Selective catalytic reduction of NO by NH_3 on titanium pillared montmorillonite

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The acidity of a titanium pillared montmorillonite (Ti-PILC) has been modified by two methods of sulfation. The acidic properties of these pillared clays have been studied by temperature-programmed ammonia desorption and FTIR analysis of pyridine adsorption. The catalytic activity of these titanium pillared clays in the selective catalytic reduction (SCR) of NO by NH_3 with or without SO_2 has been investigated. For the three titanium pillared clays, a high resistance to SO_2 presence has been observed.

Keywords: titanium pillared montmorillonite; sulfation; selective catalytic reduction

1. Introduction

Pillared interlayer clays (PILCs) have been described as a new generation of microporous materials [1–3]. Since the first work of Vaughan [4], numerous studies on pillared clays have appeared in the literature. These solids are obtained by exchanging the original interlayer cations of a smectite for polyoxocations. Various polyoxohydroxy–metal species have been intercalated in smectites, with various degrees of success. Polymeric compounds of Al, Zr, Cr, Ti are among the principal pillaring species quoted in the literature.

Titanium pillared clays have been investigated for several years and interesting textural and acidic properties have been reported [5–12] from polymeric titanium hydroxides of different origin. The properties of TiO_2 as catalyst were a principal incentive to study the titanium pillared clays.

Selective catalytic reduction (SCR) of nitrogen oxides with ammonia is of increasing industrial importance for the control of the air pollution. A comprehensive review of the subject is available [13]. The commercial catalysts are V_2O_5 with mixed WO_3 and/or MoO_3 supported on TiO_2. Various authors indicated that there is a direct correlation between the SCR activity and the Brønsted acidity of V_2O_5 [14–17], and that the Brønsted acid sites are thought to be the active sites.

It is well known that both Lewis and Brønsted acid sites exist on pillared clays [2], with a larger proportion being Lewis acid sites. The possible modification of the acidity strength of pillared clays by sulfation has been reported in the literature [18–20]. In this way, recently, the SCR activities on pillared clays and potential advantages of using pillared clays have been presented [21–23].

Various authors [16] have indicated that Brønsted sites are important for selective catalytic reduction of NO by NH_3. In this order, the increase of the SCR activity by addition of SO_2 in the reactants has been proposed [16]. The possible explanation has been the formation of surface SO_4^{2-} changing the catalyst surface acidity. On the other hand, it has been shown that SO_2 inhibit or poison the catalytic sites in conventional SCR catalysts and efforts are directed to the modification of the catalysts in order to decrease this deactivation [24].

In this work, the acidity of a titanium pillared montmorillonite has been modified by sulfation and the activity in the selective catalytic reduction (SCR) of NO by NH_3 has been investigated.

2. Experimental

The starting material used in this work was montmorillonite (Kunipia F), kindly supplied by Kunimine Co. This montmorillonite was dispersed in water and aged for at least two months. It was washed by dialysis. The solid content of the dialyzed clay dispersion was $10\ \mathrm{g}\ \ell^{-1}$.

The preparation of the intercalating solution of titanium involved the slow addition of titanium tetraethoxide to a 5 M HCl solution under vigorous stirring, so that the H/Ti mole ratio was equal to 2 [25]. This solution was used for intercalation without prior aging. The titanium solution was added to the aqueous montmorillonite suspension ($\mathrm{pH} = 1.4$) at a ratio of 10 mmol Ti (g of clay)$^{-1}$. The solid was kept in contact with the solution at room temperature for 3 h, washed by centrifugation, dried at 393 K and then calcined at 673 K.

In order to prepare two sulfated titanium pillared clays (SNTi-PILC and SHTi-PILC), the above titanium pillared montmorillonite was treated with a 0.1 N $(NH_4)_2SO_4$ (SNTi-PILC) and a 0.1 N H_2SO_4 (SHTi-PILC) solution. In both solutions, SO_4^{2-}/Ti molar ratio was 0.025. Both solids were washed by centrifugation, dried at 393 K and calcined at 673 K for 8 h.

