Catalysis Letters Vol. 86, No. 4, March 2003 (© 2003)

Selective catalytic reduction of NO by NH_3 on sulfated titanium-pillared clay

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Received 14 October 2002; accepted 13 December 2002

Structural, textural and surface properties of sulfated and non-sulfated titanium-pillared clay were correlated with catalytic tests in the reduction of NO by NH_3 in the presence of oxygen. Lower specific surface areas and basal spacings but stronger acid sites were observed on sulfated Ti-pillared clay than on Ti-pillared clay. Sulfated Ti-pillared clays were more active than Ti-pillared clay. Accordingly, it is suggested that the strong Brønsted acidity generated by sulfate is responsible for the high reactivity of sulfated Ti-pillared clay at high temperature.

KEY WORDS: titanium pillared clay; sulfation; acidity; selective catalytic reduction; NO reduction; NH_3.

1. Introduction

The reduction and/or elimination of NO emission can be considered as one of the most important keys to solving environmental problems. The selective catalytic reduction (SCR) of NO is a commercial process for stationary exhaust sources. The SCR process is based on the reaction between NO_x and NH_3 injected into the flue-gas stream to produce water and nitrogen. During selective catalytic reduction, the addition of O_2 enhances the rate of NO_x reduction [1]. Recently, several reviews which cover the various ranges of selective catalytic reduction have been published. The proposed reaction mechanism of the SCR process on metal oxide catalysts was described and critically discussed [2,3]. The commercial catalysts for the SCR process are V_2O_5–WO_3 and/or V_2O_5–MoO_3 oxides supported on TiO_2 [4–6]. The properties of TiO_2 as catalyst are the principal incentive to study titanium-pillared clays. The first study of the selective catalytic reduction of NO on pillared clays was reported by Yang *et al.* [7].

Pillared interlayer clays were obtained by exchanging the charge-compensating cations between the layers with large inorganic hydroxy cations formed by hydrolysis of metal oxides or salts. Polymeric compounds of Al [8], Zr [9], Cr [10] and V [11] are among the principal pillaring species quoted in the literature. Titanium-pillared clays (Ti-PILC) have been investigated for several years and interesting textural properties, thermal stabilities and acidities were reported [12–14]. Pillared clays have been applied in practice as catalysts for cracking, oligomerization and disproportionation reactions [15]. In recent studies, the catalytic behavior in the epoxidation of allylic alcohol [16–18], the transformation of *m*-xylene [19], the selective dehydration of 1-phenylethanol to 3-oxa-2,4-diphenylpentane [20] and the hydroxylation of phenol [21] on titanium-pillared montmorillonite have been studied.

It is known that both Lewis and Brønsted acid sites exist on pillared clays [8]. The nature and the properties of the acid sites of pillared clays depend mainly on the exchanged cations, the preparation method and the starting clay. The surface acid sites on Ti-PILC are different from those on TiO_2. Both Lewis and Brønsted acid sites exist on Ti-PILC, whereas only Lewis acid sites exist on TiO_2 [3]. Previous reports showed that several oxides, including ZrO_2, TiO_2, Fe_2O_3 and SnO_2, are able to develop very strong acidic sites on addition of a small quantity of sulfate via impregnation with H_2SO_4 and $(NH_4)_2SO_4$ [22,23]. It was also suggested that SO_4^{2-}/TiO_2 catalyst exhibits very strong acid properties and thus has considerable activity for the selective catalytic reduction of NO by NH_3 in the presence of O_2 at temperatures above 400 °C [24]. A recent study showed that an increase in the amount of SO_4^{2-} during the preparation of sulfated TiO_2 induces an increase in the total number of acid sites which are directly related with DeNOx activity [25]. The possible modification of the acid strength of Ti-pillared clays by sulfation has been reported [26]. Various authors have indicated that there is a direct correlation between the SCR activity and the Brønsted acidity of the catalysts [24,27]. This influence of acid centers was also evidenced in the selective catalytic reduction of NO by NH_3 on pillared clays [28,29].

