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Selective catalytic reduction of NO with propane on V_2O_5/SiO_2, V_2O_5/TiO_2, and V_2O_5/Al_2O_3 catalysts obtained through the sol-gel method

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ABSTRACT. Vanadium-based compounds have received a lot of attention in the last years due to their high and selective catalytic activities in major industrial reactions. The catalytic properties of V_2O_5 may be strengthened and modified when it is dispersed in pure oxides like SiO_2, TiO_2, and Al_2O_3. In this work, mixed oxides V_2O_5/SiO_2, V_2O_5/TiO_2, and V_2O_5/Al_2O_3 were prepared through the sol-gel method and obtained in nominal concentrations of 10% of V_2O_5. All samples were submitted to calcination in muffle at 400ºC for 5h. The characterization of the materials by nitrogen adsorption indicated that they present a mesoporous structure. XRD results disclosed that vanadium is highly dispersed in mixed oxide 10% V_2O_5/TiO_2. The materials obtained were studied through selective catalytic reduction (SCR) of NO with propane. It was observed that the V_2O_5/TiO_2 system presented a greater efficiency in the conversion of NO to N_2 associated to a higher dispersion of vanadium in the support, if compared with the results of other systems reported in literature.

Keywords: vanadia, mixed oxides, N_2, NO_x.

Redução catalítica seletiva de NO com propano em catalisadores de V_2O_5/SiO_2, V_2O_5/TiO_2 e V_2O_5/Al_2O_3 obtidos pelo método sol-gel

RESUMO. Compostos à base de vanádio têm recebido muita atenção nos últimos anos pelas elevadas atividade e seletividade catalíticas que apresentam em reações de grande importância industrial. As propriedades catalíticas do V_2O_5 podem ser realçadas e modificadas quando disperso em óxidos puros do tipo SiO_2, TiO_2 e Al_2O_3. Neste sentido, óxidos mistos de V_2O_5/SiO_2, V_2O_5/TiO_2 e V_2O_5/Al_2O_3 foram sintetizados pelo método sol-gel e obtidos na concentração nominal de 10% de V_2O_5. Todas as amostras foram submetidas à calcinação em mufla a 400ºC por 5h. A caracterização dos materiais pelo método da adsorção de nitrogênio indicou que os materiais apresentam uma estrutura mesoporosa. Os resultados de XRD revelaram que o vanádio encontra-se altamente disperso no óxido misto 10% V_2O_5/TiO_2. Os materiais obtidos foram estudados através de reações de redução catalítica seletiva (RCS) do NO com propano. Observou-se que o sistema V_2O_5/TiO_2 apresentou maior eficiência na conversão de NO a N_2, comportamento este, provavelmente, associado à alta dispersão do vanádio no suporte, se comparado com os demais sistemas estudados.

Palavras-chave: vanádia, óxidos mistos, N_2, NO_x.

Introduction

Vanadia systems have been extensively investigated in the last decade due to their broad applicability as heterogeneous catalysts, especially in redox reactions, such as in the selective reduction of NO_x (ANSTROM et al., 2003; BLANCO et al., 2000; BOND; FLAMERZ, 1989; BULUSHEV et al., 2002; LIN; BAI, 2003; REDDY et al., 2004; SUÁREZ et al., 2002; WILLEY et al., 1995).

NO_x emissions are mainly composed of nitric oxide (NO) and nitrogen dioxide (NO_2), which are considered two of the chief atmospheric pollutants (FINLAYSON-PITTS; PITTS JR., 1986; SEINFELD, 1986). In general, these pollutants are formed in the combustion chambers of vehicular engines as a result of the oxidation of nitrogen molecules in the air and nitrogen in the fuel (0.5-3% p/p) (SEINFELD, 1986). Nitric oxide is a significant primary pollutant emitted by both moving and stationary sources. Small quantities of NO_2 are also released together with NO, which can be converted into NO_2 in the atmosphere. Thus, NO_2 is both a primary atmospheric pollutant and one formed in chemical reactions.

Both NO and NO_2 play a major role in the formation of photochemical smog. Vehicle emissions are the main source of NO_2 in the environment, being responsible for 70% of the total NO_X emissions, together with fossil fuel-burning power plants.

