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Characterization and catalytic performance of vanadium supported on sulfated Ti-PILC catalysts issued from different Ti-precursors in selective catalytic reduction of nitrogen oxide by ammonia

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Abstract Vanadium supported on sulfated Ti-pillared clay catalysts (STi-PILCs) issued from different Ti-precursors were investigated for selective catalytic reduction (SCR) of NO by NH_3 in the presence of O_2. The STi-PILCs supports were prepared by hydrolysis of a series of organic or inorganic Ti-precursors; $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $TiCl_4$ with H_2SO_4, and then modified with vanadium introduced by impregnation method. The unpromoted and promoted vanadium pillared clays were characterized using chemical analysis, N_2-physisorption, NH_3-TPD, H_2-TPR, and tested for SCR of NO by NH_3. It was found that the textural and acidic properties of the STi-PILC materials are influenced by the nature of the Ti-precursor; and the use of Ti-methoxide allows the synthesis of STi-PILC with the highest acidity. The presence of vanadium on STi-PILC supports reduces their surface areas and porous volumes, creates new redox sites, and enhances the reducibility of the sulfate groups leading to better redox properties of the binary V-STi-PILCs. After vanadium addition, the STi-PILC materials issued from $Ti(OCH_3)_4$, exhibited higher NO reduction activity at high temperature. These results underline the importance of the Ti-precursor for the preparation of the STi-PILC support, and the role of vanadium to increase the redox properties of V-STi-PILC catalyst for the SCR of NO by NH_3.

Introduction

Pillaring is the process by which a layered compound is transformed into a thermally stable micro and/or mesoporous material with retention of the layer structure. The insertion between adjacent layers of clays various simple or mixed polycations, by ion exchange of the original interlayer cation of clays, gives after dehydratation and calcination rigid pillars. This process leads to the formation of a new generation of micro and/or mesoporous materials, known as pillared interlayered clays (PILCs) or cross linked clays. Specific properties of these solids such as structural, textural, acidic properties, and thermal stability are dependent of the nature of metal polycations used for intercalation, the method of synthesis, and the preparation conditions. The increasing number of studies on pillared clays can be explained by the growing interest of their use in environmental field as catalysts [1, 2] and adsorbents [3, 4]. It has been recently shown that Ti-PILC is one of the most successful support for vanadium leading to efficient catalysts for the selective catalytic reduction (SCR) of nitric oxide (NO) by NH_3 [5–7].

The SCR of NO by ammonia is the most adopted catalytic procedure to reduce nitrogen oxides emission, particularly NO, exhausted from stationary source [8]. This process is usually carried out with a stoichiometric molar ratio NH_3/NO and the catalytic reduction can be observed in the absence of O_2 [9]. But the presence of O_2 is necessary and enhances the rate of the SCR-NO by NH_3 reaction [10]. The most commonly used catalysts for the

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SCR industrial process are V_2O_5/TiO_2 based materials which develop a high NO removal activity and a strong resistance toward SO_2 poisoning [6]. These systems are currently modified with WO_3 or MoO_3 to enhance their acidity and their thermal stability. It is well-known that acidity and redox properties of the catalysts play a major role in the SCR-NO by NH_3 [11].

It was also shown that Ti-pillars and structural hydroxyl groups in the clay layer are the main source of acidity [12], whereas the redox properties are essentially related to the presence of vanadia species [10]. The literature reported two different methods to create Ti polycations suitable for pillaring processes: the first process used $TiCl_4$ and HCl [12–14], whereas the second method employed hydrolysis of titanium alkoxide by HCl [15, 16]. Del Castillo et al. [15] found that Ti-PILCs can be synthesized from various titanium alkoxides but the use of $Ti(OC_2H_5)_4$ with HCl yielded the best textural and thermal stability results. Valverde et al. [16] reported the preparation of Ti-PILCs by varying Ti-alkoxide hydrolyzed by HCl. The authors found that the use of $Ti(OCH_3)_4$ allows the synthesis of the Ti-PILC with the best structure, texture, thermal stability, and acidity compared to the others Ti-alkoxides.

In our previous study we have shown that the dispersion of vanadia species on the surface of the unsulfated Ti-PILC and their catalytic performance are influenced by the nature of Ti-source [17]. In this work, it appears interesting to study the effect of the Ti-precursor in the presence of sulfate groups on the characteristics of Ti-PILC supports and to compare their catalytic performances before and after vanadium addition in the SCR-NO by NH_3.

