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# Effect of vanadium on the behaviour of unsulfated and sulfated Ti-pillared clay catalysts in the SCR of NO by $NH_3$

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ABSTRACT

Vanadium supported on unsulfated and sulfated Ti-pillared clays are developed for the selective catalytic reduction (SCR) of nitrogen oxide (NO) by ammonia. The unsulfated Ti-pillared clays (TiM-PILC) were prepared by hydrolysis of titanium methoxide ($Ti(OCH_3)_4$) with HCl. The same procedure was employed using $H_2SO_4$ in order to obtain the sulfated Ti-pillared clays (STiM-PILC). All the pillared materials were characterized before and after vanadium addition by chemical analysis, XRD, $N_2$-physisorption, TGA, $NH_3$-TPD, $H_2$-TPR and UV–vis. It was found that the sulfation or the addition of a low amount of vanadium into the TiM-PILC reduces the surface area but improves the acidity of the material. The addition of vanadium to the STiM-PILC decreases the surface area, the number of acid sites and the stability of the sulfate species but enhances the redox properties of the material. The STiM-PILC and the V-TiM-PILC exhibit higher NO removal activity at high temperature than the TiM-PILC. The presence of both sulfate and a low amount of vanadium (2 wt.%) in the TiM-PILC leads to an excellent active and selective catalyst for SCR-NO with $NH_3$.

## 1. Introduction

The abatement of nitrogen oxides ($NO_x$) emissions from both mobile and stationary sources is still an environmental problem. These harmful gases have a direct impact on the human health and contribute to a variety of environmental problems such as the formation of acidic rain and the destruction of the troposphere. The application of catalytic systems for $NO_x$ abatement has been extensively studied due to the adoption of strict environmental regulations. Until today, the selective catalytic reduction (SCR) of nitrogen oxide by ammonia is recognized as the best available technology to reduce NO emitted from stationary sources [1]. It is well known that the process is based on the reaction between NO and $NH_3$ to produce $N_2$ and $H_2O$ [2]. Most of the SCR studies agree that two factors play a very important role in the reduction process: acidity and redox properties [3]. A great variety of catalysts have been reported to be active: noble metals and ion exchange zeolite as well as metallic oxides such as $V_2O_5$, $Fe_2O_3$, $Cr_2O_3$, CuO, $ZrO_2$, supported on $TiO_2$, $Al_2O_3$ and $SiO_2$ catalysts. Among the various oxide catalysts, materials containing Ti and V are known as excellent catalysts for the SCR of NO with ammonia due to their superior activity and stability [4]. Recently, vanadium supported on titanium-pillared interlayer clays materials have received much attention for the SCR of NO by $NH_3$ [5–7].

In general, two different methods for generating Ti-polycations suitable for pillaring process were reported in the literature, the first one is based on the hydrolysis of $TiCl_4$ by HCl [8,9], while the second method is the use of various Ti-alkoxides hydrolyzed by HCl [10,11]. It is worthwhile to note that the first attempt to use vanadia-doped titanium-pillared clay in the SCR process have been reported by Bahranowski et al. [12] who claimed that catalytic performance of these systems depends on the method of the preparation and on the vanadia content; the best catalyst converting 90–100% NO in the temperature range 250–350 °C, is obtained by exchange of titanium-pillared montmorillonite, prepared by $TiCl_4$/HCl solution and containing 3.4 wt.% of vanadium. Long and Yang [13] investigated $VO^{2+}$-exchanged titania-pillared clays, also prepared by hydrolysis of $TiCl_4$/HCl, and found that the increase in the Brønsted acidity with vanadium content was consistent with the increase of SCR-NO activity. The maximum activity was obtained for the catalysts with 2.1–3.5 wt.% of vanadium. More recently, we have compared the activity in the SCR-NO reaction of Ti-PILC prepared from different titanium precursors: $TiCl_4$, $Ti(OCH_3)_4$ and $Ti(OC_2H_5)_4$. We have shown that

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the nature of Ti-source plays a role in the SCR-NO activity [14]. The highest activity of Ti-PILC in the SCR reaction was obtained in the case of the sample prepared with Ti-alkoxides hydrolyzed by HCl. In the present work it appears interesting to study the effect of the sulfation and/or the addition of a low amount of vanadium (2 wt.%) on the behaviour of Ti-PILC, issued from $Ti(OCH_3)_4$ precursor, in the SCR of NO by $NH_3$.