In the last few decades, many catalysts, particularly those composed of noble metals and modified zeolitic materials with various transition metals were developed for the removal of NO (CHEUNG et al., 1996; MORETTI et al., 1999; SCHAY et al., 2002). However, the literature on the selective catalytic reduction of NO with hydrocarbons using vanadia mixed oxides as catalysts is scarce. Vanadia-based materials are known to be highly reactive in selective catalytic reduction reactions of NO by NH_3 and have been largely studied due to their environmental relevance (BLANCO et al., 2000; BOND; TAHIR, 1991; CARABA et al., 2001; DUTOIT et al., 1997; LIN; BAI, 2003; REICHE et al., 1999; SCHNEIDER et al., 1994; SUÁREZ et al., 2002; WILLEY et al., 1995). Thus, this study investigated the activity of catalysts V_2O_5/SiO_2, V_2O_5/TiO_2, and V_2O_5/Al_2O_3, which were synthesized employing the sol-gel method and were applied to the reduction of NO into N_2 in the absence of an oxidizing atmosphere using propane as a reducing agent.

Material and methods

Chemicals

All reagents and solvents used in this work had analytical grade and were purchased from Aldrich, Merck, and Acros Organics. Double distilled water with approximate resistivity of 18 MΩ.cm was obtained with a Milli-Qplus apparatus. Vanadium (V) oxide (V), used as a characterization standard, was synthesized in laboratory through NH_4VO_3 calcination at 550°C for 8h. Next, the material was thermal annealed in O_2 for 18h at 550°C to eliminate trace nitrogen (BRAUER, 1958). The other reagents were used without previous preparation.

The catalysts were prepared through the sol-gel method using 10% V_2O_5/SiO_2, 10% V_2O_5/TiO_2 and 10% V_2O_5/Al_2O_3 (wt.%) – more details can be found elsewhere in the literature (COLPINI et al., 2008b).

Catalyst preparation

For more details in the preparation of the catalysts 10% V_2O_5/SiO_2, 10% V_2O_5/TiO_2, and 10% V_2O_5/Al_2O_3 see (COLPINI et al., 2008a). Concerning mixed oxide aging, the gels were previously aged for 15 days. In this case, the samples were labeled 10VSien, 10VTien, and 10VAlen. All the mixed oxides obtained were calcined at 400°C for 5h. These samples were labeled with an additional capital C. The quantities of reagents and the preparation conditions appropriate for the materials under study are given in Table 1.

Characterization

The materials obtained were characterized by X-ray fluorescence spectroscopy, N_2 adsorption measurements (specific surface area, average pore volume and average pore diameter) and X-ray diffraction.

X-ray fluorescence spectroscopy (XRFS)

The amount of vanadium in the samples was determined by X-ray fluorescence spectroscopy in TRACOR Northern 5000 equipped with a beryllium window in vacuum chamber (0.7 Torr).

N_2 adsorption measurements

N_2 adsorption measurements: the specific surface area (S_o), average pore volume (V_p), and average pore diameter (d_p) of the mixed oxides obtained were determined in Quantachrome Corporation model Nova 1200. The (S_o) values were determined by the Brunauer, Emmett, and Teller (BET) method after previous sample activation at 150°C in vacuum for 2h.

Table 1. Amounts and compositions used in the preparation of the sol-gel.

Catalyst	VOTIP (mol) x 10^{-5}	TEOS (mol)	HCl 37% (mol) x 10^{-4}	H_2O (mol)	$NH_4OH/EtOH$ (mL)	
10VSiC	941.800	0.13	13	0.269	7.00	
Catalyst	VOTIP (mol) x 10^{-5}	TBOT (mol)	HNO_3 65% (mol) x 10^{-3}	H_2O (mol)	H_2O (mL)	MeOH (mL)
10VTiC	1023.71	0.088	7.0	0.352	0.56	220
Catalyst	VOTIP (mol) x 10^{-5}	Aluminum isopropoxide (mol)	Hexylene glycol (mol)	H_2O (mL)	EtOH(mL)	
10VAlC	1482.30	0.14	0.28	9.00	47.0	

X-ray diffraction (XRD)

Diffractograms of the materials were obtained with a Shimadzu XRD 6000 apparatus. Copper emission line (Cu Kα, $\lambda = 0.154$ nm) with emission tube acceleration of 30 kV, current of 20 mA, and scanning velocity of 2° min^{-1} was used as a radiation source.

Catalytic activity

The catalytic activity of calcined and aged-calcined 10VSi, 10VTi, and 10VAl was assessed through the reduction of nitric oxide with propane in the absence of an oxidizing atmosphere.

Tests were performed in a tubular borosilicate glass fixed-bed microreactor fed with continuous flux with a sintered porous glass plate on which the catalysts were placed. Reagents were fed into the reactor in the following proportions (v/v): 0.5% NO and 0.5% C_3H_8 (in He).

