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Catalytic activity of copper and palladium based catalysts for toluene total oxidation

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Abstract

In this study, catalysts containing 0.5 wt.% of palladium or 5 wt.% of copper were compared towards toluene total oxidation using FAU Zeolite and ZrO_2 supports. A 0.5%Pd/NaFAU and 5%Cu/ZrO_2 were found to be promising catalysts for this reaction. Palladium presented then a better affinity for FAU zeolite and copper oxide had a better affinity for zirconia. The performances of Pd based catalysts were correlated to interaction between the active phase and the support whereas the activity of copper oxide was related to oxygen mobility property of the support leading to copper oxide particles easily reducible. Support modifications, yttrium addition for ZrO_2 and cation exchange for the zeolite FAU, still enhanced the catalytic activity. Therefore, 0.5%Pd/CsFAU and 5%Cu/$Zr_{95}Y_5$ samples were found to be interesting catalysts for total VOC oxidation.

Keywords: VOC oxidation; Palladium; Copper oxide; Zirconia; Faujasite zeolite

1. Introduction

Volatile Organic Compounds (VOCs) in industrial gas represent a serious environmental problem. Catalytic oxidation is an effective way for reducing the emissions of VOCs. In this way, two kinds of catalysts are usually applied: (i) noble metal based solids which possess high activity but are expensive and (ii) metal oxides based samples which are cheaper but less active [1–3]. Supported precious metals as Pt and Pd are well established as efficient catalysts for the oxidation of different VOC [4–6]. Moreover, among the precious metals, ''Pd'' is presently the cheapest one and ''Pd'' is often more active than ''Pt'' for oxidation [7]. Among the metal oxides, copper oxide is often employed for its high activity and selectivity for VOC oxidation [8,9]. Furthermore, it is well known that supports play an important role in catalytic activity improvement, particularly in oxidation reaction [10]. Large pores zeolites are often chosen for their high surface area and acidic–basic properties allowing high metal loading and particular interaction with the active phase [11]. ZrO_2 is a very interesting material since lability and easiness to exchange oxygen atoms of the tetragonal phase make zirconia suitable for redox catalysis [12]. In this study, the activities in the toluene total oxidation of 0.5 wt.% Pd and 5 wt.% Cu deposited on zeolite NaFAU and ZrO_2 supports were compared and discussed in terms of activity and reducibility of active phases. The influence of support modification by yttrium addition for zirconia and cation exchange for the zeolite FAU, has been also evaluated in this study.

Toluene has been chosen as VOC probe molecule because aromatics are present in the industrial and automotive emissions and because toluene presents an important POCP (Photochemical Ozone Creativity Potential) [13,14]. Pores diameter of large pores zeolite Faujasite (7.5 Å) should not imply any shape selectivity for the oxidation of toluene which presents a kinetic diameter of 5.8 Å [15].

2. Experimental

Simple and mixed zirconia-yttria solids were prepared by precipitation and coprecipitation of the respective precursor salts solutions by ammonium. The samples were calcined at 600 °C. Synthesis details were reported elsewhere [10]. The samples were called ZrO_2 for pure zirconia and $Zr_{95}Y_5$ for the mixed oxide support with a molar ratio Y/Zr of 5.

HFAU zeolite was prepared from NaFAU zeolite (Si/Al = 2.43 from Union Carbide) by exchange with a 2 M solution of NH_4NO_3 (Acros) at 80 °C. Afterward the samples was filtered, washed and dried overnight at 100 °C. CsFAU was

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prepared from the parent zeolite by exchanging seven times with 0.5 M of CsCl (Prolabo) at 60 °C. After each exchange the sample was filtered, washed and heated at 350 °C. Calcination of all zeolite samples was performed under air flow with heating rate of 1 °C min^{-1} from ambient temperature till 500 °C with a hold of 4 h.

Palladium based catalysts were prepared by 0.5 wt.% aqueous impregnation using an adequate dilute solution of $Pd(NO_3)_2$ (Johnson Matthey). Afterward the samples were filtered and washed. All Pd impregnated samples were then dried overnight at 100 °C and calcined at 400 °C under air flow at 1 °C min^{-1} for 4 h. These samples were pre-reduced by H_2 before testing for oxidation reaction.

Copper based catalysts were prepared by impregnation of 5 wt.% copper (using copper nitrate solution) with the subsequent drying in air at 100 °C (24 h) and calcined at 450 °C (4 h).

