PHYSICO-CHEMICAL CHARACTERIZATION AND CATALYTIC PROPERTIES OF COPPER-DOPED ALUMINA-PILLARED MONTMORILLONITES

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Abstract—Cu-doped alumina-pillared montmorillonite samples have been prepared and characterized with X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), electron spin resonance (ESR) and inductive coupled plasma atomic emission spectroscopy (ICP AES) techniques. The results show that the catalysts are porous materials with copper species located in the interlayer, present either as isolated Cu^{2+} ions anchored at alumina pillars or as patches of amorphous CuO. Catalytic tests with hydroxylation of phenol show that the clay samples possess significant activity for dihydroxybenzene (DHB) formation, comparable with the reference TS-1 catalyst. Experiments with changing the substrate dosing indicate that adsorption and activation of phenol molecules is a necessary condition for the reaction to occur.

Key Words—Alumina, Copper, Copper Catalyst, Montmorillonite, Phenol Hydroxylation, Pillared Clay.

INTRODUCTION

Pillared interlayer clays (PILC) are characterized by high surface area, pore dimensions larger than those encountered in most zeolites and substantial intrinsic acidity. These qualities have led to numerous attempts to apply pillared clays in catalysis, mainly of the acid type (Vaughan 1988). Potential application of pillared clays in catalytic processes of a redox nature would require the PILC structure to accommodate transition metal ions known to easily change their oxidation states. In a series of recent papers we have suggested the use of pillared clays as a support for the catalytically active vanadium species (Bahranowski and Serwicka 1993; Bahranowski, Dula, Grabowski et al. 1995; Bahranowski, Dula, Komorek et al. 1995; Bahranowski et al. 1997). Many interesting results have been obtained for processes of significant practical importance: the oxidative dehydrogenation of propane to propene, and the selective catalytic reduction (SCR) of nitrogen oxide by ammonia (Bahranowski, Dula, Grabowski et al. 1995; Bahranowski et al. 1997). Recently, it has been reported by Yang et al. (1995) that Cu(II)-containing titania-pillared clays are promising as potential catalysts in SCR of NO by hydrocarbons. It seemed of interest to check on the ability of transition metal doped pillared clays to oxidize organic substrates in the liquid phase using the environmentally friendly oxidant hydrogen peroxide. We have chosen hydroxylation of phenol as a test reaction, due to its practical importance. Also, our preliminary studies (Bahranowski, Dula et al. 1996; Bahranowski, Gąsior et al. 1996) and recent reports from other laboratories indicate that pillared clays may be active in this process (Frini Srasra et al. 1995; Del Castillo et al. 1996).

About 50% of the total world production of DHBs (hydroquinone and catechol) is accomplished by means of catalytic hydroxylation of phenol with the aid of hydrogen peroxide. The reaction scheme is presented in Figure 1.

The latest industrial process, developed by Enichem (Italy), uses titanium silicalite TS-1 as a catalyst and gives the best DHB yields (Notari 1988). For this reason we relate the catalytic results obtained in this study for a series of copper-doped alumina-pillared montmorillonite clays to the performance of a TS-1 reference sample.

EXPERIMENTAL

Materials and Syntheses

The parent montmorillonite used in this study was the sodium-exchanged (less than 2 μm particle-size fraction) Milowice bentonite from the Saturn deposit in Silesia, Poland, referred to as Na-mt. The cation exchange capacity of the clay is 84 meq/100 g.

ALUMINA-PILLARED MONTMORILLONITE. Alumina-pillared clay was prepared according to the procedure described by Vaughan and Lussier (1980). Commercial

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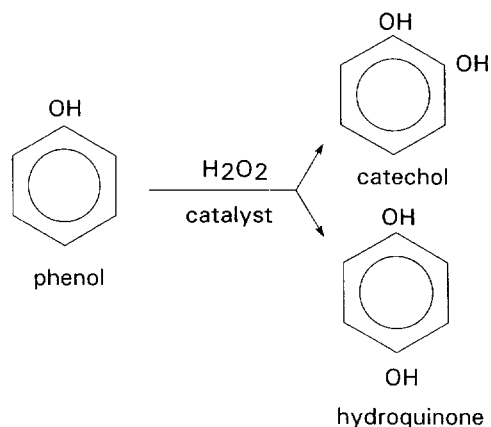
Figure 1. Reaction scheme.

aluminum chlorhydroxide known as Chlorhydrol (Reheis Chemical Company) was added with vigorous stirring to a water suspension containing about 4 g/L of Na-mt, in an amount corresponding to 0.17 g Al^{3+} per gram of clay. After thorough homogenization of the slurry (about 30 min), and adjustment of the pH to 2.0 with dilute hydrochloric acid, the mixture was allowed to age for 30 min at 70 °C, centrifuged, washed free of Cl^- and dried in air at 80 °C. This product is referred to as Al-mt, and after calcination in air at 400 °C for 3 h as Al-PILC.

