

Effect of vanadium on the behaviour of unsulfated and sulfated WTi-pillared clay catalysts for the SCR of NO with NH₃

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Abstract: Vanadium supported on unsulfated and sulfated Tungsten-Titanium-pillared clays are prepared and characterized then tested in the selective catalytic reduction of nitrogen oxide by ammonia. The structural, textural and acidic properties are largely influenced by either the presence or in the absence of sulfate. The catalytic activity in the selective catalytic reduction of NO by NH₃ indicates that vanadium supported on mixed-tungsten-titanium pillared clay exhibit higher activity than that of a similar sample prepared in the presence of sulfate groups.

Keywords: Vanadium, Tungsten, Sulfate, Titanium, catalytic activity.

I. Introduction

Nitrogen oxide, emitted from stationary plants, is one of the major sources of air pollution. The selectivity of catalytic reduction (SCR) of nitrogen oxide with ammonia is considered today as the efficient process for abating this dangerous gas. Many catalysts have been reported in literature as being active to the SCR of NO by NH₃ [1-4]. It is proved that the catalytic properties of solids can be greatly influenced by the nature of the support [1, 2].

Commercial SCR catalysts consist of TiO₂ as a support and V₂O₅/WO₃ as active catalyst compounds [2]. The catalyst activity is related to the ammonia adsorbed in Bronsted acid sites associated with V⁵⁺-OH, while WO₃ increases the number of acid sites and stabilises the Bronsted acidity of the catalyst [1, 2]. All authors agree that the active sites in the V₂O₅-WO₃/TiO₂ industrial SCR catalysts are vanadium oxide. Noticing is that TiO₂ alone contains Lewis acid sites and shows a poor catalytic activity for SCR-NO. However, after sulfation, strong Bronsted acidity is formed and SCR-NO activity is strongly enhanced [2]. Parvulescu et al. [1] present results of the DeNO_x over a series of the V₂O₅/TiO₂ catalysts containing different amounts of V₂O₅. The best catalytic results are achieved for the samples containing 1.4-6.6 wt.% of V₂O₅ deposited on titanium oxide. Furthermore, the commercial SCR catalysts contain about 0.5-1% sulphur that mainly exists on the surface in the form of sulphate [4]. The properties of TiO₂ as a support catalyst have made of Ti-pillared clays an interesting subject to study. It is well known that both Lewis and Bronsted acid sites are present in Ti-pillared clays, whereas only the first one exists in TiO₂. In fact, the number of chemical reactions of which the potential application of pillared clays, whether as catalysts or as catalyst supports, is continuously increasing [5]. Among various catalysts tested for the selective catalytic reduction of NO by NH₃, modified pillared clays have gained wide technical applications [6-17]. Moreover, the Bronsted acidity generated by the sulfation of Ti-PILC is responsible for a high activity in the selective catalytic reduction of NO by NH₃ [10]. In our previous study, it can be perceived that the addition of a higher amount of vanadium (3% and 5%) induces a decrease of NO conversion at a higher temperature (above 300°C) due to the ammonia oxidation resulting in NO [13]. In SCR-NO reaction, best activity is obtained in the case of 1.5-2% vanadium doped to sulfated Ti-PILCs [12, 13, 16, 17]. In our previous study, we have shown that the simultaneous addition of vanadium (3%) and tungsten (9%), by an incipient wetness, of the sulfated Ti-PILC has increased the Bronsted acidity and the SCR-NO activity [14]. Yet, the effect of the addition of a few amount of vanadium to the mixed tungsten-titanium-pillared clays is not investigated for NO removal activity.

Recently, new systems, mixed pillared clays such as: FeCr-pillared clay [18], FeMn-pillared clay [19], AlCu-pillared clay and AlFe-pillared clay [20], ZrTi-pillared clay [21], Pd and/or Cr supported on mixed ZrTi-pillared clay [22] and FeTi-pillared clays [23] have been prepared, and their catalytic activities have been evaluated in different reactions. A significant field in pillared clay science is dealing with a research into systems intercalated with two different elements, aiming to improve the thermal stability and the catalytic properties of the mixed PILCs [21, 24, 25]. Vicente et al., in the recent edition of Handbook of Clay Science [25] illustrate the large use of mixed pillaring agents over the past 30 years. The authors list more than 10 types of mixed pillaring agents containing aluminum as one of their components. Usually, transition metals like Cr, Fe, Zr, Cu, etc. are deposited in pillared clays by means of ionic exchange, incipient wetness, or by a dry impregnation of samples.

