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Selective catalytic reduction of nitric oxide with ammonia on vanadia/alumina catalysts

Influence of vanadia loading and secondary metal oxide additives

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A series of V_2O_5/Al_2O_3 catalysts have been examined for the selective catalytic reduction (SCR) of NO with NH_3 as a function of vanadia loading, metal oxide additives (Mo, W, Ni, Co), and reaction temperature. Increasing the vanadia loading, or surface vanadia coverage, increased the Brønsted acidity and reactivity of the V_2O_5/Al_2O_3 catalysts. Introducing additives that increased the Brønsted acidity, Mo oxide and W oxide, also increased the reactivity. Introducing additives that did not influence the Brønsted acidity, Ni oxide and Co oxide, did not affect the reactivity. However, the addition of Ni oxide and Co oxide increased the ratio of polymerized to isolated surface vanadium oxide species on alumina, which reveals that the SCR reaction is not sensitive to the surface vanadia structure on alumina. A model that explains these observations consists of a dual site: a surface redox site and an adjacent surface Brønsted acid site. Consequently, increasing the surface vanadium oxide coverage and introducing additives that increase the surface concentration of Brønsted acid sites is beneficial for the SCR of NO with NH_3.

The selective catalytic reduction (SCR) of NO_x with NH_3 over supported V_2O_5–WO_3/TiO_2 catalysts is a recent commercial technology used for the reduction of NO_x emissions from power plants. The industrial success of the SCR reaction has generated many fundamental studies of this catalysed reaction, but many questions regarding the nature of the catalytic active centre and mechanism of this reaction still remain.

Miyamoto *et al.* proposed that NH_3 is strongly adsorbed adjacent to V=O sites as NH_4^+ and that the reaction rate is directly proportional to the number of surface V=O bonds determined by the rectangular pulse technique.[1] Janssen *et al.* employed oxygen isotope experiments to probe the surface vanadium species and proposed that a pyrovanadate structure, O=V—O—V=O, was the most likely structure for the active centre.[2] Went *et al.* characterized the surface vanadium species with *in situ* Raman spectroscopy as well as temperature programmed reduction/temperature programmed oxidation and concluded that both monomeric vanadyl and polymeric vanadate surface species were present on the titania support.[3] Corresponding SCR studies suggested that the polymeric species were *ca.* 10 × more active than the monomeric species, but the polymeric species were less selective towards N_2 formation.[4] An increase in the SCR specific activity with surface vanadia coverage on titania has also been reported by other investigators.[5,6] Lietti *et al.* and Ramis *et al.* proposed that the redox properties of the catalysts are a major factor governing SCR activity and that the reaction primarily involved a coordinated ammonia species on Lewis acid sites.[6,7] The potential participation of a protonated ammonium on a surface Brønsted acid site was also proposed, because of the possible interconversion of these species.[6,7] Ramis *et al.* also proposed that promoters affect the Lewis acidity of V=O bonds, which affects the adsorption of ammonia, the first step in the SCR reaction.[8] Topsoe proposed from *in situ* FTIR studies that Brønsted acid sites are the main active centres for the SCR reaction over titania-supported vanadia catalysts.[9] The role of Brønsted acidity in the SCR reaction over supported vanadia catalysts was also proposed by several other research groups.[10–12] Model SCR studies with unsupported V_2O_5 crystals concluded that the crystallographic planes possessing V—O—V or V—OH bonds rather than V=O bonds were the selective sites for the SCR reaction.[12,13] In a recent series of detailed experiments over V_2O_5/TiO_2 catalysts, Topsoe *et al.* combined *in situ* FTIR and on-line mass spectrometry, transient and steady state, to provide convincing evidence that both surface Brønsted acid sites and surface V= sites are involved in the SCR catalytic cycle.[14,15]

The mechanism for the selective catalytic reduction of NO with NH_3 over vanadia–titania catalysts has been suggested to occur *via* an Eley–Rideal[1,2,6,7,12,15] mechanism as well as *via* a Langmuir–Hinshelwood mechanism.[4,16,17] The Eley–Rideal mechanism can be written as:

$$NH_3(g) \rightarrow NH_x(ads)$$

$$NO(g) + NH_x(ads) \rightarrow N_2(g) + H_2O(g)$$

and the Langmuir–Hinshelwood reaction can be written as:

$$NO(g) \rightarrow NO(ads)$$

$$NH_3(g) \rightarrow NH_x(ads)$$

$$NO(ads) + NH_x(ads) \rightarrow N_2(g) + H_2O(g)$$

However, significant amounts of adsorbed NO are not found on the V_2O_5/TiO_2 catalyst surface under the reaction conditions required by the Langmuir–Hinshelwood mechanism.[15] Furthermore, detailed microkinetic analysis of the SCR reaction by Dumesic *et al.* suggests that a two-step Eley–Rideal mechanism involving reaction between NH_3 and gaseous (or weakly bonded) NO is not consistent with the data.[18] The SCR kinetic data could quantitatively be described by a kinetic model involving a three-step mechanism: equilibrated ammonia adsorption, activation of adsorbed ammonia and reaction of activated ammonia with NO (gaseous or weakly adsorbed). It has been suggested that the surface sites associated with these three reaction steps involve surface Brønsted acid sites, surface V=O sites and reduced surface V=O sites.[15]

