Selective dehydration of 1-phenylethanol to 3-oxa-2,4-diphenylpentane on titanium pillared montmorillonite

A. Gil [a,*], H.L. Del Castillo [a], J. Masson [b], J. Court [b], P. Grange [*,a]

[a] Unité de Catalyse et Chimie des Matériaux Divisés, Université catholique de Louvain, Place Croix du Sud, 2/17, 1348 Louvain-la-Neuve, Belgium
[b] LEDSS, Université Joseph Fourier, 301 rue de la Chimie, St Martin d'Héres, 38041 Grenoble, France

Abstract

Activity and selectivity of titanium pillared clay (Ti-PILC) are higher than those obtained with a zeolite (Y-82) in dehydration of 1-phenylethanol. Under hydrogen, 48% conversion and 98.4% selectivity are obtained on Ti-PILC as compared with 30% conversion and 81.4% selectivity on Y-82 zeolite in the same conditions. Physico-chemical characterizations (adsorption of nitrogen and TPD of ammonia) suggests that these results may be explained by a better accessibility of the strong acid sites of the Ti-PILC.

Keywords: Dehydration; 1-Phenylethanol; Pillared clay; Titanium

1. Introduction

Pillared clays derived from smectites interlayered with inorganic polymeric cation represent a relatively new class of porous materials [1–3]. These solids behave as sieves for molecules with a shape selectivity comparable to that of the zeolites. The main difference resides in their bidimensional character. These materials can possibly replace zeolite-containing catalysts for certain reactions.

Titanium pillared clays have been investigated for several years and interesting textural and acidities properties have been reported [4–11] from polymeric titanium hydroxides of different origin. The properties of TiO_2 as catalyst were a principal incentive to study the titanium pillared clays.

In the least years, catalytic studies on pillared clays have motivated the possible use of these materials as catalysts. Pillared clays have been practically applied as catalysts for cracking, oligomerization, alkylation, disproportionation, etc. In recent works, the catalytic behaviour in the transformation of m-xylene [12], the disproportionation of alkylsilanes [13], the disproportionation of toluene [14], the dehydrocyclodimerization of propane [15] and the propene alkylation of biphenyl [16] over pillared clays and zeolites was taking into account. The relative amount and strength of the acid sites and the geometrical limitations to explain the results obtained have been proposed.

It has been shown [17] that in the dehydration of alcohols to olefins and ethers over zeolite, both reaction rate, and selectivity are strongly influenced by the pore geometry. In order to shed light

* Corresponding authors.

on the accessibility and the catalytic properties of the strong acid sites of the titanium pillared clay, the dehydration of 1-phenylethanol over a titanium pillared clay and a zeolite has been compared.

2. Experimental

The starting material used in this work was montmorillonite (Kunipia F), kindly supplied by Kunimine Co.. This commercial product is available in the sodium-exchanged form with a particle size less than 2 μm. This Na-montmorillonite was dispersed in water and aged for at least 2 months. Finally, the suspension was then washed by dialysis and the solid content of the dialyzed clay dispersion was 10 g l^{-1}.

The preparation of the intercalating solution of titanium involved the slow addition of titanium tetraethoxide to a 5 M HCl solution under stirring vigorously, so that the H/Ti mole ratio was equal to 2 [18]. This solution was used for intercalation without prior aging. The titanium 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 398 K and then calcined at 623 K for 48 h.

The zeolite studied to compare his properties with the pillared clay was supplied by Union Carbide (Y-82, SiO$_2$/Al$_2$O$_3$ = 5.9).

The basal spacing of the Ti-PILC was measured by X-ray diffraction (XRD) on a thin layer of the clay deposited on glass slides using a D-5000 Kristalloflex Siemens diffractometer with Ni-filtered Cu-K$_\alpha$ radiation.

Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP 2000M adsorption analyzer). The samples were previously degassed at 393 K for 24 h. Specific total surface areas were calculated as the sum of the specific micropore surface areas obtained by the Dubinin–Radushkevich method and the specific external surface areas obtained by the α_s-method [19] (montmorillonite and Ti-PILC) and t-method (Y-82). The specific total pore volumes were estimated from the nitrogen uptake at $P/P_0 \approx 0.99$.

