volume of as-synthesized Cr-MIL-101 which are $2563 \text{ m}^2 \text{ g}^{-1}$ and $1.44 \text{ cm}^3 \text{ g}^{-1}$, respectively; decrease to $2019 \text{ m}^2 \text{ gm}^{-1}$ and $1.19 \text{ cm}^3 \text{ gm}^{-1}$ due to formation of coke on the surface of catalyst (figure 3a). Similarly, in case of 35 wt% Cr/AC, specific surface area and pore volume of as-synthesized are $375 \text{ m}^2 \text{ g}^{-1}$ and $0.29 \text{ cm}^3 \text{ g}^{-1}$, decrease to $288 \text{ m}^2 \text{ g}^{-1}$ and $0.21 \text{ cm}^3 \text{ g}^{-1}$, respectively, which are lower than the specific surface area ($905 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.55 \text{ cm}^3 \text{ g}^{-1}$) of AC due to pore blocking by chromia (figure 3b). FT-IR pattern of Cr-MIL-101 is shown in figure 4. The

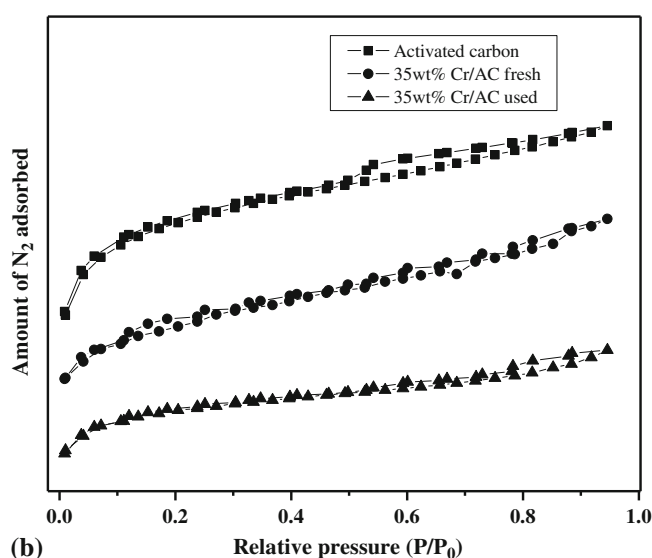


Figure 3. N_2 adsorption studies of (a) Cr-MIL-101 and (b) 35 wt% Cr/AC catalysts.

band at 1403 cm^{-1} corresponds to symmetric vibrations (O-C-O) of dicarboxylate in the framework. On the other hand, stretching and bending vibration bands corresponding to benzene ring are observed at $1600\text{--}600 \text{ cm}^{-1}$.²⁴ Thermogravimetric analyses of

Table 1. Textural properties of Cr-MIL-101, AC and 35 wt% Cr/AC.

Catalysts	Surface area ^a ($\text{m}^2 \text{ g}^{-1}$)	Average pore size ^b (n. m)	Pore volume ^c ($\text{cm}^3 \text{ g}^{-1}$)
Cr-MIL-101 (fresh)	2563	2.25	1.44
Cr-MIL-101 (used)	2019	2.36	1.19
Activate carbon (AC)	905	2.43	0.55
35 wt% Cr/AC (fresh)	375	3.09	0.29
35 wt% Cr/AC (used)	288	2.92	0.21