## 2. Experimental

### 2.1. Synthesis of catalysts

#### 2.1.1. Starting clay

The fraction with particle size smaller than 2 μm of the sodium exchanged form of a commercial montmorillonite ($KC_2$) supplied by CECA (France), was selected as starting material and referenced as Na-mont.

#### 2.1.2. Unsulfated titanium-pillared clay (TiM-PILC)

The pillaring solution was obtained by slowly adding titanium methoxide $Ti(OCH_3)_4$ into HCl solution (6 M) under vigorous stirring. Final concentrations of 0.05 M in titanium and 0.1 M in HCl were reached by adding water; an $H^+/Ti = 2$ was thus obtained. The pillaring solution was aged for 1 h then added dropwise to 0.5 L of a suspension containing 4 g of clay; in these conditions a final Ti/clay ratio of 10 mmol/g was obtained. The suspension of clay and the intercalating solution of titanium were kept in contact at room temperature for 12 h then the solid fraction was separated by centrifugation, finally washed several times with distilled water and dried at room temperature.

#### 2.1.3. Sulfated titanium-pillared clay (STiM-PILC)

The first step of the synthesis of the sulfated titanium-pillared clay is the preparation of the intercalating solution by slowly adding titanium methoxide $Ti(OCH_3)_4$ 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 STiM-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 then the solid fraction was separated by centrifugation, finally washed several times with distilled water and dried at room temperature.

#### 2.1.4. Vanadia supported on TiM-PILC and on STiM-PILC

Vanadium content (2 wt.%) was introduced into TiM-PILC and STiM-PILC by impregnation of the support with appropriate volume of $NH_4VO_3$ aqueous solution containing oxalic acid (0.1 M). The samples were then dried at 80 °C for 24 h and calcined at 450 °C for 3 h under airflow. The temperature was raised at the rate of 1 °C $min^{-1}$ up to 450 °C, maintained for 3 h. The vanadia supported on unsulfated and sulfated titanium-pillared clay catalysts are referenced V-TiM-PILC and V-STiM-PILC, respectively.

### 2.2. Characterization of catalysts

Chemical compositions of the clay samples were determined by ICP and by atomic absorption.

X-ray diffraction patterns of the samples were obtained using a Philips Panalytical instrument with Cu Kα radiation (λ = 1.5412 Å).

Textural properties of the samples (specific surface areas ($S_{BET}$), pore volumes ($V_p$) and microporous volumes ($V_{\mu P}$)) were determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2000 apparatus.

Thermogravimetric analysis was performed on a TG 209 analyser (NETZSCH). Aliquots of ≈15 mg were heated from room temperature to 900 °C in airflow (20 mL $min^{-1}$) using a heating rate of 10 °C $min^{-1}$.

Total acidity measurement was evaluated by temperature-programmed desorption (TPD) of ammonia using an AUTOCHEM 2910 (Micromeritics). Before $NH_3$ adsorption, the samples were pre-treated under airflow (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 $min^{-1}$.

UV–vis diffuse reflectances were recorded on a PerkinElmer spectrophotometer type Instrument lambda 45 coupled to an integration sphere type RSA-PE-20 in the range 200–900 nm with a speed of 960 nm $min^{-1}$ and an aperture of 4 nm.

Temperature-programmed 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.

### 2.3. 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 programmed temperature from room temperature up to 450 °C with heating rate of 6 °C $min^{-1}$. The reaction products were analysed 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).

## 3. Results and discussion

The chemical compositions of the Na-mont and of the investigated samples are presented in Table 1. Intercalation of the Na-mont with Ti-polycations resulted in an increase of $TiO_2$ content at the detriment of $Na_2O$. In the case of the sulfated samples, both $TiO_2$ and sulfate contents increased. These results indicate that unsulfated and sulfated Ti-polycations were successfully introduced in the interlayer space.

