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Preparation, characterization and catalytic performance of molybdenum supported on sulfated titanium pillared clay

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ABSTRACT

New catalysts molybdenum supported on titanium pillared clay (MoTi-PILC) were prepared in presence and absence of sulfate then characterized by different techniques. All the samples were tested in the selective catalytic reduction (SCR) of NO by ammonia. The addition of sulfate during the preparation of the materials affects the surface properties and essentially the nature of the acid sites that influences on the catalytic activity at high temperature.

Keywords: *MoTi-pillared clay, sulfatation, acidity, reducibility, SCR-NO.*

1. INTRODUCTION

Nitrogen oxides (NOx) emitted from the stationary plants and mobile sources are the major air pollutants in urban areas causing serious damages to human health and environment. The reduction of the nitrogen oxides (NO_x) by ammonia is nowadays considered as the best available technology for the abatement of these dangerous gas emitted from the stationary sources like incineration plants, oil refinery, etc. The nitrogen oxide penetrates deeply into sensitive parts of the lungs and can cause or worsen respiratory disease, such as emphysema and bronchitis, and can aggravate existing heart disease, leading to increased hospital admissions and premature death.

The selective catalytic reduction (SCR) of NO in presence of ammonia, as a reductant, has been extensively studied and developed as a potential technology for the abatement of NOx. Researchers from the laboratories of the world investigate different catalysts with low cost to find the effective ones for the NO reduction by ammonia and operating at industrial high temperature. Various reports in recent years have attracted attention to a new class of microporous and mesoporous solids by intercalating clay with different macrocations.

The pillaring process consists of converting layered clay into highly porous structure material by exchanging the compensating cations with large variety of polycations [1]. The process requires a thermal treatment in order to transform the polycations inserted between the clay layers into rigid pillars, linking permanently the silicates sheets. The obtained samples are recognized pillared inter layered clays (PILC). These materials have found a wide range of potential applications in catalytic processes [2] such as air pollution control.

In this work, sulfated and unsulfated MoTi-Pillared clays have been prepared and characterized by different techniques then tested as catalysts for the reduction of nitrogen monoxide NO by ammonia.

2. EXPERIMENTAL SECTION

In this work, the samples are prepared using a commercial Bentonite (starting clay), provided by Sigma Aldrich. The Mo-solution is prepared by dissolving ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24},4H_2O$) in distilled water. The Ti-solution is prepared by hydrolysis of $TiCl_4$ with HCl (6M) [3]. For mixed intercalation, the Mo-solution and the Ti-solution are simultaneously added to the starting clay dispersed in distilled water (2g clay/0.5L water) under vigorous stirring at room temperature. In this condition, 10% of Molybdenum and Ti/clay = 10 mmol g^{-1} was obtained. After 16 h stirring, the solid fraction was separated by centrifugation, then washed several times with distilled water and finally dried at room temperature. The samples were calcined at 400 °C for 3 h under a flow of air (1mL min^{-1}) and referenced MoTi-PILC. For the synthesis of the sulfated sample (MoSTi-PILC) the $TiCl_4$ was hydrolysed by H_2SO_4 (3M) instead of HCl (6M).

3. RESULTS SECTION

The BET surface area of the starting clay is 34 m^2 g^{-1} (Table 1). It is well known that the increase of the specific surface area, the micropore surface area and the microporous volume indicate a successful incorporation of the mixed polycations between the clay layers therefore a success of the intercalation process. The specific surface area of the sample MoTi-PILC is clearly higher than that of the starting clay and the samples prepared in presence of sulfate groups (STi-PILC and MoSTi-

PILC). The microporosity resulted from a creation of some micro and/or mesopores between the pillars in inter laminar space of the clay. In addition, the microporous structure of the pillared clay is characterized by the distance between the clay sheets and the distance between the pillars.

Table 1. Textural properties of the samples and chemical analysis of molybdenum, sulfate and titanium.

Samples	S_{BET} (m^2/g)	$S_{\mu p}$ (m^2/g)	V_p (cm^3/g)	$V_{\mu p}$ (cm^3/g)	Mo (wt.%)	SO_4^{2-} (wt.%)	Ti
Starting clay	34	6	0.069	0.002	0	0	0
STi-PILC	181	103	0.050	0.047	-	3.2	43.22
MoTi-PILC	309	140	0.100	0.061	9.9	-	39.86
MoSTi-PILC	198	86	0.058	0.038	9.8	3.7	37.15

Specific surface area (S_{BET}), micropore surface area ($S_{\mu p}$), total pore volume (V_p), micropore volume ($V_{\mu p}$)

