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Catalytic properties of Beta zeolite exchanged with Pd and Fe for toluene total oxidation

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Dealuminated beta zeolites exchanged with Pd and Fe were prepared to investigate the influence of iron and dealumination on the activity and selectivity of Pd/BEA zeolite for toluene total oxidation. The specific areas determined by BET method and EPR studies allowed to know that the palladium would be more easily agglomerated on the BEA than on the DBEA. Moreover, a quantification of the palladium saturation on the BEA zeolite was deduced by EPR. Effects of dynamic and static oxidation and weak and strong reduction treatments were studied by EPR. Several isolated and interacted Pd^+ species and hole centers were detected. The Pd was much reduced after the catalytic test in dealuminated and Fe doped samples. This result could be directly correlated to the catalytic deactivation. The deactivation could be also explain by the type of coke deposed on the catalyst and by the hydroscopic behavior of the samples. Addition of Fe or dealumination could prevent the deactivation and then lead to better catalysts for VOCs oxidation.

1. INTRODUCTION

Volatile Organic Compounds (VOCs) in industrial gas represent a serious environmental problem. An effective way of removal is complete catalytic oxidation to harmless products such as H_2O and CO_2. In order to make the reaction economically attractive, highly active catalysts at low temperatures are required. Supported precious metals such as Pt and Pd are well established as efficient catalysts for VOC combustion [1] and palladium is cheaper and often more active for oxidation than platinum [2]. Moreover, iron is often used for catalytic oxidation of VOCs [3] and could imply special properties of the catalyst for deactivation [4]. However, the support is also very important for the efficiency of the catalyst. Zeolites have a good potential for VOC adsorption but the formation of water during the combustion could be a deactivation agent [5]. Therefore, in this paper, we prepared dealuminated beta zeolites exchanged with Pd and Fe for a good activity and low deactivation. Toluene, which is often found in industrial exhausts, has been chosen as probe molecule for the catalytic oxidation test. The objective of this work is to investigate the influence of iron and dealumination on the activity and selectivity of 0.5wt%Pd/BEA zeolite for toluene total oxidation. The palladium valence was also studied for this reaction.

2. EXPERIMENTAL

2.1. Catalyst preparation

Na-Beta zeolite (Si/Al=10, from P.Q. Corporation, called BEA) was dealuminated by HCl (0.2M, 3h, 80°C) and exchanged with NaCl (1M, 2h, 60°C, 7 times) to obtain the solid called DBEA (Si/Al=66). The samples were exchanged by palladium (18h, 60°C) to have 0.5wt%Pd/DBEA. The exchange by palladium was carried with two different complexes: $Pd(NO_3)_2$ for all the catalysts and $Pd(NH_3)_4Cl_2$ only for the preparation of the solid called 0.5wt%Pd(2)/BEA to compare the influence of the both solids for the VOC oxidation. A second exchange was done by iron $(Fe(NO_3)_2,$ 24h, 25°C) to have 0.2wt%Fe,0.5wt%Pd/DBEA. β-zeolite was also exchanged in the same ways without previous dealumination (samples called .../BEA).

2.2. Catalyst characterization

The XRD patterns were obtained at room temperature with a Siemens D5000 diffractometer using Cu-Kα radiation.

Chemical elementary analysis of the samples were obtained by the research centre of Vernaison (France, CNRS).

Thermal analysis measurements were performed using a Netzsch STA 409 equipped with a microbalance. The sample (40 mg) was treated under a flow of air (75 mL.min^{-1}) and the temperature was raised at a rate of 5°C min^{-1} up to 1000°C.

The specific areas of solids are determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at -196°C is pure nitrogen.

The electron paramagnetic resonance (EPR) measurements are performed at 20°C on a EMX Bruker spectrometer. A cavity operating with a frequency of 9.3 GHz (X-band) is used. The magnetic field is modulated at 100 kHz. Precise g values are determined from precise frequency and magnetic field values. Reduction studies of the catalysts followed by EPR were carried on a vacuum ramp with 5 vol%H_2 in N_2 or pure H_2.