Temperature-programmed ammonia desorption (TPD) experiments were performed to characterize the acidic properties of catalysts. In each TPD experiments, a sample weighing about 0.1 g ($200 < d_p < 350\ \mu$m) was placed in the cell, which was evacuated at 673 K for 150 min and then cooled to 373 K. Ammonia gas at 65 Torr (1 Torr = 133.3 N m^{-2}) was adsorbed at 373 K for 15 min. The sample was kept in the stream state flow, prior to heating at a rate of 4 K min^{-1} to 973 K. As H$_2$O, which was produced from dehydroxylation, was desorbed simultaneously after heating at 673 K with NH$_3$, the ammonia TPD spectrum was compared with the spectrum obtained with the same catalyst which had not adsorbed NH$_3$. In all cases, the molecules desorbed were detected by a thermal conductivity detector (Intersmat IGC 120ML) and the NH$_3$ was determined by the Kjeldhal method.

The catalyst was calcined at 673 K for 12 h, then cooled in a desiccator under vacuum. Before introduction of 1-phenylethanol, the reactor containing a suspension of the catalyst (0.1 g) in cyclohexane (135 ml) was purged with a flow of hydrogen followed by a pretreatment at room temperature for 1 h with stirring under a hydrogen pressure of 0.9 MPa. Temperature was then raised to 353 K and 1-phenylethanol (42 mmol) was introduced as the reaction proceeded, samples were with drawn from the reaction mixture and analyzed by gas liquid chromatography. For the GLC a packed column (4 m × 1/8 in) with OV 210 10% + XE 60 5% on chromosorb WHP 80/100 was used with nitrogen as carrier gas at a flow of 20 ml min^{-1}. The temperature conditions were as follows: isothermal at 378 K during 20 min, heating up to 453 K at a rate of 10 K min^{-1}. Dodecane was used as internal standard. Authentic samples of 3-oxa-2,4-diphenylpentane and 3-oxa-2-phenylpentane were prepared according to the procedure described by Kim [20], they have

Table 1

Specific surface areas, specific pore volumes and basal spacings [$d(001)$] for the samples indicated

Sample	$A_{\mu p}$ [a.1] (m^2 g^{-1})	$V_{\mu p}$ [b.1] (ml g^{-1})	A_{ext} [a.2] (m^2 g^{-1})	V_{pTotal} [b.2] (ml g^{-1})	A_{Total} [a.3] (m^2 g^{-1})	$d(001)$ [c] (Å)
Na-montmorillonite	23	0.008	6	0.040	29	12.0
Ti-PILC	313	0.160	45	0.242	358	22.2
Y-82	591	0.186	61	0.323	652	–

[a] Specific surface areas: [a.1] specific surface areas; [a.2] specific external surface areas; [a.3] specific total surface areas.
[b] Specific pore volumes: [b.1] specific micropore volumes; [b.2] specific total pore volumes.
[c] Basal spacings.

Table 2

Amounts of ammonia desorbed from 373 to 673 K and from 673 to 973 K for the samples indicated

Sample	μmol$_{NH_3}$ g^{-1} 373–673 K	673–973 K	Total	μmol$_{NH_3}$ m^{-2} 373–673 K	673–973 K	Total
Na-montmorillonite	52	[a]		1.82	[a]	
Ti-PILC	527	190	717	1.47	0.53	2
Y-82	1464	303	1767	2.48	0.51	3

[a] Not measured.

been used for the quantitative measurements of the reaction products.

3. Results

Table 1 presents the specific surface areas (A), specific pore volumes (V) and basal spacings [$d(001)$] of the samples studied. The standard adsorption isotherm of nitrogen on Na-montmorillonite calcined at 1073 K was used as reference.