CU-DOPED PILLARED MONTMORILLONITES. Copper was introduced into the pillared clay by means of cationic exchange with calcined Al-PILC samples. The exchanged samples are reported as Cux-(Al-PILC), where x is the weight percentage of CuO. Al-PILC was treated with 0.1 M $Cu(NO_3)_2$ (Merck) solution, centrifuged, washed 10 times with distilled water, dried in air at 50 °C and calcined in air at 400 °C for 3 h. The calcined product is referred to as Cu1.1-(Al-PILC). In order to increase the copper content the exchange/drying/calcination procedure was repeated twice with the Cu1.1-(Al-PILC) sample. Samples Cu2.0-(Al-PILC) and Cu2.3-(Al-PILC) were obtained this way.

REFERENCE SAMPLES. Cu-exchanged montmorillonite was obtained by stirring Na-mt with a 0.1 M solution of $Cu(NO_3)_2$, followed by washing with distilled water. After calcination in air at 400 °C for 3 h it was used as a reference in the ESR investigation. TS-1 (Si/Ti $\approx$ 80), synthesized according to the known standard procedure (Thangaraj et al. 1991), and characterized with XRD, infrared (IR), ultraviolet-visible (UV-VIS) and scanning electron microscopy (SEM) to ascertain that it is free from any crystalline or amorphous impurities, was used in the reference catalytic experiments. The size of TS-1 crystallites was in the range 0.5–1.0 μm.

Physicochemical Characterization

XRD analyses were performed on oriented samples prepared by spreading the sample suspension on a glass slide, followed by drying at room temperature. The XRD patterns were obtained with a DRON-3 diffractometer using Ni-filtered Cu$K\alpha$ radiation.

Chemical analysis was carried out on an ICP-AES Plasma 40 Perkin Elmer spectrometer, after dissolution of the samples in a mixture of concentrated acids (HF and $HClO_4$).

The ESR spectra were recorded at room and liquid nitrogen temperatures with an X-band SE/X (Technical University Wroclaw) spectrometer. Diphenylpicrylhydrazyl (DPPH) and nuclear magnetic resonance (NMR) field marker were used to determine the resonance frequency. The ESR parameters were determined from the best fit computer simulations. The programs SIMAX and COMBI, kindly made available by Dr. José C. Conesa from Instituto de Catalisis y Petroleoquimica, CSIC, Madrid, Spain, were used for computations.

Specific surface area and porosity measurements were determined with the aid of a computer-controlled multifunctional Micrometrics ASAP 2000 apparatus. The samples were outgassed at 200 °C in an automatic mode. Nitrogen adsorption isotherms recorded at −196 °C were used to determine all texture parameters. Specific surface area was calculated using the BET method in the relative pressure range 0.06–0.22, and micropore (<17 Å) volume by the "t" method in the relative pressure range 0.06–0.60, both according to the standard procedures offered by Micrometrics software.

Catalysis

Catalytic reactions were carried out for 60 min in a batch microreactor in the temperature range 75–92 °C under a flow of argon. The amount of the catalyst was 0.05 g. The total volume of reagents was 1.6 mL. Acetone was used as a solvent. Hydrogen peroxide (30%) was added dropwise to the reaction mixture under vigorous stirring (1000 rpm). The molar ratio of phenol: acetone:water:H_2O_2 was 1:0.32:1.41:0.27. Products were separated with a Varian 3400 gas chromatograph and analyzed with an Incos 500 Finnigan mass spectrometer.