The temperature of the reaction was varied from 150 to 500°C and the total gas flux used was 42 mL $min.^{-1}$. Before the reaction was initiated, the catalyst was activated under oxygen flux at 500°C for 30 min., followed by cooling down to 30°C. The catalyst, 200 mg, was mixed with 200 mg of quartz to prevent the formation of hot spots.

Catalytic test line

In the catalytic test line (Figure 1), the pressure and the flow of each gas of the feeding system (Figures 1-1 and 1-2) were controlled on a panel. The gas mixture runs either through a saturator to remove water vapor (Figure 1-4) or directly to the reactor (Figure 1-5). This reactor is inside an oven (Figure 1-6) with a PID temperature control system and a forced air ventilation system to ensure that the temperature of the catalytic bed is homogeneous. At the reactor outlet, the effluent mixture runs through two injection valves (Figure 1-7), one with six paths (FID sampling) and one with ten paths (TCD sampling), heated with electric resistances to a constant temperature of 150°C by means of a PID temperature controller. After passing through the injection valves, the mixture is analyzed by gas chromatography in a SHIMADZU GC-17A (Figure 1-8) fit with flame ionization (FID) and thermal conductivity (TCD) detectors interfaced with a computer (Figure 1-9). Dedicated software furnishes the mass composition of the effluent mixture by integrating the chromatogram peaks.

The effluent mixture of the reactor was separated with a 0.32 mm diameter and 30 m long alumina/KCl capillary column and two stainless steel columns packed with haysep D and a 13X molecular sieve. The capillary column was connected to the FID for the separation of hydrocarbons. NO, N_2O, N_2, O_2, CO, CO_2, and C_3H_8, were separated in packed columns coupled to the line operated in reverse flux and connected to the TCD. The temperature of the three columns was kept at 60°C.

Equations used for results calculation

The catalytic activity in the reduction of NO in the presence of hydrocarbons and in the absence of an oxidizing atmosphere was determined as a function of the total conversion of propane and the conversion of NO into N_2 by gas chromatography as follows:

$$\text{HC Conversion} = \left[\frac{[\text{HC}]_{\text{initial}} - [\text{HC}]_{\text{final}}}{[\text{HC}]_{\text{initial}}}\right].100\% \qquad (1)$$

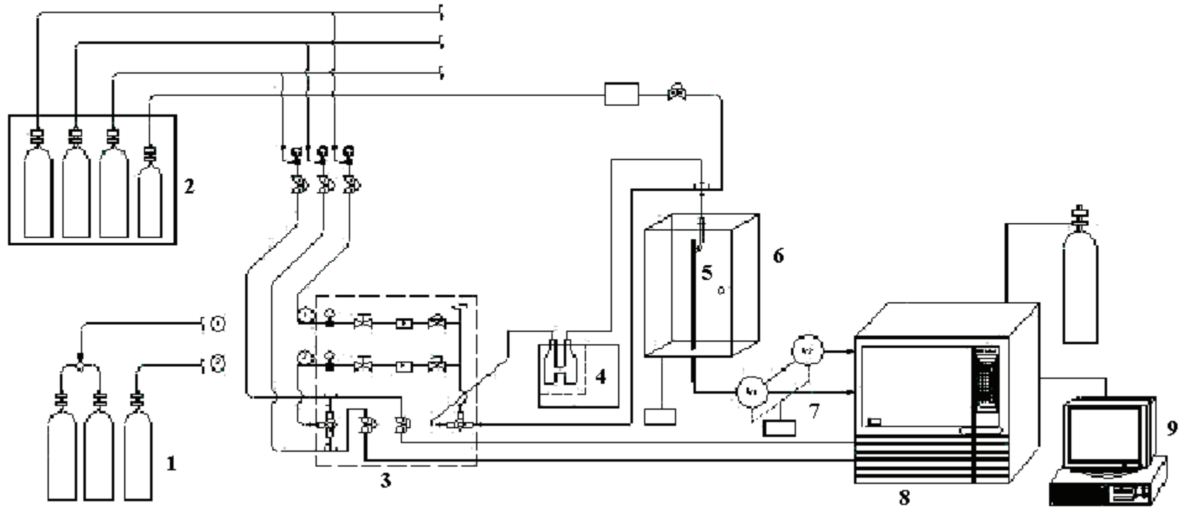

Figure 1. Catalyst test line diagram.

$$\text{Conversion of NO into } N_2 = \left[\frac{2.[N_2]\text{produced}}{\text{NO}}\right].100\% \qquad (2)$$

where:

[NO] = NO concentration in the reactor feed stream;

$[N_2]$ = N_2 concentration in the reactor outlet stream;

[HC] = hydrocarbon concentration in the gas stream.