But, until now, there has not been any published work either describing the preparation method and the catalytic activity of mixed tungsten-titanium-pillared clay or studying the effect of vanadium addition on the physicochemical properties of these pillared clays. There has not been any publication of any scientific work dealing with the SCR-NO reaction on mixed tungsten-titanium-pillared clay prepared in the presence or in the absence of sulphate or any study about the effect of vanadium addition on the catalytic activity of these systems.

II. Experimental

2. 1. Synthesis of catalysts

2. 1. 1. Starting clay

The clay used in this work is an industrial-treated-montmorillonite Clarsol, referenced as KC2, provided by CECA (France). Before its use, the clay is purified by sedimentation to remove the fraction less than 2 μm . Then, it is exchanged three times with Na^+ ions by stirring in NaCl solution (1 M) for 24h. Carrying dialysis, the suspension obtained is washed several times with distilled water until it becomes free from Cl^- ions (as indicated in the test with silver nitrate solution). The solid is separated by centrifugation and dried at room temperature. The chemical analysis is subject to an exchange capacity of 80 meq./100 g. This initial material is referenced as In-clay.

2. 1. 2. Mixed WTi-pillared clay prepared in the presence and in the absence of SO_4^{2-} groups

The W-solution is prepared by dissolving ammonium metatungstate $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ in distilled water (10^{-2}M). The sulphated Ti-solution is obtained by a slow addition of TiCl_4 into H_2SO_4 solution (3M) under vigorous stirring. Final concentrations of 0.82M in titanium and 0.2M in acid are reached by adding water. H^+/Ti value of 0.24 is thus achieved [10].

The W-solution and the sulphated Ti-solution are simultaneously added in a drop per 500cm^3 of a suspension containing 2 g of the initial clay under vigorous stirring at room temperature. Consequently, the percentage of tungsten (15%) added to the clay suspension with a final Ti/clay ratio of 10 mmol/g is obtained. After 24 h stirring, the solid fraction is separated by centrifugation and filtration. Then, it is washed several times with distilled water and dried at room temperature. All these samples are calcined at 400°C with a heating rate of 2°C min^{-1} for 3h under air flow. The free tungsten prepared sample is referred to as sulphated Titanium pillared clay (STi-PILC), whereas the mixed-sulphated-tungsten-titanium pillared clays is referenced as SWTi-PILC.

The same procedure is used with HCl (6M) for hydrolysis of TiCl_4 in order to obtain the non sulphated samples, referenced as Ti-PILC and WTi-PILC.

2. 1. 3. Vanadium supported on PILCs

The vanadium solution is prepared at room temperature by dissolving ammonia vanadate NH_4VO_3 (1M) in an acidified water by oxalic acid. Vanadium (2%) supported on pillared clay is prepared at a room temperature under vigorous stirring by incipient wetness impregnation of the support with the vanadium solution. All samples are then dried at 80°C for 20 h, then calcined at 400°C with a heating rate of 2°C/min for 3h under air flow. The catalysts are referenced as V/Ti-PILC, V/WTi-PILC, V/STi-PILC and V/SWTi-PILC.

2. 2. Characterization

The Chemical analyses are carried out in the National Institute for Research and Physico-Chemical Analysis (INRAP) of Tunisia. The X-ray diffraction patterns are obtained using a SIEMENS D 500 instrument equipped with a mono chromated $\text{CuK}\alpha$ radiation at $\lambda = 1.541\text{\AA}$. The specific surface area, pore and micropore volume of the samples are determined by nitrogen physisorption using a Micromeritics ASAP 2020 instrument. The samples are out gassed in vacuum during 5 h at 200°C before the nitrogen physisorption. Total acidity measurement is evaluated by ammonia temperature programmed desorption (NH_3 -TPD) using an AUTOCHEM 2910 (Micromeritics). Before NH_3 adsorption, samples are pre-treated under air flow (30mL/min) at 450°C (10°C/min) for 30 min. Ammonia adsorption is carried out at 100°C by exposing to 5 vol% NH_3 in He (flow rate = 30mL/min) for 45 min and then by flushing with He (30mL/min) during 2h to remove the residues of the adsorbate in the gaseous phase and physisorbed on the catalyst surface. Finally, ammonia is desorbed in helium flow (30mL/min) from 100 to 450°C with a heating rate of 10°C/min .