Experimental

Synthesis of catalysts

Starting clay

The starting material was the commercial clay (KC_2) provided by CECA (France). It was purified and only the particle size equal or less than 2 μm was selected for pillaring process, and then was exchanged with Na^+ ions as reported in Ref. [18].

Sulfated Ti-pillared clay by hydrolysis of $TiCl_4$

The pillaring solution was obtained by slowly adding $TiCl_4$ (Fluka, 98%) to H_2SO_4 solution (3 M) under vigorous stirring. Final concentrations of 0.82 M in titanium and 0.1 M in H_2SO_4 were reached by adding water. This fresh pillaring solution was added to the suspension of clay at a Ti/clay ratio of 10 mmol/g and kept in contact at room temperature for 12 h. The solid fraction was separated by centrifugation, washed several times with distilled water, and finally dried at room temperature. The sulfated Ti-pillared clay (STi-PILC) support prepared by hydrolysis of $TiCl_4/H_2SO_4$ is referenced as STiC-PILC.

Sulfated Ti-pillared clay by hydrolysis of $Ti(OCH_3)_4$ or $Ti(OC_2H_5)_4$

The first step of the synthesis of the sulfated titanium pillared clay is the preparation of the intercalating solution by slowly adding titanium methoxide $Ti(OCH_3)_4$ (Aldrich, 95%) or titanium ethoxide $Ti(OC_2H_5)_4$ (Acros 85%) into H_2SO_4 solution (3 M) under vigorous stirring. Final concentrations of 0.05 M in titanium and 0.05 M in H_2SO_4 were reached by adding water. The second step of the synthesis of the STi-PILC sample involved exchange of the Na^+ cations situated between the clay layers with oligomeric sulfated titanium species formed in the intercalating solution. This fresh solution was added to the suspension of clay at a Ti/clay ratio of 10 mmol/g and kept in contact at room temperature for 12 h. The solid fraction was separated by centrifugation, washed several times with distilled water, and finally dried at room temperature. The STi-PILC catalysts are referenced as STiM-PILC and STiE-PILC, respectively, with M and E being the Ti-precursors: M = $Ti(OCH_3)_4$ and E = $Ti(OC_2H_5)_4$.

Vanadia supported on STi-PILC

Vanadium content (2 wt%) was introduced by impregnation of the support (STiC-PILC, STiM-PILC, or STiE-PILC) with an aqueous solution of NH_4VO_3 (Prolabo, 98%) dissolved in oxalic acid (0.1 M). All the samples were then dried at 80 °C for 24 h and calcined at 450 °C for 3 h under air flow. The temperature was raised at the rate of 1 $°C\ min^{-1}$ up to 450 °C, maintained for 3 h. The vanadia supported on sulfated titanium pillared clay catalysts prepared with different Ti-precursors are referenced as V-STiC-PILC, V-STiM-PILC, and V-STiE-PILC.

Characterization of the catalysts

Elemental analysis of the samples was carried out by atomic absorption and by inductively coupled plasma (ICP).

Isotherms of nitrogen adsorption–desorption, specific surface areas, pore volumes, and microporous volumes of the samples were determined by N_2 physisorption at 77 K using a Micromeritics ASAP 2000 apparatus.

Thermal studies were performed on a TG 209 analyser (NETZSCH). All the measurements were carried out with ≈ 15 mg of catalyst under air flow (20 $mL\ min^{-1}$) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C.

Total acidity measurement was evaluated by temperature-programed desorption (TPD) of ammonia using an AUTOCHEM 2910 (Micromeritics). Before NH_3 adsorption, the samples were pre-treated under air flow (30 mL min^{-1}) at 450 °C (ramp 10 °C min^{-1}) for 30 min. NH_3 adsorption was done at 100 °C by exposition to 5 vol.% NH_3 in He (flow rate = 30 mL min^{-1}) for 45 min and then flushed with He (30 mL min^{-1}) during 2 h to remove the remainder of the adsorbate in the gas phase and physisorbed on the catalyst surface. Finally, ammonia was desorbed in helium flow (30 mL min^{-1}) from 100 to 400 °C using a heating rate of 10 °C min^{-1}.