Toluene oxidation was carried on a fixed bed microreactor using a flow of air and 1000 ppm of toluene from ambient temperature to 300 or 350 °C (1 °C min^{-1}). The analysis of combustion products was performed evaluating the toluene conversion and selectivity from a Perkin-Elmer autosystem chromatograph equipped with TCD and FID. The existence of mass transfer limitations was checked by the use of different masses of catalysts but no limitation was detected.

Temperature Programmed Reduction (TPR), H_2 pulse chemisorption experiments and Temperature Programmed Oxidation (TPO) were carried out in an Altamira AMI-200 apparatus by passing, respectively, a 5% H_2/Ar flow (30 mL min^{-1}) and 10% O_2/He flow (30 mL min^{-1}) through the calcined sample (about 100 mg). The hydrogen and oxygen concentrations in the effluent were continuously monitored by a thermoconductivity detector (TCD).

Coke deposit was evaluate by thermal analysis: TGA under air flow from 25 to 1000 °C using a Netzsch STA 409 equipped with a microbalance differential analysis.

3. Results and discussions

It is first noticeable that for all the studied samples, CO_2 and H_2O were the only products of toluene oxidation. The results of the catalytic tests in the toluene oxidation in the presence of Pd and Cu/support samples are shown in Fig. 1. The following activity order was obtained: 0.5%Pd/NaFAU > 0.5%Pd/ZrO_2 ≫ 5%Cu/ZrO_2 > 5%Cu/NaFAU (Fig. 1).

Even at low palladium content (0.5 wt.%), palladium based catalysts exhibit a remarkable activity for toluene oxidation and much better that CuO based catalysts. However, the catalytic results evidence that the nature of support modifies in different ways the catalytic properties of palladium or copper based samples. Indeed palladium associated with zeolite leads to a more active catalyst than Pd/ZrO_2, whereas higher activity of copper oxide based solids was obtained when zirconia is used as support. The difference between palladium and copper based catalysts observed can be explained in terms of different oxidation mechanisms.

It is generally assumed that hydrocarbons catalytic oxidation on metal oxides takes place via a redox mechanism in which the determining step would be the oxygen removal of the metal oxide to oxidize hydrocarbons [10]. Then, the reducibility study of copper oxides seems to be also crucial [16] in order to explain the difference in catalytic results observed in toluene oxidation. TPR results of copper based samples are shown in Fig. 2.

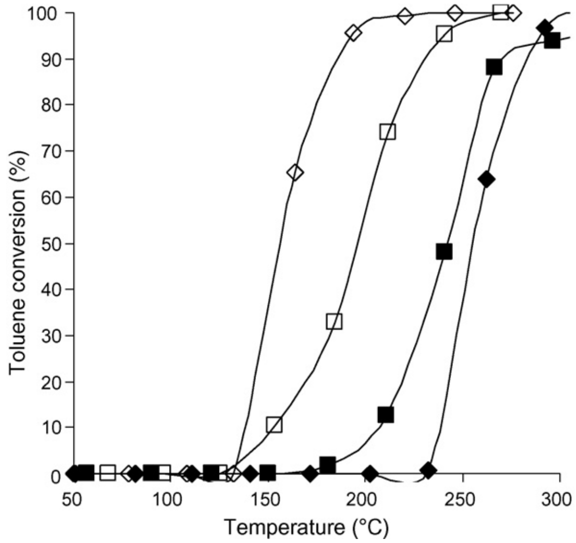

Fig. 1. Toluene conversion vs. temperature for 0.5%Pd/NaFAU (◇), 0.5%Pd/ZrO_2 (□), 0.5%Cu/NaFAU (◆) and 5%Cu/ZrO_2 (■).

Copper can be present in different forms on the support surface depending on the amount of deposited copper and on the support properties: isolated Cu^{2+} species in strong interaction with the support, Cu^{2+} clusters, small and big CuO particles. The TPR profile for CuO/NaFAU presents a large peak centered at 235 °C and a small one at about 400 °C. The large signal can be associated to big CuO particles outside the zeolite porosity, the small one corresponding to some copper species in the zeolite pores less easily reducible [17]. The Cu/ZrO_2 TPR profile presents also two peaks, the first doubled one at about 150 °C can correspond to isolated Cu^{2+} species and Cu^{2+} clusters and the much lower one at 210 °C to big CuO particles [18]. Since the