For the FTIR studies, self-supported wafers were pressed from 25 mg of each sample at a pressure of about 1 ton/cm^2 and then placed in a sample holder inside a Pyrex cell with NaCl windows, which allowed the pre-treatment of the samples (300°C in vaccum < 10^{-6} Torr for 2 h), the introduction of toluene (1 μL (9.4.10^{-6} mol) to 30 μL (28.2.10^{-5} mol)) and the recording of the spectra. The IR spectra were recorded after adsorption-desorption equilibrium of toluene using a Fourier Transform Perkin-Elmer Spectrometer Spectrum 2000 at room temperature.

2.3. Activity tests

The samples were tested in the total oxidation of toluene for 24h on stream. Before the catalytic test, the solid (200 mg) was calcined under a flow of air (4 L.h^{-1}) at 500°C (2°C.min^{-1}) during 4 hours. Toluene oxidation was carried out in a flow microreactor and studied at about 250°C. Temperature was controlled at the internal oven surface and in the catalytic bed. Toluene was mixed with a flash-injector in a flow of air (99 mL/min) adjusted by a mass flow controller. The space velocity was about 50000 h^{-1}. The analysis of combustion products was performed evaluating the toluene conversion and the CO/(CO + CO_2) molar ratio from a Perkin Elmer autosystem chromatograph equipped with TCD and FID.

Table 1
Loss of BET specific areas after Pd and Fe exchanges on BEA and DBEA (m^2/g)

	0.01wt%Pd	0.05wt%Pd	0.5wt%Pd	0.5wt%Pd + 0.2wt%Fe
BEA	52	64	112	128
DBEA	8	22	29	

3. RESULTS AND DISCUSSION

XRD patterns of the pure BEA and the dealuminated DBEA are similar. The cristallinity of the β-zeolite is then not altered by dealumination.

The thermal behaviour and the decomposition of the palladium complexes (Pd(NO$_3$)$_2$ and Pd(NH$_3$)$_4$Cl$_2$) of the samples 0.5wt%Pd/BEA, 0.5wt%Pd/DBEA and 0.5wt%Pd2/BEA are followed by thermal analysis and the TGA-DTA curves displayed two endothermic transitions for the all these samples. The first one corresponds to the loss of water at about 100°C. The samples 0.5wt%Pd/BEA and 0.5wt%Pd(2)/BEA present a water loss of about 8 % whereas the sample 0.5wt%Pd/DBEA showed only 6 % water loss. This difference is due to dealumination which implies a lower hydrophilic character and should led to less deactivation of the catalyst during oxidation of VOCs [5]. The second endothermic transition around 230°C and 320°C for 0.5wt%Pd/BEA and 0.5wt%Pd(2)/BEA is due to the decomposition of the Pd complexes, respectively, Pd(NO$_3$)$_2$ and Pd(NH$_3$)$_4$Cl$_2$.

The samples BEA and DBEA present important specific areas of, respectively, about 595 and 653 m^2/g. The losses of BET specific areas after Pd and Fe exchanges are displayed in Table 1. The decrease of surface area after Pd exchange is always higher for BEA than for DBEA. More agglomeration of Pd on BEA than on DBEA could explain this tendency. This result will be correlated to EPR measurements.