Temperature programed reduction have been carried out in the AUTOCHEM 2910 with a mixture containing 3 vol.% H_2 in Ar (15 mL min^{-1}), with a 15 °C min^{-1} temperature ramp between 50 and 800 °C. The samples were previously activated using the same procedure than for NH_3-TPD.

Catalytic test

The catalytic tests were performed in a continuous flow fixed bed microreactor operating at atmospheric pressure. The catalyst (0.050 g) was activated in situ at 450 °C under 10 vol.% O_2 in He, and then cooled to room temperature. A feed gas stream containing NO (2000 ppm), NH_3 (2000 ppm), and O_2 (3%) in He as balance gas was supplied through mass flow controllers to the microreactor. The total flow rate was 138 mL min^{-1} and the SCR was carried out on programed temperature from room temperature up to 450 °C with heating rate of 6 °C min^{-1}. The reaction products were analyzed by sampling on line with a quadruple mass spectrometer (Pfeiffer Omnistar), calibrated with standard mixtures and by recording the following masses: NO (30), N_2 (28), N_2O (44), NO_2 (46), NH_3 (17), O_2 (32), and H_2O (18).

Results and discussion

Table 1 Element analysis (wt%) of the parent montmorillonite (Na-mont) and of the samples investigated

Sample	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	TiO_2	$V_{loading}$
Na-mont	52.07	14.35	1.14	1.81	0.56	–
STiC-PILC	30.24	13.07	0.78	0.05	29.56	–
STiM-PILC	28.23	13.40	0.77	0.04	30.92	–
STiE-PILC	23.22	9.36	0.65	0.01	33.49	–
V-STiC-PILC	29.96	12.43	0.74	0.02	28.60	2.10
V-STiM-PILC	27.42	13.16	0.71	0.02	29.25	2.06
V-STiE-PILC	23.47	9.37	0.61	0.02	32.11	2.01

The results of chemical analyses of the initial clay (Na-mont) and of the investigated samples are presented in Table 1. The increase of titanium contents at the detriment of the amounts of the sodium upon intercalation is clearly shown for all the STi-PILCs and reflects the successful incorporation of the sulfated Ti-polycations in the interlayer space of the clay, by cation exchange reaction between these polycationic species and the sodium, exchangeable cation, of the initial clay (Na-mont). The impregnation of the sulfated samples by vanadium solution does not significantly alter the relative amounts of Si, Al, and Fe which suggests that the composition of the clay sheet remained constant in all the samples. Therefore, the deposition of vanadium has been realized without chemical element modification of the support.

The isotherms of nitrogen adsorption–desorption of the raw and intercalated clay, determined at 77 K, are shown in Fig. 1. The intercalated samples showed a similar shape