The basal spacing ($d_{0\,0\,1}$) reported for Ti-pillared clay obtained from $TiCl_4$ hydrolyzed by HCl is about 22–26 Å at room temperature [8,9] but this value strongly depends on the method

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

| Samples | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $TiO_2$ | $S_{loading}$ | $V_{loading}$ |
|---|---|---|---|---|---|---|---|
| Na-mont | 52.07 | 14.35 | 1.14 | 1.81 | 0.56 | – | – |
| TiM-PILC | 25.91 | 11.89 | 0.72 | 0.01 | 36.32 | – | – |
| V-TiM-PILC | 24.64 | 13.66 | 0.68 | 0.01 | 35.07 | – | 2.08 |
| STiM-PILC | 28.23 | 13.40 | 0.77 | 0.04 | 30.92 | 2.83 | – |
| V-STiM-PILC | 27.42 | 13.16 | 0.71 | 0.02 | 29.25 | 2.71 | 2.06 |

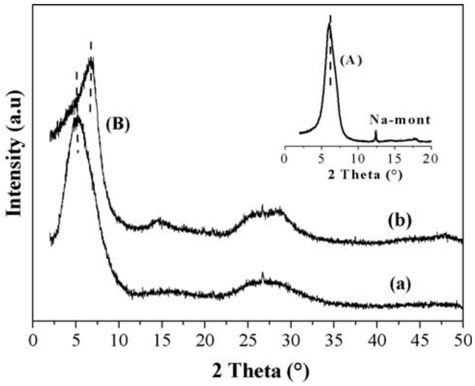

**Fig. 1.** X-ray diffractograms of (A) the parent clay (Na-mont) and (B) the samples: (a) TiM-PILC and (b) V-TiM-PILC.

of intercalation. It was shown that when using Ti-alkoxide, the basal spacing is however much lower than that obtained by intercalation using Ti-chloride precursor [10,11]. The XRD pattern of the parent montmorillonite (Na-mont) exhibits a peak at $2\theta$ about 6.5 ° (Fig. 1A) which is assigned to the basal spacing $d_{0\,0\,1}$ = 13.5 Å. This value represents the distance between the two clay layers including the thickness of the layer (9.6 Å). After intercalation the $d_{0\,0\,1}$ peak was shifted to lower $2\theta$ region (Fig. 1B, a) which is a clear indicative of the enlargement of the basal spacing of the two clay layers by titanium polycations with a low relative degree of polymerization. This lower basal spacing (17.6 Å) obtained for TiM-PILC compared to that obtained in Refs. [8,9] is therefore related to the use of Ti-methoxide precursor. It is known that the polymerization process of titanium depends on the nature of the acid used for hydrolysis of the Ti-source [10]. The Ti-polycations obtained in the presence of $H_2SO_4$ have a smaller size than those obtained with HCl at an equivalent pH of the pillaring solution [9]. In this work the basal spacing decreased after sulfation to 16.04 Å (data not shown). This lower value is therefore related to the use at the same time of the Ti-methoxide and $H_2SO_4$ in the pillaring solution. For all the samples containing vanadium (Fig. 1B, b) the basal spacing was decreased to 14 Å. The redispersion of the intercalated clay in the vanadium solution can cause some disorder in the structure.

The textural properties of the samples investigated in this work are reported in Table 2. The increase of the surface area and the micropore volume of the investigated materials compared to the parent clay indicate a successful intercalation of the Ti-polycations. It should be noticed that the unsulfated sample had a large surface area than the sulfated material. This might be due to pore blockage through progressive filling with sulfate species. The addition of vanadium on the unsulfated and the sulfated samples reduced their surface areas which can be explained by the blocking of the small pores of the solids by vanadia species. The comparison of the thermal stability of the samples was performed under similar operating conditions (Table 2). In the case of the unsulfated Ti-pillared clay (with or without vanadia), the decrease of $S_{BET}$ is mainly due to the dehydroxylation of the Ti-pillars and of vanadia species. In contrast, the surface area of the sulfated Ti-pillared clay (with or without vanadia) increased after calcinations at 450 °C, due essentially to the decomposition of sulfate species.

**Table 2**
Textural properties of the parent montmorillonite and of 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 | – | 0.084 | – | 0.007 | – |
| TiM-PILC | 282 | 249 | 0.200 | 0.193 | 0.025 | 0.004 |
| V-TiM-PILC | 221 | 210 | 0.158 | 0.182 | 0.024 | 0.001 |
| STiM-PILC | 119 | 185 | 0.062 | 0.100 | 0.045 | 0.026 |
| V-STiM-PILC | 60 | 186 | 0.038 | 0.136 | 0.016 | <0.001 |

