

Effect of Promoters on V_2O_5/SiO_2 Catalysts Active for the Selective Reduction of NO

ROBERT B. BJORKLUND,* SVEN JÄRÄS,† ULF ACKELID,*
C. U. INGEMAR ODENBRAND,‡ LARS A. H. ANDERSSON,‡ AND
JAN G. M. BRANDIN‡

**Laboratory of Applied Physics, Linköping University, S-581 83 Linköping, Sweden;*

†*Special Chemicals Division, Eka Nobel AB, S-445 01 Surte, Sweden; and*

‡*Department of Chemical Technology, Lund University, P.O. Box 124, S-221 00 Lund, Sweden*

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Vanadia catalysts supported on SiO_2 containing 3.5 wt% TiO_2 were promoted by Fe and Cu oxides. At 180°C the unpromoted and Fe-promoted catalysts exhibited the highest activities for the selective reduction of NO by NH_3 . The Fe-promoted catalyst maintained activity in the presence of SO_2 during 120 h on-stream. Electrical conductance and mass spectrometric measurements indicated that at 200°C the only reactions occurring were the formation of N_2 and H_2O from both the $NO + NH_3$ reaction and the self-reaction of NH_3 . Additional reactions forming NO and N_2O from NH_3 were observed at 350°C. Poisoning of the catalysts by SO_2 was followed by electrical conductance as a decrease in the V(IV) concentration formed from the $NO + NH_3$ reaction.

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INTRODUCTION

Although silica is a widely used support in catalysis, its utility for supporting vanadia is limited by the fact that the interaction of vanadia species with silica is weak in catalysts prepared by impregnation (1, 2). Vanadia supported on silica tends to agglomerate when exposed to elevated temperatures leading to a decrease in active surface area and catalytic activity. Some methods proposed to overcome this problem include adding titania to the silica matrix to strengthen the bonding of the vanadia to the support (3) and immobilizing vanadia in the silica matrix by using a mixed gel preparation (4). We report here a study of V_2O_5/SiO_2 catalysts where the silica contains 3.5 wt% TiO_2 (by impregnation) in order to stabilize the vanadia on the support. The catalysts exhibit high activity for the selective catalytic reduction (SCR) of nitric oxides by ammonia at temperatures less than 200°C. In a previous study of V_2O_5/SiO_2-TiO_2 cata-

lysts ((Si/Ti = 1), designated VSiTi) we showed that electrical conductance measurements could be used to describe the dispersion of vanadia on the support (5). It was also shown that the gases involved in SCR, NH_3 , NO, and O_2 affected the catalyst conductance and this information was used to describe the reaction mechanism with regard to the concentration of V(IV) ions on the catalyst surface. In the present study, we use conductance measurements to compare the mechanism for SCR at 350 and 200°C, to study the effect of promoters on the adsorption of NO and NH_3 on the catalysts, and to observe the effect of SO_2 on the NO- NH_3 reaction.

EXPERIMENTAL

The silica carrier used had a surface area of 300 m^2/g and average particle size of about 45 μm . Titania to a concentration of 3.5 wt% was deposited on the support by adding an ammonia solution to a $TiOSO_4$ solution. After the carrier was washed to

remove sulfate ion, it was impregnated with aqueous solutions of NH_4VO_3 in oxalic acid to obtain a concentration of 15.5 wt% V_2O_5 . For the catalysts containing additional promoters, the appropriate salts were added to the NH_4VO_3 solutions to obtain 0.6 wt% of Cu or Fe oxides. Finally the catalysts were dried and then heated in air for 1 h at 450°C. Surface areas for the finished catalysts were 180–200 m^2/g .

Catalysts were characterized by XRD and by FTIR using the KBr method on a Bruker 1FS 113 spectrometer. Catalytic activities were determined in a conventional down-flow fixed-bed reactor similar to the system described in Ref. (6). The following experimental conditions were used: NO 600 ppm, NH_3 600 ppm, O_2 7%, and the balance N_2 . The space velocity was 2400 h^{-1} and the reaction temperature 180°C.