Nitrogen adsorption experiments were performed at 77 K using a static volumetric apparatus (Micromeritics ASAP 2000 adsorption analyzer). The samples were previously degassed at 393 K for 8 h.

Temperature-programmed ammonia desorption (TPD) experiments were performed to characterize the acidic properties of pillared clays. In each TPD experiment, a sample weighing about 0.1 g ($200 < dp < 350$ μm) was placed in the cell, which was evacuated at 673 K for 150 min and then cooled to 373 K. Ammonia gas of 65 Torr (1 Torr = 133.3 N m^{-2}) was adsorbed at 373 K for 15 min. After removing the weakly adsorbed ammonia by helium flow at 373 K for 1 h, the samples were heated at 10 K min^{-1} and the desorbed ammonia detected by a thermal conductivity detector (Intersmat IGC 120ML) and the NH_3 was determined by the Kjeldhal method.

FTIR spectra were recorded using a Brücker FT88 spectrometer. In preparation for pyridine adsorption, samples were pressed into self-supported disks, placed in an IR cell and treated under vacuum (10^{-6} Torr) at 673 K for 4 h. After cooling to room temperature, spectrum (a) was recorded. The samples were then exposed to pyridine vapour for 5 min. Spectra (b), (c) and (d) correspond to successive outgassing (5×10^{-5} Torr) of samples at 473, 573 and 673 K, respectively.

SCR experiments were carried out in a fixed-bed reactor between 393 and 673 K and atmospheric pressure, using a mixture of NO 0.1 vol% with a NH_3/NO molar ratio of 1.06 and 0.43 vol% O_2. The catalyst amount (0.045 g, $200 < dp < 350$ μm) and the space velocity (500 h^{-1}) were kept constant for all experiments. The reaction products were analysed by an on-line mass spectrometer (QMG311 Balzers).

3. Results and discussion

The BET specific surface areas (A) of the samples studied are presented in table 1. The total amounts of NH_3 desorbed are also presented in table 1. These results indicate an increase of the total amount of NH_3 desorbed for the sulfated samples and no high differences between the two methods of sulfation.

Table 1
BET specific surface areas and acidic properties

Sample	Surface area ($m^2 g^{-1}$)	Acidity	
		(μeq. NH_3 g^{-1})	L/B
Ti-PILC	308	458	1.70
SNTi-PILC	274	573	1.37
SHTi-PILC	256	584	1.42

The infrared spectra in the 1700–1400 cm^{-1} region for SHTi-PILC calcined at 673 K, after pyridine adsorption and after subsequent desorption under vacuum for 30 min at 473, 573 and 673 K are shown in fig. 1. The general trends observed for pyridine adsorbed on titanium pillared montmorillonite evacuated at different temperatures are illustrated in fig. 1. Qualitatively, pyridine adsorption spectra exhibit the same behaviour with outgassing temperature. These spectra exhibit Brønsted [26], PYH^+, bands at 1491, 1540 and 1630 cm^{-1}; Lewis [26] acid sites, PYL, at 1448, 1491, 1610 and 1624 cm^{-1}; and physisorbed or hydrogen-bonded pyridine [26], HPY, at 1597 cm^{-1}. The Lewis/Brønsted (L/B) acid sites ratios have been determined (b spectrum) from the integral area of the bands at 1450 cm^{-1}, Lewis, and 1540 cm^{-1}, Brønsted, respectively. These ratios are also presented in table 1. These results indicate a decrease of the acid sites ratio for the sulfated samples and small differences between the two methods of sulfation.