In the preceding paper,[19] Raman and IR spectroscopy were used to characterize the interaction of additives to the alumina-supported vanadia catalysts. In the present paper, modified and unmodified alumina-supported vanadia catalysts were used to study the SCR of NO with NH_3. The present investigation was initiated to obtain fundamental insight into the nature of the active centres of supported vanadia catalysts employed in the selective catalytic reduction of NO with NH_3. The advantage of using an alumina-supported vanadia catalyst as the model system is that previous studies demonstrated that many of the catalyst properties could be varied either by changing the surface vanadia coverage or by the introduction of secondary surface-metal-oxide additives. Increasing the surface vanadia coverage on alumina increases the ratio of polymerized surface vanadia species[20] and the number of surface Brønsted acid sites,[21] but decreases the number of surface hydroxy groups on the alumina support.[21] Addition of surface nickel oxide or cobalt oxide species to the alumina supported vanadia catalyst dramatically increases the ratio of the polymerized : isolated surface vanadium species,[19] but does not introduce surface Brønsted-acid sites[22–24] and has only a minor effect on the alumina surface hydroxy group.[19] Addition of surface tungsten oxide and molybdenum oxide species to the alumina-supported vanadia catalyst increases the ratio of polymerized : isolated surface vanadium species[19] and the number of surface Brønsted acid sites,[21] but significantly decreases the number of surface hydroxy groups on the alumina support.[21] Thus, the previous characterization studies reveal that the V_2O_5/Al_2O_3 catalyst, with and without additives, is a model catalyst system that allows for the systematic variation of many of the fundamental parameters: ratio of polymerized : isolated surface vanadium species, concentration of surface Brønsted acid sites, surface-metal-oxide coverage and concentration of alumina surface hydroxy groups. The variation of these parameters helps in the fundamental understanding of the catalysts employed for the selective catalytic reduction of NO with NH_3.

Experimental

Preparation of the V_2O_5/Al_2O_3 catalysts

The γ-alumina support used was obtained from Harshaw (180 $m^2\ g^{-1}$). The supported vanadium oxide catalysts were prepared by incipient wetness impregnation of the alumina support with a solution of $VO(OPr^i)_3$ (Alpha, 95–98% purity) in methanol. Owing to the air- and moisture-sensitive nature of this alkoxide precursor, impregnation, drying (at room temperature) and heating (at 383 K for 16 h and 623 K for 16 h) were performed in a nitrogen atmosphere. The samples were finally calcined in dry air at 773 K overnight.

Preparation of modified V_2O_5/Al_2O_3 catalysts with Mo, W, Co and Ni

First, the precursors of Mo, W, Co and Ni were added to the alumina support *via* incipient wetness–impregnation with aqueous solutions of their corresponding salts: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_6H_2W_{12}O_{40}\cdot 4H_2O$, $Co(NO_3)_2$ and $Ni(NO_3)_2\cdot 6H_2O$. After the first impregnation step the samples were dried at room temperature and at 383 K, and finally calcined in dry air at 773 K overnight. Afterwards, the vanadium oxide precursor was added as mentioned above.

Gases

Gas cylinders containing pure O_2, NO (4000 ppm)–He, NH_3 (4000 ppm)–He (certified to 2% accuracy) and pure He were supplied by UCAR (Union Carbide).

Reactor set-up

The NO reduction measurements have been carried out in a reactor set-up in which it is possible to simultaneously test up to six catalysts in six parallel reactors. The apparatus, schematically shown in Fig. 1, consists of three sections: gas mixing, reactor and analysis. The gas-mixing section comprised stainless-steel tubing maintained at 383 K. The gases were fed in to a static-gas mixing tube (MT) through four mass flow controllers (Hi-Tec MFC 201). The resulting gas mixture was divided into seven streams in a splitter: six streams, adjusted by six mass flow controllers, were admitted to the six reactors and the seventh stream, consisting of excess mixture, was vented through a back-pressure controller (Tescom mod. 26-2321-24), to maintain a constant pressure in the system. The reactor section is made up of a water-cooled oven controlled by a temperature programmer–controller (West 2050) carrying six glass reactors (Duran 50) with an internal diameter of 3 mm. Within the oven, the reactor tubes extended through a cylindrical aluminium block designed to ensure a uniform temperature profile. The temperature in the oven was measured by means of a chromel–alumel thermocouple. The temperature was not found to differ from that prevailing inside the reactors under the test conditions.