In this work, the objective was to elucidate the role of sulfate on Ti-PILC in the selective catalytic reduction of NO by NH_3 in the presence of oxygen.

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1011-372X/03/0300-0251/0

2. Experimental

2.1. Catalyst preparations

The initial material used for intercalation was a volclay montmorillonite from CECA. The pillaring solution was obtained by slowly adding $TiCl_4$ to H_2SO_4 solution (6 M) under vigorous stirring. Final concentrations of 0.82 M in titanium and 0.2 M in H_2SO_4 were reached by adding water; an H^+/Ti value of 0.24 was thus obtained. The fresh pillaring solution was then added dropwise to 500 ml of a suspension containing 2 g of clay, in such quantities that final Ti/clay ratios of 10, 20 and 40 mmol/g were obtained. After stirring for 24 h, the solid fraction was separated by centrifugation and filtration, then washed several times with distilled water and dried at room temperature. The solids were calcined at 673 K in a flow of air at a heating rate of 1 K/min. The same procedure was employed using HCl for $TiCl_4$ hydrolysis in order to obtain the non-sulfated titanium-pillared clays. Two series of catalysts were prepared and the samples are referred to as S-**x**-Ti or **x**-Ti in which **x** is the Ti/clay ratio, equal to 10, 20 or 40 mmol/g clay. S-**x**-Ti and **x**-Ti stand for a preparation with H_2SO_4 and HCl, respectively, giving the two series of sulfated and unsulfated titanium-pillared clay catalysts.

2.2. Characterization of catalysts

The position of the d_{001} line in X-ray diffraction (XRD) gave the interlayer distance and consequently the pillar height. XRD patterns were recorded on a CGR Theta 60 instrument using monochromatized Cu Kα radiation at $\lambda = 1.54$ Å.

The specific surface areas of the samples were measured by the BET method from nitrogen adsorption isotherms using a Micromeritics ASAP 2000 equipment.

The quantities of titanium retained by the clay were determined by colorimetry using a Philips Pye Unicam PU 8650 spectrophotometer after dissolution of the sample in 6 M sulfuric acid at 353 K and addition of 5 ml of H_2O_2 per mg of Ti [30].

NH_3-TPD was performed to characterize the acidic properties of catalysts. In each experiment, a sample weight of about 0.150 g calcined at 673 K was placed in the cell, evacuated at 673 K for 2 h and then cooled to ambient temperature. Pure ammonia gas (50 cm^3/min) was adsorbed on the catalyst at 373 K for 20 min. Then, after sweeping NH_3 by He and stabilization of the baseline of the detector, the temperature was progressively increased up to 673 K at a constant rate of 10 K/min. The desorbed ammonia was passed through H_3BO_3 solution (20 g/l) in order to check the amount of ammonia evolved. The total NH_3 amount was titrated with sulfuric acid (5×10^{-3} M) for quantitative determination.

Infrared spectra were recorded at room temperature on a Nicolet 320 Fourier transform infrared (FT-IR) spectrometer with 2 cm^{-1} resolution. A standard pretreatment of self-supporting samples (20 mg) was used. The cell was evacuated while the temperature was increased slowly to 723 K (1 K/min) and left overnight at the same temperature. The adsorption of pyridine (3 Torr) was performed for 2 min at 373 K. IR spectra were recorded at room temperature.

XPS analysis was performed at room temperature with an SSX-100 Model 206 Surface Science Instruments (SSI) photoelectron spectrometer, interfaced to a Hewlett-Packard 9000/310 computer. The residual pressure in the spectrometer was in the range $(1.3–6.5) \times 10^{-9}$ Pa. A monochromated Al anode (energy of the Al Kα line 1486.6 eV), powered at 10 KeV and 20 mA, was used for X-ray photoelectron excitation. Samples calcined at 400 °C for 3 h were compressed in a small cup under 5 kg/cm^2 pressure for 30 s and supported on a holding carousel. The binding energies (B.E.) of Ti 2p and S 2p lines were calculated with respect to the C 1s band at 284.8 eV.