The N_2-isotherms of all samples are type IV characteristic for mesoporous materials according to the IUPAC classification. Hysteresis loops due to capillary condensation in the mesopores, which generally associated with the filling and emptying of mesopores, are type H1 characteristic for mesoporous materials (Fig. 1A). It is well known that the pores with diameters smaller than 20 Å are called micropores following the general definition in the IUPAC classification of pores, while the pores whose diameters are larger than 50 Å are called macro pores. In addition, the pores with diameter between 20 and 50 Å are described as mesopores. The starting clay (noted B-Na) has a negligible distribution of mesoporosity without microporosity, as shown by the BJH pore size distribution (Fig. 1B). However after pillaring process, the distribution of mesoporosity and microporosity increased for all the investigated catalysts. A bimodal pore size distribution with a diameter of about 20 and 40 Å exist in all the catalysts. The mesopore structure of the pillared clays is significantly affected by the presence of molybdenum and sulfate.

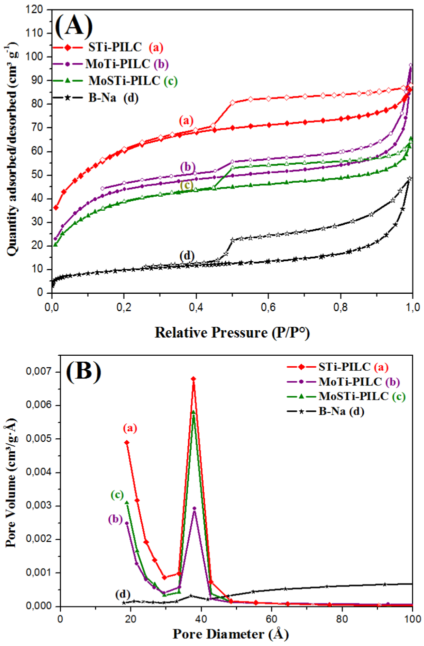

Figure 1.(A) N_2 adsorption-desorption isotherms of the solids: (a) STi-PILC, (b) MoTi-PILC, (c) MoSTi-PILC, (d) starting clay (B-Na) and (B) Pore size distribution of the same samples.

The reduction behaviour of the sulfate species in the catalysts was studied by means of H_2-TPR; reduction curves of the MoTi-PILC and the sulfate samples are shown in Fig. 2. The TPR profile of MoTi-PILC shows a weak peak at 470 °C which is attributed to the reduction of molybdenum [4]. Therefore, the intensity of this peak became more predominant after sulfate addition, indicating that the reduction of sulfate species occurs in the same temperature range. In our previous work, we demonstrated the reduction of sulfate to essentially SO_2 with few H_2S formation over sulfated titanium pillared clay [5].

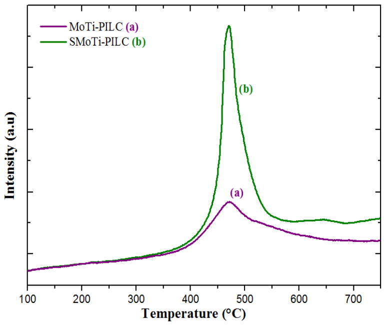

Figure 2.H_2-TPR profiles of the samples prepared in presence and absence of sulfate.

It should be noticed that the surface acidity is one of the important properties required on the catalyst for chemical reactions needing acid sites like the reduction of NO by ammonia. It was assumed that one NH_3 molecule reacts with one acid site to calculate the total number of acid sites. The molybdenum increases further the total acidity of the sample compared to the sulfated solids (Table 2). This result reveals that molybdenum in MoTi-PILC contributes to the improvement of the number of acid sites on the catalyst surface. The unexpected acidity of the sample MoSTi-PILC can be explained by the diffusion limitation of NH_3, due probably to the pore diameter and to the accumulation of sulfate groups covering some acid sites arising by molybdenum which restricts the available active sites for adsorption of ammonia. More recently we have demonstrated that the high microporosity arising by the well distribution of the pillars between the clay sheets as well as the existence of a moderate acidity on WTi-PILC enhanced the catalytic activity in the SCR of NO by ammonia [6].

Table 2. The acid properties of the investigated samples**.**

Samples	Acidity (μmol NH_3 g^{-1})	Acid sites (site nm^{-2})
Starting clay	-	-
STi-PILC	200	1.2

MoTi-PILC	499	1.87
MoSTi-PILC	302	1.82

The NH_3-TPD profiles of the investigated catalysts are shown in Fig. 3. The shape of desorption patterns obtained for the MoTi-PILC is very different from those recorded for samples containing sulfate groups. However, the NH_3-TPD profile of this solid (MoTi-PILC) contains at least two maxima. The first peak is centred at about 180°C, while the second one, much broader, appeared at temperature above 350°C. The low temperature peak can be related to the desorption of ammonia either physisorbed or linked to weak Bronsted acid sites, while the second peak at high temperature can be attributed to NH_3 desorbed from strong Lewis acid sites.

