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N_2O formation in the ammonia oxidation and in the SCR process with V_2O_5-WO_3 catalysts

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Abstract

Commercial catalysts based on vanadia and tungsta supported on titania are generally employed in the selective catalytic reduction (SCR) of nitrogen oxides present in the stack gases of power stations; similarly, they are active for the oxidation of traces of ammonia and the elimination of dioxins and furans. When these catalysts are used for gas purification in the presence of ammonia, they can produce nitrous oxide that is released to the atmosphere. In order to evaluate the formation of nitrous oxide during the total ammonia oxidation and SCR of nitrogen oxides with ammonia, a series of V_2O_5-WO_3/TiO_2 catalysts were prepared and tested under conditions close to those found in their industrial use. The results confirm that nitrous oxide formation mechanisms in both processes were clearly related to the active phase composition, increasing the formation of this undesired compound as the vanadia loading in the catalyst was raised. With the oxidation of trace ammonia, nitrous oxide is formed from the adsorption of two ammonia molecules over polymeric vanadyl species. For the SCR process, nitrous oxide is also formed by nitric oxide molecules adsorbed on adjacent centres of the polymeric vanadia.

Keywords: Nitrous oxide; Ammonia oxidation; Selective catalytic reduction; Vanadia; Tungsta

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1. Introduction

For many years, nitrous oxide (N_2O) was considered as a relatively innocuous chemical species due to the ignorance of this compound as a potential contributor to environmental problems and as such received little interest among the scientific and technological community [1]. However, during the last decade, a growing concern for the emissions of this gas has been registered since its identification as one of those responsible for the destruction of the stratospheric ozone layer, also as a promoter of the greenhouse effect.

The formation of nitrous oxide has been observed in the catalytic elimination of ammonia traces from gaseous effluents [2], such as those from the selective catalytic reduction (SCR) of nitrogen oxides with ammonia [3]. Catalysts based on V_2O_5-WO_3 supported on TiO_2 are generally used in the SCR process to eliminate nitrogen oxides present in waste gases from fossil fuel fired power stations [4]. Furthermore, the use of V_2O_5/TiO_2 catalysts has been generalized in purification units that operate at low temperature (~200 °C) for the treatment of effluent gases from nitric acid plants. In a series of pioneer works on the oxidation of ammonia, a great number of catalysts in which V_2O_5, WO_3 and TiO_2 were found to be active oxides in this process were compared [5].

Recently, the formation of nitrous oxide during ammonia oxidation with vanadia-tungsta catalysts has been described, where it was observed that the selectivity to this compound increased with the vanadia loading in the catalyst and the reaction temperature [6]. However, the mechanism by which this phenomenon took place was not discussed. The formation of nitrous oxide has been observed also in the SCR processes, with V_2O_5/TiO_2 catalysts [7] and V_2O_5-WO_3/TiO_2 catalysts [8].

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Bearing in mind these considerations, the purpose of this work was to study the formation of nitrous oxide in the total oxidation of ammonia traces and in the selective catalytic reduction process of nitrogen oxides using catalysts, based on titania as support with different contents of vanadia and tungsta as active phase. In this work, we attempt to illustrate the criterion by which the optimum composition of these catalysts can be chosen since until recently their design has only been based on the benefits that they present for the main reaction without any thought for the eventual formation of any undesirable products, such as nitrous oxide, whose emissions participate in the degradation of the atmosphere.

2. Materials and methods

2.1. Catalyst preparation

For this study, a series of vanadia and tungsta supported on titania catalysts were prepared. The raw materials were a hydroxylated titanium gel, with approximately 50% water content and an average particle size of 90% <40 μm after drying and calcining at 500 °C (manufactured by Tioxide, UK), ammonium metavanadate (Panreac) and ammonium metatungstate (Panreac). The titanium oxide content of all the catalysts was maintained at 90 wt.%, varying the vanadia and tungsta contents to produce the five studied compositions: Ti:V:W 90:0:10, 90:2:8, 90:5:5, 90:8:2 and 90:10:0, respectively.