The analysis section consists of a mass spectrometer (a preferred analysis technique in SCR) controlled by an IBM-PC/AT computer. An air-actuated multiposition valve (Valco SD type) selects one of the product streams for admission to the mass spectrometer. This took place by differential pumping through a capillary tube, of length 1.10 m and internal diameter 0.15 mm, and a small orifice. Calibration mixtures were used to quantify product concentrations. An internal-standard technique was also applied to improve the accuracy of the

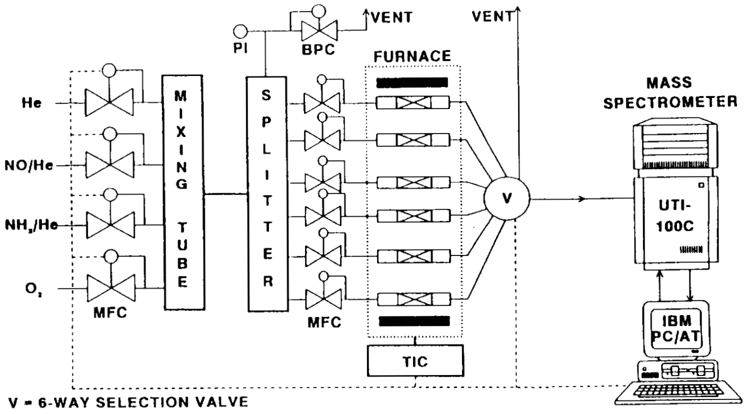

Fig. 1 Reactor set-up for SCR reaction

Table 1 Standard conditions of activity measurements

NO content (ppm)	500
NH_3 content (ppm)	550
O_2 content (%)	2
He content	balance
temperature/K	423–773
pressure/atm	1
flow rate/cm^3 (STP) min^{-1} (34 mmol s^{-1})	50

measurements. Over the concentration range studied (0–1000 ppm), the NO and NH_3 response was linear. The computer communicates with all sections of the set-up by an interface (RTI-802, RTI-820 and STB-HL) from Analog Devices.

Activity measurements

One of the six reactors was kept empty and served as a reference. The standard conditions of the activity measurements are given in Table 1. An excess of NH_3 was used to determine the NO removal efficiency without any reaction limitations due to the reducing agent. Testing of the catalysts started at 423 K and the temperature was increased to 773 K in six steps of 50 K at a rate of 4 K min^{-1}. At each step the catalyst activity was monitored for 1.5 h. A number of increasing and decreasing cycles were performed on some catalysts and no significant change in conversion was observed at a particular temperature. The testing of the catalysts was carried out such that the catalyst bed always contained 0.8 mg V_2O_5. Alumina was added to keep the bed geometry unchanged. Mass-transfer gradients were found to be absent for the conditions used in the present investigation.

After correction of the MS signals for background, blank and contributions from the fragmentation of other species, the NO conversion was calculated as follows:

$$X_{NO} = 1 - S_{NO}/S_{NO\,blank} \quad (1)$$

where S_{NO} is the corrected MS signal. The selectivity was calculated as follows:

$$S = 1 - C_{N_2O}/(C^{\circ}_{NO} - C_{NO}) \quad (2)$$

assuming that NO and NH_3 react on a 1 : 1 basis to yield N_2 and N_2O, where C_i is the concentration of component i in the product stream, and $C^{\circ}_{NO} = 500$ ppm in this case.

Calculation of turnover frequency was performed by assuming a first-order reaction mechanism as found for V_2O_5/Al_2O_3 catalysts by Wong and Nobel.[25] The turnover frequency is defined as the number of moles of NO converted per mole of vanadium atom per second.

Results

Vanadium oxide/alumina catalyst system

Previous studies reveal that only surface vanadium oxide species are formed on the present series of V_2O_5/Al_2O_3 up to a loading of 20% V_2O_5. Above 20% V_2O_5, crystallites of bulk V_2O_5 are observed and the monolayer capacity has been exceeded on this alumina support. The activity of the series of V_2O_5/Al_2O_3 catalysts, 1–20% V_2O_5, were studied as function of vanadium oxide loading for the SCR reaction at various temperatures. As the vanadia loading is increased from 1 to 20% V_2O_5, the activity, (mol NO converted g^{-1} h^{-1}), of the V_2O_5/Al_2O_3 catalysts increases more than an order of magnitude and consequently, the activity is predominantly due to the surface vanadia species. Thus, the activity data can be converted to turnover frequencies (TOF) based on the vanadia coverage.

The TOF at various temperatures of the series of unmodified 1–20% V_2O_5/Al_2O_3 catalysts were calculated using first-order kinetics for the SCR reaction and are presented in Fig. 2. From Fig. 2, the TOF frequency of the V_2O_5/Al_2O_3 series increases and then decreases as the temperature of the reaction is increased reaching a maximum value at 623 K. The TOF as a function of vanadia loading also increases and decreases as the vanadia loading is increased and reaches a maximum value for the 15% V_2O_5/Al_2O_3 sample. Such an optimum value of TOF as a function of temperature (623 K) and vanadia loading (15%) can be explained by considering that significant amounts of ammonia oxidation occurs at higher temperatures or vanadium oxide loadings, and/or when a key intermediate is formed over a well defined temperature range only. The former case appears to be more likely for the SCR reaction over vanadia/alumina catalysts since higher temperatures and higher vanadia loadings are known to lead to the oxidation of ammonia.