Electrical conductance measurements were made in a stainless-steel cell which we have described previously (7). Preliminary measurements indicated that it was necessary to partially sinter the catalysts in order to obtain measurable conductances. Catalyst powders were first ground for 10 min in an agate ball mill and then pressed into thin tablets at 10 ton pressure for 16 h. The tablets were placed in an oven at 530°C for 16 h. Gold contacts were evaporated onto both sides of small tablets (about $0.2 \times 0.2 \times 0.03$ cm, weight about 5 mg) which were then positioned in the measurement cell two at a time and heated to 350°C in flowing 10% O_2 in Ar and held there for 16 h. Gases used were Ar, O_2 , 21% O_2/Ar , 2600 ppm NO/Ar, and 2700 ppm NH_3/Ar from Alfax AB. Several mass flow regulators from Bronkhorst High-Tech B.V. were used to vary the concentration of the different gases at a total constant flow through the cell of 100 ml/min. Switching valves from Bürkert were used to introduce and take away gases from the carrier flow. All flow regulators and valves could be controlled manually or by computer. Conductance measurements were made at a constant dc potential of 1 V.

Analysis of the calcined catalysts by XRD

TABLE 1
Conversion of NO at 180°C

Catalyst ^a	Time on stream		
	20 h	40 h	200 h
V . . .	96	95	95
V Cu	75	74	—
V Fe	92	93	97

^a 15.5% $\text{V}_2\text{O}_5/\text{SiO}_2$ (3.5% TiO_2) with Cu or Fe promoters.

showed no peaks which could be attributed to a crystalline vanadia phase being present. This was confirmed by the absence of a band at 1020 cm^{-1} in the infrared spectra which has previously been assigned to crystalline $\text{V} = \text{O}$ (8).

RESULTS AND DISCUSSION

Since the goal of this work was to develop a catalyst for 90% NO conversion at temperatures lower than 200°C, the catalysts were tested in an integral mode. Table 1 lists total NO conversions obtained over the different catalysts during a test period of 200 h. Highest activities were obtained over the unpromoted and Fe-promoted catalysts. For VFe, the activity was observed to increase during the 200-h test period. VCu had the lowest activity.

Electrical conductance measurements were made on tablets which had been sintered at 530°C. XRD measurements showed evidence for a crystalline vanadia phase being present after sintering. The surface areas for the catalysts after sintering were about 45 m^2/g . Table 2 shows conductances for the catalysts at 200 and 350°C in a gas stream of 1.5% O_2/Ar . Results for a 15% $\text{V}_2\text{O}_5/\text{SiO}_2\text{-TiO}_2$ catalyst (15 VSiTi) which we have described earlier (5) is included for comparison. There were no significant differences in conductances for the silica-supported catalysts. The VSiTi catalyst exhibited considerably lower conductance than the others since it had not undergone any sintering treatment.

TABLE 2
Conductance, G , and Conductance Changes, ΔG , in the Presence of Gases

	Catalyst ^a	G (μS) ^b	$\Delta G(\text{NO})$	$\Delta G(\text{NH}_3)$	$\Delta G(\text{NO} + \text{NH}_3)$
			G	G	G
350°C	V	2.5	0.2	3.1	2.9
	V Cu	2.3	0.5	7.0	7.1
	V Fe	1.1	0.0	4.0	4.6
	15 VSiTi ^c	0.05	0.2	3.3	2.7
200°C	V	0.5	0.2	0.4	4.7
	V Cu	0.7	0.0	1.0	5.1
	V Fe	9.3	0.0	0.3	3.3
	15 VSiTi ^c	0.5 ^d	0.0	1.0	6.0

^a 15.5% $\text{V}_2\text{O}_5/\text{SiO}_2$ (3.5% TiO_2) with Cu or Fe promoter.

^b MicroSiemens = 10^{-6} ohm⁻¹.

^c 15% $\text{V}_2\text{O}_5/\text{SiO}_2\text{-TiO}_2$.

^d NanoSiemens = 10^{-9} ohm⁻¹.

V_2O_5 exhibits n -type semiconductor properties due to the hopping of electrons between vanadium ions in different valence states, $\sigma \propto \text{V(IV)}/[\text{V(IV)} + \text{V(V)}]$ (9). For vanadia dispersed on a support, the distance between V ions and the physical contact between catalyst grains play an important role in determining the conductance. We have previously given a more complete description of the conductance mechanism in supported vanadia catalysts based on previous work with vanadia-containing glasses (5). This description could possibly be extended and make use of glasses containing double redox pairs (10), such as Fe and V, as models for the promoted vanadia catalysts. However, since the concentrations of promoter ions were fairly low in the present study, it was our goal to test whether conductance measurements could be used to observe small effects caused by the presence of promoter ions during gas adsorption.

