

NOTES

HYDROXYLATION OF PHENOL ON TITANIUM PILLARED MONTMORILLONITE

Key Words—Titanium Pillared Montmorillonite, Sulphation, Hydroxylation of Phenol.

Pillaring of smectites by complex inorganic cations yields porous solids that possess some of the properties of zeolites, strong acidity and regular porosity (Vaughan 1988). The size of the micropores is determined by the nature of the species of the intercalation (Gil et al. 1995). This new class of microporous solids shows interesting properties toward adsorption and catalysis.

The oxidation of phenol by hydrogen peroxide (H_2O_2) is a widely applied process in the chemical industry for the preparation of the dihydroxylated derivatives. This oxidation process is frequently reported as taking place through the decomposition of H_2O_2 , with formation of an unstable electrophilic intermediate, which attacks the phenol nucleus to give a phenoxy ion. This ion can be considered as the precursor of the products usually formed by this process, which are hydroquinone, catechol and benzoquinone. This distribution of the products is affected by the nature of the solvent (Thangaraj et al. 1991a; Tuel et al. 1991). Within protic solvents such as methanol, hydroquinone prevails over catechol, or while within an aprotic solvent such as acetone, catechol prevails over hydroquinone. Other conditions for good activities for phenol hydroxylation over substituted molecular sieves are typically, a positive dispersion of Ti species and a hydrophobic character support. The catalytic activity of the titanium silicalites in the hydroxylation of phenol was enhanced significantly by increasing the Ti content. As the Ti oxide, the amorphous Ti silicalite and physical mixtures of silicate and Ti oxide were inactive in this reaction, it was proposed (Thangaraj et al. 1990, 1991a) that the Ti ions associated with the silicalite framework structure was responsible for the observed catalytic activity. This positive dispersion of Ti species can also be obtained with the intercalating process in the titanium pillared clays (Ti-PILC).

Within the recent literature (Taramasso et al. 1983; Peregó et al. 1986; Reddy et al. 1990; Romano et al. 1990; Thangaraj et al. 1991b), the titanium-silicalite zeolites have been applied as catalysts for the hydrox-

ylation of phenol by H_2O_2 . We report our preliminary findings on the catalytic activity and selectivity of a Ti-PILC and its modification by sulphation in the hydroxylation of phenol. The effect of the solvents methanol or acetone on the distribution of the products was also studied.

EXPERIMENTAL

The starting material was montmorillonite (Kunipia F), supplied by Kunimine Co. This montmorillonite was dispersed in water and aged for at least 2 mo. It was washed by dialysis. The solid content of the dialyzed clay dispersion was 10 g/l.

The preparation of the intercalating solution of Ti involved the slow addition of titanium tetraethoxide to a 5M HCl solution with vigorous stirring, so that the H/Ti mole ratio was equal to 2 (Del Castillo and Grange 1993). This solution was used for intercalation without prior aging. The Ti solution was added to the aqueous montmorillonite suspension (pH = 1.4) at a ratio of 10 mmol Ti/g of clay. The solid was kept in contact with the solution at room temperature for 3 h, washed by centrifugation, dried at 120 °C and then calcined at 400 °C.

To prepare sulphated titanium pillared clays (SNTi-PILC) a similar procedure was used. A 0.1 M $(NH_4)_2SO_4$ solution was added to the Ti solution used for intercalation. Within this solution, SO_4^{2-}/Ti molar ratio was 0.075. After 3 h of reaction, the solid was washed by centrifugation, dried and calcined using the same conditions stated above.

The basal spacing of the samples was measured by X-ray diffraction (XRD) on a thin layer of the clay deposited on glass slides using a Kristalloflex 805-Siemens diffractometer with Ni filtered Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation.

Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP 2000 adsorption analyzer). The samples were previously degassed at 120 °C for 8 h.

Table 1. BET specific surface areas, basal spacings and acidic properties, the total ammonia desorbed.

Sample	Surface area (m ² /g)	d ₀₀₁ (Å)	Acidity (μeq.NH ₃ /g)
Ti-PILC	308	21.0	458
SNTi-PILC	268	19.6	526

Temperature-programmed ammonia desorption (TPD) experiments were performed to characterize the acidic properties of catalysts. In each TPD experiment, 0.1 g (200 < dp < 350 μm) of solid was treated under helium flow at 400 °C for 150 min and then cooled to 100 °C. Ammonia gas of 65 Torr (1 Torr = 133.3 N/m²) was adsorbed at 100 °C for 15 min. After removing the weakly adsorbed ammonia by helium flow at 100 °C for 1 h, the samples were heated at 10 K/min and the desorbed ammonia was detected by a thermal conductivity detector (Intersmat IGC 120ML) and the NH₃ was also determined by the Kjeldhal method.