Table 2 presents the amounts of NH$_3$ desorbed between two temperature ranges: 373–673 K and 673–973 K. The total amount desorbed is also presented. It can be seen, the high acidity that presents the zeolite as if one compares with Ti-PILC and Na-montmorillonite. This difference is
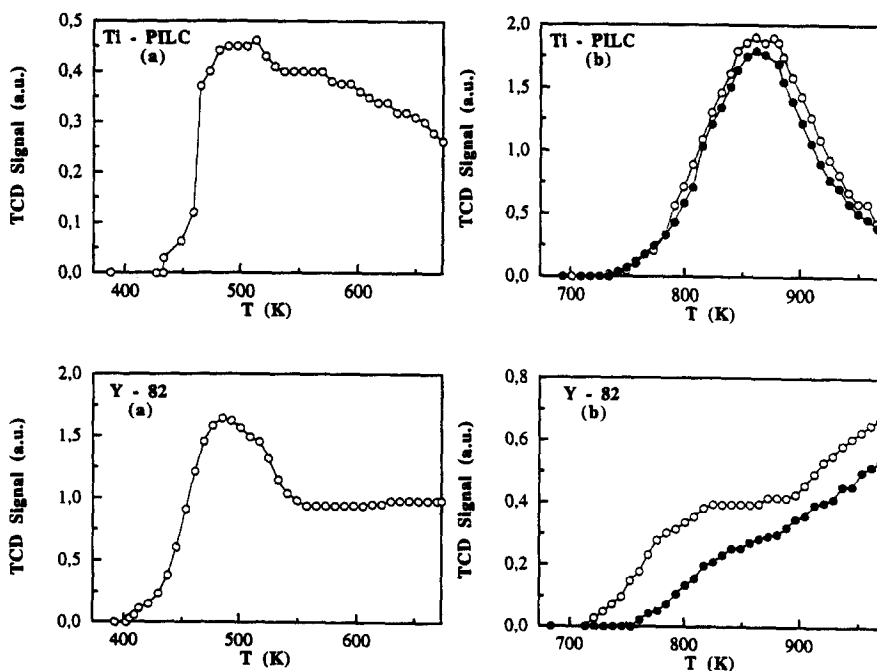

Fig. 1. Ammonia TPD experiments of Ti-PILC and Y-82. (a) Temperatures from 373 to 673 K and (b) temperatures from 673 to 973 K. In (b) the open symbols correspond to the ammonia TPD experiments for the samples and the solid symbols correspond to the blank experiments.
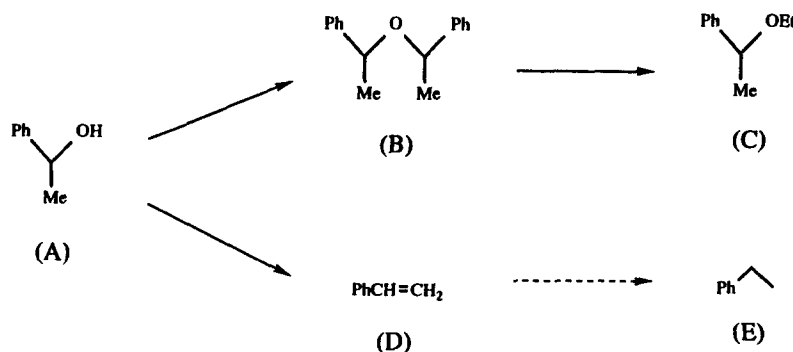
Fig. 2. Reaction scheme.

Table 3
Yield (%) of **B**, **C**, **D** and **E** as a function of the conversion of **A** (%) over PILC

Time (h)	A	B	C	D	E	(B+C)/(D+E)
0.5	10.1	9.9	0	0.20	0	50
1	17.8	17.5	–	0.30	0.01	56
2	23.5	23.0	–	0.44	0.02	50
4	40.3	39.6	–	0.66	0.05	56
5	47.9	47.1	–	0.71	0.06	61
6	53.6	52.7	–	0.86	0.08	56
8	67.2	66.0	–	1.08	0.12	55

Table 4
Yield (%) of **B**, **C**, **D** and **E** as a function of the conversion of **A** (%) over Y zeolite