RESULTS AND DISCUSSION

The XRD diagram of Al-PILC is presented in Figure 2. The most intense low-angle reflection at 18.6 Å corresponds to the d(001) basal spacing of the pillared sample and is followed by higher-order reflections at 9.3 Å (002 plane), 6.2 Å (003 plane), 4.7 Å (004 plane) and 3.1 Å (006 plane). The narrow reflection at 3.3 Å is due to the quartz impurity. Assuming a layer thickness in montmorillonite of 9.6 Å, the interlayer
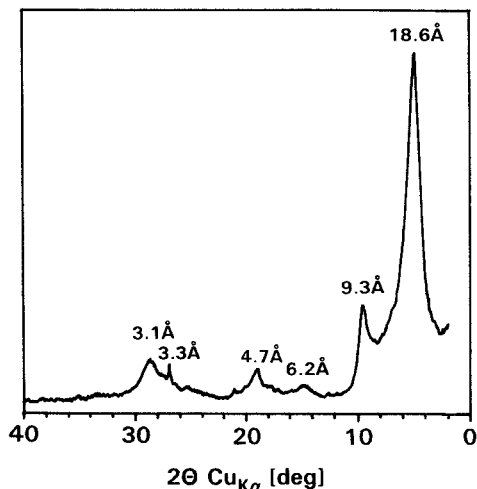
Figure 2.   Powdered XRD pattern of Al-PILC sample.

Table 1.   Basal spacing $d(001)$, specific surface area S_{BET}, micropore volume $V_{micropore}$, micropore surface area $S_{micropore}$, and copper content of the investigated clay samples.

Sample	$d(001)$ [A]	S_{BET} [m²/g]	$V_{micropore}$ [cm³/g]	$S_{micropore}$ [m²/g]	CuO [wt%]
Na-mt	12.5	31.4	—	—	—
Al-PILC	18.6	211.2	0.058	142.4	—
Cu1.1-(Al-PILC)	18.6	184.3	0.049	104.7	1.05
Cu2.0-(Al-PILC)	18.5	167.6	0.042	88.8	1.95
Cu2.3-(Al-PILC)	18.5	161.1	0.040	85.8	2.31

distance of ~9 Å can be evaluated. Addition of copper by exchange procedure does not affect the character of the XRD pattern. Table 1 shows the $d(001)$ basal spacings, BET surface area, micropore volume and the content of copper in the investigated catalysts. The values of $d(001)$ and the BET specific surface areas of pillared materials show an increase with respect to the parent Na-mt sample. Both results confirm that the pillaring procedures were effective. Comparison of the data obtained for the Cu-doped series with those of Al-PILC shows that an increase in copper content is accompanied by a gradual decrease of BET surface area and of micropore volume. Since the experimental procedure used for insertion of copper, that is, cation exchange followed by thorough washing, prevents a preferential adsorption of copper ions at the outer surfaces of the clay crystallites, the data of Table 1 may be taken as an indication that copper introduced into the pillared matrix occupies the interlayer area.

Dehydration/dehydroxylation processes accompanying the calcination of copper-doped pillared clays leave essentially 2 possibilities for anchoring the Cu(II) species: 1) coordinated to the oxygens of the silicate layer, or 2) coordinated to a pillar. To gain some insight into the location and nature of the copper centers, ESR investigations, presented in detail elsewhere (Bahranowski, Dula et al. 1996), have been undertaken. Figure 3 shows, as an example, the ESR spectrum of Cu1.1-(Al-PILC) catalyst recorded at −196 °C. The signal is anisotropic, with clearly defined $g_\parallel$ and $g_\perp$ regions, as expected for a Cu²⁺ in an axial symmetry. As shown in Figure 3 (insert), it can be deconvoluted into 2 components. One, with $g_\parallel$ = 2.369, $g_\perp$ = 2.085 and resolved hyperfine structure around $g_\parallel$ ($A_\parallel$ = 158.1 × 10⁻⁴ cm⁻¹), the other, with $g_\parallel$ = 2.301, $g_\perp$ = 2.142, broad and structureless. The appearance of the resolved signal indicates that part of