All the catalysts were obtained by the same procedure, blending the raw materials in the appropriate amounts to form a paste with adequate rheological properties for extrusion through a die with a 1 mm diameter orifice. After careful drying at ambient temperature, the materials were subsequently heated to 110 °C to remove the excess water then finally calcined at 500 °C.

2.2. Catalytic activity measurements

The measurements of catalytic activity, for the oxidation of ammonia traces and for the SCR of nitric oxide, were carried out in a stainless steel micro-reactor with an isothermal temperature profile. In this reactor of 20 cm length and 1 cm diameter, approximately, 0.5 g of catalyst was employed. In the assays carried out in the presence of nitric oxide, the ammonia was fed directly to the reactor inlet, thus, avoiding the formation of ammonium salts. The detection and quantification of NO, NO_2, N_2O, N_2, NH_3, H_2O and O_2 at the entrance and exit of the micro-reactor was carried out by mass spectrometry using a Balzers Omnistar with a Channeltron detector of high sensitivity. The following experimental conditions were employed: space velocity, under normal conditions (GHSV), 15,000 h^{-1}; linear velocity, 0.1 m s^{-1}; pressure, 0.1 MPa; reaction temperature, 180–350 °C. The gas composition in the ammonia oxidation tests was the following: $[NH_3]$ = 500 ppm; $[O_2]$ = 3 vol.%; [Ar] = balance. In the selective catalytic reduction experiments, the following gas composition was used: [NO] = $[NH_3]$ = 1000 ppm; $[O_2]$ = 3 vol.%; [Ar] = balance.

2.3. Characterisation

The pore volumes and pore size distributions between 300 μm and 7.5 nm were determined by mercury intrusion porosimetry (MIP) on samples dried overnight at 150 °C with a Fisons Instruments Pascal 140/240 device. The specific surface area and pore size distribution in the micro (0–2 nm) and mesopore (2–50 nm) diameter ranges were determined by nitrogen adsorption/desorption isotherms measured with a Carlo Erba Sorptomatic 1800 on samples previously outgassed overnight at 300 °C to a vacuum of >0.1 Pa. The surface areas of the samples (S_{BET}) were determined by the BET method from the corresponding nitrogen adsorption isotherm. Combination of the nitrogen adsorption and mercury porosimetry results leads to the determination of the total pore volume. The results from this textural analysis are collated in Table 1.

Diffuse reflectance UV–vis spectra were obtained with a Shimadzu UV-2401PC UV–vis spectrometer equipped with an integration sphere diffuse reflectance attachment. The catalysts were used as powders and a halon white (PTFE) reflectance standard used to record the baseline. The reflectance spectra were taken over the range 12,500–45,000 cm^{-1} (230–800 nm) and converted into Kubelka–Munk function $F(R)$.

3. Results and discussion

3.1. Ammonia oxidation

In order to determine the catalyst behaviour in the ammonia oxidation process, a series of experiments between

Table 1
Textural properties of the catalysts

TiVW catalyst	BET area (m^2/g)	Mesopore volume (cm^3/g)	Macropore volume (cm^3/g)	Total pore volume (cm^3/g)
90:0:10	116	0.18	0.26	0.44
90:2:8	110	0.24	0.24	0.48
90:5:5	91	0.26	0.29	0.55
90:8:2	37	0.24	0.34	0.58
90:10:0	22	0.12	0.44	0.56