TG patterns of the parent montmorillonite and of the pillared materials are shown in Fig. 2. In the case of the Na-mont (Fig. 2A), the weight loss observed at 110 °C is attributed to the departure of adsorbed water and the second weight loss observed at around 550 °C is due to the dehydroxylation of the clay structure. The TiM-PILC sample shows a monotonous weight loss up to 800 °C, due to the dehydration, the dehydroxylation of the Ti-pillars and the dehydroxylation of the clay structure. After vanadia addition to the TiM-PILC, a new weight loss appeared around 180 °C which can be attributed to the dehydroxylation of vanadia species. The TGA plot of the sulfated titanium-pillared clay (Fig. 2B) shows a weight loss starting at around 500 °C. This marked weight loss is not observed in the case of the unsulfated TiM-PILC and is attributed to the decomposition of the sulfate species. In the case of the V-STiM-PILC sample, the weight loss attributed to the decomposition of sulfate was shifted to lower temperature suggesting that the presence of vanadia species decreases the thermal stability of the sulfate groups. This result can be explained by a strong interaction between vanadia and sulfate species.

The acidity is one of the important properties required from Ti-PILC used as catalysts. It is well known that the surface acidity of the catalyst plays a major role in the process of selective reduction of NO by ammonia. The $NH_3$-TPD patterns of the samples are shown in Fig. 3. The Ti-pillared materials show a much higher acidity than that of the initial clay (Na-mont). This result indicates that the total acidity is enhanced by pillaring of the montmor-

