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Catalytic performance of $Al_2O_3/SiO_2/TiO_2$ loaded with V_2O_5 for the selective catalytic reduction of NO_x with ammonia

Nicolaos Economidis, Robert F. Coil, Panagiotis G. Smirniotis*

Chemical Engineering Department, University of Cincinnati, Cincinnati, OH 45221-0171, USA

Abstract

In this work, various $Al_2O_3/SiO_2/TiO_2$ nanocomposites prepared from organic precursors through a sol–gel method and loaded with vanadium were studied for the selective catalytic reduction of NO_x with ammonia as a reductant. The coexistence of Al and Si as heteroatoms in the titania matrix resulted in lower levels of activity than titania catalysts due to the low crystallinity of titania in the polyoxide supports. Catalytic experiments indicate that the level of NO_x conversion and N_2 selectivity for the Al-rich or Si-rich catalysts are comparable under identical operating conditions. However, the NO_x conversion over the SiO_2-rich polyoxides passes through a maximum for composites with atomic composition Ti:Si:Al=30:5:1. This behavior is strongly related with the BET surface area of each catalyst. The NO_x conversion and N_2 selectivity over the Al-rich catalysts follows very closely their BET surface area as well. The Brønsted acidity of the support, which is introduced by the addition of Si and the Al dopants, seems to play a secondary role in the catalyst performance. The addition of Si and Al as heteroatoms decreases the temperature window for optimum performance in comparison with earlier studies for SCR reactions. FT-IR, XRD, BET and TEM were used for the characterization of our catalysts. © 1998 Elsevier Science B.V.

Keywords: SCR of NO_x; Polyoxide-based catalysis; Acidity; Si and Al heteroatoms

1. Introduction

Selective catalytic reduction (SCR) is one of the most widely used methods of removing NO_x from flue gases [1–4]. Vanadia based catalysts have been extensively studied and found to be highly effective for the reduction of NO_x [5–11]. The most widely studied support for vanadium has been TiO_2 because it is resistant to sulfur poisoning and disperses effectively V_2O_5. However, titania does have some drawbacks, namely it is expensive, non-resistant to sintering, and has relatively low surface area [12,13].

Mixed oxides of TiO_2–SiO_2 have been studied by other researchers as $DeNO_x$ catalysts [10,12,14–16]. It was demonstrated earlier that there are a number of benefits associated with SiO_2 such as better mechanical strength, significantly higher BET surface area, and higher Brønsted acidity. Mixed oxides of TiO_2–Al_2O_3 have been investigated extensively by Centi et al. [17]. It was found that Al_2O_3 rendered the binary oxide catalyst resistant to SO_2 poisoning. It was proposed that the Al_2O_3 component (no CuO was added to the catalyst) attracts the generated surface sulfate species formed originally on vanadia, thus shielding the active vanadium sites. However, the incorporation of a heteroatom in the TiO_2 matrix

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*Corresponding author.

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results in reduced crystallinity of titania. Many researchers have observed that titanias with relatively low crystallinity do not disperse vanadia very effectively [14,16]. Knowing the potential benefits of the mixed oxides as supports for SCR, we decided to synthesize and study $Al_2O_3/SiO_2/TiO_2$ mixed oxides as potential supports for this reaction in the presence of NH_3. We found that supports synthesized via a sol–gel co-precipitation procedure involving organic precursors of aluminum, silicon, and titanium acquire much greater BET surface area and Brønsted acidity. In this study we report the catalytic performance of these supports loaded with vanadia for the SCR of NO. We found that the incorporation of Si and Al as dopants in the support and also the BET surface area of the catalyst play an important role in the catalyst performance.

2. Experimental

2.1. Catalyst preparation

A sol–gel method involving organic precursors was used to homogeneously co-precipitate the mixed oxide supports [18]. The organic precursors used were titanium isopropoxide (TIOP) from Aldrich (97%), tetraethyl orthosilicate (TEOS) from Aldrich (98%), and aluminum tri-sec butoxide (ALTSB) from Aldrich (97%). All the precursors were dissolved in 2-propanol at the appropriate concentrations and mixed vigorously for 1 h. The solution was then added dropwise to a known amount of distilled water. Under these conditions, the precipitation took place rapidly. The solution underwent vigorous mixing for 12–18 h and then aged for an additional 24 h. The synthesized material was dried overnight, ground, and sieved (80 mesh size). The supports were calcined in air at 450°C for 4 h. From transmission electron spectroscopy experiments we observed that the primary particles of the synthesized materials are spherical with size in the range 10–25 nm.

A known amount of the support (dry basis) and distilled water were added to oxalic acid (Fisher Scientific, 99%) at a molar ratio of support to oxalic acid equal to 6:1. Ammonium metavanadate (NH_4VO_5, Aldrich 99+%) was dissolved in water and then added to the support solution. Both solutions were brought to 70°C before mixing. The final solution turns yellow-green instantly upon addition of the vanadium precursor solution and heating, and then gradually turns to green as it is mixed until the water has completely evaporated.