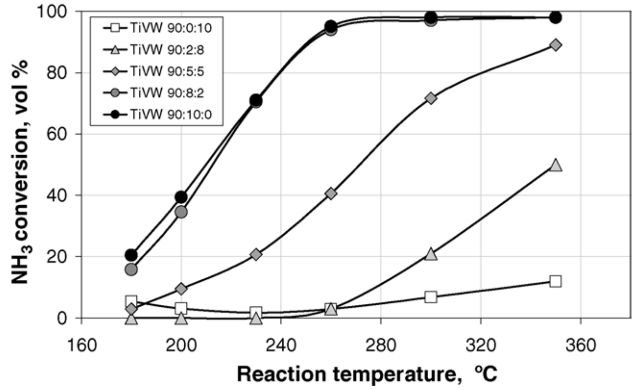


Fig. 1. Ammonia conversion vs. reaction temperature. *Operating conditions:* space velocity at normal conditions (GHSV), 15,000 h^{-1}; linear velocity, 0.1 m s^{-1}; pressure, 0.1 MPa. *Feed composition:* $[NH_3]$ = 500 ppm; $[O_2]$ = 3 vol.%; [Ar] = balance.

180 and 350 °C were carried out. As may be observed, from the results shown in Fig. 1, the ammonia conversions increased as the vanadia loading was raised up to 8 wt.%. The sample with only tungsta had a very low activity indicating that although ammonia could be adsorbed over the Brønsted acid sites, since this material has no redox capability the ammonia cannot be reduced. However, in the binary systems, ammonia can adsorb over the Brønsted sites of both the vanadia and tungsta and subsequently react by a redox mechanism of the vanadia to produce both nitrogen and water [9].

For the two catalysts with the higher vanadia contents, significant amounts of nitrous oxide were also produced when the reaction took place at temperatures greater than 260 °C. The selectivity to (a) nitrogen and (b) nitrous oxide obtained during the ammonia conversion experiments are shown in Fig. 2. It can be observed that the selectivity to nitrogen was around 90%, up to an operating temperature of 240 °C for all the catalysts, then, fell abruptly for samples with the higher vanadia contents.

Various authors [10] have described that the dispersed vanadia on titania (anatase) is present as isolated vanadyl and polymeric V_xO_y species, increasing the presence of the latter as the vanadia content was increased. From our results, it can be seen that the formation of nitrous oxide is favoured by the increased surface density of the polymeric species, since this facilitates the close proximity of active centres capable of adsorbing two ammonia molecules. Furthermore, the abrupt fall in the specific surface area at vanadia loadings greater than 5 wt.% would lead to a higher surface density of the vanadyl species. The reaction between the adsorbed ammonia and the polymeric vanadyl species to give nitrous oxide could take place according to Scheme 1.

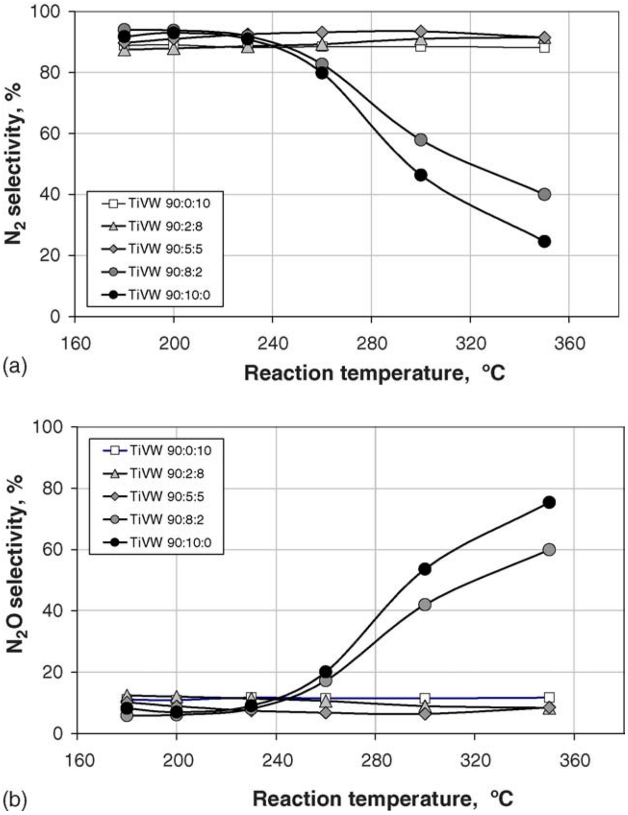
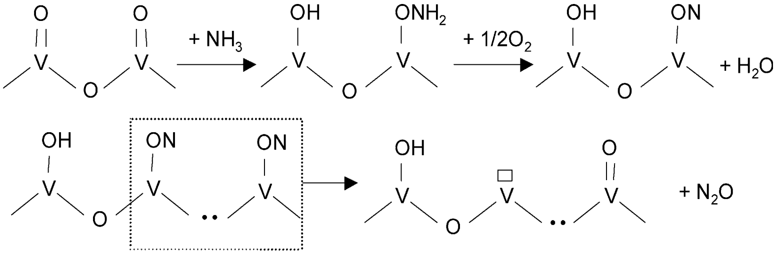