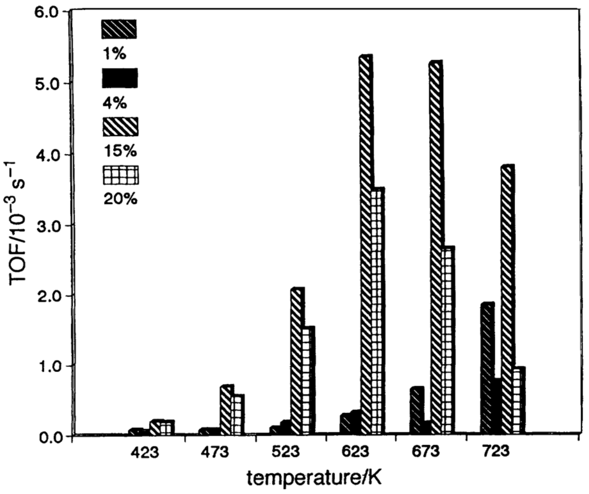

Fig. 2 TOF for the SCR of NO with NH_3 as a function of temperature and loading for the V_2O_5/Al_2O_3 catalysts

Selectivity towards N_2 formation over the same series of V_2O_5/Al_2O_3 catalysts was also studied as a function of different reaction temperatures and are shown in Fig. 3. The selectivity of NO conversion to N_2 was generally high for the V_2O_5/Al_2O_3 catalysts (>95%) in the low-temperature range (<473 K). However, the selectivity decreases at higher temperatures (>623 K) to lower values. In general, the drop in selectivity is due to the formation of N_2O at high temperatures.

V_2O_5/Al_2O_3 catalyst modified with Mo oxide and W oxide additives

The influence of modification of V_2O_5/Al_2O_3 with Mo oxide and W oxide additives is shown in Fig. 4 for different reaction

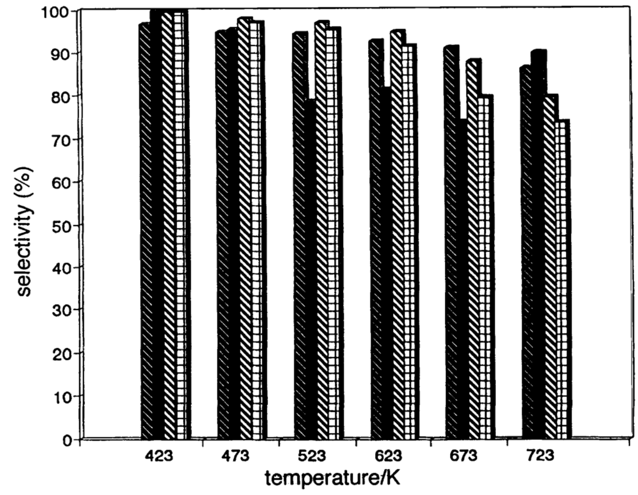

Fig. 3 Selectivity as a function of temperature and loading for the V_2O_5/Al_2O_3 catalysts. Legends as Fig. 2.

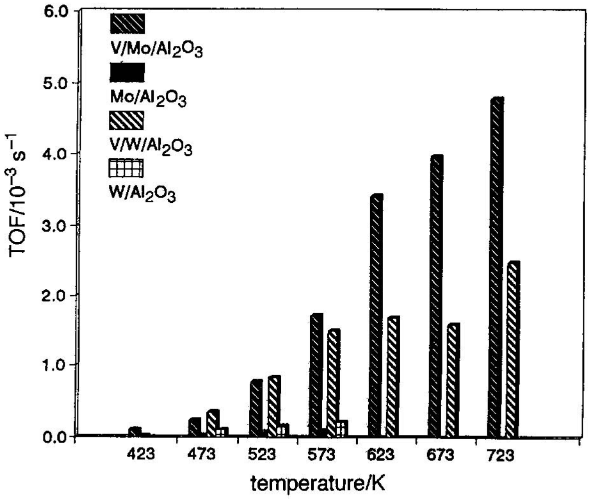

Fig. 4 TOF for the SCR of NO with NH_3 as a function of the temperature for the 5% V_2O_5/Al_2O_3 catalyst with Mo oxide (10% MoO_3) and W oxide (5% WO_3) additives

temperatures. The catalytic results for the unmodified V_2O_5/Al_2O_3 catalyst demonstrate that a 5 wt.% V_2O_5/Al_2O_3 catalyst is almost inactive (see Fig. 2). However, modification of the 5% V_2O_5/Al_2O_3 catalysts with Mo oxide (10% MoO_3) and W oxide (5% WO_3) additives results in considerably enhanced catalytic activity. The catalytic activity attributable to the alumina-supported Mo oxide and W oxide catalysts, in the absence of vanadia, is negligible as shown in Fig. 4.