2.3. Catalytic activity measurements

SCR experiments were carried out in a tubular continuous-flow fixed-bed reactor between 373 and 673 K operating under atmospheric pressure. The total flow rate was controlled by a flow meter (100 cm^3/min). The gas mixture was NO (0.1 vol%), NH_3 (0.11 vol%) and O_2 (2.5 vol%), in helium. A catalyst amount of 0.150 g was calcined at 673 K and the space velocity were kept constant for all experiments. Each catalyst was heated for 1 h at 373 K under helium before adding the charge. All reported conversions were measured at the steady state, under our experimental conditions, after 1 h at a given temperature. The reaction products were analyzed using a quadrupole mass spectrometer (QMC 311, Balzers).

3. Results and discussion

The textural, structural and acidic properties of sulfated titanium pillared clay compared with unsulfated samples are reported in table 1. The large surface areas indicate successful pillaring. The Ti-pillared clay had a larger BET surface areas and pore volumes than sulfated Ti-PILC. Specific surface areas above 300 m^2/g are obtained for unsulfated samples, which are characterized by an intense diffraction line at 25–29 Å with 48% TiO_2 retained by the clay. For the sulfated Ti-PILC, the interlayer distances are reduced compared with the non-sulfated samples. Their specific surface areas are smaller in all cases and a decrease in TiO_2 retained by the clay is evidenced. An increase in sulfate content with the added Ti/clay ratio during the preparation

Table 1
BET specific surface area, total pore volume, basal spacing, TiO_2 retained by the clay and acidic properties of the catalysts investigated

Sample	Ti/clay (mmol/g)	S_{BET} (m^2/g)	V_p (cm^3/g)	d_{001} (Å)	TiO_2 (wt%)	NH_3 (μmol/g)
10-Ti	10	316	0.166	24.8	39.3	513
20-Ti	20	351	0.153	25.7	48.6	498
40-Ti	40	308	0.115	29.9	48.4	486
S-10-Ti	10	255	0.146	22.0	38.9	646
S-20-Ti	20	137	0.082	16.2	32.9	813
S-40-Ti	40	100	0.058	15.4	40.0	900

induces a decrease in the pore volume, indicating that sulfate particles blocked some small pores in the pillared clay.

X-ray powder diffraction patterns of 10-Ti and S-10-Ti are shown in figure 1. For the non-sulfated Ti-PILC, the X-ray diffractogram contains two lines. The first, at 24.8 Å, is attributed to the layers intercalated by titanium polycations and the other is due to unpillared clay. Subtracting 9.6 Å, the thickness of the clay layer, we obtain an interlayer distance (*i.e.*, the titania pillar height) of about 15.2 Å. The diffractogram of S-10-Ti shows that the line corresponding to the pillared clay is less intense and is reduced to a shoulder centered at 22 Å, whereas the line corresponding to the unpillared clay is increased. This evolution results from the different nature of the polymeric species formed in the solution in both cases. The Ti polymers obtained with H_2SO_4 seem to have a smaller size than those obtained with HCl. These results seem to indicate that the polymerization process of titanium depends on the nature of the anions in solution.

In order to evaluate the total acidity, NH_3-TPD was carried out. The amount of NH_3 desorbed is also presented in table 1, which shows an increase in NH_3 adsorbed by the sulfated samples and no great differences in acidity between the unsulfated samples. Furthermore, for sulfated Ti-PILCs the amount of ammonia desorbed increases with S/Ti atomic ratio (table 2). It is evidenced that the amount of desorbed ammonia increases with the added amount of sulfate ion during the preparation. In other words, the different Ti/clay ratios also led to different amounts of sulfuric acid added. Accordingly, the number of acidic sites observed in sulfated samples results from the addition of SO_4^{2-} species. These results are in agreement with those reported on the development of very strong acid sites by sulfation of TiO_2 [23]. It was also shown by Jung and Grange [25] that on bulk TiO_2 the amount of NH_3 desorbed up to 500 °C increases with increase in sulfate content.