2.2. X-ray diffraction

The percentage of crystallinity and the phases of titania were identified with X-ray diffraction. The experiments were performed with a Siemens D-500 Diffractometer equipped with a CuK_α source. The anatase phase of titania was identified by the peak at $\theta=25.3^\circ$ while the rutile phase was identified by the peak at $\theta=27.5^\circ$ [19]. For the quantitative determination of the non-crystalline titania and percentage of the anatase and the rutile phases, we prepared calibration curves from mixtures with variable concentrations of highly crystalline anatase (Aldrich 99.99%) and rutile (Kemira 99%) titanias. The calibration was based on the intensity counts of each peak.

2.3. FT-IR spectroscopy

FT-IR spectroscopy was used for the characterization of the acidic properties of the supports and the catalysts. The experiments were performed with a Bio-Rad spectrophotometer (FTS-040). Self-supported wafers were formed by pressing 10±1 mg of powder and were placed in a bakeable high-vacuum cell with CaF_2 windows. The wafers were treated with ultrapure He at 550°C for 1 h in order to remove any impurities. The sample was cooled down to 150°C and anhydrous ammonia was admitted to the cell for 1 h followed by a He purging step to remove any physisorbed ammonia. From the recorded spectra, conclusions for the Lewis acid sites (band at 1605 cm^{-1}) and the Brønsted acid sites (band at 1427 cm^{-1}) of the catalysts [6] were derived.

2.4. Catalytic studies

The catalytic experiments were conducted in a plug flow differential reactor under atmospheric pressure. The catalytic setup used in the present work is shown in Fig. 1. Four anticorrosive mass flow controllers regulated the flow rates of oxygen (Wright Bros., 4.18% in He), ammonia (Matheson, 3.89% in He),

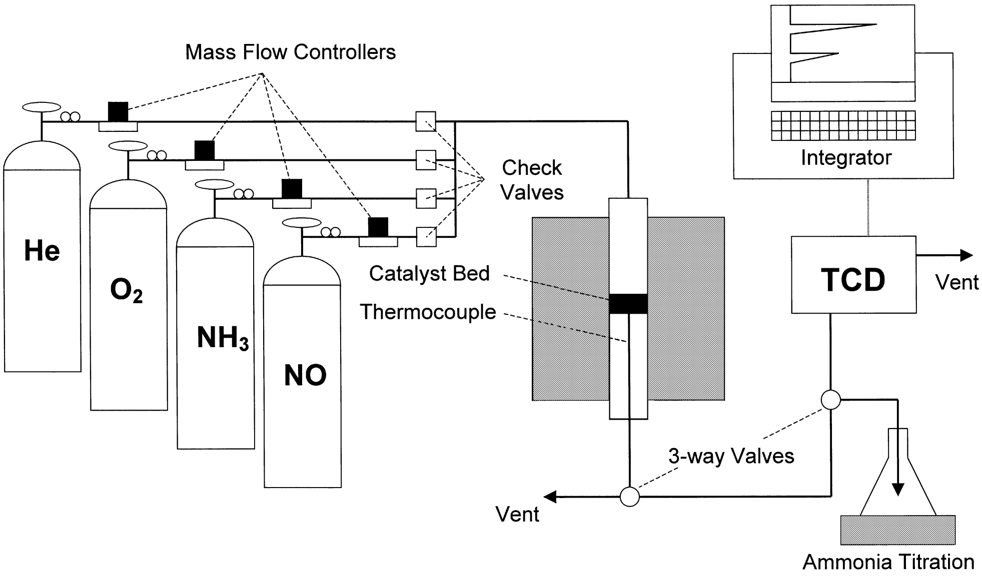

Fig. 1. Schematic of the catalytic setup.

and nitric oxide (Air Products, 2.0% in He). The reaction mixture was fed into the reactor (1/4 in. ceramic alumina tube) through stainless steel tubing. Ultrahigh purity He (Wright Bros., 99.995%) was used as the balance gas. The inlet concentrations of the NO, O_2, and NH_3 were 2000 ppm. For the catalytic experiments 50 mg of catalyst (dry basis) were loaded in the reactor unless otherwise specified. The density of the catalysts used for the estimation of gas hourly space velocity was about 0.68 g/cm^3. The GHSV for the present study was kept at 30 000 h^{-1}.