Fig. 2. Selectivity to: (a) N_2 and (b) N_2O, during ammonia oxidation as a function of the temperature.

3.2. Selective catalytic reduction process

The NO conversion results obtained during the SCR process between 200 and 350 °C are shown in Fig. 3. The catalysts prepared with vanadia present a common pattern of activity with maximum conversion values between 260 and 300 °C. The different textural properties of these catalysts do not seem to affect the catalytic behaviour for this reaction under the assayed operation conditions. The data suggest



Scheme 1.

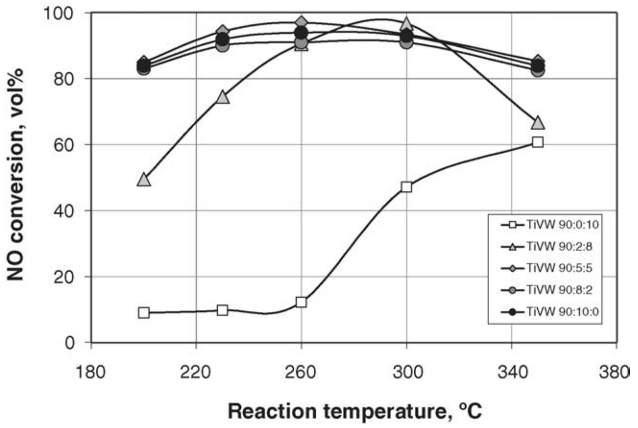


Fig. 3. Nitric oxide conversion vs. reaction temperature. *Operating conditions:* space velocity at normal conditions (GHSV), 15,000 h^{-1}; linear velocity, 0.1 Nm s^{-1}; pressure, 0.1 MPa. *Feed composition:* [NO] = [NH_3] = 1000 ppm; [O_2] = 3 vol.%; [Ar] = balance.