The addition of sulfate into the MoTi-PILC increased the intensity of the second peak which is shifted to higher temperature. It is associated to the strongly adsorbed ammonia on physically powerful Lewis acid sites. The change in the NH_3-TPD profiles can be explained by the transformation of the surface acidity after addition of sulfate in presence of molybdenum. This suggests that the incorporation of sulfate and molybdenum in Ti-PILC produces more strong acid sites leading to a catalyst with excessive acidity at high temperature.

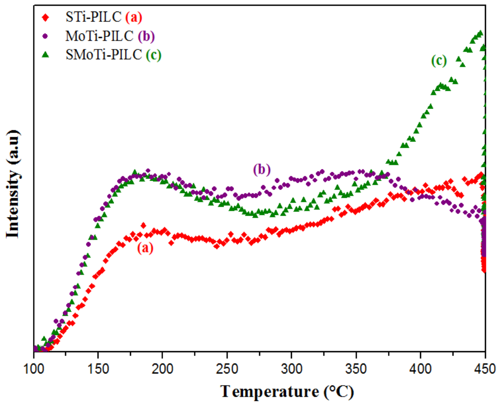

Figure 3.NH_3-TPD profiles of the investigated samples.

The catalytic activity of each sample is tested in the reduction of NO by ammonia. As seen in Fig. 4, it is relatively clear that no NO conversion was observed over the starting clay (B-Na) even at high temperatures. In our previous works, it was demonstrated that Ti-PILC was no active in the SCR-NO and Ti-pillars do not play a role in the SCR-NO despite the existence of Lewis acidity on its surface. However, in this work for all the investigated samples, the NO conversion begins at 200 °C and increases with temperature reaching the highest maximum of 98% at 450°C, only in the case of the MoTi-PILC catalyst. This fact is due to molybdenum addition to Ti-PILC, to its moderate acidity distributed on its large specific surface area and essentially to its large surface microporosity. The unexpected lower catalytic activity of MoSTi-PILC is probably due to the difficult diffusion of the reactants in the pores and to highly constraint formation of the products as a consequence of the small micropore structure (Table 1). Furthermore the strong acid sites arising after sulfation are probably responsible of the low activity of the sulfated samples.

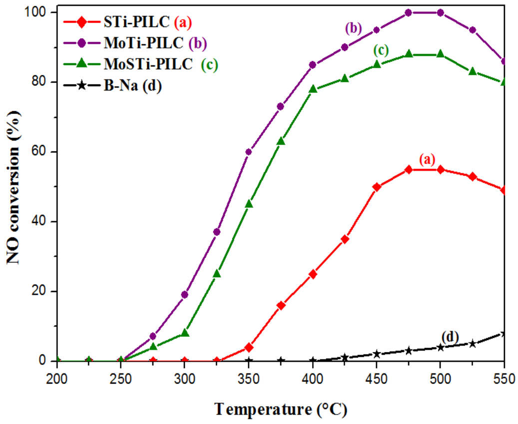

Figure 4.NH_3-SCR of NO reaction over the investigated samples.

The acidity and reducibility of the oxides catalysts like WO_3/TiO_2 or MoO_3/TiO_2 are well known as the key factors of the activity in the SCR-NO by ammonia. However, in the case of the MoTi-pillared clay catalyst, we discover that the micropore structure generated after pillaring process and the moderate acidity arising by molybdenum play a major role in the catalytic activity for the SCR-NO by NH_3. The well distribution of the MoTi-pillars between the clay layers is responsible of the creation of a high microporosity in the pillared clays [7].In summary, enhanced moderate acidity and microporosity after simultaneous addition of Mo and Ti to the clay allows to a catalyst with high efficiency in the selective catalytic reduction of NO by ammonia. This result demonstrates that the active sites in the SCR of NO are Bronsted acid sites while the stronger Lewis acid sites observed in MoSTi-PILC are low active in the SCR-NO, despite the high reducibility of the sulfated sample. The elevated microporosity generated by the well distribution of the mixed MoTi-pillars in the pillared clay (MoTi-PILC) plays a crucial role in the catalytic activity of this material.

4. CONCLUSIONS

The molybdenum addition enhanced the NO removal activity of the titanium pillared clay, while the sulfate addition has a negative effect on the catalytic activity. When both molybdenum and sulfate exist simultaneously on the surface of the titanium pillared clay, the molybdenum species seems to play a more important role for NO removal activity than the sulfates groups.

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6. ACKNOWLEDGEMENTS

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