At the beginning of the catalytic tests, the gas mixture was analyzed at 150ºC and the data obtained was used as a reference (blank) for the calculations for the other temperatures.

Results

Table 2 shows the results of V_2O_5 concentrations on the calcined mixed oxides with 10% V_2O_5 nominal content as measured by XRFS. This table also presents specific surface area (S_o), average pore volume (V_p), and average pore diameter (d_p) measurements. The diffractograms of the catalysts at different temperatures are presented in Figures 2 and 3. Figure 4a illustrates the conversion curves of NO into N_2 as a function of temperature for calcined and aged-calcined catalysts 10VSi, 10VTi, and 10VAl. Figure 4b shows the conversion curves of propane for the reduction of NO.

Discussion

Materials characterization

N_2 adsorption measurements

The type of isotherm obtained (type IV, according to IUPAC classification) is characteristic of mesoporous materials (20-500 Å) – more details can be found elsewhere in the literature (COLPINI et al., 2008b).

The characteristics associated with the sol–gel method explains the results shown in Table 2. The considerably high specific surface area values of the mixed oxides synthesized indicate a highly porous structure. Table 2 shows that the specific surface area of the mixed oxides increases in the following order: $V_2O_5/TiO_2 < V_2O_5/Al_2O_3 < V_2O_5/SiO_2$.

The values of S_o can be considered high if compared with literature data for similar oxides obtained using other methods. As for example, mixed vanadia oxides obtained through impregnation method: 5% V_2O_5/SiO_2, 5% V_2O_5/TiO_2, and 5% V_2O_5/Al_2O_3, gave areas of 190, 40 and 112 m^2 g^{-1}, respectively (COLPINI et al., 2008b).

Literature reports that small variations in experimental conditions, such as in temperature, solvent type, catalyst concentration, external agents, etc., significantly modify the textural properties (specific surface area, pore size and distribution) of the obtained solids (CORRIU; LECLERCQ, 1996).

The results showed that the production of mixed vanadium oxides with high surface area and pore volume through the sol-gel method was efficient. It also proved the methodology to be advantageous for a better control of these textural properties as a function of the vanadium content and the calcination temperature.

Table 2. XRFS analysis, specific surface area (S_o), pore volume (V_p) and average pore diameter (d_p) of the materials synthesized.

Catalyst	V_2O_5 (wt%)	S_o (m^2 g^{-1})	V_p (cm^3 g^{-1})	d_p(Å)
10VSiC	8.15	591.10	5.095×10^{-1}	34.48
10VTiC	6.17	86.15	9.160×10^{-2}	42.53
10VAlC	14.15	487.70	5.501×10^{-1}	45.11

X-ray diffraction (XRD)

The X-ray diffractograms of the materials under study were interpreted in relation to the diffractograms of standards (V_2O_5, TiO_2, and Al_2O_3) published by JCPDS, 1997. Figure 2 presents the X-ray diffractograms of 10VSi samples calcined at 800 and 1,100ºC. The diffractograms of the samples of 10VSi calcined at 200, 400, 600, and 800ºC showed that the materials were predominantly amorphous. Only after calcining at 1100ºC the crystalline regions of V_2O_5 and SiO_2 observed (Figure 2c) were defined. The broad peak from 10VSi (Figure 2b) in the $2\theta = 21.0^o$ region that appeared when the sample was calcined at 800ºC is associated with the amorphous phase of silica. The diffractogram in Figure 2c shows a peak at $2\theta = 21.7^o$ which is probably due to V_2O_5 crystallites or crystalline silica in the form of α-crystobalite (21.9, 28.4, and 31.3º) (DUTOIT et al., 1997; GIAKOUMELOU et al., 2004; JCPDS, 1997; PÂRVULESCU et al., 2004; WANG et al., 2003). Sample V_2O_5, which was used to obtain the diffractograms shown in Figures 2a and 3c was synthesized in the laboratory as described in section 2.1 of the Experimental section.

More details on the diffractograms of the material 10VTien calcined at different temperatures can be found elsewhere in the literature COLPINI et al. (2008a).