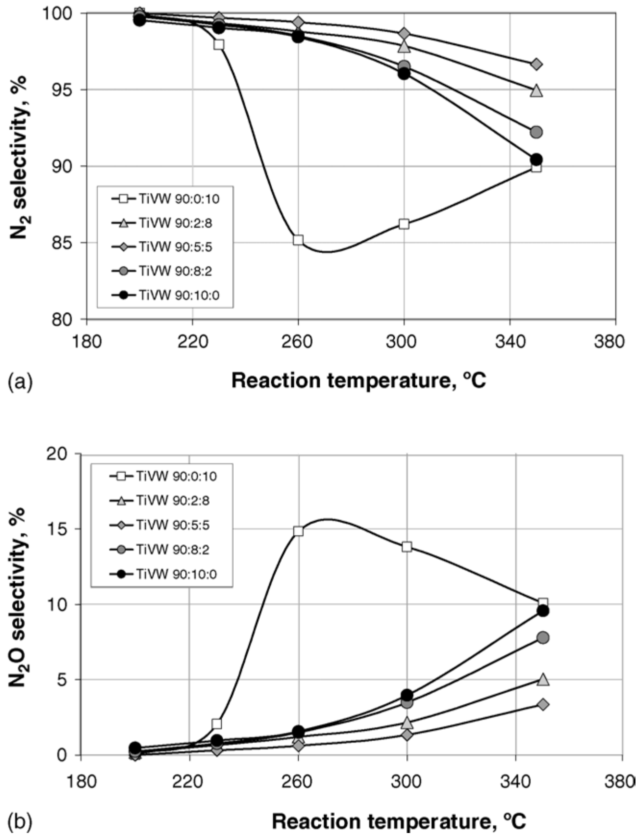


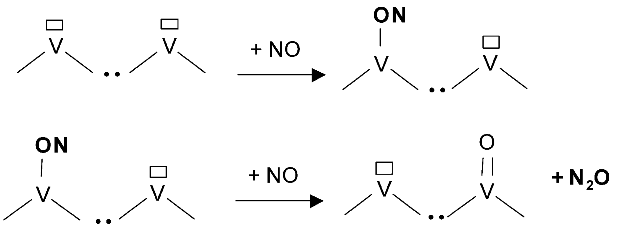
Fig. 4. Selectivity to: (a) N_2 and (b) N_2O, during selective catalytic reduction of nitric oxide as a function of the temperature.

that the overall process was controlled by external diffusion phenomena. At temperatures above 290 °C, a slight decrease in the nitric oxide conversion was observed due to oxidation of ammonia, used as the reducing agent, becoming significant. The different behaviour in the catalytic activity of the TiVW 90:0:10 catalyst was due to the absence of the redox properties in this material, leading to an activity pattern very different with respect to samples containing vanadia. However, this catalyst still had an ammonia absorption capacity due to the presence of Brønsted acid sites of the tungsta.

The selectivity to nitrogen and nitrous oxide are shown in Fig. 4a and b, respectively. It can be observed that above 260 °C, the formation of nitrous oxide begins to become significant and that increased vanadia loading and reaction temperature promote this phenomenon. The data obtained with the TiVW 90:0:10 catalyst may be related with the reactivity of ammonia absorbed on the Brønsted acid sites of the tungsta. These results demonstrate that the formation of nitrous oxide in the SCR process of nitrogen oxides with ammonia differs slightly from that observed during the ammonia oxidation process. Since the disappearance values of NO in terms of conversion remain almost constant between 260 and 300 °C, but in this temperature interval, a significant increase in the selectivity to nitrous oxide takes place, it is necessary to suppose that there are different mechanisms for the formation of nitrous oxide during ammonia oxidation but without discarding this mechanism as responsible for part of the nitrous oxide formed in the overall process.

The reaction could be based on the adsorption of nitric oxide molecules on reduced centres of polymeric vanadyl species that lead to the formation of nitrous oxide according to Scheme 2.

In a similar way to that described for ammonia oxidation, the increase in the vanadia content led to an increase in the density of polymeric vanadyl species on the surface of the catalyst, especially, at vanadia contents greater than 5% due to the corresponding fall in the specific surface area, facilitating the adsorption of NO on active centres within close proximity. The first stage in the nitrous oxide formation process was the same as that proposed in the previous scheme. This was confirmed by an experiment carried out with the TiVW 90:8:2 catalyst, in the microreactor, where the catalyst was previously reduced with ammonia then subsequently purged with argon and finally exposed to a flow containing 1000 ppm of nitric oxide in Ar. From Fig. 5, the small amount of nitrous oxide generated during the oxidation with nitric oxide of this previously reduced catalyst may be noted. This experiment confirms the possibility that under certain reduction conditions, a nitrous oxide molecule can be formed by the interaction of two adjacent V–ON groups.



Scheme 2.