^aBET method

^bBJH method

^cAt P/P_0 of 0.99

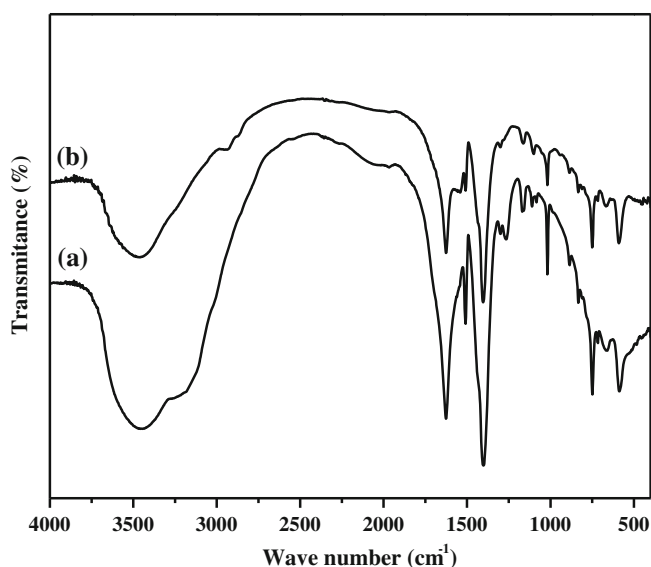


Figure 4. FT-IR analysis of Cr-MIL-101, (a) fresh and (b) used catalyst

Cr-MIL-101 and 35 wt% Cr/AC are depicted in figure 5. Removal of guest water molecules at 323–373 K and elimination of OH/F groups at 523–673 K for Cr-MIL-101 are observed, which leads to decomposition of the framework.^{25,26} However, in the case of 35 wt% Cr/AC, weight loss in the range of 373–473 K indicates decomposition of nitrate group leading to formation of Cr₂O₃ on AC.

The vapour phase cyclodehydration of 1, 4-butanediol has been studied over Cr-MIL-101 and 35 wt% Cr/AC catalysts in the temperature range of 513–523 K (scheme 1). Cr-MIL-101 shows highest conversion of 99% of 1,4-butanediol at 513 K with 100% selectivity

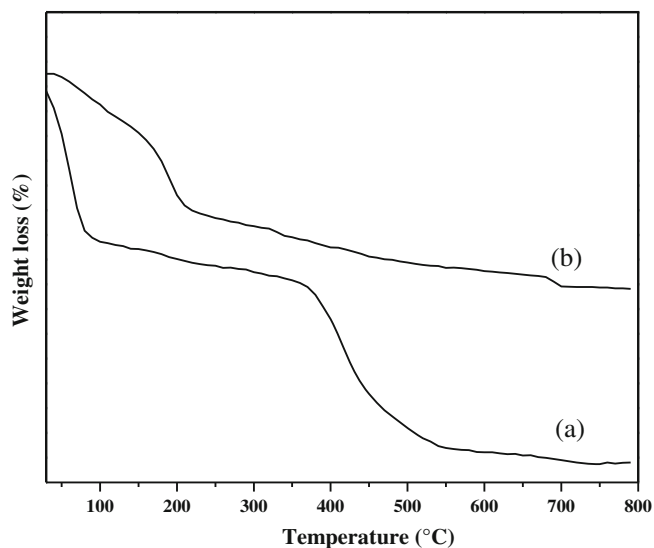
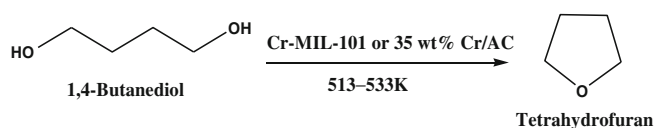


Figure 5. TGA analysis of (a) Cr-MIL-101 and (b) 35 wt% Cr/AC catalysts.



Scheme 1. Cyclodehydration of 1, 4-butanediol to tetrahydrofuran.

of tetrahydrofuran (THF). However, conversion of 1,4-butanediol is only 28% when 35 wt% Cr/AC is used as a catalyst (figure 6). Catalytic activity of Cr-MIL-101 and 35 wt% Cr/AC is compared with various rare earth metal oxides and the results are summarized in table 2.^{27–31} The lowest conversion of 1,4-butanediol (40.3%) and selectivity of THF (2.7%) was reported over Yb₂O₃ among all other rare earth metal oxides due to higher basic nature of the catalyst. Decrease in number of acidic site with loading of 1.5 mol% of Na in ZrO₂ resulted in increase in selectivity of 3-buten-1-ol. Cyclodehydration of 1,4-butanediol at temperature of 698 K shows 73.4% of conversion and 7.4% selectivity of THF and formation of by products such as 3-buten-1-ol and 1,3-butadiene over CeO₂ due to redox properties of the catalyst. The above results clearly confirm that Cr-MIL-101 shows superior catalytic activity over 35 wt% Cr/AC and other rare earth metal oxide catalysts due to presence of coordinated unsaturated chromium sites in Cr-MIL-101 catalyst. Interestingly, TOS results in figure 7 indicates there is no loss in catalytic activity and selectivity in THF for 10 h over Cr-MIL-101 catalyst.