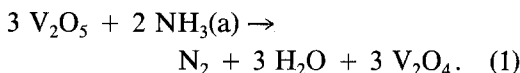
Catalysts were exposed at 350 or 200°C to 300 ppm NO, 300 ppm NH_3 , or 300 ppm NO + 300 ppm NH_3 in a carrier gas of 1.5% O_2/Ar . Table 2 shows the conductance increases observed, ΔG , after 3-h exposure to the different gases relative to the conduc-

tance, G , in the carrier gas. All conductance increases were reversible when the different gases were removed from the carrier gas. As shown in Table 2, small increases in conductance were observed during NO exposure for catalysts V and VCu at 350°C and for catalyst V at 200°C. Larger increases were observed for all catalysts during NH_3 and NO + NH_3 exposures. It should be noted that catalysts V and 15 VSiTi, which each had a vanadia content of 15%, had nearly identical $\Delta G/G$ values at 350°C despite their different support compositions.

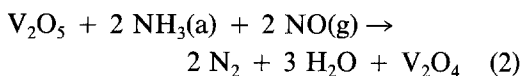
We have previously described how the conductance increases observed during NO and NH_3 exposures of VSiTi catalysts were the result of reduction of vanadia (5). From the results in Table 2, it can be concluded that promotion with Cu enhances the reducing effect of NH_3 relative to the unpromoted and Fe-promoted catalysts. It has been shown that Cu-containing catalysts such as CuY are active for the NO- NH_3 reaction by a template mechanism where the Cu cation coordinates reacting molecules as ligands in its coordination sphere (11). Promotion by Cu ions can thus affect the adsorption of gases on the vanadia catalysts, but it is the subsequent reduction of vanadia which is

detected by the conductance measurements.

It was found that the following sequence of gases: (a) 300 ppm NH₃, (b) 300 ppm NH₃ + 300 ppm NO, (c) 300 ppm NO, O₂ removed, (d) NO removed, O₂ returned in a carrier gas of 1.5% O₂/Ar provided information about changes in the catalysts during SCR. During segment (a), the conductance increased for all catalysts, which is in agreement with the mechanism proposed by Janssen *et al.* (12) for the adsorption of NH₃ alone on vanadia catalysts:



After the V(IV) concentration has increased during segment (a), it is expected to decrease during (b) when NO is introduced into the gas stream according to the reaction (12)



since fewer V(IV) ions are produced per adsorbed NH₃ in (2) than in (1). It is assumed that O₂, and possibly NO, continuously oxidizes V(IV) to V(V). A small decrease in conductance during segment (b) was observed at 350°C for catalyst V but increases were observed for catalysts VCu and VFe (Fig. 1, Table 2). This is in contrast to the behavior of VSiTi catalysts where the same sequence of gases yielded conductance decreases during (b) (5). For these catalysts with vanadia supported on a coprecipitated SiO₂-TiO₂ carrier the NO-NH₃ reaction was limited to reactions (1) and (2) at 350°C (6). The catalysts VCu and VFe supported on TiO₂ containing silica were not as selective at 350°C. The further increase in conductance on going from (a) to (b) in Fig. 1 indicates that the reactions occurring on the surface when NO is added to the NH₃-reduced catalysts are additive, i.e., the self-reaction of NH₃ does not decrease when NO is introduced. The number of V(IV) ions produced during segment (b) in Fig. 1 is thus

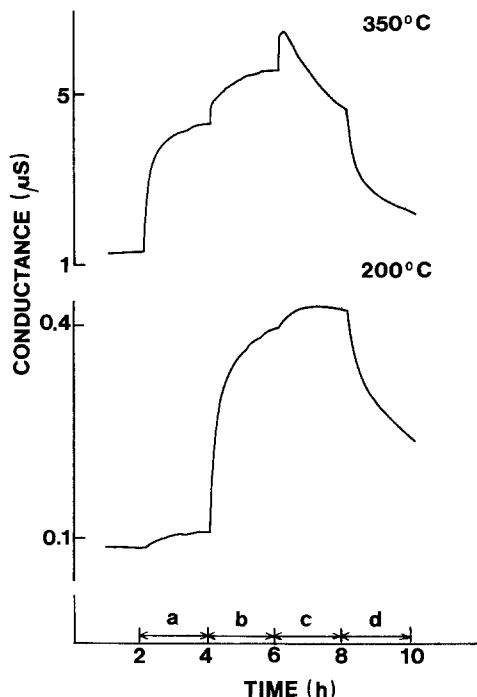


FIG. 1. Conductance of the VFe catalyst at 350 and 200°C in a gas flow of 1.5% O₂/Ar with the following gases added for 2-h periods: (a) 300 ppm NH₃, (b) 300 ppm NH₃, 300 ppm NO, (c) 300 ppm NO, O₂ removed, (d) O₂ returned, NO removed.