An Omega temperature controller was used to control the furnace temperature. A type K thermocouple is inserted directly into the catalyst bed. Prior to the catalytic experiments the catalyst was activated in situ by passing oxygen for 1 h at 530°C. The reactor effluent was analyzed with a thermal conductivity detector. Nitrogen and oxygen are separated with a Carboxen 1000 column (Supelco, stainless steel 1/8 in., 15 ft long, 60/80 mesh), and the nitrous oxide with a Porapak-Q column (Altech, stainless steel 1/8 in., 12 ft long, 100/120 mesh). The columns operated in parallel for the analysis of each sample at any given time on stream. A special sampling configuration was used in order to allow the storage of the sample for the injection into both columns. Titrations were used for the determination of NH_3 and gave very satisfactory and reproducible results. By using a three-way valve, the effluent from the reactor passes through a solution of boric acid for a certain amount of time. The amount of ammonia reacted with the boric acid was determined by measuring the amount of dilute hydrochloric acid solution required to bring the pH to its initial value. Phenol Red was used as an indicator. The definitions of NO_x conversion and nitrogen selectivity are as follows:

$$NO_x \text{ conversion} = \frac{NO_{in} - NO_{x,out}}{NO_{in}} \times 100, \qquad (1)$$

$$N_2 \text{ selectivity} = \frac{N_2}{N_2 + N_2O} \times 100. \qquad (2)$$

The moles of NO_x (including NO and NO_2) in the reactor effluent can be determined from a balance of nitrogen atoms:

$$NO_{x,out} = NO_{in} + NH_{3,in} - 2(N_{2,out}) - 2(N_2O_{out}) - NH_{3,out}. \qquad (3)$$

3. Results and discussion

3.1. *Effect of* Si *content on the* NO_x *conversion and product selectivities*

The effect of the silicon composition on the NO_x conversion and N_2 selectivity at 460°C is presented in Fig. 2. The NO_x conversion passes through a maximum (Ti:Si:Al=30:5:1) with respect to the silicon content. We observed that initially by increasing the Si content of the ternary polyoxides the conversion increases. Further increase of the conversion is hindered by the surface area reduction of the catalysts. The conversion acquires relatively low values in comparison with earlier work [20,21] utilizing highly crystalline anatase TiO_2 catalysts. High NO_x conversion and yield for N_2, namely about 90%, was observed as well [22] over V_2O_5/TiO_2 (rutile phase). Moreover, it was also found that the rutile phase of TiO_2 loaded with V_2O_5 was more active than anatase for this reaction on a unit surface area basis [23]. For our experiments presented in this work, the crystallinity of titania (anatase or rutile phases) of the mixed oxides was low [18]. A comparison of the supports involved in our study with crystalline titania (P25, Degussa) is presented in Fig. 3. More specifically, for the mixed oxides synthesized in our work, XRD studies indicate that anatase is the only crystalline phase of titania. It was found that the incorporation of silicon results in a significant decrease of the anatase content of the mixed oxides. This was a result of the coexistence of heteroatoms (Si or Al) in the titania matrix. We found that even low concentrations of Si and/or Al can retard the crystallization of titania into the anatase or rutile phases, thus generating amorphous titania. For the mixed oxide with composition Ti:Si:Al=30:2:1 the percentage of anatase TiO_2 was about 20 wt% while the rest of the titania was amorphous. The increase of the Si concentration of the mixed oxides results in even higher decrease of the titania crystallinity. Many investigators demonstrated that crystalline titania is needed to stabilize active surface vanadia species [14,16,24,25]. As a result of the low titania crystallinity of the synthesized mixed oxides, the vanadia probably does not disperse well on the support.

It is known that the theoretical amount of vanadia on titania corresponds to 0.145 wt% V_2O_5 per m^2 [26].

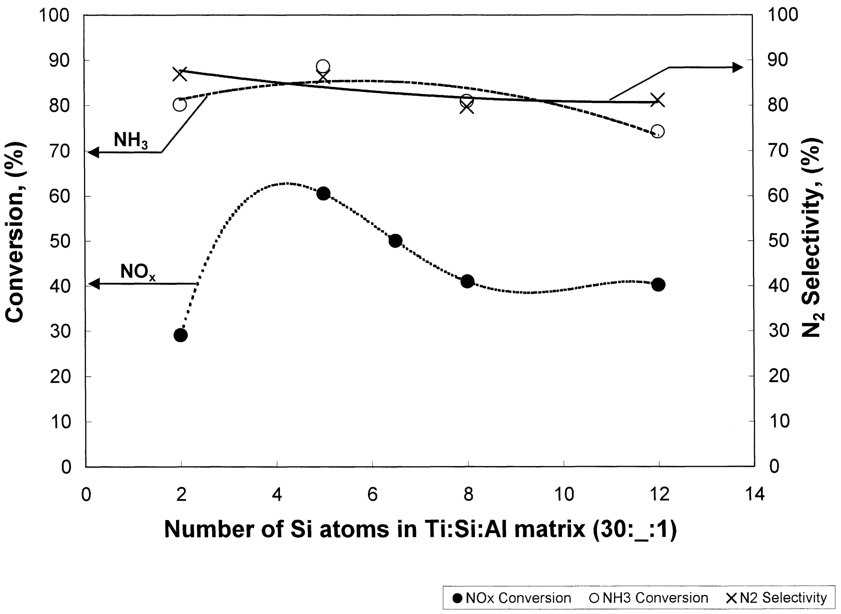

Fig. 2. NO_x and NH_3 conversions, and N_2 selectivity versus the silicon content of mixed oxides synthesized from organic precursors (without Si prehydrolysis) at 460°C. The atomic ratio of the other compounds of the matrix was Ti:Al=30:1 (2 h time on stream, GHSV=30 000 h^{-1}, V_2O_5 loading=5 wt%).