On the other hand, catalytic activity of Cr-MIL-101 and 35 wt% Cr/AC has also been tested for dehydration

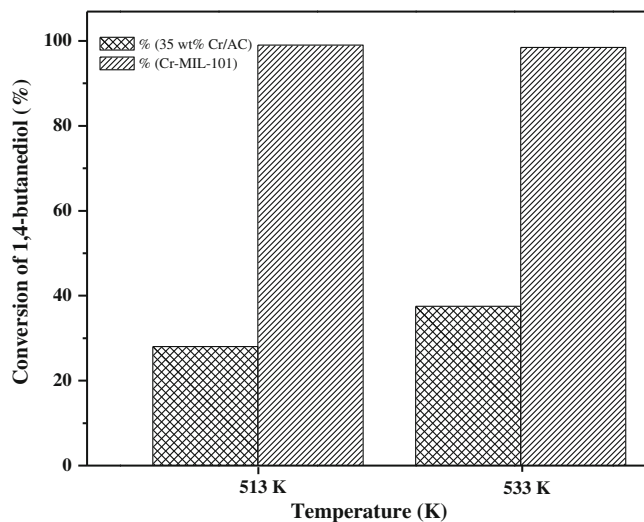
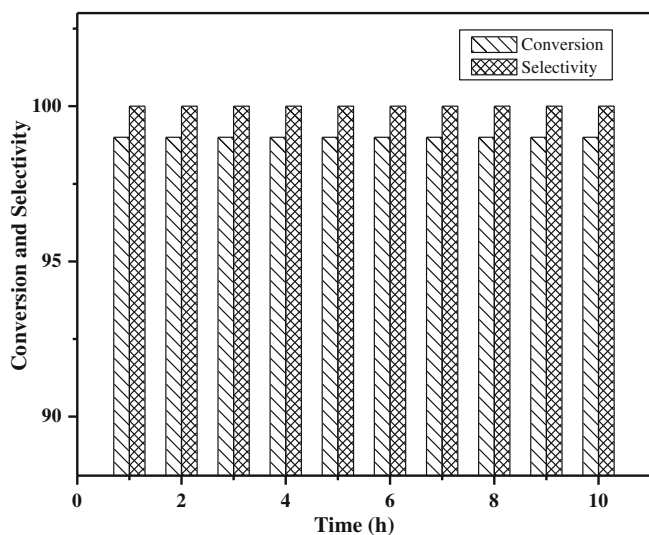
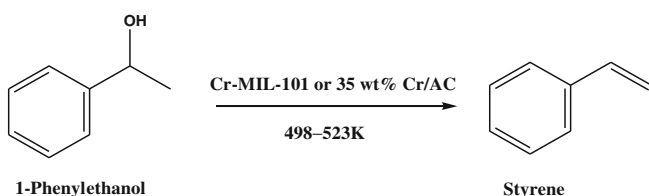
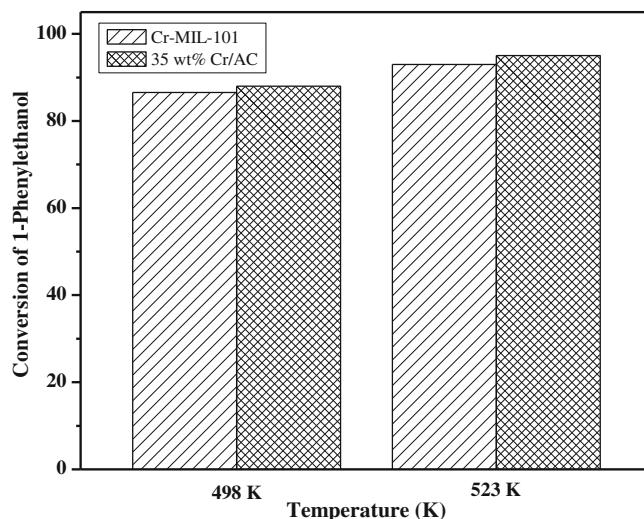
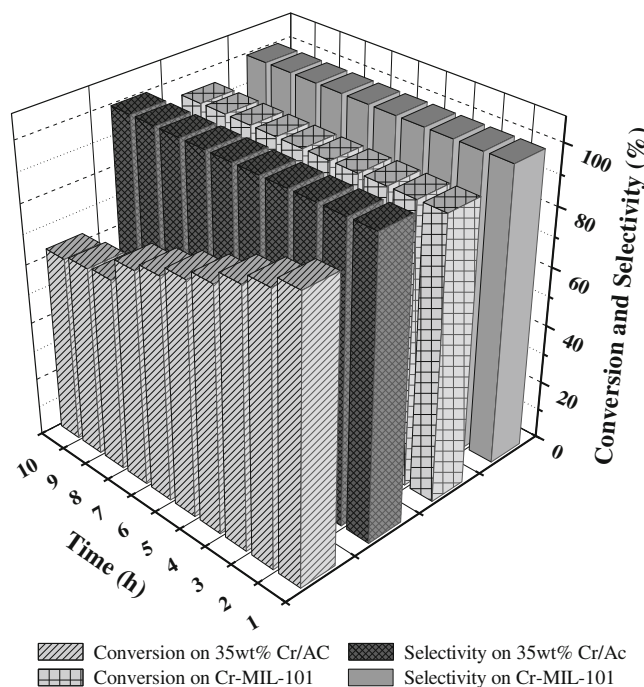