The catalytic properties of the 2 Ti-PILC were evaluated by the study of the hydroxylation of phenol. One-half g of catalyst, 10 g of phenol and 10 g of solvent (methanol or acetone) were introduced in a 50 cm³ flask equipped with a magnetic stirrer at 70 °C. A solution of H₂O₂ (30%) was added to the reactor to a ratio of 0.2 H₂O₂/phenol. The liquid samples were regularly withdrawn with a filtering syringe and analyzed by gas chromatography (Delsi Instruments DI 200) with a DB-5.625 column (30 m × 0.25 mm, df = 0.25 μm). Selectivities were defined as the mole fraction of the reacted phenol, which was converted into a given product.

RESULTS AND DISCUSSION

The BET specific surface areas and the total amounts of NH₃ adsorbed of the samples studied are presented in Table 1. These results indicate a decrease of specific surface areas and basal spacings for the Ti-PILC after sulphation. The results also indicate an increase of the total amount of NH₃ desorbed for the sulphated sample.

The main products from the hydroxylation of phenol are hydroquinone, catechol and benzoquinone. The reaction scheme is presented in Figure 1. Some non-identified products were also detected. These products could be related to cracking and condensation of the reactants and the products of reaction.

The overall phenol conversions after 24 h of reaction for both samples are presented in Table 2. Ti-PILC and SNTi-PILC show similar phenol conversions after 24 h of reaction in methanol and acetone. SNTi-PILC presents a phenol conversion of 21% after 2 h of reaction in methanol. For the other reactions, the phenol conversion slightly increases after 10 h of reaction. The low activity of the Ti-PILC can be related to the

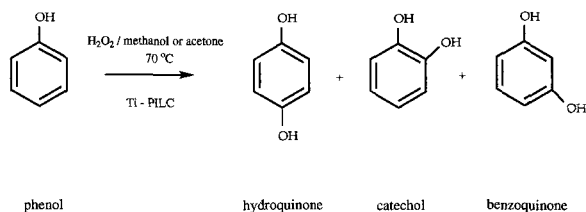


Figure 1. Reaction scheme.

acidity and, in the same order, to the strong adsorption of the products of reaction on the surface.

The selectivities of Ti-PILC and SNTi-PILC in methanol are presented in Figure 2. At low phenol conversions, hydroquinone is the main reaction product for the 2 catalysts.

The selectivities of Ti-PILC and SNTi-PILC in acetone are presented in Figure 3. At low phenol conversions, benzoquinone is the main reaction product for both catalysts. As the phenol conversion increases, the main products are hydroquinone and catechol. The selectivities of hydroquinone and catechol for Ti-PILC are very similar. SNTi-PILC shows a higher selectivity for hydroquinone and catechol than Ti-PILC for the 15 to 20% phenol conversion range. The changes of selectivity can also occur by the consecutive oxidation of the products.

When the influence of the solvent on the selectivities is compared, an important effect is observed. Hydroquinone is the main product obtained when methanol is used as solvent. No modification in the selectivities is observed when Ti-PILC and SNTi-PILC are used as catalysts in this solvent. For acetone, catechol is the main product when SNTi-PILC is used as a catalyst. The selectivities for hydroquinone and catechol are similar when Ti-PILC is used as a catalyst in acetone.

The hydroxylation of phenol to form hydroquinone and catechol has been postulated (Notari 1989) to occur via formation of titanium-peroxo species, which facilitate the direct insertion of oxygen into the aromatic ring. The selectivities observed in methanol and acetone can be related to the nature of the solvents. When the reaction is carried out in methanol, a protic solvent, the hydroquinone is the main product in the reaction for Ti-PILC and SNTi-PILC. The formation of H-bonded between the methanol and the phenol can explain these results of selectivity. When the reaction

Table 2. Overall phenol conversions (%) in methanol and acetone as solvents.

Sample	Methanol	Acetone
Ti-PILC	22 [†]	22.5
SNTi-PILC	24	20

[†] Overall phenol conversions (%) after 24 h of reaction.