the introduced copper ions exist as isolated copper centers. To facilitate the interpretation of the data, the calcined Cu-exchanged non-pillared montmorillonite, in which Cu centers are attached to silicate layers only, has been used as a reference. The ESR signal produced by this sample ($g_\parallel$ = 2.387, $g_\perp$ = 2.083, $A_\parallel$ = 129.0 × 10⁻⁴ cm⁻¹) differs considerably from the resolved spectrum present in the pillared montmorillonite. This leads to a conclusion that the isolated copper ions are anchored at the pillars rather than at the surface of a silicate layer. The lineshape and parameters of the broad, unresolved signal fall into the range observed for clustered copper ions experiencing exchange interactions (Fujiwara et al. 1967). Indeed, the value of G = $g_\parallel$ − 2/$g_\perp$ − 2 calculated for this signal is less than 4 which, according to Hathaway and Billing (1970), is an indicator of significant exchange interactions. This result shows that besides the isolated cupric ions giving resolved hyperfine patterns and associated with the pillars, part of the copper forms clusters responsible for the broad, structureless component of the ESR spectrum. When the Cu content in the samples increases, the contribution from clustered species, as evidenced by ESR, increases as well. Since preparation conditions of the catalysts involve calcination in air at 673 K, the clustered species are believed to exist as patches of amorphous CuO.

The results of the catalytic hydroxylation of phenol, expressed in terms of yield of dihydroxybenzenes, are
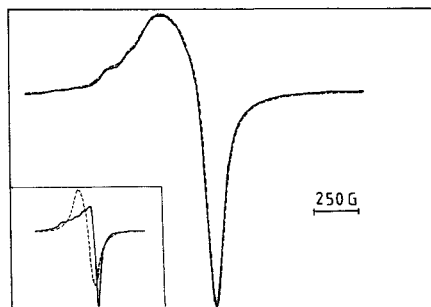

Figure 3.   ESR spectrum of Cu1.1-(Al-PILC) recorded at −196 °C. Solid line = experimental, dashed line = calculated. Insert shows the spectrum components: resolved signal = solid line, broad signal = dashed line.
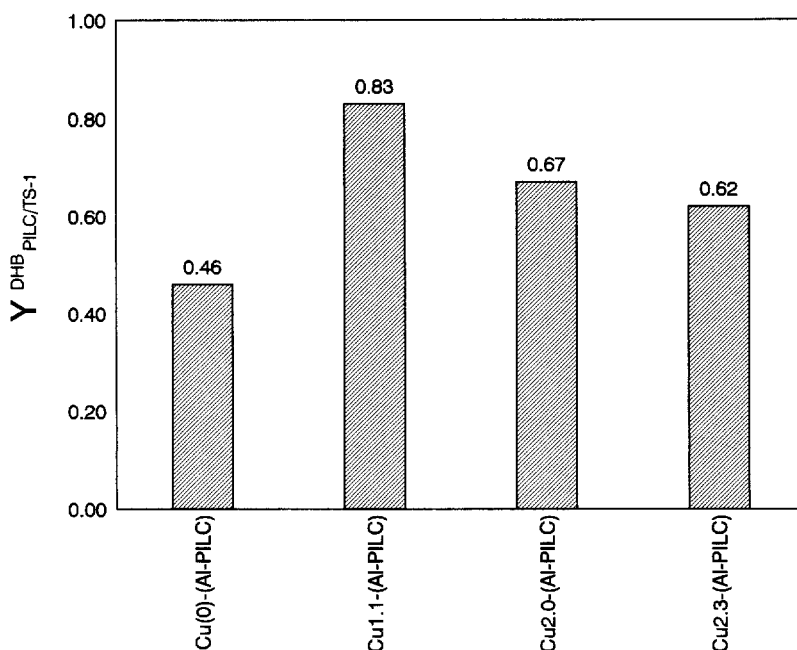
Figure 4.   Yield of dihydroxybenzenes over PILC catalysts relative to the performance of TS-1 catalyst. Reaction carried out at 92 °C for 60 min.

presented in Figure 4. All data are given in relative units with respect to the performance of a TS-1 catalyst on which the DHB yield was 12.9, and the H_2O_2 selectivity (hydrogen peroxide utilized in the formation of DHBs) 54%. Undoped Al-PILC samples show certain activity in the hydroxylation process. Addition of copper clearly improves the catalytic properties of the pillared material. For example, the yield of dihydroxybenzenes for the Cu1.1-(Al-PILC) catalyst is only slightly lower than for the TS-1 sample. Contrary to our expectations, further increase in the Cu content does not improve the catalytic performance of pillared clays. Instead, a fall in catalytic activity is observed. From the physico-chemical characterization data it is known that the higher the copper content, the larger the contribution from clustered Cu(II) ions. Consequently, an ever increasing number of copper centers, located below the cluster surface, are catalytically not active. Clusters of amorphous CuO may also cause a local blocking of the micropores, thus cutting off some of the active copper species.