The overall NO conversion for the three titanium pillared montmorillonites as a function of the temperature of reaction is shown in fig. 2. The overall NO conversion when SO_2 (0.4 vol%) is or is not present in the reaction is shown in this figure. Also, two successive tests are carried out, the first in presence of SO_2 and the second without SO_2. For the three samples, an increase of the overall NO conversion with the temperature of reaction has been observed. Only differences in the overall NO

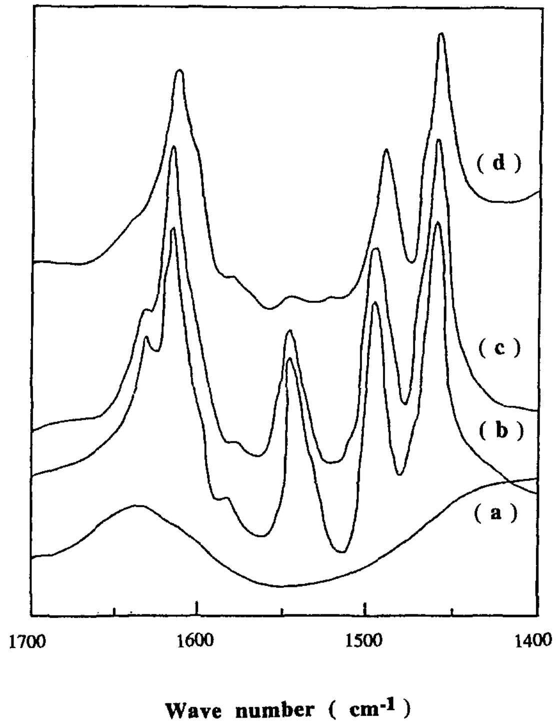

Fig. 1. FTIR spectra of pyridine adsorbed on SHTi-PILC. Pillared clay spectra before pyridine adsorption (a), pillared clay exposed to pyridine and outgassed at 473 K (b), 573 K (c) and 673 K.

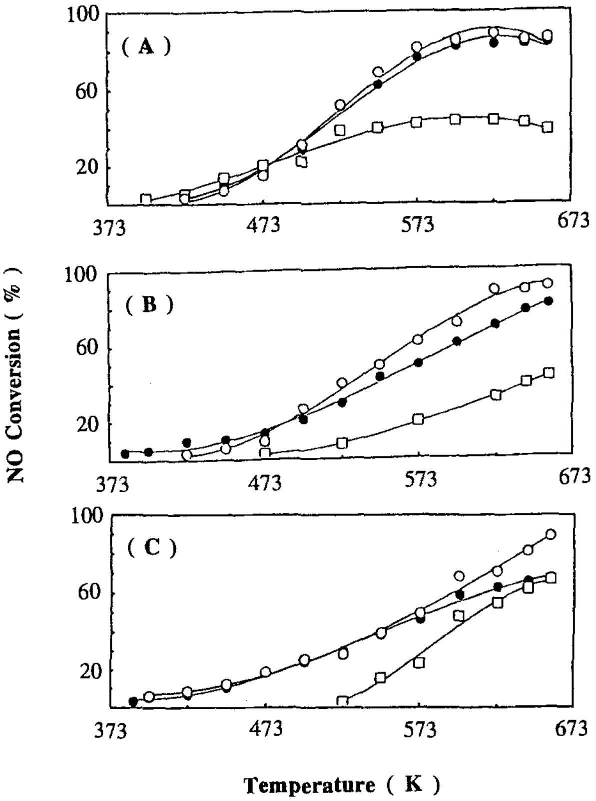

Fig. 2. Selective catalytic reduction of NO by NH_3. (A) Ti-PILC, (B) SHTi-PILC and (C) SNTi-PILC. NO conversion without SO_2 (●) and with SO_2 (□) in the feed. NO conversion (○) after test with SO_2 presence.

conversion can be observed between 250 and 673 K. Ti-PILC is more active at lower temperatures than SNTi-PILC and SHTi-PILC, but all catalysts show a similar overall NO conversion at 673 K. When the temperature of reaction is 673 K, only N_2 and H_2O are observed. When the reaction is carried out in presence of SO_2, traces of NO_2 are observed at temperatures higher than 623 K. If we compare the SCR activities at 673 K of the Ti-PILC with and without the presence of SO_2, SHTi-PILC shows higher resistance for the SO_2 effect with respect to Ti-PILC and SNTi-PILC. The main differences correspond at low temperatures. This behaviour can be related to an inhibition mechanism because SCR activities are recovered when SO_2 is not present and the NH_3 oxidation in presence of SO_2 is observed. For all pillared clays, the catalytic test after inhibition with SO_2 shows a higher NO conversion than when the reaction is carried out with the fresh catalysts. A slight increase of the acidity can explain these conversions.