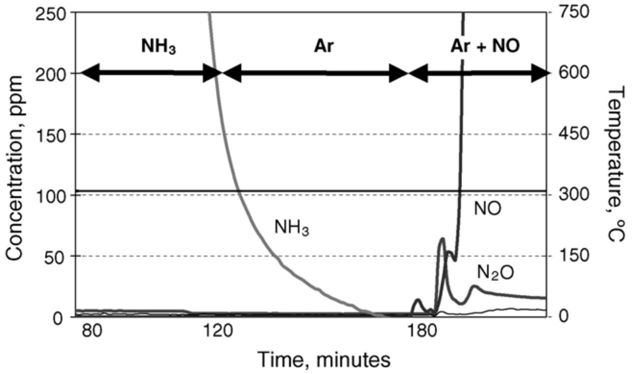


Fig. 5. Programmed experiment with three steps. First step: ammonia feed of (1000 ppm), using Ar as carrier, for 2 h at 350 °C to reduce the active sites. Second step: ammonia removal from the stream by a gas purge with Ar for 1 h at 350 °C. Third step: the reactor was fed with 1000 ppm of NO + Ar as carrier at 350 °C. *Operating conditions:* temperature, 350 °C; space velocity at normal conditions (GHSV), 20,000 h^{-1}; linear velocity, 0.1 m s^{-1}; pressure, 0.1 MPa.

In Fig. 6, the UV–vis spectra between 350 and 800 nm for the five catalysts and a sample of titania with no vanadia or tungsta incorporation are shown. The UV–vis spectrum of titania presents an absorption edge with an onset close to 400 nm and an absorption maximum at 320 nm (due to the charge transfer $O^{2-} \rightarrow Ti^{4+}$ corresponding to the excitation of electrons form the O 2p valence band to the Ti 3d valence band and a shoulder at 260 nm due to the bending of the Ti 3d orbital of the Ti ions. The position of this band with its corresponding energy gap of 3 eV characterises titania as an intrinsic semiconductor [11].

The UV–vis spectrum of bulk vanadia (where vanadium ions show coordination six) has an intense absorption between 200 and 600 nm, extending into the visible region, giving rise to its characteristic orange colour. This absorption is due to the charge transfer from valence band of O 2p to the empty orbital V 3d, with a maximum at 320 nm and two shoulders at 250 and 450 nm [12]. Analyses of salts where the V^{5+} ion has tetrahedral coordination show absorption at values lower than 400 nm, having been deduced as a general rule that the higher the coordination of V^{5+} ion, the higher are the wavelengths found for their absorption edge in UV–vis [13].

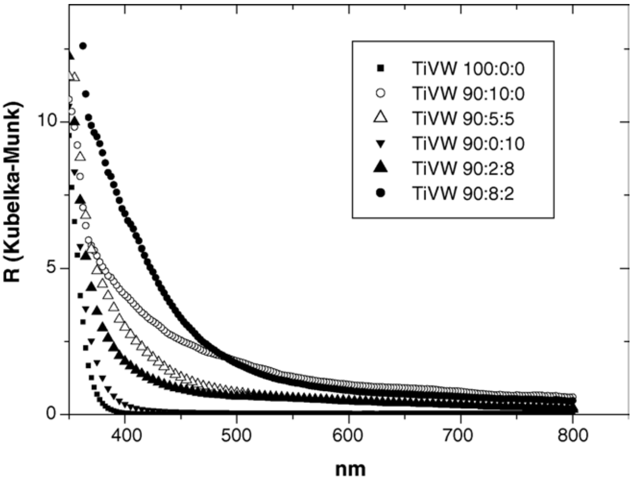


Fig. 6. UV–vis spectra between 350 and 800 nm for the five catalysts and a sample of titania.

In the case of bulk tungsta, where the W^{6+} ion has coordination six, an absorption can be observed between 200 and 400 nm, with a maximum at 320 nm and a shoulder at 250 nm, corresponding to the charge transfer from the valence band O 2p to the empty orbital W 5d [14].

As described in the literature, the addition of tungsta to titania scarcely varies the absorption edge of titania, because the charge transfer transitions $O^{2-} \rightarrow W^{6+}$ of tungstyl centres are superimposed on the band of bulk titania. Thus, sample TiVW 90:0:10 was white-like titania, due to the lack of absorption bands in the visible region of the spectrum [15].