the sum of the self-reaction from segment (a) plus new V(IV) ions produced by reaction (2). In this system the NH₃ self-reaction may result in other products, such as NO, in addition to N₂ as recently described by Vogt *et al.* (13).

To test this hypothesis, mass spectrometric measurements were made of the products desorbing from the catalysts during conductance measurements. This was done by introducing the gases into the spectrometer through a capillary leak tube positioned near the catalyst sample in a system similar to that described in Ref. (14). It was not possible to quantify the ion currents observed at the different masses observed in terms of NO conversion. However, it was clear that at 350°C the catalysts exhibiting an increase in conductance upon going from segment (a) to segment (b) (see columns for

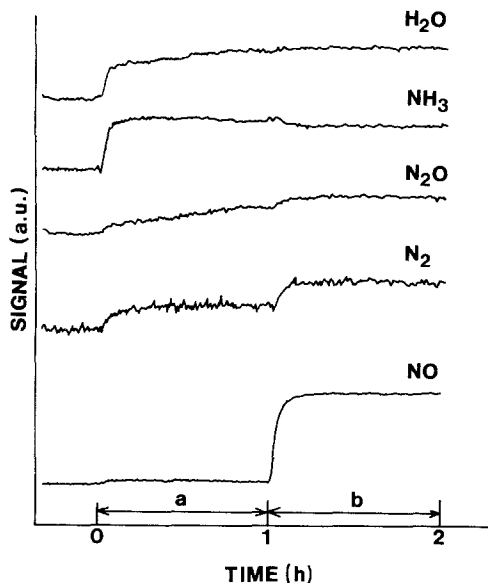


FIG. 2. Mass spectrometer signal for masses 18 (H_2O), 16 (NH_3), 44 (N_2O), 28 (N_2), and 30 (NO) during exposure of catalyst VFe at 350°C to (a) 300 ppm NH_3 and (b) 300 ppm NH_3 + 300 ppm NO in 1.5% O_2/Ar carrier gas. Note that mass 16 also contains a contribution from O_2 . Although the O_2 concentration in the gas stream entering the reactor was constant during the measurements, the adsorption of NH_3 can displace O_2 from the catalyst surface thereby increasing the O_2 concentration near the capillary inlet.

NH_3 and $\text{NO} + \text{NH}_3$ in Table 2) converted NH_3 during segment (a) to several products. This is shown in Fig. 2 for catalyst VFe, where NH_3 was converted to N_2 , N_2O , and NO during segment (a). Catalysts exhibiting decreases in conductance upon going from segment (a) to segment (b) were found to produce only N_2 and H_2O at 350°C during segment (a).

Exposure of the catalysts to NH_3 at 200°C resulted in small increases in conductance (Table 2, Fig. 1, segment (a)). Since reaction (1) requires a certain lateral mobility in order for adsorbed NH_3 to produce N_2 and V(IV) ions it can be concluded that the relatively low $\Delta G(\text{NH}_3)$ values at 200°C indicated that NH_3 was strongly adsorbed on the V and VFe catalysts at this temperature. When NO was added to the gas flow during segment (b) the conductances increased for all

catalysts indicating that the reaction between adsorbed NH_3 and gaseous NO described in reaction (2) was occurring. Since activity for NO reduction is related to availability of adsorbed NH_3 to react with NO , one possible reason for the lower activity observed for the VCu catalyst could be the higher activity for reaction (1) exhibited by this catalyst as compared to the V and VFe catalysts.