The diffractograms of the VAl samples calcined at 400ºC revealed an amorphous material (Figure 3a). The crystalline regions of γ-Al_2O_3 were defined only for 10VAl samples calcined at 800ºC (Figure 3b). The peaks at $2\theta = 20.0$, 21.8, 26.2, 32.7, and 34.4º indicate the presence of V_2O_5 crystallites (CHARY et al., 2003; JCPDS, 1997).

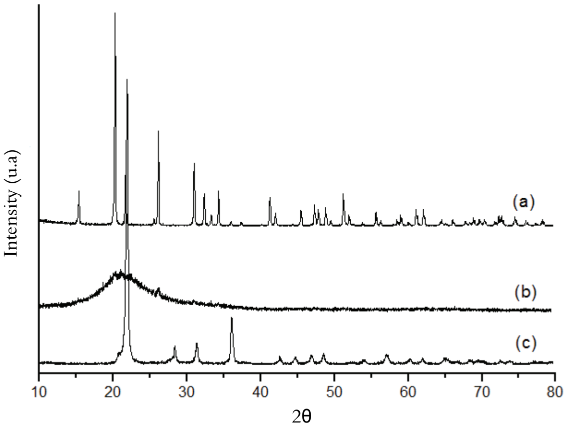

Figure 2. X-ray diffractograms of materials: (a) V_2O_5, (b) 10VSi calcined at 800°C and (c) 10VSi calcined at 1,100°C.

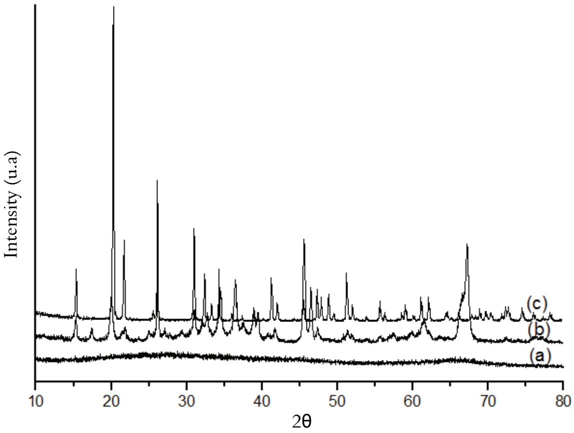

Figure 3. X-ray diffractograms of materials: (a) 10VAl calcined at 400°C, (b) 10VAl calcined at 800°C and (c) V_2O_5.

Selective catalytic reduction of NO with propane

The mixed 10VSi presented low catalytic activity for the conversion of NO into N_2 when compared to the catalytic performance of the others calcined and the aged-calcined materials, as shown in Figure 4a. Additionally, aging of the material did not contribute to increased catalytic activity. Conversely, the conversion of NO into N_2 was much higher and aging resulted in an elevated NO conversion ratio for the 10VAl catalysts. Nevertheless, the 10VTi catalysts showed the best catalytic performance for the conversion of NO into N_2. In this case, aging also led to increased activity.

The elevated efficiency of the 10VTi system when compared to the other systems under study, 10VSi and 10VAl may be attributed to the strong specific interaction between vanadium and titania in this type of composites (BOND, 1997; CENTI et al., 1991; CHARY et al., 1998; WACHS et al., 2000). Literature reports that vanadium forms a highly dispersed VO_x monolayer on the TiO_2 layer, which explains the performance of the 10VTi catalytic system (BOND, 1997). The similar electronegativities of titanium and vanadium result in similar bond polarities for Ti-O and V-O and allow the vanadium oxide monolayer to act as if it were an extension of the crystalline lattice of TiO_2. In the case of alumina, V_2O_5 dissolves in the pure oxide and forms a solid solution, while the energy of interaction of SiO_2 is so low that it induces the formation of V_2O_5 microcrystals and poor dispersion. Anatase presents an intermediate behavior, while rutile behaves like SiO_2 (ROUTRAY et al., 2004).

There is controversy regarding the nature and the functionality of the active sites of these catalysts. However, the reaction mechanisms involving the surface V^{4+}/V^{5+} redox pair have been largely accepted as a better explanation for the performance of the 10VTi system (ANDERSON, 1982; CENTI et al., 1991). The strong interaction between vanadium and titanium affords vanadium on the two surface oxidation states, (IV) and (V), which are strongly influenced by the crystallographic nature of the support and the preparation method.

These results, along with the XRD data, confirm that vanadium is highly dispersed in the 10VTi catalyst, which results in its unsurpassed catalytic performance.