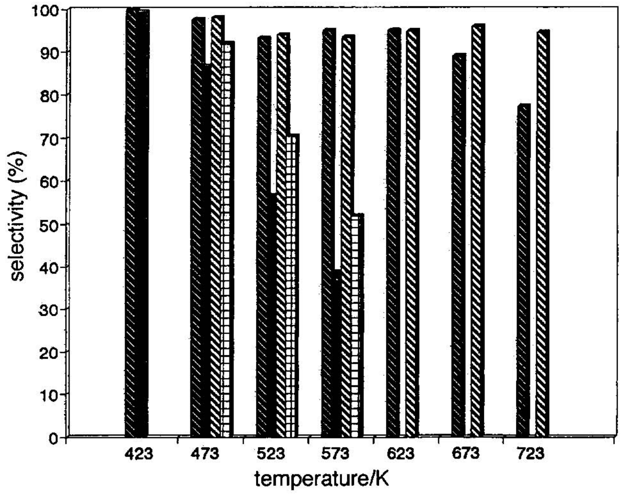

Fig. 5 Selectivity as a function of temperature for the 5% V_2O_5/Al_2O_3 catalysts with Mo oxide and W oxide additives. Legends as Fig. 4.

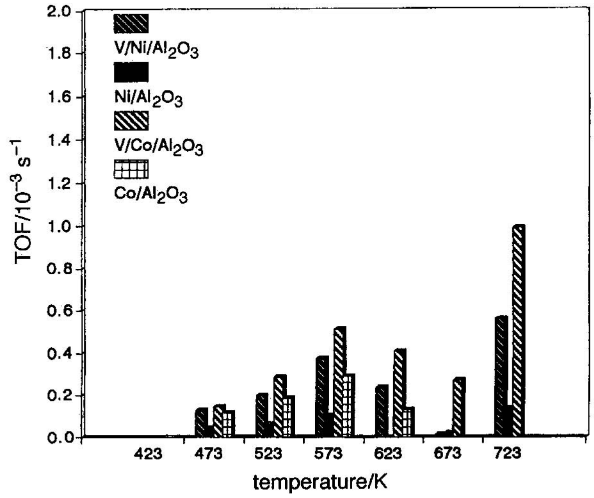

Fig. 6 TOF for the SCR of NO with NH_3 as a function of the temperature for the 5% V_2O_5/Al_2O_3 catalysts with Ni oxide (6% NiO) and Co oxide (5% CoO) additives

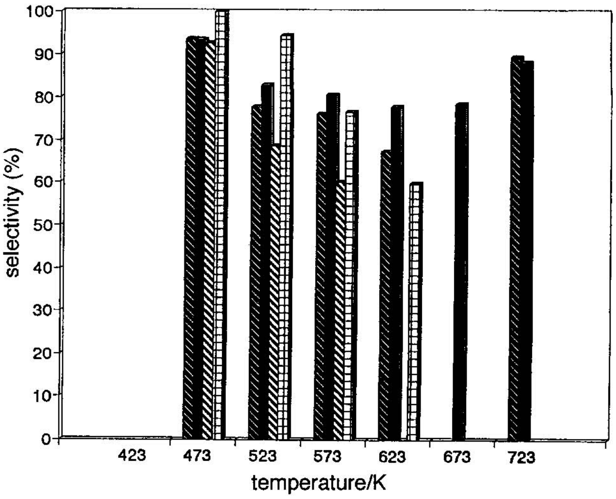

Fig. 7 Selectivity as a function of temperature for the 5% V_2O_5/Al_2O_3 catalysts with Ni oxide and Co oxide additives. Legends as Fig. 6.

The selectivity of the modified V_2O_5/Al_2O_3 catalysts, Fig. 5, was comparable to that of the best performing unmodified catalysts shown in Fig. 3, with the W oxide modified V_2O_5/Al_2O_3 catalysts showing better selectivity at higher temperatures (>623 K) and the Mo oxide modified V_2O_5/Al_2O_3 catalyst showing similar behaviour to the unmodified V_2O_5/Al_2O_3 catalyst. The selectivity of the alumina-supported Mo oxide and W oxide catalysts, without vanadia, decreases considerably above 450 K. Thus, V_2O_5/Al_2O_3 catalysts modified by Mo oxide and W oxide additives exhibit enhanced catalytic activity with the W oxide modified V_2O_5/Al_2O_3 catalysts exhibiting superior performance at higher temperatures.