A test was made in a down-flow reactor to compare the activity at 200°C of the Fe catalyst before and after sintering. The space velocity was 53855 h^{-1} and gas concentrations were the same as for segment (b) in Fig. 1. After 1 h on stream, the total conversion of NO over the catalyst which had been sintered was 8% as compared to 33% for the nonsintered catalyst. Surface

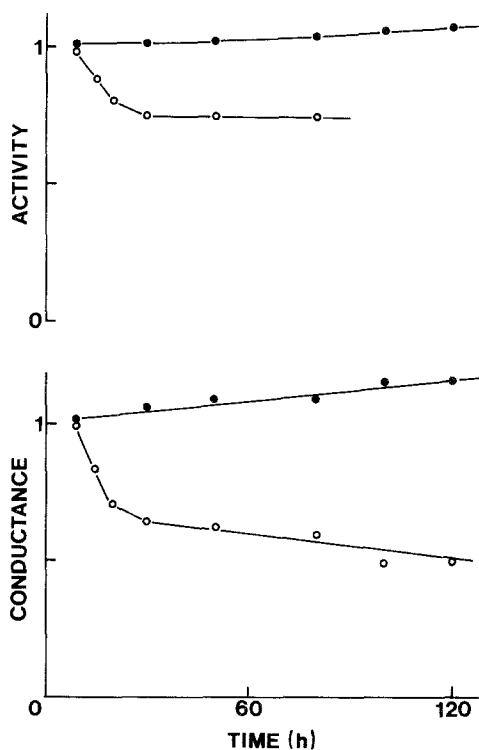


FIG. 3. Activities and $\Delta G(\text{NO} + \text{NH}_3)/G$ values for the VFe (●) and VCu (○) catalysts normalized to the values when 500-ppm SO_2 was added to the $\text{NO} + \text{NH}_3$ containing gas flow over the catalysts at $t = 9 \text{ h}$.

area was 180 m²/g before sintering and 45 m²/g afterward. Mass spectrometric measurements on catalysts during conductance measurements indicated that only N₂ and H₂O were formed during both segments (a) and (b). Thus selectivities for reactions (1) and (2) were high at 200°C. Additional reactions were possible at 350°C, as shown in Fig. 2, where the crystalline phase introduced by the sintering treatment could influence the product distribution (15). Based on these results, we conclude that the catalyst sintering lowered the surface area and activity for NO conversion at 200°C by a factor of 4. The crystalline vanadia phase produced by the sintering affected selectivity at 350°C. The sintering also altered the grain boundaries in the catalysts which are an important factor for determining electrical conductance in pressed powder samples (16).

Segment (c) in Fig. 1 shows the result of removing NH₃ and O₂ from the gas flow. The conductance decrease observed at 350°C indicates that NO alone can oxidize V(IV) ions in agreement with previous reports (12). At 200°C the reoxidation of the reduced catalysts by NO alone was very slow. In segment (d) of Fig. 1, O₂ is returned to the gas flow and a faster decrease in conductance occurs relative to the decrease in segment (c) at both 200 and 350°C.

The influence of SO₂ on the NO–NH₃ reaction was studied by introducing 500 ppm SO₂ into the gas stream through the reactor under the conditions described above. Figure 3 shows the activities normalized to the activity when SO₂ was first introduced for the VFe and VCu catalysts during 120 h on-stream. Activity for the VFe catalyst increased slightly during the on-stream period while activity for the VCu catalyst decreased rapidly after SO₂ was introduced. The unpromoted V catalyst maintained the original activity for about 20 h after SO₂ introduction, followed by an activity decrease.

In order to determine whether electrical measurements could detect the effect of SO₂

on the catalysts, a similar test was made by introducing SO₂ into the gas flow through the conductance cell. Figure 3 shows $\Delta G(\text{NO} + \text{NH}_3)/G$ values normalized to the values when SO₂ was introduced for the VFe and VCu catalysts. In agreement with the activity results, the normalized ΔG values increased for the VFe catalyst during the test, but decreased for the VCu catalyst. Infrared measurements failed to show the presence of any sulfur-containing compounds on either catalyst after the test. The conductance decrease for the VCu catalyst shown in Fig. 3 is therefore not the result of accumulation of sulfur on the catalyst but simply reflects the decrease in activity for the catalyst shown in the upper curves of Fig. 3 which caused a lowering of the V(IV) ion concentration according to reaction (2). Electrical conductance measurements can thus be used to observe the effect of SO₂ on the SCR reaction based on the decrease in V(IV) ion concentration when the catalyst deactivates. This is a somewhat different effect from what we have previously observed for the deactivation of supported Ni and Co catalysts by H₂S during the CO + H₂ reaction where accumulation of S on the catalysts led to a conductance increase (7).

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