Time (h)	A	B	C	D	E	(B+C)/(D+E)
1	12.9	10.7	1.36	0.83	0.04	14
2	18.0	15.2	1.84	0.94	0.07	17
4	23.9	19.3	3.10	1.37	0.18	14
5	29.7	24.2	3.64	1.65	0.21	15
6	35.9	29.9	3.92	1.80	0.25	17
7	39.7	33.4	4.13	1.79	0.30	18
9	45.9	38.9	4.60	1.99	0.38	18
22.3	70.1	59.1	6.56	3.19	1.28	15
25	72.4	60.7	6.86	3.33	1.52	14
28	76.2	64.0	7.06	3.41	1.76	14
30.5	80.2	67.7	7.33	3.33	1.83	15

smaller if one compares the ammonia desorbed as μmol m^{-2}. In the 673–973 K range, the ammonia amounts desorbed as μmol m^{-2} are almost identical in Ti-PILC and in Y-82, therefore the densities of strong acid sites expressed by square metre are very similar in both samples.

Fig. 1 shows the results of the NH$_3$ TPD experiments for Ti-PILC and Y-82. Included in the figures (b) are curves for blank samples in the absence of adsorbed ammonia. This behaviour of the blank samples has been attributed to volatile products resulting from structural rearrangement [21].

Fig. 2 shows the most likely overall reaction scheme that is proposed.

Table 3 and Table 4 show the evolution of the reaction products with the time.

4. Discussion

4.1. Physico-chemical characterization

In a previous work [22], the analysis and comparison of the microporosity between Ti-PILC and Y-82 has been presented. In this work, it has been observed that the microporosity of these samples is important and makes a difference. These differences can be observed in Table 1. Nevertheless, the adsorption isotherms at low pressures indicated that the microporosity of the samples is very different. Two micropore sizes for Ti-PILC and one micropore size for Y-82 were observed. However, also differences between the micropore sizes have been observed. The zeolite presents a smaller micropore size than the pillared clay.

Both samples present differences in the TPD of ammonia. The spectra obtained over the temperature range 373–673 K indicate a very wide desorption band for Ti-PILC, suggesting a wide

distribution of the strength of the acidic sites. A difference in intensity can also be observed. Quantification of the ammonia desorbed over the temperature range 373–673 K reveals that the amount of NH_3 chemically bound to Y-82 is approximately three times that for Ti-PILC (Table 2). This result indicates the presence of a substantially larger number of acid sites for Y-82. Small differences between the samples and the blank can be observed in the spectra obtained at the temperature range 673–973 K. This behaviour indicates a significant presence of the volatile products for Y-82 [21].

4.2. Dehydration of 1-phenylethanol

The dehydration of 1-phenylethanol (**A**) was performed over Ti-PILC and over Y-82 zeolite under the same conditions i.e. in a stirred batch reactor at 353 K under 0.9 MPa of hydrogen. The products found (Fig. 2) were 3-oxa-2,4-diphenylpentane (**B**), 3-oxa-2-phenylpentane (**C**), styrene (**D**) and ethylbenzene (**E**). No detectable amounts of unidentified products were detected in the reaction mixtures. As expected **B** was obtained in equal amounts of the meso form and of the racemate, but the diastereoisomers are not differentiated in the yield of **B** (Tables 1 and 2).

One can see that the dehydration of 1-phenylethanol to styrene is low over Ti-PILC and that 3-oxa-2-phenylpentane is not observed over this catalyst, therefore the selectivity in **B** with Ti-PILC is higher than that obtained with Y-82 zeolite. Thus 48% conversion and 98.4% selectivity are obtained on clay for a reaction time of five hours as compared with 30% conversion and 81.4% selectivity in exactly the same conditions. From these results it appears also that Ti-PILC presents a higher activity in the dehydration of 1-phenylethanol than Y-82 zeolite.

In our opinion, 3-oxa-2-phenylpentane results form the hydrodealkylation of 3-oxa-2,4-diphenylpentane, however benzene which should be obtained, cannot be observed since the reactions were carried out in cyclohexane. One can see that this compound (**C**) was not observed over Ti-

PILC. The ratio $(\mathbf{B} + \mathbf{C}) / (\mathbf{D} + \mathbf{E})$ remained constant over both catalysts for extents of the dehydration going from 10% up to 80%, therefore the formation of **B** and **D** are two competitive parallel reactions, and according to the catalyst these two compounds can react further affording **C** and **E**, respectively.