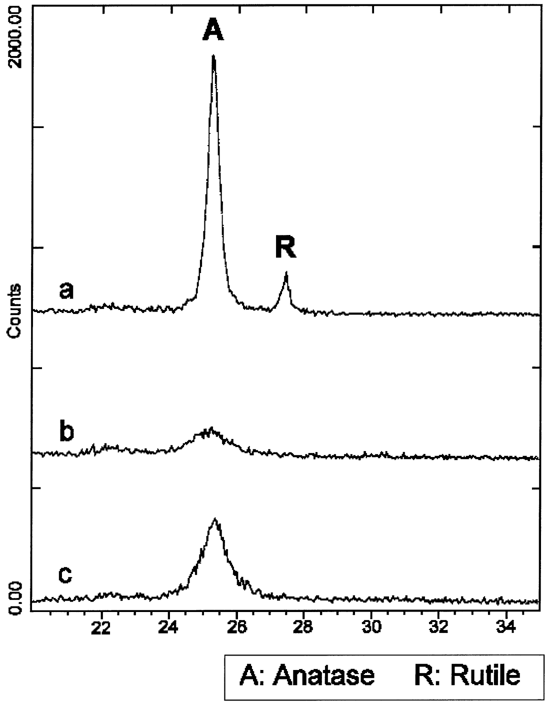

Fig. 3. XRD spectra of (a) TiO_2 (P25, Degussa), (b) TiO_2-based polyoxide (Ti:Si:Al=30:5:1), and (c) TiO_2-based polyoxide (Ti:Si:Al=30:2:5).

Of course, our supports contain Al_2O_3 and SiO_2 and therefore the above theoretical loading cannot be applied for the exact numerical estimation of the vanadia required. For the present catalysts, the surface area of the supports including the Al_2O_3 and SiO_2 is larger than 100 m^2/g (Table 1), which indicates that relatively large loadings are needed in order to approach monolayer V_2O_5 coverage. The BET surface area of each catalyst is lower (Table 1) than that of the support for any silicon composition. The reduction of the BET area after the loading of vanadia is due to the partial plugging of the pores of the support. Other researchers [16,27] found a similar to ours trend, namely the BET surface area of vanadia $DeNO_x$ catalysts decreased after the vanadia was loaded on the support. The maximum of the NO_x conversion observed with the Si composition is associated with the maximum of the BET surface area of the catalyst (Table 1) observed for this composition of the support. The nitrogen selectivity reaches relatively high levels (about 85%) under the present operating conditions.

Table 1
BET surface area of the supports and the catalysts (V_2O_5 loading=5 wt%) as a function of the composition of dopants

Composition (atomic ratio)	BET surface area (m^2/g) (support)	BET surface area (m^2/g) (support and V_2O_5)
Si-*rich mixed oxides*		
Ti:Si:Al=30:2:1	150	84
Ti:Si:Al=30:5:1	138	101
Ti:Si:Al=30:8:1	141	90
Ti:Si:Al=30:12:1	118	50
Al-*rich mixed oxides*		
Ti:Si:Al=30:2:1	148	87
Ti:Si:Al=30:2:2	117	61
Ti:Si:Al=30:2:5	119	90
Ti:Si:Al=30:2:8	140	106

Note: The BET surface area of the vanadia support was determined after calcination of the catalyst in air at 530°C for 1.5 h.

For the same content of aluminum in the composites the nitrogen selectivity as well as the NH_3 conversion remain approximately unchanged as a function of the silicon content of the polyoxides. This indicates that ammonia is effectively utilized in the SCR reaction since the molar ratios of NO and NH_3 fed into the reactor were the same. The concentration of the N_2O increases with the silicon content of the support (Table 2).

For this set of experiments we kept the aluminum composition constant in order to isolate the effect of Si

Table 2
N_2O concentration over the polyoxides with increasing Si, and increasing Al concentration at 530°C (the V_2O_5 loading was 5 wt%)

Composition (atomic ratio)	N_2O (ppm)
Si-*rich mixed oxides*	
Ti:Si:Al=30:2:1	207
Ti:Si:Al=30:5:1	203
Ti:Si:Al=30:8:1	238
Ti:Si:Al=30:12:1	254
Al-*rich mixed oxides*	
Ti:Si:Al=30:2:1	274
Ti:Si:Al=30:2:2	311
Ti:Si:Al=30:2:5	150
Ti:Si:Al=30:2:8	160