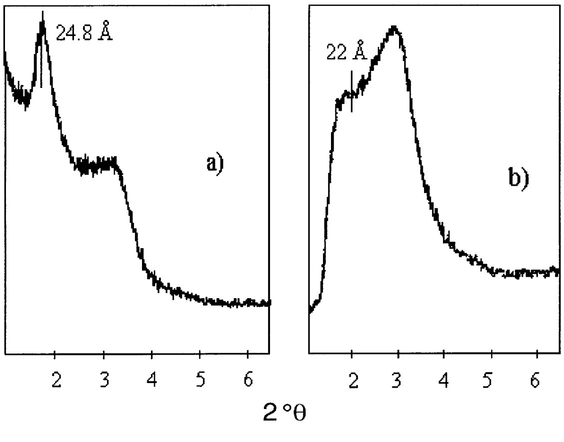

Figure 1. XRD patterns of (a) 10-Ti and (b) S-10-Ti.

In order to investigate the effect of sulfate on the generation of Brønsted and Lewis acid sites, FT-IR spectra of adsorbed pyridine at 373 K were measured for the unsulfated and sulfated Ti-pillared clay (figure 2). It is well known that the bands near 1490 and 1550 cm^{-1} are indicative of pyridinium ion formation (Brønsted acid sites). Those near 1440 and 1490 cm^{-1} are assigned to pyridine coordinated to Lewis acid sites. Upon pyridine adsorption, protonated and coordinated pyridine are formed on the Brønsted acid sites and Lewis acid sites, respectively. Strong Lewis acid sites are obtained in all samples whatever the mineral acid used for hydrolysis. A rather different behavior is observed for the Brønsted acidity. When sulfur is introduced on Ti-pillared clay, the amount of Brønsted acidity further increases, along with a slight decrease in Lewis acidity. By comparison, TiO_2 has only Lewis acid sites [3]. The strong Lewis acidity observed in all Ti-PILC can be related to the acidic properties of TiO_2. It is known that pillars are considered as the major source of Lewis acidity on pillared clays [8]. In the case of sulfated Ti-pillared clay, the strong Brønsted acid sites are generated

Table 2
Values of S/Ti XPS atomic ratio, amounts of ammonia desorbed from 373 to 673 K and number of acidic sites for the sulfated samples

Sample	S/Ti XPS atomic ratio	S/Ti bulk	NH_3 ($\mu mol/m^2$)	Acidic sites ($sites/nm^2$)
S-10-Ti	0.163	0.047	2.5	1.5
S-20-Ti	0.306	0.096	5.9	3.5
S-40-Ti	0.521	–	9.0	5.4

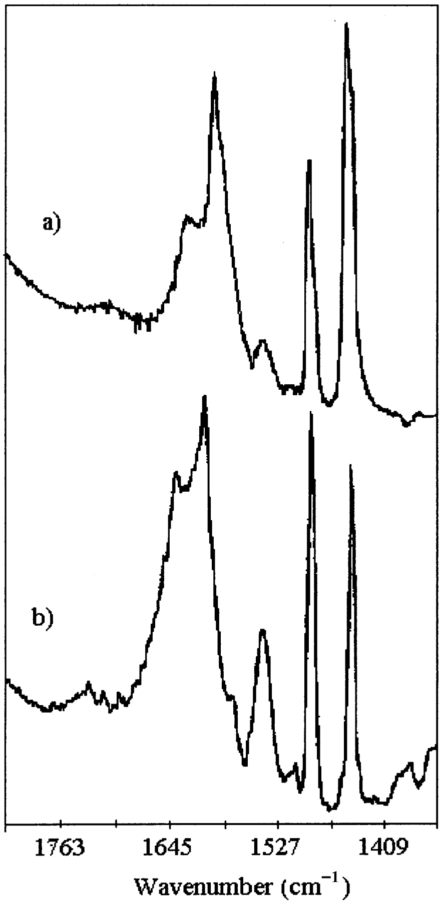

Figure 2. FTIR spectra of pyridine adsorbed on (a) 10-Ti and (b) S-10-Ti.

by doping titanium-pillared clay with trace amounts of SO_4^{2-}.