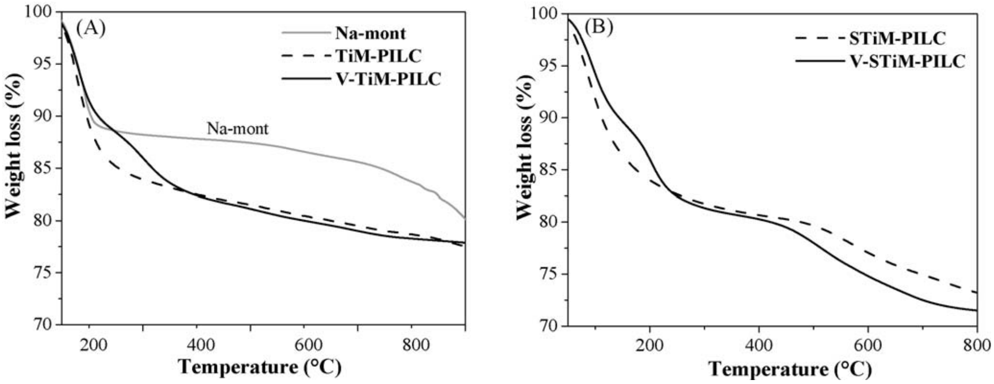

**Fig. 2.** TGA curves of the samples.

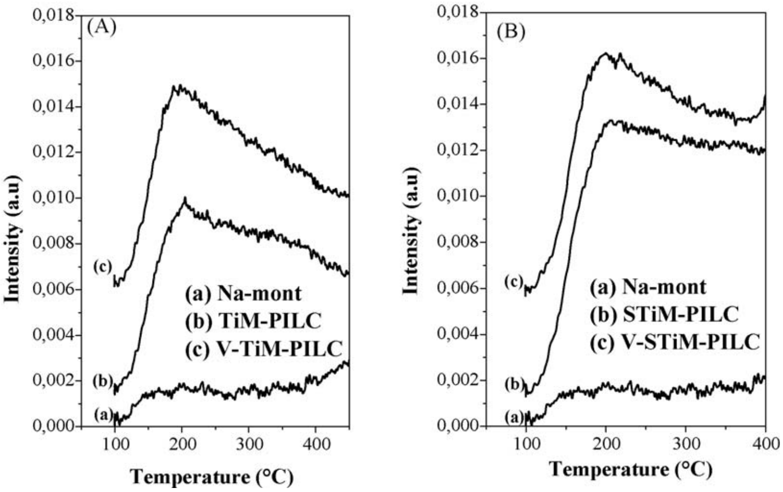

**Fig. 3.** $NH_3$-TPD profiles of the samples.

illonite. The Ti-pillaring process creates both weak acid sites (ammonia desorbed between 100 and 250 °C) and medium strength acidity (ammonia desorbed between 250 and 400 °C). The ammonia desorption profile suggest that there are at least two distinct $NH_3$ species adsorbed on the catalyst surface. It is well known that the Ti-pillars are the major source of Lewis acidity, while a weak Brønsted acidity can be arises from structural hydroxyl groups of the clay layers. When sulfate was introduced on Ti-PILC, the amount of Brønsted acidity further increased [9]. The stronger Brønsted acidity of sulfated Ti-PILC has been proposed to be responsible for the high SCR-NO activity of sulfate Ti-pillared clay [15]. The $NH_3$ desorption profile of Ti-pillared clay (Fig. 3A) shows two unresolved maxima. The first peak centred at about 200 °C can be related to ammonia desorbed from weak Brønsted acid sites while the second peak much broader centred at about 350 °C can be attributed to the desorption of $NH_3$ strongly adsorbed on Lewis acid sites [16–17]. The addition of vanadium into the titanium-pillared clay have an effect on the total acidity, it induces an increase of the intensity of the first peak due to the weaker acid sites and a slight decrease of the intensity of the second peak due to the ammonia strongly adsorbed at temperature above 300 °C. Fig. 3B shows that the sulfation of the clay material enhances significantly its surface acidity as also observed by FT-IR study for the sulfated Ti-PILC prepared by hydrolysis of $TiCl_4$/$H_2SO_4$ [15]. When vanadium was supported on the sulfated titanium-pillared clay, the number of acid sites weakly diminishes leading us to conclude that the deposition of vanadia obstructs some pores of the solids and suppresses some acidic sites arising from the pillars and/or the sulfates species.

Fig. 4 shows the diffuse reflectance UV–vis spectra of the parent montmorillonite (Na-mont) and of the investigated samples. The Na-mont displays a characteristic broad band centred at about 245 nm (Fig. 4A) which was assigned to ($Fe^{3+} \rightarrow O^{2-}$, $OH^-$ or $OH_2$) charge transfer band for iron present in the octahedral layer of the montmorillonite [18]. Before vanadia addition, the spectra of the unsulfated and the sulfated Ti-pillared clays are similar and show two peaks centred at around 260 and 320 nm, which can be assigned to octahedral isolated Ti species and to anatase crystal form, respectively. Note that the weak shoulder at around 210 nm can be attributed to tetrahedral isolated Ti species. For the samples containing vanadium, also two peaks situated around 350 and 400 nm were found. These bands can be attributed to low polymerized vanadia chains and domains vanadium in tetrahedral and square-pyramidal configurations, respectively [19]. All the spectra of the vanadium containing samples show a shoulder around 475 nm which could suggest the presence of octahedrally coordinated crystalline $V_2O_5$ [19]. Note that the deposition by impregnation of small amount of vanadia onto the unsulfated and the sulfated TiM-PILC surface causes a partial intensity decrease of the main absorption which can result from the interruption of Ti–O–Ti chains due to the incorporation of vanadia species.

The reduction behaviour of the sulfate and vanadia species in the catalysts was studied by means of TPR; reduction curves of the investigated catalysts are shown in Fig. 5. The TPR profile of the TiM-PILC shows a weak reduction peak at 520 °C which is attributed to the reduction of iron species, present in the clay [14]. Therefore, the relative intensity and surface area of the peak became more predominant after vanadia addition, which suggests