In conclusion, the modification of the acidic properties by two methods of sulfation in a titanium pillared montmorillonite has been presented. The three titanium pillared clays have been tested and compared for their SCR activities, and a high resistance at 673 K to SO_2 presence for SHTi-PILC has been observed.

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References

[1] T.J. Pinnavaia, Science 220 (1983) 365.
[2] F. Figueras, Catal. Rev. Sci. Eng. 30 (1988) 457.
[3] M.L. Occelli, in: *Studies in Surface Science and Catalysis*, ed. S. Kaliaguine (Elsevier, Amsterdam, 1988) p. 101.
[4] D.E.W. Vaughan, P.K. Maher and E.W. Albers, US Patent 3,775,345 (1973).
[5] J.P. Sterte, Clays Clay Minerals 34 (1986) 658.
[6] M.L. Occelli, J. Molec. Catal. 35 (1986) 377.
[7] A. Bernier, L.F. Admaiai and P. Grange, Appl. Catal. 77 (1991) 269.
[8] M.L. Occelli, in: *Proc. Int. Clay Conf.*, eds. L.G. Shultz, H. Van Olphen and F.A. Mumpton (Blomington, Indiana, 1987) p. 319.
[9] L. Khalfallah Boudali, A. Ghorbel, D. Tichit, B. Chiche, R. Dutartre and F. Figueras, Microporous Mater. 2 (1994) 525.
[10] K. Bahranowski and E.M. Serwicka, Coll. Surf. A 72 (1993) 153.
[11] S. Yamanaka, Y. Inone, M. Hattori, F. Okuma and M. Yoshikawa, Bull. Chem. Soc. Jpn. 65 (1992) 2494.
[12] S.-J. Jong, J.-T. Lin and S. Cheng, in: *Zeolites and Microporous Crystals*, Studies in Surface Science and Catalysis, Vol. 83, eds. T. Hattori and T. Yashima (Elsevier, Amsterdam, 1993).
[13] H. Bosch and F. Janssen, Catal. Today 2 (1990) 369.
[14] R.A. Rajadhyaksha and H. Knözinger, Appl. Catal. 51 (1989) 81.
[15] R.A. Rajadhyaksha, G. Hausinger, H. Zeilinger, A. Ramstetter, H. Schmelz and H. Knözinger, Appl. Catal. 51 (1989) 411.
[16] J.P. Cheng and R.T. Yang, J. Catal. 125 (1990) 411.
[17] N.Y. Topsøe, J. Catal. 128 (1991) 499.
[18] E.M. Farfán-Torres, E. Sham and P. Grange, Catal. Today 15 (1992) 515.
[19] E.M. Farfán-Torres and P. Grange, in: *Catalytic Science and Technology*, eds. S. Yoshida, N. Takezawa and T. Ono (Kodansha, Tokyo, 1991) p. 103.
[20] A. Clearfield, H.M. Aly, R.A. Cahill, G.P.D. Serrette, W.-L. Shea and T.-Y. Tsai, in: *Zeolites and Microporous Crystals*, Studies in Surface Science and Catalysis, Vol. 83, eds. T. Hattori and T. Yashima (Elsevier, Amsterdam, 1993) p. 433.
[21] R.T. Yang, J.P. Chen, E.S. Kikkinides, L.S. Cheng and J.E. Cichanowicz, Ind. Eng. Chem. Res. 31 (1992) 1440.
[22] L.J. Csarnecki and R.G. Anthony, AIChE J. 36 (1990) 794.
[23] J.P. Chen, M.C. Hausladen and R.T. Yang, J. Catal. 151 (1995) 135.
[24] H. Matralis, S. Fiasse, Ph. Bastians, M. Ruwet, P. Grange and B. Delmon, Catal. Today 17 (1993) 141.
[25] H.L. del Castillo and P. Grange, Appl. Catal. A 103 (1993) 23.
[26] E.P. Parry, J. Catal. 2 (1963) 371.