on the catalyst performance. It should be noted that many other investigators have reported relatively low conversion levels for SiO_2/TiO_2-based supports for the selective catalytic reduction of NO_x to N_2 [7,14,20]. The crystallinity of our supports is low (compare curve (a) with (b) and (c) of Fig. 3) and is responsible for the relatively low activity observed. However, the level of activity achieved is higher than what one would expect by comparing the anatase content of these polyoxides (about 20%) with that of P25 which is 85%. From FT-IR studies performed in our laboratory [18] we observed that the relative ratio of Brønsted acid sites (band at 1427 cm^{-1}) to Lewis acid sites (band at 1605 cm^{-1}) increases with the silicon content. In contrast, we observed that pure titania (P25) had negligible Brønsted acidity, something which agrees with previous investigations [28]. Other researchers [29] reported an increase of the Brønsted acidity of the oxides. This observation is in contradiction to the Lewis acidity predicted by Tanabe's [30] hypothesis. The incorporation of Si in a Ti-rich matrix will generate a positive charge difference and the impurity cation (Si) will act as a Lewis site. It was proposed [29] that this positive charge is balanced by hydroxyl groups, thus generating Brønsted acidity. Other groups observed a "boost" of the acidity by incorporating Si into a titania matrix as well [31]. However, it should be noted that for our catalysts (relatively low titania crystallinity) following the procedure described above for the loading of vanadia, the activity of the catalyst for NO_x transformation depends strongly on its BET surface area.

3.2. *Effect of the temperature on the behavior of mixed oxides with* Ti : Si : Al = 30 : 5 : 1

The effect of the reaction temperature on the NO_x conversion and the product selectivities is presented in Fig. 4 for polyoxides with concentration Ti:Si:Al=30:5:1 under the same GHSV. For these experiments we used higher vanadia loading (12 wt%) than the previous ones. At temperatures below 340°C, the N_2 selectivity acquires the highest value. The selectivity of N_2 decreases monotonically with temperature; this change is emphasized at temperatures above 370°C. A similar behavior was observed by Ciambelli et al. [7] for V_2O_5/TiO_2 catalysts with relatively high loadings of vanadia. However, other researchers [27] observed a broad maximum of the nitrogen selectivity for temperatures

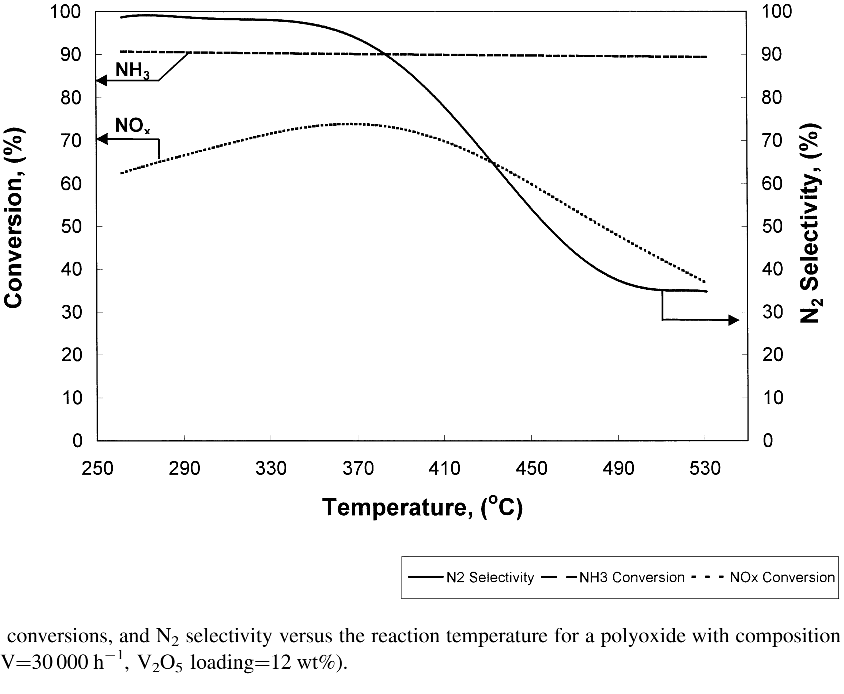

Fig. 4. NO_x and NH_3 conversions, and N_2 selectivity versus the reaction temperature for a polyoxide with composition Ti:Si:Al=30:5:1 (2 h time on stream, GHSV=30 000 h^{-1}, V_2O_5 loading=12 wt%).

around 300°C for vanadia loaded on SiO_2/TiO_2. The NO_x conversion increases and passes through a maximum at about 370°C. It decreases at higher temperatures because of the increase of the NH_3 oxidation reaction occurring at temperatures above 410°C (Fig. 4). Other investigators observed the maximum of the NO_x conversion at temperatures around 350°C over V_2O_5/TiO_2 [22], and over $V_2O_5/SiO_2/TiO_2$ [27,32,33].