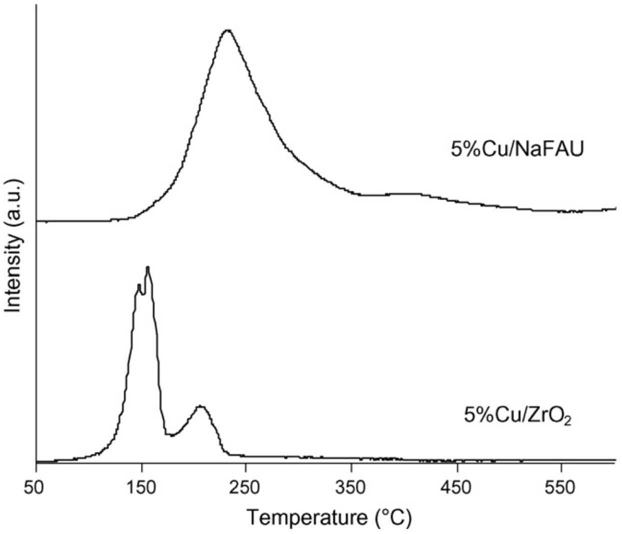

Fig. 2. TPR profiles of 5%Cu/NaFAU and 5%Cu/ZrO_2.

Table 1
Surface areas, palladium dispersions and particle sizes of Pd based catalysts after calcination at 400 °C

Catalyst	S_{BET} (m^2/g)	Palladium dispersion[a] (%)	Palladium particle size[a] (nm)
Pd/ZrO_2	88	15	7.4
Pd/HFAU	589	34	3.2
Pd/NaFAU	714	22	4.8
Pd/CsFAU	414	12	9.9

[a] Determined from H_2 chemisorption at 100 °C.

activity of oxide catalysts towards total oxidation reactions is mainly correlated to the reducibility of the active species, the higher activity of 5%Cu/ZrO_2 can then be reliable to the reduction of copper species which happens at lower temperature than CuO on zeolite support [18].

For noble metals the mechanism of oxidation is quite different and undergoes by a first oxidation of Pd^0 by O_2 to form very active $[Pd^{2+}O^{2-}]$ which oxidize the hydrocarbon and the Pd^{2+} cation is reduce to Pd^0 [19]. Therefore, the reduction step is less important than for metal oxides whereas the oxidation step is crucial. TPR results for Pd based catalysts (not shown) cannot explain the better activity of 0.5%Pd/NaFAU because palladium oxide species are always reduced at the same range of temperature (at around 0 °C) and then at lower temperature than the toluene oxidation reaction.

Therefore, the activity order can be partially correlated to the high surface area of the zeolite which leads to a higher dispersion of palladium particles (22%) than on ZrO_2 (15%). Surface areas, palladium dispersions and particle sizes of palladium based catalysts are summarized in Table 1.

For further studies, a modification of the supports was performed to enhance activity of 0.5%Pd/NaFAU and 5%Cu/ZrO_2 which are found to be promising catalysts for toluene complete oxidation. In this way, NaFAU zeolite was modified by exchanging Na^+ by Cs^+ and H^+ cations to obtain Pd supported catalyst with different support-palladium interaction according to different acidic–basic properties of the zeolite [20].

Toluene oxidation over Pd/zeolite FAU catalysts are displayed in Fig. 3 with the following activity order: 0.5%Pd/CsFAU $\geq$ 0.5%Pd/NaFAU $>$ 0.5%Pd/HFAU.

The catalytic activity cannot be simply explained by the results of surface areas and Pd dispersion measurements since among zeolite based catalysts, 0.5%Pd/CsFAU presents the lowest surface area and Pd dispersion (Table 1). TPO measurements have been performed for Pd/zeolite FAU and the results are shown in Fig. 4. A positive signal at around 250 °C is observed and can be attributed to Pd oxidation into PdO. The temperature range corresponding to such oxidation is close to that related to toluene conversion (Fig. 3); this correlation evidencing that the oxidation step of Pd particles is crucial for the oxidation reaction. Furthermore, a shift of about 20 °C to higher temperature is observed for 0.5%Pd/HFAU TPO signal. Since it has been provided evidences that the acidic–basic properties of the support influenced the Pd oxidation and that the co-existence of Pd and PdO species on the Pd surface was important for VOC oxidation [21], we can conclude that the differences observed in the catalytic performances can be also correlated to the more difficult PdO oxidation for 0.5%Pd/HFAU sample than for 0.5%Pd/CsFAU and 0.5%Pd/NaFAU solids.