2. 3. SCR of NO by NH_3

Catalytic tests are performed in a continuous flow of fixed bed microreactor operating at an atmospheric pressure. The catalyst (0,050g) is activated in situ at 450°C under He then cooled to room temperature. A feed gas stream containing NO (1000 ppm), NH_3 (1000 ppm), and O_2 (3%) in He as balance gas is supplied to the micro reactor through mass flow controllers. The total flow rate is was 138 mL min^{-1} and the

SCR is carried out at programmed temperature from room temperature up to 450 °C with heating rate of 6°C min⁻¹. The reaction results are analysed by on line sampling with a quadruple mass spectrometer (Pfeiffer Omnistar), calibrated with standard mixtures and in the following masses: NO (30), N₂ (28), N₂O (44), NO₂ (46), NH₃ (17), O₂ (32) and H₂O (18).

III. Results and discussion

3. 1. Characterization of the catalysts

The insertion of large polycations between the clay sheets is only observed for the samples containing tungsten, WTi-PILC and SWTi-PILC (Fig. 1). Usually, a more intense (001) peak at lower 2θ, indicates a successful intercalation process and a good dispersion of pillars between the layers. The second peak at higher 2θ is also perceived, either associated with the layers which remain unexchanged, containing water and probably a small amount of Na⁺ or with the ones exchanged by cations with a low degree of polymerization. These results demonstrate the beneficial effect of tungsten in enhancing the pillars height and obtaining a good distribution of pillars between the clay sheets, regardless of the absence or the presence of sulphate groups.

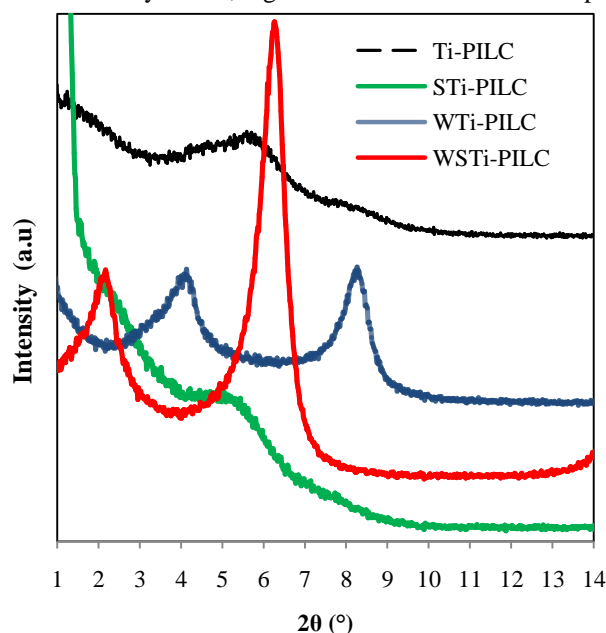


Fig. 1: X-Ray diffractograms of the pillared clay supports.

The results of the chemical analysis of sodium, titanium, sulfate and tungsten are illustrated in Table 1. The decrease of sodium content in the initial clay on cationic exchange can be observed, proving the insertion of mixed-pillars between the clay sheets, thus a success of pillaring process.

Table 1: Textural properties of the initial clay and the samples calcined at 400°C with main chemical composition.

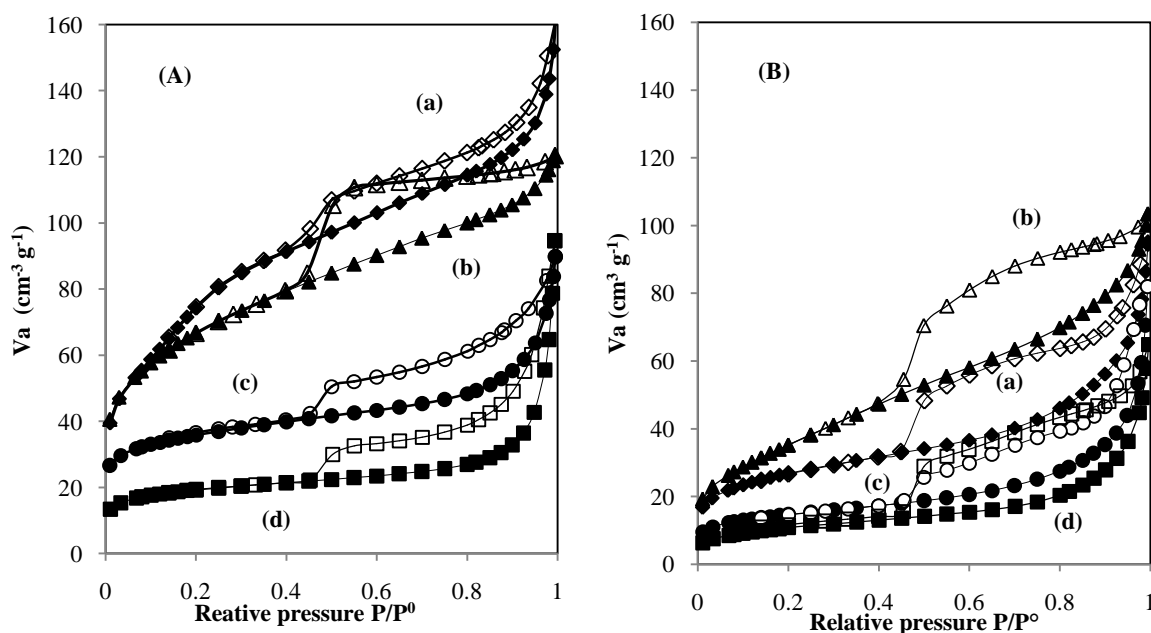
Samples	S _{BET} (m ² /g)	V _{up} (cm ³ /g)	V _p (cm ³ /g)	Na (wt.%)	Ti (wt.%)	W (wt.%)	SO ₄ ²⁻ (wt.%)
In-clay	25	0.0050	0.09430.36	0.14	0	0	
Ti-PILC	281	0.0001	0.21400.09	25.05	0	0	
STi-PILC	239	0.0161	0.1771	0.08	22.22	0	0.61
WTi-PILC	124	0.0281	0.1123	0.01	14.60	4.07	0
WSTi-PILC	68	0.0135	0.0858	0.18	7.61	1.08	0.48