Fig. 1 shows the EPR spectra of 0.5%Pd/BEA recorded at T=293K for different treatment conditions : calcined at 773K under air (a); evacuated 293K (b); reduced at 523K (c) and reduced at 773K (d). All the spectra are composed of three signals A, B and S. The A signal centred at g = 4.30 could be attributed to isolated Fe^{3+} ions presented as impurity in the solids [7]. The B signal has a g = 2.09±0.01 and a δH = 1300G and is most remarkable in calcined and evacuated at 293K samples. Intensity of this signal (i) increases slightly with decreases of measurement temperature (exchange interaction with antiferromagnetic component); (ii) increases with increase the % of Pd exchanged up to 0.05w% and further stays still up to 0.5w% of Pd (saturation effect in quantity of paramagnetic Pd agglomerates); (iii) increases with increase of the reduction treatment (Fig. 2). On the base of these facts, we can suppose that some of the Pd ions are present in an oxidation state ≠ 2 (may be in 3 or certainly 1) and are under the influence of the strong exchange interaction with ferrimagnetic or antiferromagnetic component. The interaction in Pd ions system should be antiferromagnetic because the decrease of the measurement temperature from 293K to 77K leads to a slight increase of the signal intensity (i). The same type of magnetic interaction has been observed in small Pd particles [8]. The absence of the structure peculiarities for B signal does not allow to determine unambiguously the valence state of Pd ions as it has been made in other works [9]. However, the number of this type of palladium species (B) was calculated as a function of the %Pd exchange on BEA and the saturation of this Pd species is found between 0.01 and 0.05 wt%Pd exchange (ii). Signal S with the parameters g=2,0045 and δH = 15G and Lorentian line shape is observed in EPR spectra of all the samples after the reduction treatment at T=523K and higher. The intensity of this signal increases with increase of the exchange ratio

of Pd and the reduction treatment temperature (Fig.2). It should be noted that identification of the narrow symmetric line with $g \cong g_e$ is difficult, but Lorentian shape of signal indicates the exchange interaction between the corresponding paramagnetic species. In our case taking into account the condition of reduction treatment and composition of studied solids, it should be the oxygen located hole for corresponding defect centres [10]. It must be noted that the increase of number of S centres is in inverse proportion to quantity of agglomerated B centres (iii), i.e. the reduction of agglomerated Pd ions from paramagnetic state to diamagnetic one leads to appearance of the defects of S type. The dealuminated sample 0.5%Pd/DBEA shows the same types of EPR spectra as the 0.5%Pd/BEA ones under vacuum and reduction treatment. The difference in quantity of signal B and signal S for these treatments are shown in fig. 2. It may be noted that the dealumination of the samples leads to a decrease of quantity of agglomerated Pd ions under all the conditions of treatment (in 1.6 time on average) and their easier reduction just up zero at 773K, an increase of S type of paramagnetic species under the same conditions (in 1.67 time on average). This result is correlated to the above BET study. After dynamic oxidation of 0.5%Pd(2)/BEA at 773K under flow of air and vacuum treatment at T=773K, only weak signal A is present. After the vacuum treatment at 673 and 77K with or without previous calcination, several EPR signals of paramagnetic defect species appears. Signal S' with g=2.0036, $\delta H = 15G$ and Lorentian line shape as the signal S may be also attributed to a oxygen located hole centre. This defect is more intense in the previously calcined samples. Under static oxidation (O_2, 2h, 293K), the signal S' completely disappears even without vacuum treatment (Fig.3). The static oxidation does not lead to creation of new paramagnetic species, on the contrary it eliminates the existed above defect species. Fig.3 shows the spectra EPR at T=77K of statically oxide Pd(2)/BEA under the weak (3%H_2/Ar, p=200torr, T=293K) reduction conditions for different times of reduction. The large variety of Pd^+ centres are manifested themselves in these spectra. The impurity of Fe^{3+} (signal A) and agglomerated Pd (signal B) are also present in whole EPR spectra (not shown), but the signals of defect S and S' are absent.
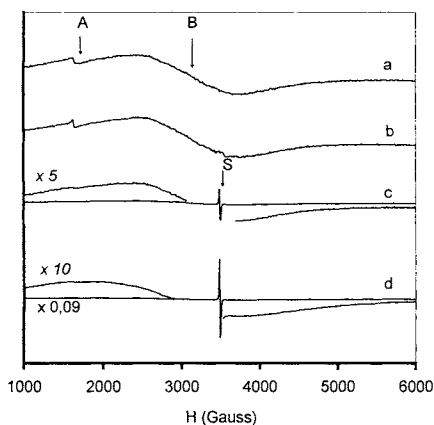