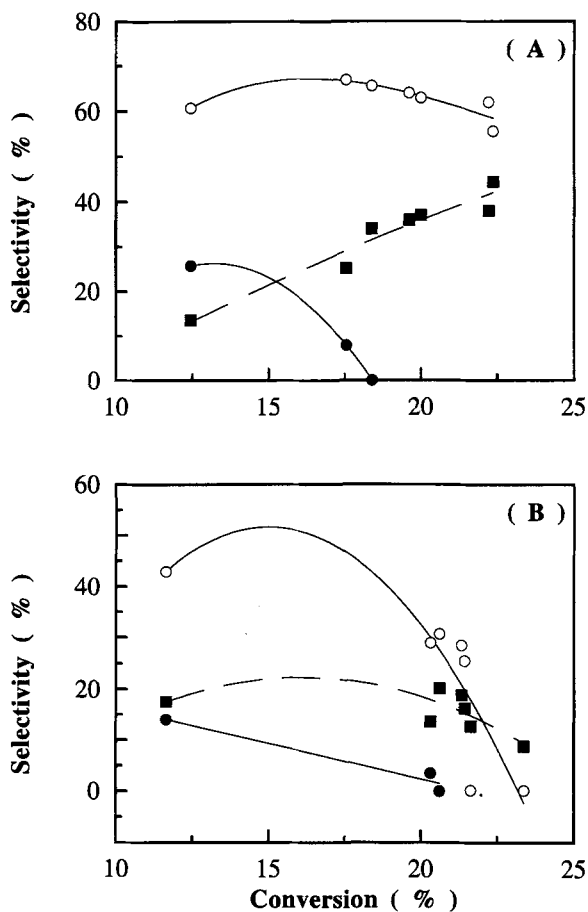


Figure 2. Key: Hydroquinone (○); catechol (■); and benzoquinone (●) selectivities for the hydroxylation of phenol in methanol as solvent. Ti-PILC (A) and SNTi-PILC (B).

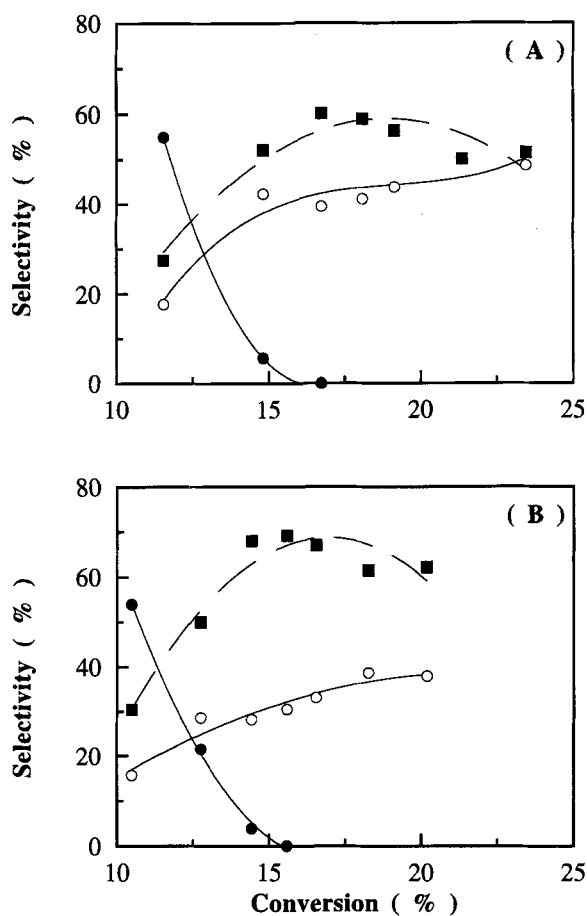


Figure 3. Key: Hydroquinone (○); catechol (■) and benzoquinone (●) selectivities for the hydroxylation of phenol in acetone as solvent. Ti-PILC (A) and SNTi-PILC (B).

is carried out in acetone, an aprotic solvent, only SNTi-PILC shows catechol as the main product of reaction. For Ti-PILC, hydroquinone and catechol show similar selectivities. Within this solvent, the nature of Ti-PILC and SNTi-PILC can affect the selectivities. In this way, the acidity of SNTi-PILC can explain the higher selectivity to catechol than observed for Ti-PILC (Thangaraj et al. 1990).

Recently, the role of the acidity of Ti catalysts has been discussed for this reaction (Thangaraj et al. 1990; Germain et al. 1995). The authors demonstrated that the acidity of the catalyst presents an important effect upon the induction period of the reaction and upon the autocatalysis phenomenon. In the same way, the acidity also intervenes in the over-oxidation of phenol.

Therefore, the effects of the nature of the solvent in the hydroxylation of phenol on 2 titanium pillared montmorillonites have been studied. It has been observed that the nature of the solvent affects the product distribution. When acetone is used as solvent, the possible effect of the acidity of the catalyst must also be

considered to explain the distribution of the products. The hypothesis is that in the presence of acetone, the interaction between the Brönsted sites of the surface catalyst and the phenol is favored. The action of the titanium-peroxo species is facilitated and, as the sulphation of Ti-PILC produces an increase of the Brönsted sites (Yamaguchi 1990), the catechol selectivity for SNTi-PILC increases. Conversely, the low activity of the Ti-PILC can be related to the acidity that, as well as the microporous nature, produces a strong adsorption of the products of reaction. This is the main difference of this microporous solid from the titanium-silicalite zeolites described in the literature.

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