The BET surface area of the initial clay is 25 m²/g. The increase of the specific surface area results in the pillaring process (Table 1). For the mixed catalyst, the surface area decreases sharply after tungsten addition due to the filling of the interlayer space by the large WTi-pillars, as shown in the X-ray results. However, a significant decrease in the surface area is also noticed in the catalysts after vanadium addition due to the blocking of some pores by the vanadium species (Table 2).

Table 2: Textural properties of vanadium supported on PILCs calcined at 400°C.

Samples	S_{BET} (m ² /g)	V_{up} (cm ³ /g)	V_{p} (cm ³ /g)
V/Ti-PILC	96	0.0086	0.1139
V/STi-PILC	131	0.0084	0.1438
V/WTi-PILC	52	0.0065	0.0825
V/WSTi-PILC	39	0.0013	0.0692

The N₂ adsorption-desorption isotherms of our catalysts are presented in Fig. 2. According to the IUPAC classification of type IV adsorption isotherms of all the samples, they are typical of mesoporous solids. Hysteresis loops are of type H3 due to capillary condensation in the mesopores generally associated with their filling and emptying, characterizing mesoporous materials. In all isotherms, the desorption branch shows an obvious inflection at about P/P^0 of 0.4-0.5. This result is also observed in many different types of layered materials. According to the IUPAC classification of pores, those with a diameter ranging from 20 to 50 Å are described as mesopores while the ones with a diameter less than 20 Å are referred to as micropores. For all PILCs, the microporous structure is commonly characterized by the distance between the clay layers and that between the pillars. Pores with diameters larger than 50 Å are classified as macro pores. The analysis of the BJH pore size distribution (Fig. 3) shows a narrow distribution of mesopores with a diameter ranging from 30 to 50 Å and a maximum diameter of 40 Å. The Ti-PILC shows a bimodal pore size distribution with maxima of about 20 and 40 Å. The first maximum is significantly decreased after the addition of sulfate and tungsten. The BJH pore size distributions of vanadium supported PILCs are monomodal, with maxima of about 35 and 40 Å. This progressive disappearance of the micropores after vanadium addition could result from the progressive filling of the micropores with vanadia species.


Fig. 2: N₂ adsorption-desorption isotherms of the samples: (A): (a) Ti-PILC, (b) STi-PILC, (c) WTi-PILC, (d) WSTi-PILC and (B): (a) V/Ti-PILC, (b) V/STi-PILC, (c) V/WTi-PILC, (d) V/WSTi-PILC.

The surface acidity is one of the most important properties required on the catalyst in favour of reaction requiring acid sites like the selective catalytic reduction of NO (SCR-NO) by ammonia. For understanding of the influence of the sulfate and tungsten on the surface acidity of the mixed catalysts, we calculated the concentration of surface acidity and the surface concentration of W and S (Table 3). It was assumed that one NH₃ molecule reacts with one acid site. From this table, it is clear that the surface acidity is enhanced by introducing sulfate groups. Therefore, the addition of sulfate generated more acid sites than with the introduction of vanadium.