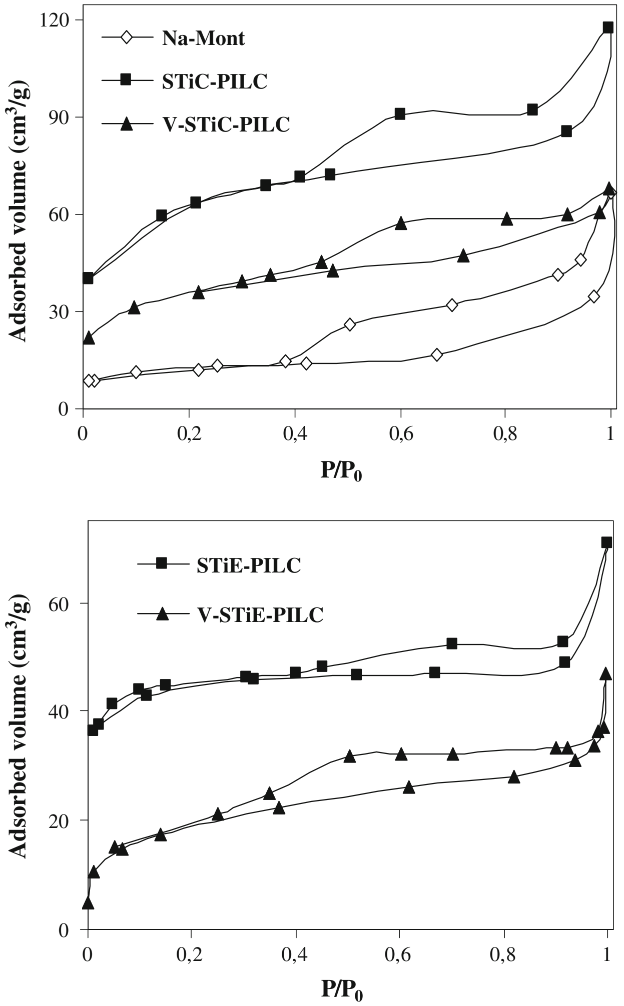


Fig. 1 Nitrogen adsorption–desorption isotherms of the samples

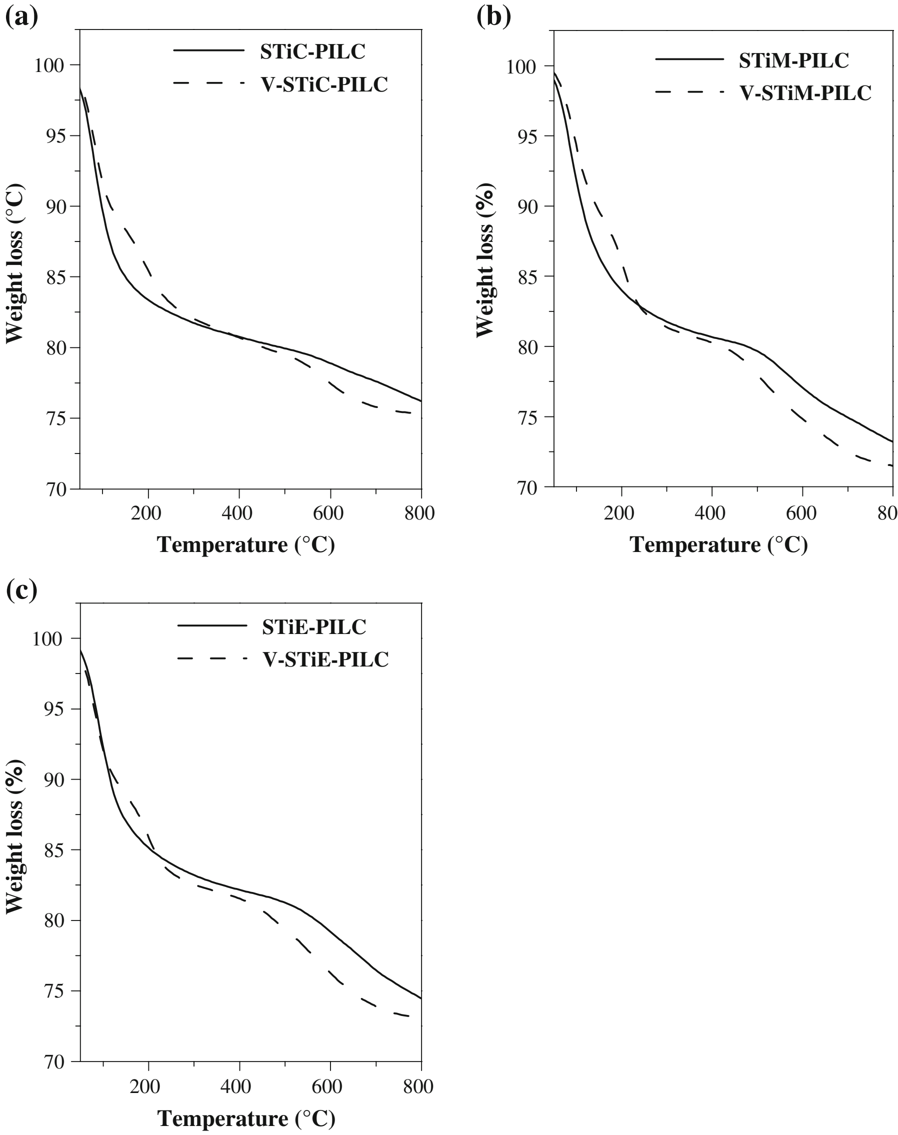
Table 2 Textural properties of the parent montmorillonite and of the samples investigated