In the case of the sample that contained only titania and vanadia (TiVW 90:10:0), the absorption edge was displaced to values higher than 550 nm, indicating the existence of an elevated percentage of vanadia in the form of crystallites (which have been described as having low catalytic activity in the SCR reaction compared with dispersed vanadyl species). This behaviour has been explained because the 3d orbitals have energies slightly lower than that of the conduction band of Ti 3d and perturb it. Accordingly, these samples are brown. In the material with a small amount of tungsta, TiVW 90:8:2, there was no dispersion of the vanadium species, even though the amount of these is lower, as shown by the absorption edge being even higher than that for the TiVW 90:10:0 sample with wavelengths higher than 480 nm.

On analysing sample TiVW 90:5:5, the absorption edge was strongly decreased at values higher than 500 nm, corresponding to the much higher dispersion of the vanadia species. Not surprisingly even higher dispersion of the vanadia species were found in sample TiVW 90:8:2, with an additive effect of the low amount of vanadia and higher surface area.

4. Conclusions

The catalytic oxidation of ammonia increases with the reaction temperature and the vanadia content in catalysts of V_2O_5-WO_3/TiO_2. However, the increased vanadium oxide content leads to nitrous oxide selectivity values greater than 40% under the studied operating conditions. The selection of a catalyst for the elimination of ammonia traces should be made, therefore, keeping in mind not only ammonia conversion values but also the selectivity to nitrogen. A reaction scheme that justifies the formation of nitrous oxide in this process, in function of the increase of polymeric vanadyl species on the catalytic surface is proposed.

In the case of the selective catalytic reduction of nitrogen oxides, the catalysts showed nitric oxide conversion values that were independent of the active phase content. However, the selectivity to nitrous oxide became significant when the vanadia content in the catalysts was equal or superior to 8 wt.% and the reaction temperature higher than 300 °C. To explain the formation of nitrous oxide in this process, it is proposed that besides being generated from the adsorbed ammonia, it might also be generated from oxidation of reduced sites of the catalyst by nitric oxide. It would be useful to study the effect of the vanadia content on the formation of nitrous oxide with real gases, since the presence of SO_2, water vapour and other compounds in the effluent could significantly affect the proposed mechanisms.

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References

[1] F. Kapteijn, L. Singoredjo, N.J.J. Dekker, Y.J.A. Moulijn, Ind. Eng. Chem. Res. 32 (1993) 445.
[2] N.I. Il'Chenko, G.I. Golodets, I.M. Avilova, Kinet. Catal. 16 (6.) (1976) 1455.
[3] J. Blanco, P. Avila, S. Suarez, J.A. Martín, C. Knapp, Appl. Catal. B Environ. 28 (3–4) (2000) 235.
[4] P. Forzatti, L. Lietti, Heter. Chem. Rev. 3 (1996) 33.
[5] N.I. Il'chenko, Russ. Chem. Res. 45 (12) (1976) 1119.
[6] I. Nova, L.-D. Acqua, L. Lietti, E. Giamello, Y.P. FForzatti, Appl. Catal. B Environ. 35 (2001) 31.
[7] A. Baiker, B. Handy, J. NIckl, M. Schraml-Marth, Y.A. Wokaum, Catal. Lett. 14 (1992) 89.
[8] L.J. Alemany, F. Berti, G. Busca, G. Ramis, D. Robba, P. Toledo, M. Trombetta, Appl. Catal. B 10 (1996) 299.
[9] H. Topsoe, J. Catal. 216 (2003) 155.
[10] J. Svachula, L.J. Alemany, N. Ferlazzo, P. Forzatti, E. Tronconi, Y.F. Bregani, Ind. Eng. Chem. Res. 32 (1993) 826.
[11] J.B. Torrance, P.L. Chinnarong, R.M. Metzger, J. Solid State Chem. 90 (1991) 168.
[12] G. Catana, J. Phys. Chem. 102 (1998) 8005.
[13] B.M. Reddy, I. Ganesh, B. Chowdhury, Catal. Today 49 (1999) 115.
[14] M.A. Larrubia, G. Busca, Mater. Chem. Phys. 72 (2001) 337.
[15] D.S. Kim, M. Ostromecki, I.E. Wachs, J. Mol. Catal. A 106 (1996) 93.