V_2O_5/Al_2O_3 catalyst modified with Ni oxide and Co oxide additives

The influence of modification of a 5% V_2O_5/Al_2O_3 catalyst with Ni oxide (6% NiO) and Co oxide oxide (5% CoO) additives is shown in Fig. 6. The level of activity for the modified V_2O_5/Al_2O_3 catalysts is similar for unmodified 5% V_2O_5/Al_2O_3 and Al_2O_3 supported Ni oxide and Co oxide in the absence of vanadia. However, the selectivity of the Al_2O_3-supported Ni oxide and Co oxide in the absence of vanadia is significantly lower than that of the corresponding unmodified 5% V_2O_5/Al_2O_3 catalyst (Fig. 7). Thus, V_2O_5/Al_2O_3 catalysts modified by Ni oxide and Co oxide do not exhibit enhanced catalytic activity and selectivity.

Discussion

The V_2O_5/Al_2O_3 catalyst of the present study exhibited a significant increase in the TOF of the SCR reaction with surface vanadium oxide coverage similar to that observed for V_2O_5/TiO_2 catalyst system.[4,26] Parallel studies with methanol oxidation over the same catalysts did not reveal a significant change in TOF with surface vanadium oxide coverage,[27] which suggests that all the surface vanadium oxide species on the alumina surface, isolated as well as polymerized, possess the same redox potential. Consequently, the varying TOF for the SCR reaction must be due to factors other than changes in the redox activity of the surface vanadia species on alumina.

IR studies of the supported V_2O_5/Al_2O_3 catalysts reveal that increasing the surface vanadium oxide coverage simultaneously decreases the number of surface hydroxy groups and increases the number of Brønsted acid sites.[21] The surface hydroxy groups decrease monotonically with surface vanadium oxide coverage, but the Brønsted acid sites are only present at high vanadia coverages. These observations suggest that the SCR reaction probably requires a dual site to proceed efficiently: a redox site (provided by the surface vanadium oxide site) and a Brønsted acid site (only present at high surface vanadium oxide coverages). This is consistent with the observation that the 1 and 4% V oxide–alumina catalysts were not active for the SCR reaction since both samples possessed surface vanadium oxide redox sites, but no Brønsted acid sites.[21] The slight decrease in SCR activity of the 20% V_2O_5/Al_2O_3 catalyst is not clear at present since this catalyst did not possess microcrystalline V_2O_5 particles[20] and it appears to be related to the oxidation of ammonia, as stated above. Thus, these studies with changing surface vanadia coverage suggest that for the SCR reaction an efficient active centre contains dual sites: a surface redox site and an adjacent surface Brønsted acid site.

The above model of an efficient active centre for the SCR reaction is further supported by studies with the modified V_2O_5/Al_2O_3 catalysts. The addition of Mo and W oxides results in high surface coverages in the metal oxide overlayer on Al_2O_3, and significantly increases the surface Brønsted acid sites.[21,22] The addition of Mo oxide and W oxide to the 5% V_2O_5/Al_2O_3 catalysts results in significantly higher TOF of the SCR eaction, see Fig. 4. Note that the influence of Mo oxide is somewhat more pronounced than that of W oxide, because of the higher surface coverage of Mo rather than W (a factor of three on a molar basis).[19] Furthermore, note also that the alumina-supported Mo oxide and W oxide catalysts in the absence of vanadia are not active for the SCR reaction, because of their much lower redox potentials relative to the V_2O_5/Al_2O_3 catalyst.[28,29] Addition of Ni and Co oxides does not influence the surface Brønsted acid sites and no effect is observed on the TOF of the SCR reaction, see Fig. 6. However, the addition of Ni and Co oxides has a dramatic effect on the ratio of polymerized : isolated surface vanadium oxide species as revealed from Raman studies.[19] This demonstrates that the ratio of polymerized : isolated surface vanadium oxide species does not affect the TOF of the SCR reaction. Thus, the SCR reaction appears to be structure insensitive with regard to the specific surface vanadium oxide molecular structure.

The role of the surface hydroxy group density on the SCR reactivity is not absolutely clear from the present studies since consumption of surface hydroxy groups generally coincides with the appearance of the Brønsted acid sites. In the case of addition of Mo and W oxides, the surface hydroxy group density decreased significantly and the Brønsted acid site density increased simultaneously. For the Ni and Co oxide modifiers, the surface hydroxy group density was not significantly altered and no Brønsted acid sites are formed. Thus, these two effects, the increase in surface Brønsted acid sites and decrease in surface hydroxy group sites may always occur simultaneously and it may not be possible to determine independently the contribution of the surface hydroxy groups on the SCR reaction. A possible role of the surface hydroxy groups is their ability to assist in the chemisorption of water,[30] which may result in blocking adsorption sites for NO_x and NH_3 on the catalyst surface.