The concentration of N_2O acquires very low values at low temperatures but increases with temperature (Fig. 5). Our polyoxide supports as catalysts shift the maximum of the N_2O production to higher temperatures in comparison with the case of P25 titania. The conversion of ammonia remains at high levels and is practically unchanged with respect to the reaction temperatures. At low temperatures the ammonia is utilized for the transformation of NO_x to N_2 while at higher temperatures ammonia is partially oxidized. It is worth noting that the increase of the vanadia loading of the catalyst has a negative effect on the nitrogen selectivity. By comparing the N_2 selectivity for the catalyst with Ti:Si:Al=30:5:1 of Fig. 2 (V_2O_5 loading=5 wt%, 460°C) with that of Fig. 4 (V_2O_5 loading=12 wt%) at 460°C, one can observe that it dropped from about 85% to 50%, respectively at comparable levels of conversion. We believe that this behavior is a combined result of the decrease of the BET surface area and the number of Brønsted sites. Indeed, in Fig. 6 one can notice that the increase of the vanadia loading results in a significant decrease of the amount of Brønsted acid sites (band 1427 cm^{-1}). The number of Lewis sites decreases also, but to a much less extent than that of the Brønsted ones.

3.3. *Effect of the* Al *content on the* NO_x *conversion and product selectivities*

The increase of the aluminum content of the mixed oxides results in a slightly different trend in comparison with that of the previous case under the same GHSV. The NO_x conversion passes through a broad minimum and then it increases slowly (Fig. 7) with the aluminum content being in close relation to the BET surface area of the catalysts (Table 1). Of course, the NO_x conversion does not acquire very high values, even for supports with the highest aluminum content, because of the low crystallinity of the titania phase of the polyoxides. Other investigators [34] found that the vanadia disperses well on Al_2O_3, and that the BET

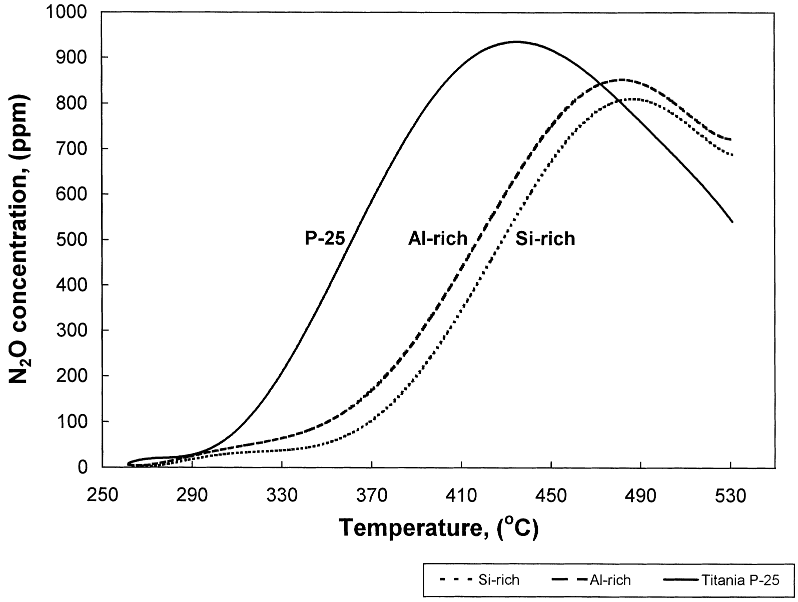

Fig. 5. N_2O concentration over the polyoxides as a function of the reaction temperature for (a) polyoxide with composition Ti:Si:Al=30:5:1, (b) polyoxide with composition Ti:Si:Al=30:2:5, and (c) TiO_2 (P25, Degussa). The V_2O_5 loading was 12 wt%.

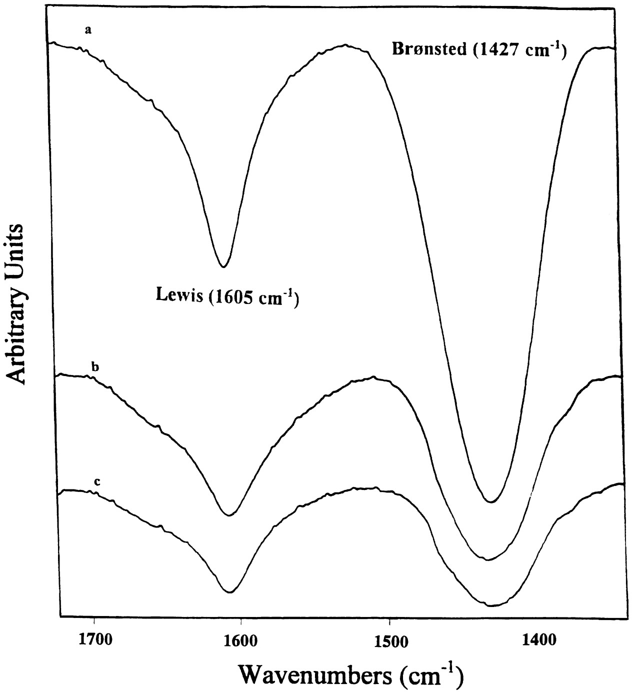

Fig. 6. FT-IR spectra of mixed oxides with composition Ti:Si:Al=30:15:1 as a function of the vanadia loading: (a) without vanadia, (b) 5 wt%, and (c) 12 wt%.