Figure 1: EPR spectra at 293K of Pd/BEA zeolites (a) calcined at 500°C under air ; (b) treated under vacuum at 293K ; reduced under H_2 at (c) 523K, (d) 773K.
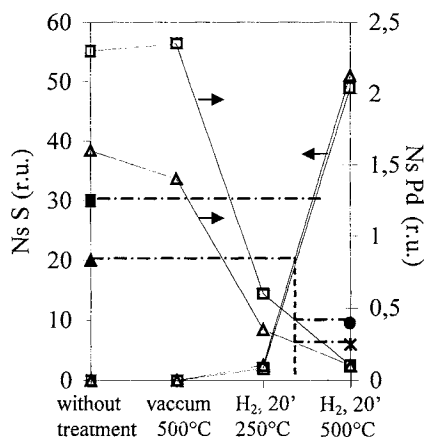
Figure.2 Dependence of the quantity of agglomerated paramagnetic Pd species (N_sPd) and of S species (N_sS) on treatment condition for $\triangle$: DBEA and $\square$: BEA.

The observed EPR signals with parameters : signals C ($g_{||}$=2.628; $g_\perp$=2.124), signal D ($g_{||}$=2.496), signal E ($g_{||}$=2.434) ; signal F ($g_{||}$=2.356) may be attributed to isolated Pd^+ [9] species in different local symmetry environment. It must be noted that the first appearance (perpendicular component of C signal) of Pd^+ is observed even after 5 minutes of reduction under the weak reduction condition. Further treatment during 50min at T=293K leads to increase of intensity of Pd^+ EPR spectra (C-F), which partially disappear (species E and F) during the longer reduction (5 h). The further increase of reduction time up to 15 h results in complete disappearance of all above observed Pd^+ species and appearance of a new radical G signal ($g_{||}$=1.988; $g_\perp$=2.0505) which is similar to signal observed earlier in [9] but under different (oxidation) treatment conditions and is attributed to Pd^{2+}-O_2^- radical.

Fig.4 shows EPR spectra of the Pd(2)/BEA reduced under the strong reduction conditions (H_2, 100torr) at T=293 and 393K for different times. A first 5 h reduction leads to appearance of a new Pd^+ centre (signal H: $g_{||}$=2,444; $g_\perp$=2.0944) or a transformation of one of precedent (C, D or E) ones and increase of intensity of earlier observed F centres. A continuous increase of reduction time up to 15 h eliminates the H signal. At the same time the beginning of the interaction between the Pd^+ ions is manifested itself in EPR spectra by appearance of a signal I with isotropic g_{iso}=2.128. The increase of the reduction temperature up to T=393K leads to consecutive increase of quantity of Pd^+ ions which are under an influence of others (Fig.4c, d). The appearance and increase of I species proves that under the noted reduction conditions, we can continue the progressive reduction of palladium species, i.e. there is an important reserve of Pd^{2+} not yet reduced. The reduction effect on Pd after the catalytic test will be discuss later.
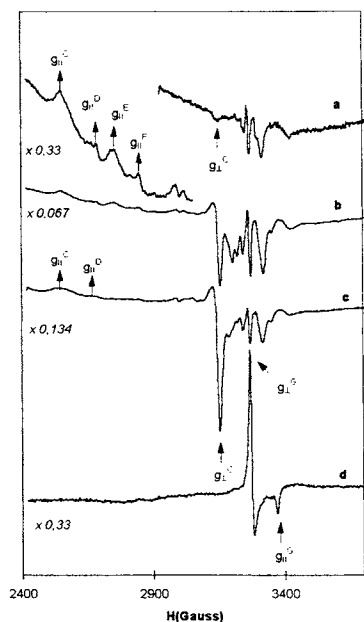

Figure 3. EPR spectra of statically oxided Pd(2)/BEA under the weak reduction during (a) 5 min ; (b) 50 min ; (c) 5 h ; (d) 15 h.