Besides Pinard et al. observed almost the same activity order for Pt/FAU exchanged with Cs^+, Na^+ and H^+ for total oxidation of chloromethane and explained this activity order by the basicity which increases with the decrease of the electronegativity of the compensating cation from the protonated Pt/HFAU to the Pt/CsFAU sample [20]. Moreover, it has been shown from XPS results the presence of an electronic shift from the zeolite framework to the Pt particles enhancing with the basicity increase from Pt/HBEA to Pt/NaBEA and Pt/CsBEA [22]. The similar performances of 0.5%Pd/NaFAU and 0.5%Pd/CsFAU catalysts can be then explained by the similar electronegativities of Na and Cs (0.9 and 0.7, respectively).

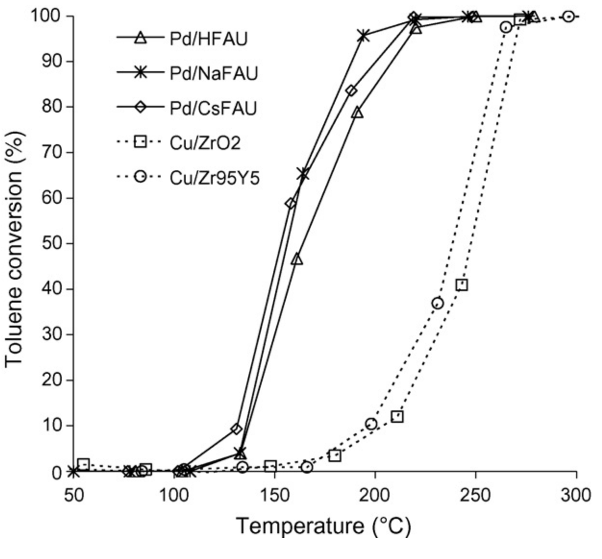

Fig. 3. Toluene conversion over 0.5%Pd/zeolite FAU and over 5% Cu/ZrO_2 and 5%$Cu/Zr_{95}Y_5$.

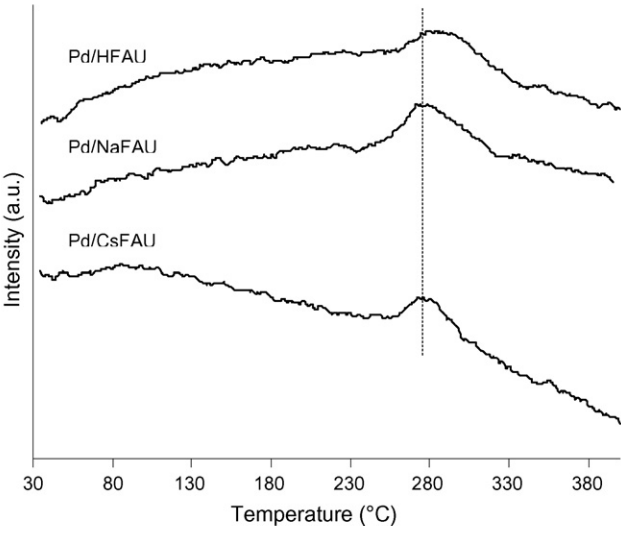

Fig. 4. TPO profiles of 0.5%Pd/zeolite FAU.

Table 2
Thermal analysis under air after toluene test

Catalyst	Mass loss (%) after toluene test
Pd/HFAU	3.8
Pd/NaFAU	2
Pd/CsFAU	1.2

The quantity of coke deposit can be evaluated by thermal analysis. The weight loss (%) corresponding to coke combustion around 400 °C are presented in Table 2. Dégé et al. [4] observed also the combustion of coke coming from xylene total oxidation on Pd/HFAU at about 400 °C. Coke is more retained on acidic form of the zeolite [23] but also on the lower active catalysts. The more acidic Pd/HFAU should then lead to a more desactivable catalyst for VOC deep oxidation [24].

ZrO_2 support was also modified by doping with Y_2O_3 before impregnation of copper. The comparison of toluene total oxidation between 5%Cu/ZrO_2 and 5%Cu/$Zr_{95}Y_5$ shows an enhancement of the activity due to the addition of yttrium to zirconia (Fig. 3). However, the very similar TPR profiles of these both catalysts [18] cannot explain the difference of activity.