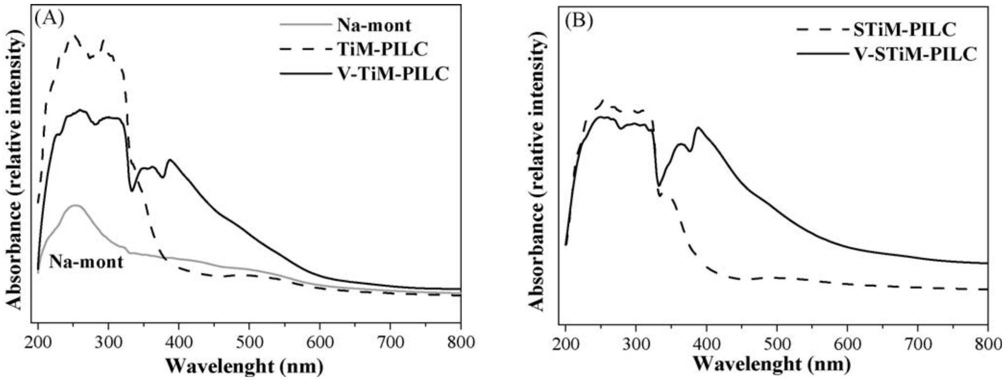

**Fig. 4.** UV–vis spectra of the samples.

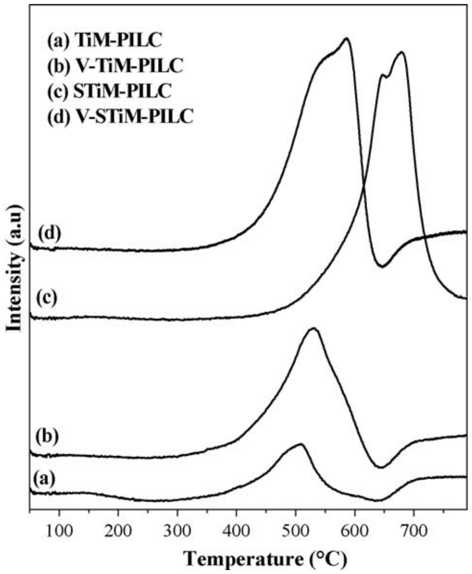

**Fig. 5.** $H_2$-TPR profiles of the samples.

that the reduction of vanadia species occurs in the same temperature range and demonstrates an easier access of hydrogen to the vanadium species well dispersed on the surface of the support. In the case of the STiM-PILC sample a new reduction peak begin at about 450 °C, reaches two maxima at around 640 and 678 °C which can be assigned to the decomposition of sulfate species. It was shown in our earlier work that the hydrogen consumption is due to the reduction of sulfate to essentially $SO_2$ with few $H_2S$ formation over sulfated Ti-pillared clay prepared from another titanium precursor ($TiCl_4$) [20]. By comparison, the maximum reduction temperature observed in this work using $Ti(OCH_3)_4$ in the pillaring solution is higher than that observed with Ti-chloride. Thus, it seems that the stability of the sulfate species is dependent of the Ti-precursor used for the preparation of Ti-pillared clay material. This TPR peak position was shifted towards lower temperature after vanadium deposition. However the reduction of sulfate completely hides the reduction of vanadium. On the other hand, the presence of vanadia species influences the reduction behaviour 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 V-STiM-PILC materials.

The SCR activities of the investigated samples are shown in Fig. 6. The TiM-PILC exhibits smaller activity in SCR-NO reaction. Furthermore, when a small amount of vanadia was added to the pillared material, the NO conversion increased significantly with temperature reaction. The increase of SCR activity can be related to the redox properties of vanadia species. The sulfated titanium-pillared clay exhibits a higher NO removal activity at high temperature than the unsulfated sample. We can assume that this improvement of activity is due to the increase in acidity, which is known to be one of the keys features of the SCR reaction mechanism. The presence of both sulfate and a low amount of vanadia (2 wt.%) onto the titanium-pillared clay allows a good balance between redox and acidic sites leading to an excellent catalyst for SCR-NO with $NH_3$. In this later case, NO reduction exceeds 97% in 380–450 °C temperature range. It should be underlined that no $NO_2$ formation was observed for all the SCR experiments of this study. On the other hand, $N_2O$ formation was observed on 3% vanadium sample only. On this sample, $NH_3/NO$ consumed is higher than 1 due to the secondary reaction of $NH_3$ oxidation [21] which starts at around 350 °C and is responsible for the formation of $N_2O$ observed.

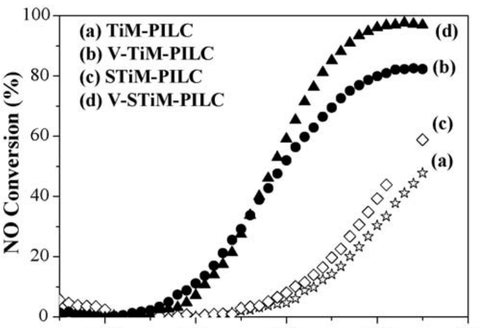

**Fig. 6.** NO conversion for SCR reaction.

## 4. Conclusion

It was found that the sulfation of titanium-pillared clay leads to a decrease of the surface area but enhances significantly the number of acidic sites of the solid. The addition of a low amount of vanadium (2 wt.%) to the unsulfated Ti-pillared clay gradually reduces the surface area but improves the number of Brønsted acidic sites. In the case of sulfated Ti-pillared clay the addition of the same amount of vanadium decreases both the surface area and the number of acidic sites but enhances the redox properties of the material. The sulfated Ti-pillared clay exhibits a higher NO removal activity at high temperature than the unsulfated Ti-pillared clay due to the increase of its surface acidity. The presence of both sulfate and a low amount of vanadium (2 wt.%) in the titanium-pillared clay, prepared by $Ti(OCH_3)_4$ source, allows a good balance between redox and acid sites leading to an excellent catalyst for SCR-NO with $NH_3$.

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