Figure 6. Effect of temperature on cyclodehydration of 1, 4-butanediol using Cr-MIL-101 and 35 wt% Cr/AC.

Table 2. Comparison of Cr-MIL-101 with literature reported catalysts in cyclodehydration of 1,4-butanediol over various oxide catalysts.

Catalyst	Temperature (K)	Con. (%)	Selectivity			References
			THF	3-Buten-1-ol	Others	
10 wt% La/ZrO ₂	598	94.4	65.9	34.1	0.0	27
Yb ₂ O ₃	648	40.3	2.7	81.7	15.6	28
ZrO ₂	623	86.4	44.9	48.0	7.1	29
Na-ZrO ₂	648	90.1	28.0	62.1	9.9	30
CeO ₂	698	73.4	7.4	55.8	36.8	31
Cr-MIL101	513	99	100	-	-	Present study
35 wt% Cr/AC	513	28	100	-	-	Present study

of 1-phenylethanol in the temperature range of 498–523 K (scheme 2). Figure 8 shows the effect of temperature on 1-phenylethanol conversion over Cr-MIL-101 and 35 wt% Cr/AC. Although, maximum selectivity is obtained for both the catalysts, conversion of 1-phenylethanol over 35% Cr/AC is 95% at 523 K, which is slightly higher than conversion obtained over Cr-MIL-101 catalyst. However, the TOS activity studies for 10 h indicate that decrease in 1-phenylethanol conversion from 93% to 63% is observed over 35% Cr/AC, due to formation of coke (figure 9). Interestingly, activity and selectivity are maintained for 10 h without

**Figure 7.** Time on stream on 1,4-butanediol using Cr-MIL-101 catalyst.**Scheme 2.** Dehydration of 1-phenylethanol to styrene.**Figure 8.** Effect of temperature on dehydration of 1-phenylethanol using Cr-MIL-101 and 35 wt% Cr/AC.**Figure 9.** Time on stream on 1-phenylethanol using Cr-MIL-101 and 35 wt% Cr/AC.

any loss when Cr-MIL-101 is used as catalyst. Results conclude that ordered porous cage structure with high surface area and more number of coordinated unsaturated chromium sites in Cr-MIL-101 favours higher activity.

4. Conclusion

In summary, a facile porous metal organic framework Cr-MIL-101 catalysed synthesis of tetrahydrofuran and styrene through dehydration reaction of 1,4-butanediol and 1-phenylethanol, respectively has been developed. Catalytic activity and selectivity are strongly influenced by ordered porous structure and coordinated unsaturated chromium sites of Cr-MIL-101 catalyst. Among the catalysts used in the present study, Cr-MIL-101 showed high conversion and selectivity under optimized reaction conditions, which is an interesting alternative to many current methodologies.