Samples	S_{BET} (m^2/g)		V_p (cm^3/g)		$V_{\mu p}$ (cm^3/g)	
	25 °C	450 °C	25 °C	450 °C	25 °C	450 °C
Na-mont	48	–	0.007	–	0.084	–
STiC-PILC	195	186	0.152	0.148	0.048	0.033
STiM-PILC	119	185	0.062	0.100	0.045	0.026
STiE-PILC	121	185	0.078	0.102	0.028	0.024
V-STiC-PILC	114	172	0.103	0.134	0.019	0.019
V-STiM-PILC	60	186	0.038	0.136	0.016	<0.001
V-STiE-PILC	64	201	0.057	0.109	0.001	0.005

corresponding to type II (according to IUPAC classification) which is characteristic of systems with large pore size range. It can be seen that the slope of the isotherms ($P/P_0 < 0.4$) increased in the intercalated samples compared to the raw clay as a consequence of the incorporation of sulfated titanium polycations between the layers of the clay which creates some degree of mesoporosity in these materials. On the other hand, the hysteresis loop exhibited H3 type, behavior characteristic of layered materials having slit-shaped pores and plate-like particles with space between the parallel plates. This fact is consistent with the expected structure for materials prepared by expanding a layer structure.

The textural properties of the samples depend on the nature of the pillars between the clay sheets (Table 2). The surface areas of all the STi-PILCs are clearly higher than that of the initial clay. The increase of the surface area and the microporous volume indicate a successful incorporation of the sulphated Ti-polycations between the layers of the clay. The addition of vanadium to the STi-PILCs

Fig. 2 TGA curves of the samples



supports reduce their surface areas, pore volumes, and micropore volumes due to the pore blockage by vanadia species. Thermal treatment at 450 °C (Table 2) affects the textural properties of the samples. Therefore, the increase of the surface area for all the STi-PILCs after calcination is related to the removal of water from polycationic species and to the decomposition of the sulfate groups. In the case of vanadia doped STi-PILCs, the increase of the surface areas and pore volumes can be explained by the removal of water from vanadia species filling the pores and/or to the decomposition of both sulfate groups and vanadia species.

The TG curves of the STi-PILC samples were performed in air atmosphere in the 50–800 °C temperature range (Fig. 2). For all STi-PILCs, two major weight loss regions have been observed. The first weight loss in the temperature range of 50–500 °C is attributed to the removal of water molecules present in the interlayer clay and coordinated to the pillars as well as to the dehydroxylation of the sulfated Ti-pillars. However, the second weight loss, starting at around 500 °C, is assigned to the dehydroxylation of clay sheets and to the decomposition of sulfate species and clay sheets [19]. Nevertheless, the second weight loss was greater for the STi-PILC issued from Ti-alkoxide than that issued from $TiCl_4$, resulting of decomposition of more sulfate species present in the interlayer region of the pillared clay. It seems that the nature and the number of the sulfated Ti-polycations introduced in the interlayer region of the clay were affected