These ratios are representative of the relative rates of etherification and olefin production, thus the ether selectivity is three times higher over Ti-PILC than over Y-82 zeolite. Assuming that etherification proceeds by an Eley–Rideal mechanism, this reaction would be favored in the catalyst with the largest pore system. This assumption is borne out experimentally, since Ti-PILC which presents a larger micropore size than the zeolite [22] displays the highest ether selectivity. Thus **B** can readily form and pass out of the cavities of Ti-PILC whereas it has difficulty forming and leaving the pores of Y-82 zeolite.

5. Conclusions

The results obtained in this work indicate that the dehydration of 1-phenylethanol is affected by the structure of the microporous solids. The activity and selectivity of a titanium pillared clay are higher than those obtained with a zeolite, in the same conditions. The zeolite shows a substantially larger number of acid sites than the titanium pillared clay, but the pillared clay shows a better accessibility of its acid sites.

Acknowledgements

References

[1] T.J. Pinnavaia, Science, 220 (1983) 365.
[2] F. Figueras, Catal. Rev.-Sci. Eng., 30 (1988) 457.

[3] D.E.W. Vaughan, in W.H. Flank and T.E. Whyle, Jr. (Eds.), ACS Symposium Series, 368, American Chemical Society, 1988, p. 308.

[4] J.P. Sterte, Clays Clay Minerals, 34 (1986) 658.

[5] M.L. Occelli, J. Mol. Catal., 35 (1986) 377.

[6] A. Bernier, L.F. Admaiai and P. Grange, Appl. Catal., 77 (1991) 269.

[7] M.L. Occelli, in L.G. Shultz, H. Van Olphen and F.A. Mumpton (Eds.), Proc. of the Int. Clay Conf., Bloomington, IN, 1987, p. 319.

[8] L. Khalfallah Boudali, A. Ghorbel, D. Tichit, B. Chiche, R. Dutartre and F. Figueras, Microporous Mater., 2 (1994) 525.

[9] K. Bahranowski and E.M. Serwicka, Colloid. Surf. A, 72 (1993) 153.

[10] S. Yamanaka, Y. Inone, M. Hattori, F. Okuma and M. Yoshikawa, Bull. Chem. Soc. Jpn., 65 (1992) 2494.

[11] S.-J. Jong, J.-T. Lin and S. Cheng, in T. Hattori and T. Yashima (Eds.), Studies in Surface Science and Catalysis, Vol. 83, Elsevier–Kodansha, Amsterdam–Tokyo, 1993.

[12] R. Molina, A. Shutz and G. Poncelet, J. Catal., 145 (1994) 79.

[13] F. Bouchet, H. Fujisama, M. Kato and T. Yamaguchi, in J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Eds.), Studies in Surface Science and Catalysis, Vol. 84, Elsevier, Amsterdam, 1994.

[14] H. Auer and H. Hofmann, Appl. Catal. A, 97 (1993) 23.

[15] S.M. Bradley and R.A. Kydd, J. Catal., 142 (1993) 448.

[16] J.-R. Butruille and T.J. Pinnavaia, Catal. Today, 14 (1992) 141.

[17] D.E. Bryant and W.L. Kranich, J. Catal., 8 (1967) 8.

[18] H.L. del Castillo and P. Grange, Appl. Catal. A, 103 (1993) 23.

[19] S.J. Gregg and K.S.W. Sing (Eds.), Adsorption, Surface Area and Porosity, Academic Press, London, 1991, Ch. 4.

[20] S. Kim, K.N. Chung and S. Yang, J. Org. Chem., 52 (1987) 3917.

[21] J.-R. Butrille, L.J. Michot, O. Barrès and T.J. Pinnavaia, J. Catal., 139 (1993) 664.

[22] A. Gil, A. Massinon and P. Grange, Microporous Mater., 4 (1995) 369.