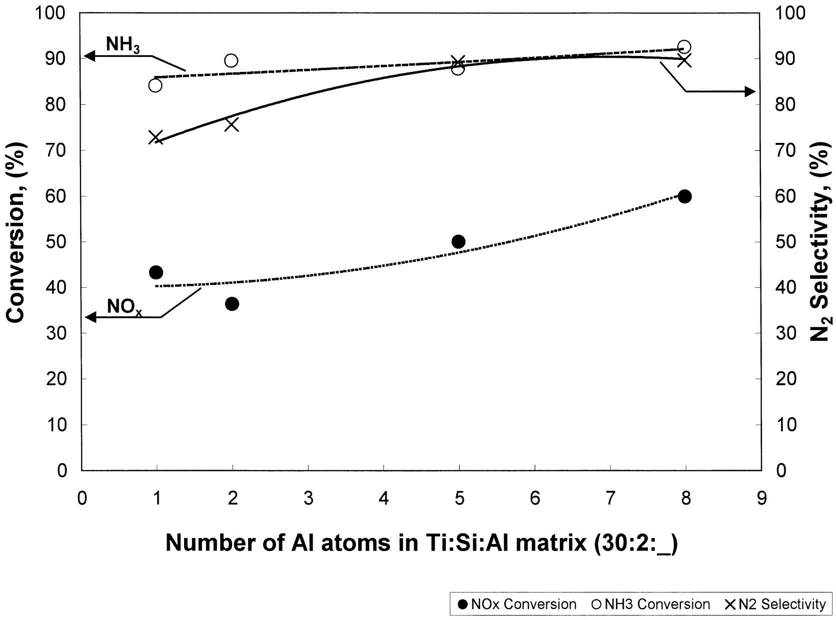

Fig. 7. NO_x and NH_3 conversions, and N_2 selectivity versus the Al content of mixed oxides synthesized from organic precursors (with Si prehydrolysis) at 460°C. The atomic ratio of the other compounds of the matrix was Ti:Si=30:2 (2 h time on stream, GHSV=30 000 h^{-1}, V_2O_5 loading=5 wt%).

area of the catalysts decreases only slightly due to the vanadia loaded. This was because VO_x monolayers are particularly stable on TiO_2 and on Al_2O_3 but they are not readily formed on SiO_2 [25,35]. Roozeboom et al. [37] came to a similar conclusion for the monolayer stability of vanadia upon thermal treatment, and it was found that the monolayer stability decreases in the order $Al_2O_3 > TiO_2 > CeO_2 \gg SiO_2$. In contrast to our findings, Centi et al. [17] observed a different trend for the conversion over Al_2O_3–TiO_2 polyoxides loaded vanadia. The NO_x conversion was found to decrease monotonically with increase in the Al content of the composites.

In the present work we found that the increase of the Al concentration of the support results in an increase of the N_2 selectivity, which approaches a plateau value for high aluminum contents. This trend differs from that observed over the Si-rich supports where the N_2 selectivity was practically unchanged with the silicon content. The NH_3 conversion increases slightly with the aluminum concentration. This trend was as expected and it indicates that ammonia is utilized selectively in transforming NO into N_2. One can observe that the nitrous oxide decreases in general with the content of Al (Table 2). Wong and Nobe [8] observed that V_2O_5/Al_2O_3 generates less N_2O than V_2O_5/TiO_2 under identical operating conditions, even though the latter catalyst was slightly more active.

3.4. *Effect of temperature on the behavior of mixed oxides* (Ti : Si : Al = 30 : 2 : 5)

The NO_x conversion increases with the reaction temperature and passes through a maximum at about 370°C and then drops sharply (Fig. 8). One can notice that the behavior of these materials as a function of temperature is almost identical to that observed for the Si-rich supports. Earlier studies [36] involving V_2O_5/Al_2O_3 catalysts for SCR reactions of NO with NH_3 also indicated that the NO_x conversion passed through a maximum versus temperature. However, the location of the maximum was shifted to a higher temperature than that observed in our work. The decrease of the NO_x conversion for temperatures above 390°C is related with the increase of ammonia oxidation. It is worth noting that the NO_x activity at the optimum temperature reaches a conversion of about 75%. This value is comparatively high if one considers the low levels of crystallinity of the titania in these polyoxides. We believe that the increased number of Brønsted sites