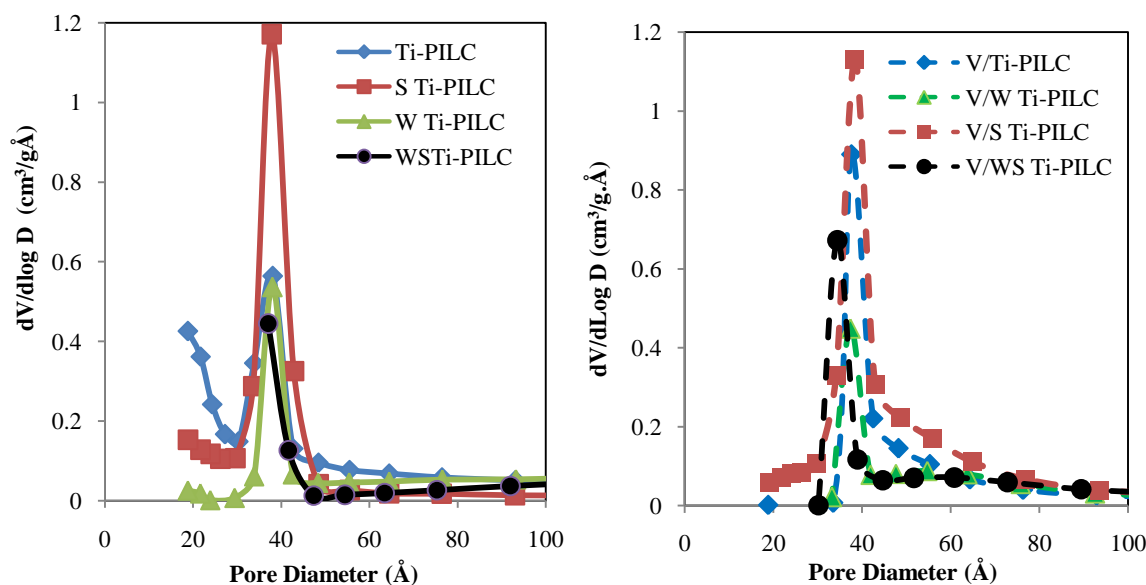


Fig. 3: Pore size distribution of the investigated samples calcined at 400°C.

Table 3: Total acidity and surface concentration of tungsten and sulfate.

Samples	Total acidity ($\mu\text{mol NH}_3 \text{ g}^{-1}$)	Surface concentration of W and S		
		($\mu\text{mol NH}_3 \text{ m}^{-2}$)	W ($\mu\text{mol m}^{-2}$)	S ($\mu\text{mol m}^{-2}$)
WTi-PILC	150	1.21	1.79	0
WSTi-PILC	435	6.44	0.87	2.21
V/WTi-PILC	200	3.84	4.260	
V/STi-PILC	566	4.32	0	0.72

The NH_3 -TPD patterns of the samples are illustrated in Fig. 4. The Ti-PILC without tungsten is presented as a reference. The NH_3 -TPD profile of this support contains at least two maxima. The first peak is centered at about 230°C, while the second one, appears at a temperature above 300°C. The low peak temperature can be related to the desorption of ammonia either physisorbed or linked to weak Bronsted acid sites. The second peak at a high temperature can be attributed to NH_3 desorbed from stronger Lewis acid sites [14]. The existence of both Lewis and Bronsted acid sites in the Ti-PILC surface is analyzed in our previous work [10]. After sulfation, both Bronsted and Lewis acid sites are increased [10, 16]. The shape of desorption patterns obtained for mixed WTi-PILC differs from those recorded for others pillared clays. The change in the NH_3 -TPD profiles is due to the progressive transformation of the surface acidity after tungsten addition surprisingly, in the case of WTi-PILC, the acidity increases. The shape of desorption patterns of WTi-PILC is largely moved to higher temperature indicating the ammonia desorption from strong acid sites and demonstrating the presence of strong Lewis acidity in the catalyst surface. By contrast the addition of tungsten to sulphate Ti-pillared clay (SWTi-PILC) increases significantly the Bronsted acidity and that of Lewis. This suggests that the simultaneous incorporation of tungsten and sulphate with titanium into the clay suspension produces a solid which exhibits more acid sites.