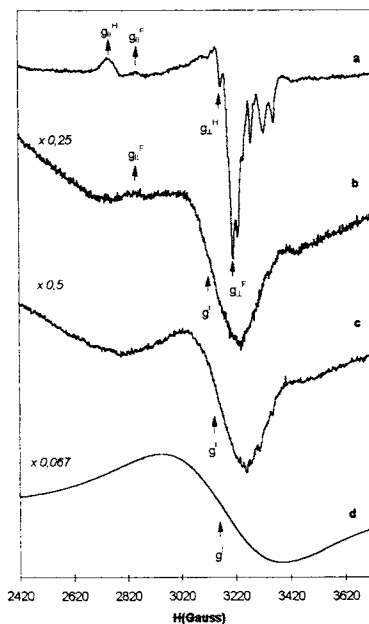Figure 4. EPR spectra at 77K under the strong reduction of sample fig.3d at (a) T=293K, 5 h ; (b) T=293K, 15 h ; (c) T=393K, 1 h ; (d) T=393K, 3 h.

The IR spectra of adsorbed toluene on the samples displayed two characteristic bands at 1650 cm^{-1} and 1490 cm^{-1} corresponding to C-C ring vibrations [6] but also C-H stretching vibrations bands of the aromatic ring between 3050 and 3020 cm^{-1}. The characteristic bands of adsorbed toluene are not shifted from one to another studied sample. The study of the intensity of toluene sorbed peaks with increasing amounts of toluene in the cell shows different behaviours of the solids. Adsorbed toluene is visible when 1µL (9.4.10^{-5} moles) is injected in the cell for 0.5wt%Pd/DBEA whereas 5µL and 10µL of toluene are the minimum amounts respectively for 0.5wt%Pd/BEA and 0.2wt%Fe,0.5wt%Pd/BEA. The toluene is then more easily adsorbed on 0.5wt%Pd/DBEA and that adsorption is more difficult on the Fe exchanged catalyst. Nevertheless, the sample 0.5wt%Pd/BEA was saturated with adsorbed toluene before 0.5wt%Pd/DBEA and 0.2wt%Fe,0.5wt%Pd/BEA.

The toluene total oxidation was studied by the conversion of toluene at 250°C versus time on stream for the calcined catalysts 0.5wt%Pd/BEA, 0.5wt%Pd2/BEA, 0.5wt%Pd/DBEA and 0.2wt%Fe,0.5wt%Pd/BEA (Fig.5). Although the oxidation of the toluene on these catalysts was producing only water and CO$_2$, all the toluene was not converted at the beginning of the experiment. After 3 minutes under flow, 96% of the toluene was oxidized on 0.5wt%Pd(2)/BEA, 94% on 0.5wt%Pd/BEA, 90% on 0.5wt%Pd/DBEA and only 80% on 0.2wt%Fe,0.5wt%Pd/BEA. However, this conversion increased to 100% for all the catalysts after some time on stream : after 5 hours for 0.5wt%Pd/BEA and 0.5wt%Pd/2BEA but only after 10 h for 0.5wt%Pd/DBEA and 0.2wt%,0.5wt%Pd/BEA. The total conversion is nevertheless not stable during our experiment for the both more active catalysts at the beginning of the experiment (0.5wt%Pd/BEA and 0.5wt%Pd(2)/BEA). The deactivation could be partially explained by the DTA curves of the sample after the catalytic test (Table 2). Two exothermic transitions at about 250 and 500°C and only one at 500°C are present for, respectively, the dealuminated 0.5wt%Pd/DBEA sample and the non-dealuminated samples (0.5wt%Pd/BEA and 0.2wt%Fe,0.5wt%Pd/BEA). These transitions should correspond to the combustion of some deposed cokes on the catalysts.
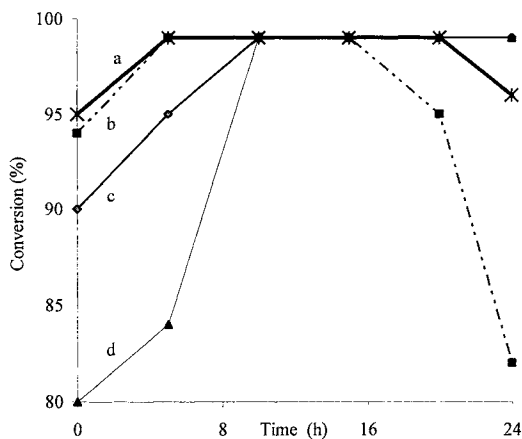

Figure 5 : Toluene conversion at 250°C versus time on stream
a : 0.5%Pd(2)/BEA, b : 0.5%Pd/BEA, c : 0.5%Pd/DBEA, d : 0.5%Pd,0.2%Fe/BEA.