The present model for the SCR reaction indicates that an efficient active centre for the SCR reaction consists of a dual site composed of a surface redox site and an adjacent surface Brønsted acid site. This dual site model accounts for many of the reactivity patterns observed over the years for supported vanadium oxide catalysts. It explains the increase in TOF of the SCR reaction with surface vanadium oxide coverage,[4,26] which is due to an increase in the surface Brønsted acid sites at high surface coverages. Completely replacing vanadium oxide with other redox sites (Mo, Cr, W, *etc.*) usually decreases the TOF of the SCR reaction, because other surface metal oxides do not possess such a high surface redox potential as surface vanadium oxide[31] and do not usually possess as many surface Brønsted acid sites.[20] Additives that increase the surface density of Brønsted acid sites (W and Mo) will increase the TOF of the SCR reaction. Recent studies, involving W oxide and Nb oxide modifed V_2O_5/TiO_2 catalysts, suggest that the additives need not produce Brønsted acid sites (Nb oxide), but should be non-reducible.[32] Moisture inhibits the SCR reactivity even though the number of acid sites increases in the presence of moisture,[33] because water also coordinates to the surface redox sites that essentially blocks or competes with these sites for the reactants.[30] The specific oxide support is also known to influence the reactivity[34] and this occurs because the specific oxide support affects the reactivity of the surface redox site[29,35] in addition to the Brønsted acid site.[36]

Although an efficient active centre for the SCR reaction over supported V_2O_5/Al_2O_3 catalysts appear to involve a pair of sites: a surface redox site and an adjacent Brønsted acid site, the SCR reaction can apparently also occur over other types of active centres. In the case of V_2O_5/SiO_2 catalysts, the surface vanadia species are isolated,[37] do not possess Brønsted acid sites,[32] and are able to convert NO and NH_3 to N_2. However, the SCR reaction over V_2O_5/SiO_2 catalysts is not efficient, exhibits a TOF that is approximately a factor of three lower than V_2O_5/TiO_2 catalysts and is less selective.[32] Recent studies involving MnO_2/Al_2O_3 catalysts have shown very high SCR TOFs even though the catalysts do not possess Brønsted acid sites.[38] This suggests another mechanism may be operative for the SCR reaction over MnO_2/Al_2O_3 catalysts. For supported vanadia catalysts, however, the SCR reaction only occurs efficiently over an active centre possessing a pair of sites: a surface redox and an adjacent Brønsted acid site (ref. 14, 15 and this work).

The dual-site mechanism for the selective catalytic reduction of NO_x with NH_3 also accounts for the selectivity patterns observed in this study. At low temperatures, the SCR selectivities of the V_2O_5/Al_2O_3 catalysts and the W oxide and Mo oxide modified V_2O_5/Al_2O_3 catalysts are very high and not significantly influenced by surface coverage or the additive. At high temperatures, however, the differences in the SCR selectivities between these catalysts increased. The selectivities generally decreased with an increasing concentration of surface redox sites, which apears to be due to oxidation of ammonia to N_2O (high surface vanadia and molybdena coverage). High concentrations of surface tungsten oxide did not decrease the selectivity, because it is a surface Brønsted acid site that is very difficult to reduce. The addition of the surface Co oxide and Ni oxide modifiers to the V_2O_5/Al_2O_3 catalysts generally decreased the SCR selectivity, because these modifiers introduced surface redox sites and did not create any surface Brønsted acid sites. Thus, an efficient SCR catalyst must contain a balance between surface redox and surface Brønsted acid sites to be selective towards N_2 over a wide temperature range.

Conclusions

The selective catalytic reduction of NO with NH_3 was studied over alumina-supported vanadium oxide catalysts as a function of surface vanadium oxide coverage and additives (W, Mo, Ni and Co oxides). The SCR TOF and selectivity generally increased with surface vanadium oxide coverage at low temperatures. At high temperatures, the selectivity decreases owing to oxidation of ammonia to N_2O (especially for high vanadium oxide coverages). The SCR activity and selectivity of the supported V_2O_5/Al_2O_3 catalysts were also found to increase with the addition of surface W oxide and Mo oxide, but not with the addition of surface Ni oxide and Co oxide. These observations are consistent with an SCR reaction model that requires a dual site: a surface redox site and an adjacent surface Brønsted acid site. Increasing the surface vanadia coverage, as well as Mo and W oxide additives, introduces surface Brønsted acid sites, which are responsible for the enhanced reactivity and selectivity. Additves that do not introduce Brønsted acid sites, surface Ni oxide and Co oxide, do not enhance the SCR activity and selectivity. The surface Ni oxide and Co oxide additives also changed the ratio of isolated : polymerized surface vanadia species, but did not influence the SCR reactivity. This suggests that the SCR reaction is not sensitive to the specific surface vanadium oxide molecule structure.