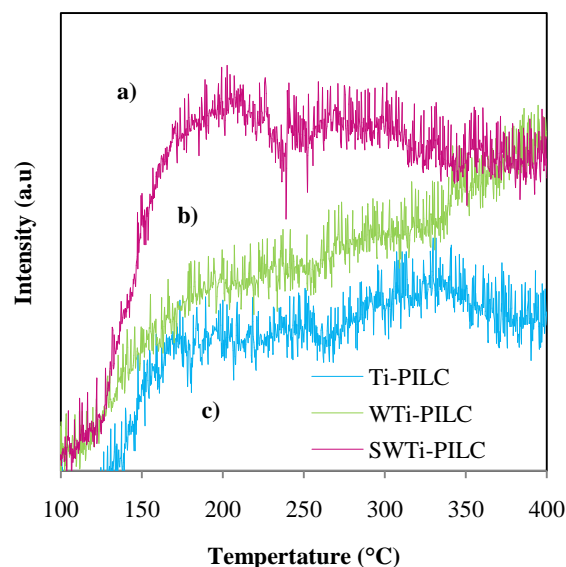


Fig. 4: NH_3 -TPD profiles of the PILCs supports: a) SWTi-PILC, b) WTi-PILC and c) Ti-PILC (reference).

After vanadium addition, the NH_3 -TPD profiles are significantly changed (Fig. 5). The addition of vanadium slightly increases the Bronsted surface acidity however a surprising rise of Lewis acidity is only observed in the case of V/SiTi-PILC. It seems that Lewis acid sites arising from sulfated pillars are not covered by vanadium. The pillars are considered as the major source of Lewis acidity [10].

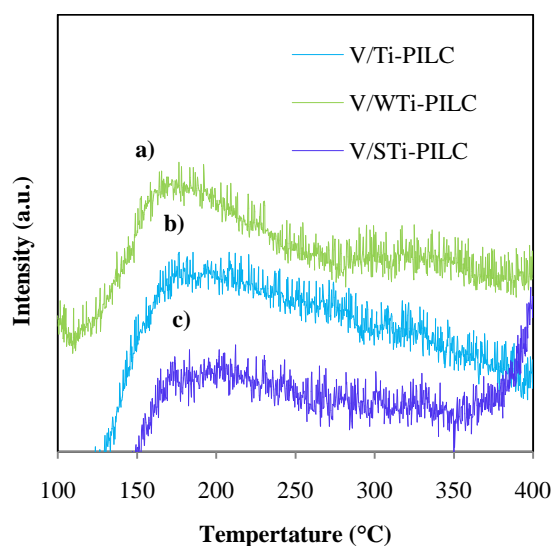


Fig. 5 : NH_3 -TPD profiles of vanadia supported on PILCs catalysts :a) V/WTi-PILC, b) V/Ti-PILC and c) V/SiTi-PILC.

3. 2. Catalytic test

For the selective catalytic reduction (SCR) of NO by ammonia, it is well known that the surface acidity of the catalyst is required for having high reduction of nitrogen oxide by ammonia. We reported in our previous work that the SCR activity of the Sulfated Ti-PILC is directly related to the total acidity [10]. To examine the effect of tungsten in the mixed WTi-pillared clay, prepared either in the absence or in presence of sulphate. All samples are evaluated before the addition of vanadium. The sulphated samples are more active than the non sulphated ones but the NO conversion do not exceed 50% for all the PILC supports. Noticing is that the quantity of sulfate groups used in this work is lower compared to those used in our previous study [10, 12].

After addition of a few amount of vanadium (2%), the activity is significantly increased for all the samples, mainly in the case of V/WTi-PILC (Fig. 6). The NO conversion is rapidly increased and it remains constant at 80% in the temperature range 200-400°C. This result can be explained by the beneficial effect of vanadium addition on the best support WTi-PILC, having a well dispersion of mixed WTi-pillars between the clay sheets and a sufficient surface acidity for the reduction of NO by NH_3 .