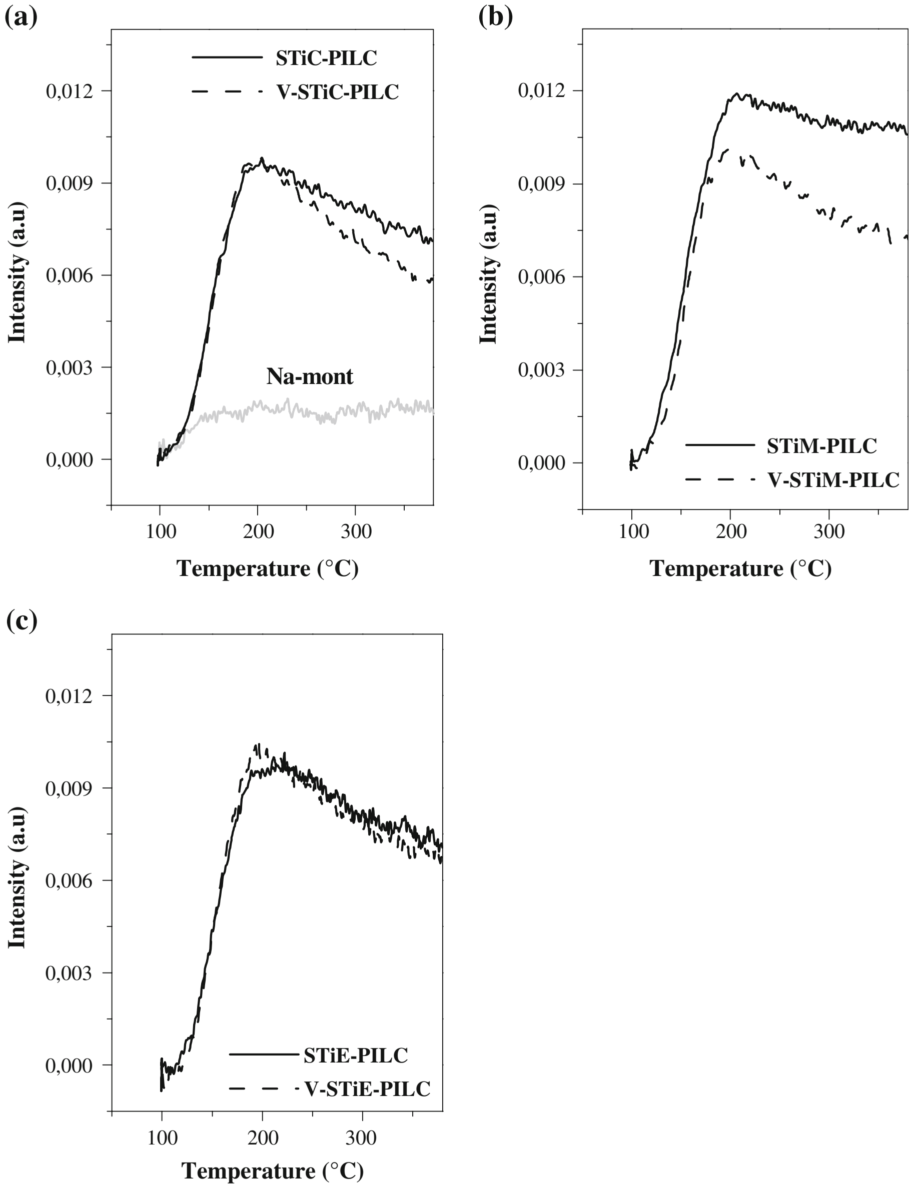


Fig. 3 NH_3-TPD profiles of the samples

by the nature of titanium source used in the preparation of the STi-PILC support. After vanadium addition, the weight loss attributed to the decomposition of sulfate was shifted to lower temperature suggesting a strong interaction between vanadia species and sulfate group. It seems that the presence of vanadium on the STi-PILC materials is responsible of the decrease of the sulfate stability.

The NH_3-TPD profiles of the original clay and of the investigated catalysts are shown in Fig. 3. Desorption of ammonia was performed up to 400 °C to avoid sulfate decomposition. All the sulfated Ti-pillared materials show a higher acidity than that of the initial clay (Na-mont). The generation of highly acidic sites of the sulfated Ti-pillared materials can be related to the Ti-pillars and essentially to the introduction of sulfate groups. It was reported that the Ti-pillars are the main source of Lewis acidity, while a weak Brønsted acidity can arise from structural hydroxyl groups of clay layers [20]. It was also shown that the sulfation of Ti-PILC increased significantly the Brønsted acidity [12, 21, 22]. The surface acidity of the Ti-PILCs issued from $Ti(OCH_3)_4$ is significantly higher than those of the samples prepared with other Ti-source. Thus, it seems that the surface acidity of the sulfated titanium pillared clay is dependent on the nature of the titanium precursor. As also shown in Fig. 3, the addition of a small amount of vanadium (2 wt%) decreases the total amount of NH_3 adsorbed on the pillared clay surface. This decrease is more pronounced in the case of the sample issued from $Ti(OCH_3)_4$ than the other samples containing the same amount of vanadium. The change in the NH_3-TPD profiles after vanadium addition can be explained by the progressive transformation of the surface acidity. It seems that the strong acid sites arising from the sulfated Ti-pillars are covered by relatively weak acid sites arising from vanadia species.

The TPR profiles of the STiM-PILC and STiE-PILC samples (Fig. 4) are similar and show two unresolved reduction peaks with two maxima at around 640 °C and 678 °C assigned to the decomposition of sulfate species into essentially SO_2 and few H_2S [22]. The reduction temperature obtained in this study is higher than that observed in Ref. [22] for the STi-PILC prepared from $TiCl_4$ as titanium source. Thus, it seems that the stability of the sulfate species is dependent on the titanium precursor. This TPR peak position was shifted toward lower temperature after vanadium addition indicating that vanadia species influence the reduction behavior of the sulfate. This result agrees with the fact that the strong interaction between vanadium and sulfate species enhances the sulfate reduction leading to better redox properties of the vanadium supported on sulfated Ti-PILC materials.