The activity can be explained firstly by the addition of yttrium to zirconia which enhances the stability of the tetragonal phase and induces a beneficial effect on the specific areas from 65 m^2/g for 5%Cu/ZrO_2 to 80 m^2/g for 5%Cu/$Zr_{95}Y_5$. Secondly, it has been shown also that the number of anionic vacancies, evidenced by Zr^{3+} (EPR measurements) and created by the substitution of Zr^{4+} by Y^{3+}, increased the support oxygen mobility and then the activity for VOC oxidation [10].

4. Conclusion

A 0.5%Pd/NaFAU and 5%Cu/ZrO_2 were found to be promising catalysts for toluene complete oxidation. The catalytic potential of Pd active phase was correlated to a good dispersion whereas the activity of copper oxide was rather correlated to oxygen mobility property of the support leading to small copper species easily reducible. However, the activity of Pd/NaFAU can be enhanced by ion exchange with less electronegative cation as Cs^+. To enhance the oxygen mobility property and specific surface of ZrO_2, yttrium was introduced into ZrO_2 and then the activity of 5%Cu/$Zr_{95}Y_5$ for toluene oxidation increased.

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References

[1] P. Gélin, M. Primet, Appl. Catal. B 39 (2002) 1.
[2] T. Maillet, C. Solleau, J. Barbier, D. Duprez, Appl. Catal. B 14 (1997) 85.
[3] S.C. Kim, J. Hazard. Mater. B91 (2002) 285–299.
[4] P. Dégé, L. Pinard, P. Magnoux, M. Guisnet, Appl. Catal. B 27 (2000) 17.
[5] J.C.-S. Wu, Z.-A. Lin, J.-W. Pan, M.-H. Rei, Appl. Catal. A 219 (2001) 117.
[6] J. Carpentier, J.-F. Lamonier, S. Siffert, E.A. Zhilinskaya, A. Aboukaïs, Appl. Catal. A 234 (2002) 91.
[7] J.R. Gonzalez-Velasco, A. Aranzabal, J.I. Gutiérrez, R. Lopez-Fonseca, M.A. Gutiérrez-Ortiz, Appl. Catal. B 19 (1998) 189.
[8] M. Baldi, E. Finocchio, F. Millela, G. Busca, Appl. Catal. B 16 (1998) 43.
[9] M.M. Günter, T. Ressler, R.E. Jentoft, B. Bems, J. Catal. 203 (2001) 133.
[10] M. Labaki, S. Siffert, J.-F. Lamonier, E. Zhilinskaya, A. Aboukaïs, Appl. Catal. B 43 (2003) 261.
[11] J. Jacquemin, S. Siffert, J.-F. Lamonier, E.A. Zhilinskaya, A. Aboukaïs, Stud. Surf. Sci. Catal. 142 (2002) 699.
[12] A. Martinez-Arras, M. Fernandez-Garcia, C. Belver, J.C. Conesa, J. Soria, Catal. Lett. 65 (2000) 197.
[13] R.G. Derwent, M.E. Jenkin, S.M. Saunders, Atmos. Environ. 30 (1996) 181.
[14] R.G. Derwent, M.E. Jenkin, S.M. Saunders, M.J. Pilling, Atmos. Environ. 32 (1998) 2429.
[15] D.W. Breck, Zeolite Molecular Sieves, Structure Chemistry and Use, Wiley, New York, 1974.
[16] Lj. Kundakovic, M. Flytzani-Stephanopoulos, Appl. Catal. A 171 (1998) 13.
[17] A.P. Antunes, M.F. Ribeiro, J.M. Silva, F.R. Ribeiro, P. Magnoux, M. Guisnet, Appl. Catal. B: Environ. 33 (2001) 149.
[18] M. Labaki, J.-F. Lamonier, S. Siffert, A. Aboukaïs, Thermochim. Acta 427 (2005) 193.
[19] P. Dégé, Thesis of Poitiers University, France, 1999.
[20] L. Pinard, J. Mijoin, P. Magnoux, M. Guisnet, C. R. Chimie 8 (2005) 457.
[21] K. Okumura, T. Kobayashi, H. Tanaka, M. Niwa, Appl. Catal. B: Environ. 44 (2003) 325.
[22] S. Siffert, J.-L. Schmitt, J. Sommer, F. Garin, J. Catal. 184 (1999) 19.
[23] M. Guisnet, P. Dégé, P. Magnoux, Appl. Catal. B 20 (1999) 1.
[24] L. Becker, H. Förster, Appl. Catal. A: Gen. 153 (1997) 31.