The only hydroxylated products appearing in the course of reaction are catechol and hydroquinone. The catechol/hydroquinone ratio depends on the catalyst; that is, for TS-1 and (Al-PILC) samples it is close to 1, while for the Cu-doped pillared clays it is 1.2–1.4.

Reducing the duration of reaction at 92 °C to 10 min gives a $Y^{DHB}_{PILC}/Y^{DHB}_{TS-1}$ ratio of 1.07, to be compared with 0.83 after 60 min catalytic run. This shows that initially the transformation of phenol occurs faster on the Cu1.1-(Al-PILC) catalyst than on the TS-1 ref-

erence sample. This effect is even more pronounced when the temperature of reaction is lowered to 75 °C. Under such conditions the $Y^{DHB}_{PILC}/Y^{DHB}_{TS-1}$ ratio after 10 min is 2.3, and only after 30 min does this value go down to 0.92. We associate this observation with the fact that on the copper-containing PILC catalysts a substantial nonselective decomposition of hydrogen peroxide quickly occurs. For instance, during the first 10 min of reaction at 92 °C, the conversion of H_2O_2 over TS-1 sample is 45%, of which ~44% participates in DHB formation, to be compared with 90% conversion over Cu1.1-(Al-PILC) with selectivity to dihydroxybenzenes of 22%. However, upon addition of fresh portions of H_2O_2, the pillared clay catalyst shows again high activity in DHB formation, indicating that the fall of the $Y^{DHB}_{PILC}/Y^{DHB}_{TS-1}$ ratio with time is not due to the deactivation of the catalyst.

Stoichiometry of the hydroxylation reaction usually suggests that 1 molecule of hydrogen peroxide is necessary to convert 1 molecule of phenol to a DHB product. Previous studies (Romano et al. 1990) demonstrated in the case of TS-1 catalyst that optimum results are obtained when phenol is used in excess, with the amount of hydrogen peroxide corresponding to ~30% of the required quantity. The same proportions have been used in the present study. It seemed worthwhile to check on the influence of increased hydrogen peroxide concentration on the activity of investigated catalysts. For this reason, catalytic tests with twice the amount of hydrogen peroxide have been carried out. The results show that at 92 °C the use of different

reaction mixture compositions substantially changes the relative activity of Cu1.1-(Al-PILC) catalyst versus the TS-1 sample. Under such conditions the performance of the clay catalyst is clearly better than that of TS-1, and the $Y^{DHB}_{PILC}/Y^{DHB}_{TS-1}$ ratio after 60 min of reaction is 1.6.

Bearing in mind the relative simplicity of preparation of PILC materials in comparison to the synthesis of titanium silicalite, the results presented above show that Cu-doped alumina-pillared montmorillonite can be considered as an interesting alternative to TS-1 catalysts in the process of phenol hydroxylation with hydrogen peroxide.

Although no mechanistic studies have been undertaken during this study, the catalytic performance of investigated pillared clay samples and of the TS-1 catalyst depends on many factors, of which the most important are catalyst pretreatment before reaction and order of substrate dosing. For optimum results the catalysts have to be purged with argon at the temperature of reaction for at least 1 h. Phenol also has to be added before injection of hydrogen peroxide solution. Both effects suggest that stripping the catalyst active centers of adsorbed species to enable adsorption and activation of phenol molecules is a necessary condition for the reaction to proceed with high efficiency.

CONCLUSIONS

Physicochemical characterization of Cu-doped alumina-pillared samples shows that the catalysts are porous materials with copper species located in the interlayer, present either as isolated Cu^{2+} ions anchored at alumina pillars or as patches of amorphous CuO. Catalytic tests of hydroxylation of phenol show that the clay samples possess significant activity for the formation of dihydroxybenzenes. The yield of dihydroxybenzenes on the best pillared clay catalyst reaches 83% of the value obtained for the reference TS-1 sample. Experiments with change of substrate dosing indicate that adsorption and activation of phenol molecules is a necessary condition for the reaction to occur.

ACKNOWLEDGMENT

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