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References

- Long J R and Yaghi O M 2009 *Chem. Soc. Rev.* **38** 1213
- Wang H, Du Z and Duan Q 2002 *Chem. Ind. Eng. Prog.* **21** 836
- Ferry G, Draznieks C M, Serre C, Millange F, Dutour J, Surble S and Margiolaki I 2005 *Science* **309** 2040
- Boehm H P, Knozinger H, Anderson J R and Boudart M 1984 *Catal. Sci. Technol.* **4** 40
- Hunter S E, Ehrenberger C E and Savage P E 2006 *J. Org. Chem.* **71** 6229
- Mabry M, Prichard W and Ziemecki S 1985 *E.I. DuPont de Nemours and Company USP 4* **550** 185
- Mabry M, Prichard W and Ziemecki S 1986 *E.I. DuPont de Nemours and Company USP 4* **609** 636
- Herbert Muller 2002 *Encyclopedia of Industrial Chemistry*. (Wiley)
- Li H, Yin H, Jiang T, Hu T, Wu J and Wada Y 2006 *Catal. Commun.* **7** 778
- Nazmul A K, Jin S H and Sung H J 2011 *Bull. Korean Chem. Soc.* **32** 1327
- Chang J S, Hong D Y, Vislovskiy V P and Park S E 2007 *Catal. Survey Asia* **11** 59
- Boelens M, Horton A D, Nisbet T M and Van Fort A B 2005 *Process for Preparing Styrene. World Patent WO* 054157 A1
- Lamson J, Hall R H and Yats L D 1977 U.S. Patent **4049** 736
- Bos A and Koradia P B 2009 World Patent WO 074461 A1
- Korchak E I 1967 U.S. Patent **344** 2963
- Sakthivel A, Badamali S K and Selvam P 2002 *Catal. Lett.* **80** 1
- Michorczyk P, Ogonowski J, Kustrowski P and Chmielarz L 2008 *Appl. Catal. A* **349** 62
- Nataliya V M, Konstantin A K, Sergey S A, Yurii A C, Maxim S M, Alexander G S, Vladimir P F and Kholdeeva A 2010 *Inorg. Chem.* **49** 2920.
- Maksimchu N V, Timofeeva M N, Melgunov M S, Shmakov A N, Chesalov Y A, Dybtsev D N, Fedin V P and Kholdeeva O A 2008 *J. Catal.* **257** 315
- Li H, Yin H, Jiang T, Hu T, Wu J and Wada Y 2006 *Catal. Commun.* **7** 778
- Siva Kumar V, Nagaraja B M, Shashikala V, Padmasri A H, Shakuntala Madhavendra S, David Raju B and Rama Rao K S 2004 *J. Mol. Catal. A* **223** 313
- Yang J, Zhao Q, Li J and Dong J 2010 *Micropor. Mesopor. Mater.* **130** 174
- Henschel A, Gedrich K, Kraehnert R and Kaskel S 2008 *Chem. Commun.* 4192
- Zhang Z J, Huang S S, Xian S K, Xi H X and Li Z 2011 *Energy Fuels* **25** 835
- Qing L, Liqi N, Shudong Z, Mengna T, Yao S and He Y 2013 *Scientific Rep.* **3** 2916
- Hwang Y K, Hong D Y, Chang J, Jhung S H, Seo Y K, Kim J, Vimont A, Daturi M, C Serre and Ferey G 2008 *Angew. Chem. Int. Ed.* **47** 4144
- Inoue H, Sato S, Takahashi R, Izawa Y, Ohno H and Takahashi K 2009 *Appl. Catal. A: General* **352** 66
- Igarashi A, Sato S, Takahashi R, Sodesawa T and Kobune M 2007 *Catal. Commun.* **8** 807
- Yamamoto N, Sato S, Takahashi R and Inui K 2005 *Catal. Commun.* **6** 480
- Yamamoto N, Sato S, Takahashi R and Inui K 2006 *J. Mol. Catal. A* **243** 52
- Sato S, Takahashi R, Sodesawa T and Yamamoto N 2004 *Catal. Commun.* **5** 397