Figure 5 shows the results of the selective catalytic reduction (SCR) of NO by ammonia. In the case of the STi-PILC catalysts issued from different Ti-precursors, the SCR-NO activity increases with increasing temperature reaction up to 450 °C. The NO conversion remains quite

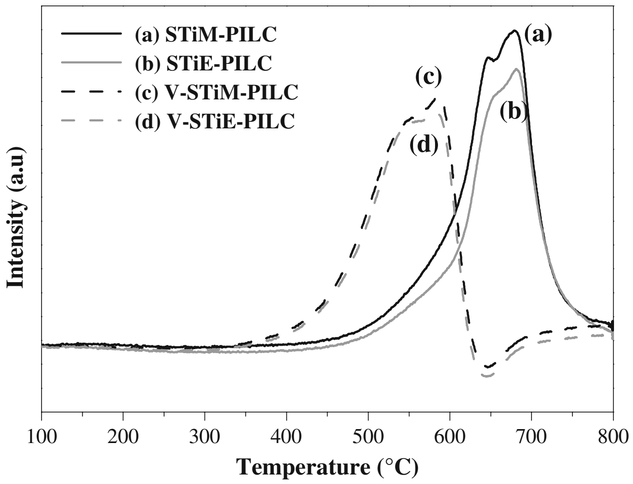


Fig. 4 H_2-TPR profiles of the samples

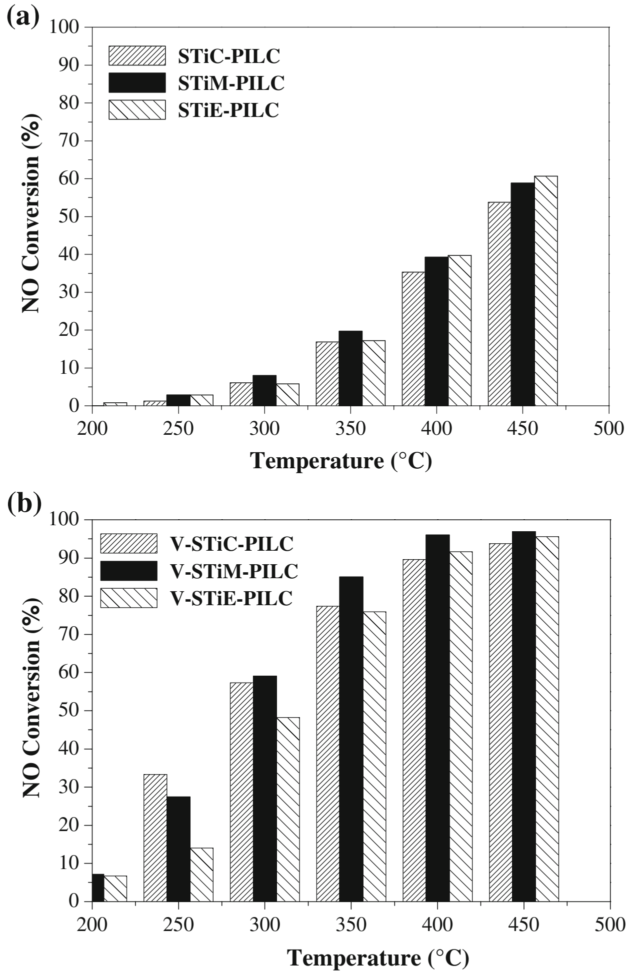


Fig. 5 NO conversion for SCR reaction

low below 350 °C and does not exceed 60% at 450 °C. The catalytic activity of the investigated samples is mainly related to their surface acidity generated by the sulfate groups. As mentioned earlier, the STi-PILC exhibited a higher NO removal activity at high temperature than the unsulfated Ti-pillared clay [19]. We have demonstrated a direct correlation between the SCR activity and acidity enhanced after sulfation [19]. In this study, the acidity and the SCR-NO activity of the catalyst synthesised from organic Ti-precursor was higher than that obtained from inorganic Ti-precursor. This result indicates that the nature of Ti-source, in presence of the sulfate groups, plays a role in the SCR-NO process. After vanadium addition (2 wt%) onto the sulfated Ti-PILCs (Fig. 5b), the activity increased significantly with reaction temperature. The NO conversion is more important in the case of the samples synthesized from titanium alkoxide suggesting that the well dispersion of vanadium species on the surface of the catalyst is affected by the nature of Ti-precursor. It should be underlined that NO_2 and N_2O formation were not observed for all the SCR experiments of this study. The N_2O formation was observed only on catalysts containing higher vanadium content (>2 wt%) [22]. It has been reported that N_2O appears usually when NO/NH_3 ratio is higher than 1 [23]; higher than our conditions. It was also shown in our earlier study that the addition of higher amount of vanadium (3 and 5%) induced a decrease of NO conversion at higher temperature (above 300 °C) due to the NH_3 oxidation by O_2 giving NO [22]. Jung and Grange [24] reported that the oxidation of NH_3 over V_2O_5 began at 350 °C yielding few NO, N_2, and N_2O. The authors showed that the conversion of NH_3 to NO was largely increased above 400 °C. By contrast, in this study we have not observed a decrease of NO conversion due to ammonia oxidation at higher temperature on all catalysts investigated containing a low amount of vanadium (2 wt%) in the presence of sulfate.