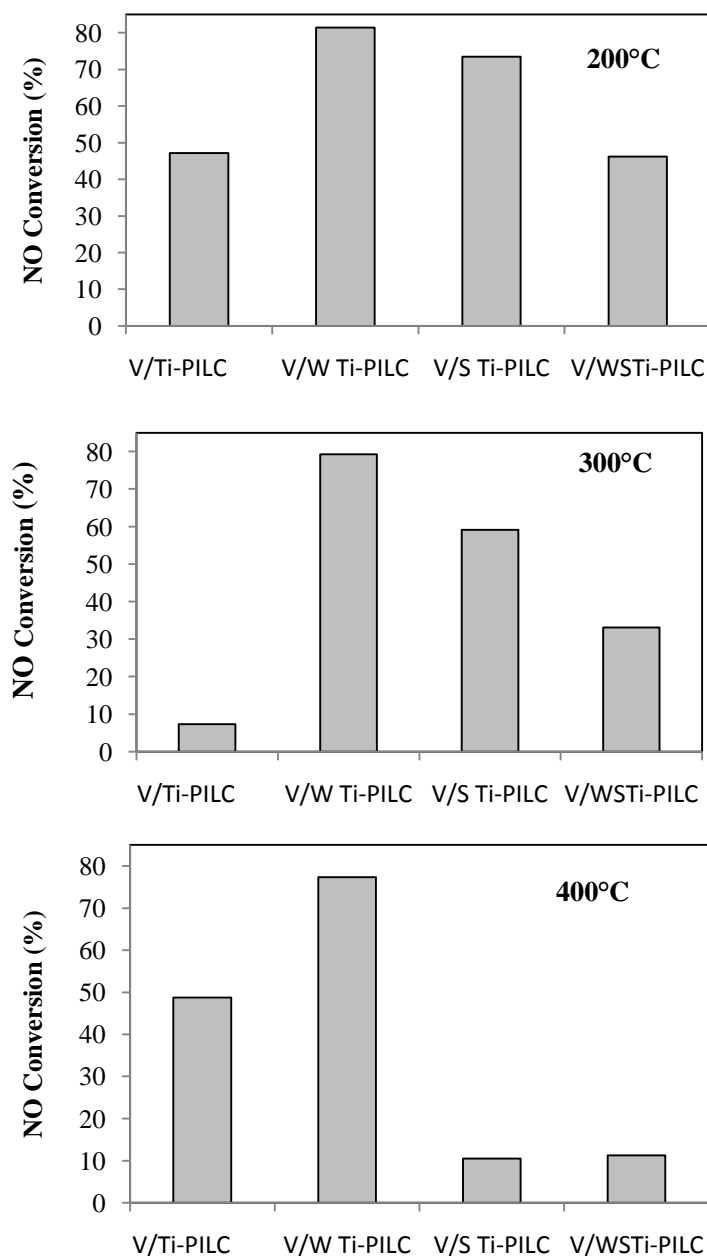


Fig. 6 :SCR-NO over vanadium supported on PILCs catalysts.

The NO conversion of V/WTi-PILC is found to be better than V/STi-PILC. The presence of sulfate, tungsten and titanium in the pillared clay results in a solid with low activity in the reduction of NO even after vanadium addition (V/SWTi-PILC). Noticing is that the low NO conversion is partly related to the conglomeration on the surface covering the active sites. In addition, partial pore blocking due to the accumulation of tungsten species and sulfate groups, that restrict the available active acid sites for the catalytic reaction, may be the reason behind the observed low NO conversion on V/SWTi-PILC. To summarize, the excess of acidity from mixed tungsten-titanium pillars, sulfate groups and vanadium species is not beneficial for the pillared clays catalysts for the SCR-NO reaction.

As a result, the good activity of V/WTi-PILC is related to the combination of the high-quality of microporosity and the good dispersion of mixed WTi-pillars (as observed in XRD results) which favors the contacts of reactants with active acid sites on the catalyst surface. The SCR-NO reaction appears to be faster when the total acidity is moderate and the acid sites are well dispersed on the surface. We note that microporous structure of pillared clays is usually characterized by the distance between the pillars and within the clay sheets. The reactant diffusion inside the pores of V/WTi-PILC may be fast in comparison to V/SWTi-PILC suggesting that there is an optimum of activity as a function of the acid sites. The partial pore

blocking and the accumulation of mixed species on the surface of V/SWTi-PILC restrict the available active acid sites that become inaccessible for reaction. The moderate surface acidity of the non-sulfated sample (V/WTi-PILC) is powerful enough to catalyze the SCR-NO.

The increased distance of the interlayer in WTi-PILC allows the insertion of more reactants within the micropores leading to a high conversion of them. It is concluded that the uniform dispersion of the WTi-pillars, the well pore structure and the moderate surface acidity of WTi-pillared clay have made of this sample an excellent support for vanadium. The V/WTi-PILC catalyst needs further investigation in other catalytic tests requiring surface acidity. In the future, the mixed WTi-PILC can be used as a catalyst support of other transition metal.

IV. Conclusion

The results of this work can be considered as the first report studying the mixed WTi-pillared clay prepared in the absence and the presence of SO_4^{2-} groups. The tungsten is simultaneously added with titanium to the clay suspension in order to prepare mixed WTi-pillars between the clay sheets. The structural, textural, acidic and catalytic properties are largely influenced by either the presence or in the absence of sulfate. The catalytic activity in the SCR of NO by ammonia indicates that vanadium supported on mixed-tungsten-titanium pillared clay exhibit higher SCR-NO activity than that of a similar sample prepared in the presence of SO_4^{2-} . The highest efficiency of the best catalyst (V/WTi-PILC) is directly related to a good support with a uniform dispersion of large mixed WTi-pillars prepared in the absence of sulfate and to its moderate surface acidity. The results of this first study reveal that the vanadium supported on mixed WTi-pillared clay becomes very attractive as a catalyst of other chemical reaction requiring surface acidity.