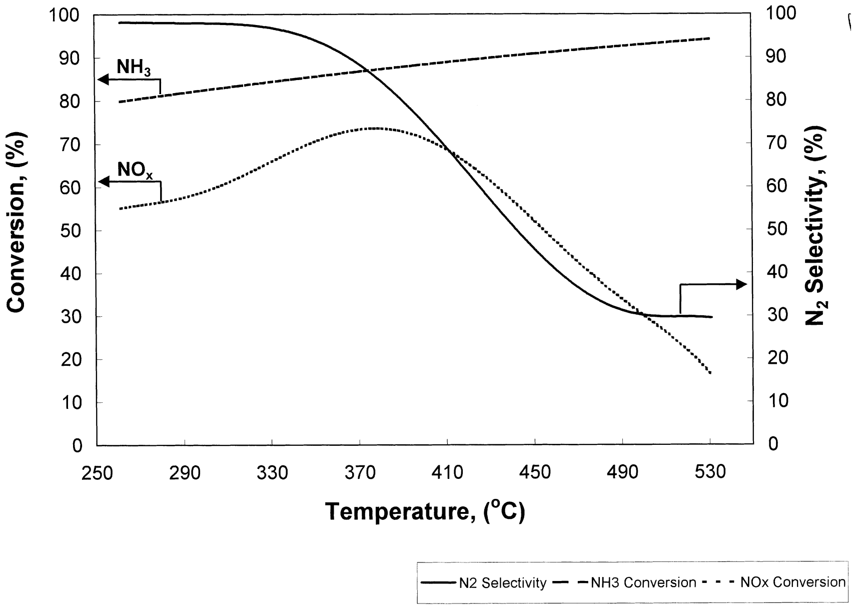

Fig. 8. NO_x and NH_3 conversions, and N_2 selectivity versus the reaction temperature for a polyoxide with composition Ti:Si:Al=30:2:5 (2 h time on stream, GHSV=30 000 h^{-1}, V_2O_5 loading=12 wt%).

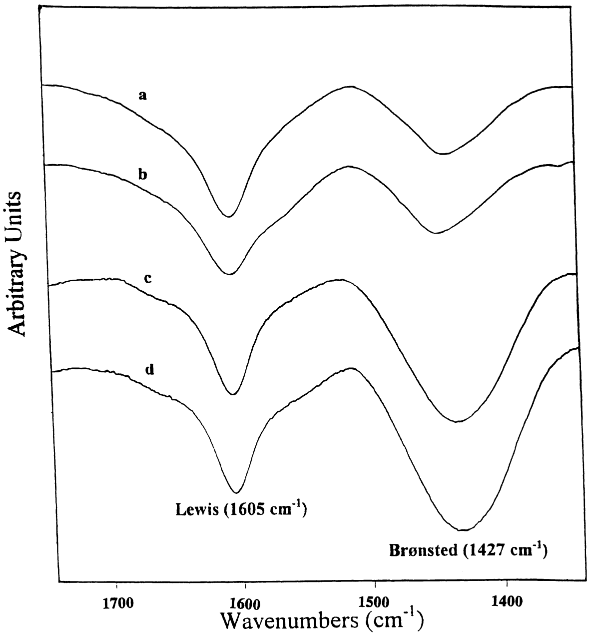

Fig. 9. FT-IR spectra of mixed oxide supports with variable Al composition: (a) Ti:Si:Al=30:2:2, (b) Ti:Si:Al=30:2:5, (c) Ti:Si:Al=30:2:8, and (d) Ti:Si:Al=30:2:15.

has a positive impact on the catalyst performance. Indeed, our FT-IR studies indicate (Fig. 9) that the Brønsted sites of the supports increase with aluminum content. The number of Lewis sites does not change significantly with the Al content. The effect of the vanadia loading on the nitrogen selectivity of these catalysts is the same with that described earlier in this paper. A comparison of the N_2 selectivity at 460°C for the support with Ti:Si:Al=30:2:5 shows that it drops from 90% to about 40% by increasing the vanadia loading from 5 to 12 wt%, respectively. The same support without vanadia gives zero NO_x conversion and negligible ammonia oxidation. This indicates that an optimum vanadia loading does exist. Wachs et al. [35] also found that there is such an optimum loading of vanadia which maximizes the turnover frequency for the SCR reaction. That maximum was attributed to a decrease of the dispersion of the vanadia species. It seems that for our catalysts, vanadia loadings below 12 wt% can provide better performance. The nitrogen selectivity decreases monotonically with the reaction temperature as a result of the partial transformation of NO_x and NH_3 to N_2O (Fig. 5).

For the present work the oxygen concentration was kept at 2000 ppm. In order to test the effect of oxygen on our experiments we increased the oxygen concentration up to 20 000 ppm for a set of experiments with a mixed oxide with composition Ti:Si:Al=30:2:8 (5 wt% V_2O_5). The reactor space time and all the other operating parameters were kept the same. We observed that the increase of the oxygen concentration in this range does not play any role on the NO conversion and the product selectivities.

4. Conclusions

The effect of heteroatoms (Si, Al) as dopants to a TiO_2-rich matrix was investigated for the selective catalytic reduction of NO_x to N_2 in the presence of ammonia. The conversion levels were lower than those reported in earlier studies utilizing highly crystalline titania as support. Similar conversion levels were observed for the mixed oxides possessing either high Si or high Al content. However, the NO_x conversion passes through a maximum with respect to the Si content while it increases with the Al concentration. Although the nitrogen selectivity remains practically unchanged with the silicon content, higher aluminum concentrations in the polyoxides result in a monotonic increase of the nitrogen selectivity. It was also shown that the performance of the catalyst was strongly related with their BET surface area. The loading of vanadia also has an important impact on the performance of the catalyst.

Acknowledgements

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