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References

1 A Miyamoto, Y. Yamazaki, M. Inomata and Y. Murakami, *J. Phys. Chem.*, 1981, **85**, 2366.
2 F. J. J. G. Janssen, F. M. G. van den Kerkhof, H. Bosch and J. R. H. Ross, *J. Phys. Chem.*, 1987, **91**, 5921.
3 G. T. Went, L.-J. Leu and A. T. Bell, *J. Catal.*, 1992, **134**, 479.
4 G. T. Went, L.-J. Leu, R. R. Rosin and A. T. Bell, *J. Catal.*, 1992, **134**, 492.
5 B. E. Handy, M. Maciejewski and A. Baiker, *J. Catal.*, 1992, **134**, 75.
6 L. Lietti, J. Svachula, P. Forzatti, G. Busca, G. Ramis and F. Bregani, *Catal. Today*, 1993, **17**, 131.
7 G. Ramis, G. Busca, F. Bregani and P. Forzatti, *Appl. Catal.*, 1990, **64**, 259.
8 G. Ramis, G. Busca and F. Bregani, *Catal. Lett.*, 1993, **18**, 299.
9 N.-Y. Topsoe, *J. Catal.*, 1991, **128**, 499.
10 R. A. Rajadhyaksha and H. Knozinger, *Appl. Catal.*, 1989, **51**, 81.
11 J. P. Chen and R. T. Yang, *J. Catal.*, 1990, **125**, 411.
12 M. Gasior, J. Haber, T. Machej and T. Czeppe, *J. Mol. Catal.*, 1988, **43**, 359.
13 U. S. Ozkan, Y. Cai and M. Kumethekar, *Appl. Catal. A: General*, 1993, **96**, 365.
14 N.-Y. Topsoe, H. Topsoe and J. A. Dumesic, *J. Catal.*, 1995, **151**, 226.
15 N.-Y. Topsoe, J. A. Dumesic and H. Topsoe, *J. Catal.*, 1995, **151**, 241.
16 J. A. Odriozola, H. Heinemann, G. A. Somorjai, J. F. Garcia de la Banda and P. Pereira, *J. Catal.*, 1989, **119**, 71.
17 M. Takagi, T. Kawai, M. Soma, T. Onishi and K. Tamaru, *J. Catal.*, 1979, **57**, 528.
18 J. A. Dumesic, N.-Y. Topsoe, T. Slabiak, P. Morsing, B. S. Clausen, E. Tornqvist and H. Topsoe, in *Proceedings of the 10th International Congress on Catalysis*, Budapest, 1992, ed. L. Guczi, F. Solymosi and P. Tetenyi, Akademia Kiado, Budapest, 1993, p. 1325.
19 M. A. Vuurman, D. J. Stufkens, A. Oskam, G. Deo and I. E. Wachs, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3259.
20 M. A. Vuurman and I. E. Wach, *J. Phys. Chem.*, 1992, **96**, 5008.
21 A. M. Turek, I. E. Wachs and E. Decanio, *J. Phys. Chem.*, 1992, **96**, 5000.
22 A. M. Turek and I. E. Wachs, unpublished results.
23 P. M. Boorman, R. A. Kydd, Z. Sarbak and A. Smogyvari, *J. Catal.*, 1986, **96**, 15.
24 F. E. Kiviat and L. Petrakis, *J. Phys. Chem.*, 1973, **77**, 1232.
25 W. Wong and K. Nobe, *Ind. Eng. Chem. Prod. Res. Dev.*, 1992, **25**, 179.
26 A. Baiker, B. Handy, J. Nickl, M. Schraml-Marth and A. Wokaun, *Catal. Lett.*, 1992, **14**, 89.
27 G. Deo and I. E. Wachs, *J. Catal.*, 1994, **146**, 323.
28 G. Deo and I. E. Wachs, *J. Catal.*, 1994, **146**, 335.
29 I. E. Wachs, G. Deo, D. S. Kim, M. A. Vuurman and H. Hu, *J. Mol. Catal.*, 1993, **83**, 443.
30 J-M. Jehng, G. Deo, B. M. Weckhuysen and I. E. Wachs, *J. Mol. Catal.*, in the press.
31 L. Wang, PhD Thesis, University of Wisconsin, Milwaukee, USA, 1982.
32. I. E. Wachs, G. Deo, B. M. Weckhuysen, M. A. Vuurman, M. de Boer, A. Andreini and M. Amiridis, *J. Catal.*, in the press.
33 N. Y. Topsoe, T. Slabiak, B. S. Clausen, T. Z. Srnak and J. A. Dumesic, *J. Catal.*, 1992, **134**, 742.
34 H. Bosch and F. J. J. G. Janssen, *Catal. Today*, 1988, **2**, 369.
35 G. Deo and I. E. Wachs, *J. Catal.*, 1991, **129**, 307.
36 J. Datka, A. M. Turek, J. M. Jehng and I. E. Wachs, *J. Catal.*, 1992, **135**, 186.
37 N. Das, H. Eckert, H. Hu, I. E. Wachs, J. F. Walzer and F. Feher, *J. Phys. Chem.*, 1993, **97**, 8240.
38 F. Kapteijn, A. Dick van Langeveld, J. A. Moulijn, A. Andreini, M. A. Vuurman, A. M. Turek, J-M. Jehng, A. M. Turek and I. E. Wachs, *J. Catal.*, 1994, **150**, 94.

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