The losses of cokes of, respectively, 1.7% + 2.3% = 4% and 3.7% for 0.5wt%Pd/DBEA and 0.2wt%Fe,0.5wt%Pd/BEA samples are similar whereas a higher quantity is found on 0.5wt%Pd/BEA. This difference could explain the deactivation observed. But also because the first type of coke present on 0.5wt%Pd/DBEA is already decomposed at 250°C and that temperature is the oxidation temperature of toluene in the catalytic test. The second type of coke decomposed at 500°C is then more stable. Another explanation of the deactivation could be also due to the formation of water during the toluene oxidation. Non-dealuminated samples after the catalytic test present higher water losses (corresponding to an endothermic transition at about 80°C). The water formed during the toluene oxidation is more sorbed on the more hydroscopic samples and then could decrease the activity of the catalysts.

Moreover, the EPR spectra of these samples after the catalytic test still present another result. In Table 3, there are the number of B (N_sPd) and S centres (N_sS) species of the samples after the toluene catalytic test. The toluene oxidation reaction produces a reduction effect for all the studied catalysts. In Fig.2, the quantity of paramagnetic species B' (g=2.25-2.34, δH=1100-1200 G) which have been attributed in [9] to palladium clusters, and S species after the test are presented. The catalytic effect is then similar to the reduction treatment at ~573K. The value of S centres (Ns) increases after test in order successive : Pd(2)/BEA to Pd/BEA to PdFe/BEA to Pd/DBEA. For the quantity of B centres the order is inverse. So the agglomerated Pd ions are in order more reduced from Pd(2)/BEA to Pd/BEA to PdFe/BEA and to dealuminated Pd/DBEA sample. This result could be directly correlated to the catalytic deactivation observed for Pd(2)/BEA and Pd/BEA after 24 h on stream (Fig. 5). In fact, the more the palladium is reduced, the more its activity for oxidation reaction [11]. Therefore, the addition of 0.2wt% of Fe or the zeolite dealumination could prevent the deactivation and then lead to better catalysts.

Table 2 : DTA results on used catalyst

	Water loss (80°C)	Coke 1 loss (250°C)	Coke 2 loss (500°C)
Pd/BEA	8.9%	0%	4.7%
PdFe/BEA	8.0%	0%	3.7%
Pd/DBEA	5.8%	1.7%	2.3%

Table 3 : Number of B (N_sPd) and S (N_sS) centres after the toluene catalytic test

	g factor (S)	N_sS (r.u.)	g factor (Pd^+)	N_sPd (r.u.)
Pd(2)/BEA	2.0046	2.15	2.34	0.327
Pd/BEA	2.0045	1.98	2.25	0.352
PdFe/BEA	2.0046	2.34	2.28	0.289
Pd/DBEA	2.0030	3.16	2.30	0.233

4. CONCLUSION

This study has shown that an addition of iron or the dealumination of the zeolite could prevent the deactivation of Pd/BEA for toluene total oxidation. Palladium would be more easily agglomerated on the BEA than on the dealuminated BEA (BET and EPR measurements). Moreover, the palladium saturation in function of the wt% of exchanged Pd on the BEA zeolite was deduced by EPR. Several isolated and interacted Pd^+ species and hole centers were also detected by EPR under dynamic and static oxidations and weak and strong reduction treatments. Moreover, the Pd was much reduced after the catalytic test in dealuminated and Fe doped samples. This result could be directly correlated to the catalytic deactivation of the other samples. The deactivation could be also explain by the type of coke deposed on the catalyst and by the hydroscopic behavior of the samples.

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