The calcined and the aged-calcined catalyst, 10VTi, had the highest conversion rates, followed by calcined and aged-calcined catalysts, 10VAl and 10VSi (Figure 4b).

Figure 4a also shows that the NO-N_2 conversion rate of the VTi catalysts decreased over 450°C. This effect is related to the decrease in the concentration of propane due to the increase in its consumption in the oxidation reaction at high temperatures. Another factor related to catalytic activity is the adsorption of NO, which is similar to the case at high temperatures. Both the amount of NO adsorbed onto the surface of the metal and the conversion rate decreased.

The comparison of the activities of the investigated catalysts shows that the NO conversion rate depends on the temperature and the type of support employed (Table 3). The VTi catalysts had the highest NO-N_2 conversion rates. As previously mentioned, the XRD results allowed attributing the catalytic performance to the elevated dispersion of vanadium on the TiO_2 support. Obviously, a greater dispersion resulted in more V^{4+} and V^{5+} species in the catalysts and VTi allowed for an increase in the number of active sites for NO_x reactions.

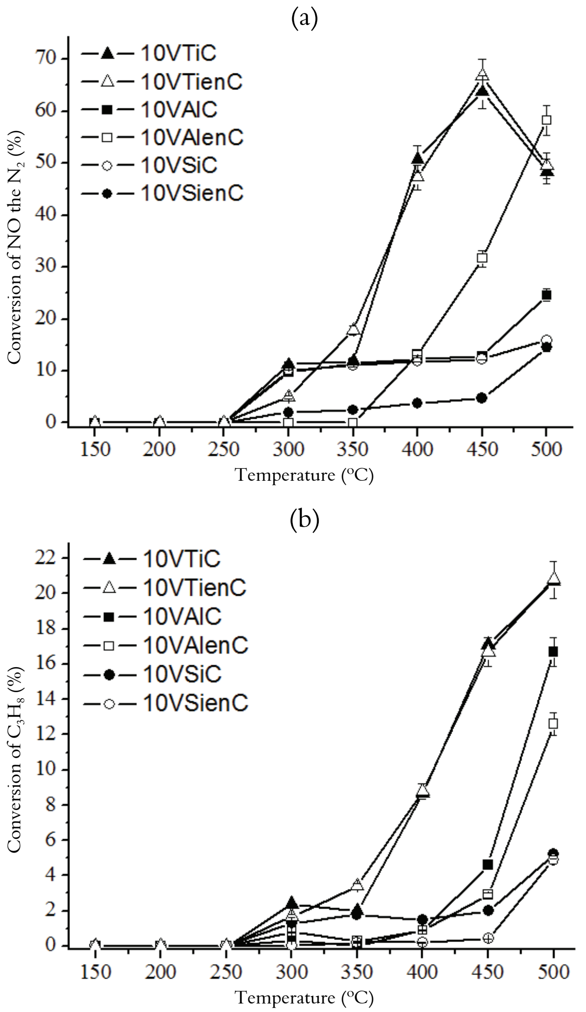

Figure 4. (a) Conversion of NO into N_2 and (b) conversion of propane as a function of temperature using catalyst 10VSi, 10VTi, and 10Val calcined and aged-calcined.

Table 3. NO-N_2 conversion ratio of the investigated vanadia catalysts.

Catalyst	Conversion of NO into N_2 (%)				
	300°C	350°C	400°C	450°C	500°C
10VSiC	10.0	11.1	11.8	12.3	15.9
10VSienC	2.0	2.5	3.7	4.7	14.5
10VTiC	11.2	11.9	50.8	63.7	48.4
10VTienC	5.0	17.8	47.3	66.7	49.6
10VAlC	9.8	11.4	12.4	12.8	24.6
10VAlenC			13.2	31.6	58.3

Conclusion

This work demonstrated the successful preparation of catalysts through the sol-gel method. Specific surface area measurements showed that the materials obtained were porous and particulated, supporting the use of the sol–gel method to produce vanadium mixed oxides with enhanced catalytic properties.

The XRD diffractograms revealed that the mixed VSi oxides are amorphous and after thermal treatment over 800°C, the V_2O_5 crystallites separate. Mixed VTi oxides presented only TiO_2 anatase and rutile peaks, indicating that it is highly dispersed in these materials. The mixed VAl oxides were amorphous below 800°C, and over this temperature, V_2O_5 crystallites appeared.

VTi catalysts gave the highest NO-N_2 conversion rates in the reduction of NO with propane. This catalytic performance can be attributed to greater dispersion of vanadium in these materials.

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