Conclusions

The most important conclusions drawn from the present study may be summarized as follows:

- The presence of sulfate group in the structure of the Ti-polycations is a key factor for the activity at high temperature of the sulfated Ti-PILC in the SCR-NO by NH_3.
- The surface acidity of the STi-PILC and its SCR-NO activity seem to depend on the nature of the Ti-precursor used in the pillaring process.
- The deposition of a low amount of vanadium influences both the surface acidity of the STi-PILC and the reducibility of the sulfate group and enhances significantly the SCR-NO activity.
- The highest acidity and the best activity in the SCR-NO by NH_3 were obtained in the case of the sulfated Ti-PILC issued from $Ti(OCH_3)_4$ and promoted with 2 wt% of vanadium.

References

1. Cheng S (1999) Catal Today 49:303
2. De Stefanis A, Tomlinson AAG (2006) Catal Today 114:126
3. Heylen I, Vansant EF (1997) Microporous Mater 10:41
4. Lenoble V, Bouras O, Deluchat V, Serpaud V, Bollinger B (2002) J Colloid Interface Sci 255:52
5. Long RQ, Yang RT (2000) Appl Catal B 24:13
6. Chae HJ, Nam IS, Ham SW, Hong SB (2004) Appl Catal B 53:117
7. Khalfallah Boudali L, Ghorbel A, Grange P, Figueras F (2005) Appl Catal B 59:105
8. Forzati P (2000) Catal Today 62:51
9. Najbar M, Banas J, Korchowiec J, Bialas A (2002) Catal Today 73:249
10. Topsøe NY, Topsøe H, Dumesic JA (1995) J Catal 151:226
11. Grzybek T (2007) Catal Today 119:125
12. Khalfallah Boudali L, Ghorbel A, Tichit D, Chiche B, Dutartre R, Figueras F (1994) Microporous Mater 2:525
13. Sterte J (1986) Clays Clay Miner 34:658
14. Bernier A, Admaiai LF, Grange P (1991) Appl Catal 77:269
15. Del Castillo HL, Gil A, Grange P (1997) J Phys Chem Solids 58:1053
16. Valverde L, Sanchez P, Dorado F, Asenico I, Romero A (2003) Clays Clay Miner 51:41
17. Arfaoui J, Khalfallah Boudali L, Ghorbel A, Delahay G (2008) J Phys Chem Solids 69:1121
18. Arfaoui J, Khalfallah Boudali L, Ghorbel A (2006) Catal Commun 7:86
19. Arfaoui J, Khalfallah Boudali L, Ghorbel A, Delahay G (2009) Catal Today 142:234
20. Chmielarz L, Kustrowski P, Zbroja M, Lasocha W, Dziembaj R (2004) Appl Catal B 53:47
21. Del Castillo HL, Gil A, Grange P (1997) Catal Lett 43:133
22. Khalfallah Boudali L, Ghorbel A, Grange P (2006) Appl Catal A 305:7
23. Lietti L, Forzatti P (1994) J Catal 147:241
24. Jung SM, Grange P (2002) Appl Catal B 36:325