References

- [1] V.I. Părvulescu, P. Grange, P. Delmon, *Catal. Today* 46 (1998) 233.
- [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B* 18 (1998) 1.
- [3] P. Granger, V. I. Părvulescu, *Chem. Rev.* 111 (2011) 3155.
- [4] P. Forzatti, L. Lietti, E. Tronconi, in: I. T. Horvath *Industrial Encyclopedia of Catalysis*, 1st ed. Wiley, New York, 2002.
- [5] G. Centi, S. Perathoner, *Microp. Mesop. Mater.* 107 (2008) 3-15
- [6] Grzybek, *Catal. Today* 119 (2007) 125-132.
- [7] K. Bahranowski, J. Janas, T. Machej, E. M. Serwicka and L. A. Vartikian, *Clay Minerals* 32 (1997) 665.
- [8] R. Q. Long, R. T. Yang, *Appl. Catal. B* 24 (2000) 13.
- [9] L. Khalfallah Boudali, A. Ghorbel, P. Grange, S. M. Jung, *Stud. Surf. Sci. Catal.* 143 (2002) 873.
- [10] L. Khalfallah Boudali, A. Ghorbel, P. Grange, *Catal. Lett.* 86/4 (2003) 251.
- [11] H. J. Chae, In-S Nam, S.-W. Ham, S. B. Hong, *Appl. Catal. B* 53 (2004) 117.
- [12] L. Khalfallah Boudali, A. Ghorbel, P. Grange, F. Figueras, *Appl. Catal. B* 59 (2005) 105-111.
- [13] L. Khalfallah Boudali, A. Ghorbel, P. Grange, *Appl. Catal. A* 305 (2006) 7-14.
- [14] L. Khalfallah Boudali, A. Ghorbel, P. Grange, *C. R. Chimie* 12 (2009) 779-786.
- [15] J. Arfaoui, L. Khalfallah Boudali, A. Ghorbel, G. Delahay, *J. Phys. Chem. Sol.*, 69 (2008) 1121-1124.
- [16] J. Arfaoui, L. Khalfallah Boudali, A. Ghorbel, G. Delahay, *Catal. Today* 142 (2009) 234-238.
- [17] J. Arfaoui, L. Khalfallah Boudali, A. Ghorbel, G. Delahay, *J. Mater. Sci.*, 44 (2009) 6670-6676.
- [18] T. Mishra, K. M. Parida, *J. Coll. Inter. Sci.* 301 (2006) 554-559.
- [19] T. Mishra, P. Mohapatra, K. M. Parida, *Appl. Catal. B* 79 (2008) 279-285.
- [20] L. A. Galeano, A. Gil, M. A. Vicente, *Appl. Catal. B* 100 (2010) 271-281.
- [21] K. Bahranowski, W. Włodarczyk, E. Wisła-Walsh, A. Gawel, J. Matusik, A. Klimek, B. Gil, A. Michalik-Zym, R. Dula, R.P. Socha, E.M. Serwicka, *Microp. Mesop. Mater.* 202 (2015) 155-164.
- [22] A. Michalik-Zym, R. Dula, D. Duraczyńska, J. Krysiak-Czerwenka, T. Machej, R.P. Socha, W. Włodarczyk, A. Gawel, J. Matusik, K. Bahranowski, E. Wisła-Walsh, L. Litynska-Dobrzynska, E.M. Serwicka, *Appl. Catal. B* 174 (2015) 293-307.
- [23] Y. Lia, X. Cai, J. Guo, S. Zhou, P. Na, *Appl. Surf. Sci.* 324 (2015) 179-187.
- [24] A. Gil, L.M. Gandia, M.A. Vicente, *Catal. Rev.* 42 (2000) 145-212.
- [25] M.A. Vicente, A. Gil, F. Bergaya, in: F. Bergaya, G. Lagaly (Eds.), *Handbook of Clay Science*, Elsevier Ltd., Amsterdam, Oxford, 2013, pp. 523-557.

Figure captions

Figure 1: X-Ray diffractograms of the pillared clay supports.

Figure 2: N_2 adsorption-desorption isotherms of the samples (A): (a) Ti-PILC, (b) STi-PILC, (c) WTi-PILC, (d) WSTi-PILC and (B): (a) V/Ti-PILC, (b) V/STi-PILC, (c) V/WTi-PILC, (d) V/WSTi-PILC.

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