Table 3 summarizes the XPS binding energies and concentrations (in parentheses) of Ti and S present on the surface of the fresh and used titanium-pillared clay catalysts. The binding energy (B.E.) of the Ti 2p photoelectrons, identical for all the samples, corresponds to bulk TiO_2 [31]. The intensity of this band increases with the titanium content, and reflects an increase in the concentration of titanium species. The Ti oxidation state remains unchanged, near 459 eV, for both sulfated and unsulfated catalysts before and after SCR reaction.

Table 3
XPS binding energies and surface composition of Ti 2p and S 2p present on the surface of titanium-pillared clay before and after SCR reaction

Sample	Binding energy (eV)[a]			
	Ti 2p		S 2p	
	Fresh	Used	Fresh	Used
10-Ti	459.1 (3.4)	459.2 (3.4)	–	–
20-Ti	459.0 (3.9)	459.1 (3.8)	–	–
40-Ti	459.1 (4.8)	459.0 (5.0)	–	–
S-10-Ti	459.3 (3.6)	459.2 (3.4)	169.2 (0.6)	169.0 (0.5)
S-20-Ti	459.2 (3.0)	459.2 (3.4)	169.1 (0.9)	169.2 (0.9)
S-40-Ti	459.2 (3.2)	459.3 (3.6)	169.1 (1.6)	169.3 (1.4)

[a] Values in parentheses are surface concentrations (%).

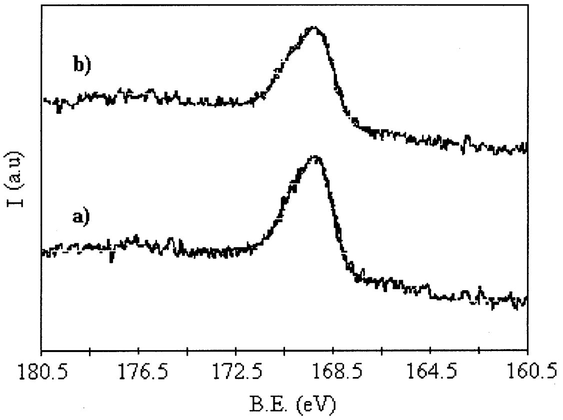

Figure 3. The S 2p spectra in XPS of sulfated Ti-PILC: (a) fresh S-20-Ti catalyst and (b) after SCR reaction.

The S 2p line was also analyzed by XPS, and a binding energy near 169.2 eV was observed for all samples containing sulfur (figure 3), indicating one sulfate species on the surface. No XPS peaks at 161–162 eV, for sulfide, or 164 eV, for elemental sulfur, are observed, indicating that S is in the +6 oxidation state on the catalyst. After SCR reaction, the same species, at the same concentration, are still present.

To examine the effect of sulfate ion on the surface of Ti-pillared clay for NO removal by NH_3, all samples were evaluated, as shown in figure 4. For all catalysts, the NO conversions under steady-state conditions increased with increasing temperature. The unsulfated titanium-pillared clays are active in the SCR reaction of NO by NH_3, but their NO conversions are small at 573–673 K. An increase in the titanium content for the non-sulfated samples leads to a substantial decrease in the activity for SCR of NO. This result shows that titanium does not play a major role in the SCR process.

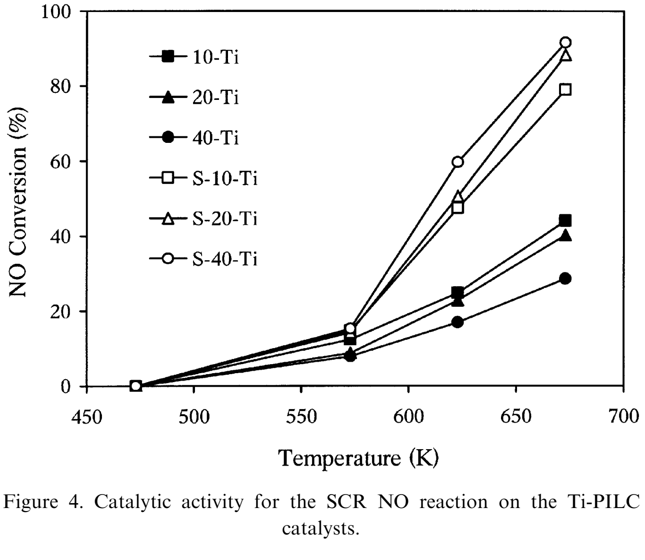

Figure 4. Catalytic activity for the SCR NO reaction on the Ti-PILC catalysts.

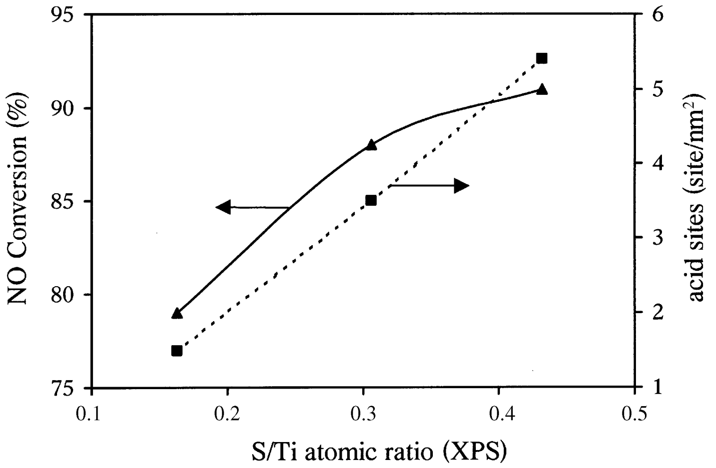

Figure 5. NO conversion and acid sites *versus* S/Ti XPS atomic ratio of sulfated Ti-PILC at a reaction temperature of 673 K.

For comparison, the catalysts containing sulfur exhibit higher NO removal activity than those without sulfur. This indicates that the sulfate on the surface of Ti-pillared clay plays an important role for NO removal activity. The increase in activity is consistent with the amount of ammonia adsorbed, as shown by the TPD study. However, there is a direct correlation between the SCR activity and the acidity enhanced by the sulfation. Accordingly, the increase in sulfate amount, which can be evaluated from the S/Ti atomic ratio obtained by XPS, is closely related to acidity and activity. An increase in the overall NO conversion with increasing S/Ti atomic ratio was observed for the sulfated Ti-PILC (figure 5). These results strongly confirm that the high catalytic activity for the SCR process on titanium-pillared montmorillonite is directly related to the extent of sulfation. The FT-IR investigations showed that the introduction of sulfated ions on the Ti-pillared clay increased the strength of Brønsted acidity. The high catalytic activity of sulfated Ti-PILC in the selective catalytic reduction of NO can be correlated with its strong Brønsted acidity.

4. Conclusions

Based on the results of this study, it is concluded that the addition of sulfate to Ti-pillared clay increases the SCR activity significantly. This reaction shows that coordination sites on titanium centers do not appear to play a role in the primary catalytic step and high catalytic activity is observed only for the sulfated titanium-pillared clay catalysts. The enhancement of the acidic properties in titanium-pillared montmorillonite cannot be related to the poor acidic sites of TiO_2, but results from the sulfation of Ti-pillared clay. The increase in the Brønsted acidity after sulfation was consistent with the increase in SCR activity. Along with results on the SCR activity, we concluded that active sites for this reaction on titanium-pillared clays are Brønsted acid sites.

Acknowledgments

We thank the CGRI (Commissariat Général aux Relations Internationales, Communauté Française de Belgique/Région Wallonne) and the FNRS (Belgium) for financial support.

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