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Preparation and Performance of a Silica-Supported V_2O_5 on TiO_2 Catalyst for the Selective Reduction of NO with NH_3

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A preparation technique is described in which a layer of TiO_2 completely covering the support can be deposited onto silica. Onto the support thus modified, V_2O_5 can be applied to result in a catalyst suitable for the selective catalytic reduction (SCR) of NO_x with NH_3. To obtain the required selectivity in the reduction of NO_x the silica surface must be completely covered with TiO_2. Catalysts prepared according to the above procedure exhibit good activity and a completely selective reduction of NO to N_2 at temperatures to 350°C. At higher temperatures selective oxidation of the NH_3 to N_2 is observed.

INTRODUCTION

One of the options for postcombustion control of NO_x emission is the selective catalytic reduction of NO_x (SCR) (*1*). In contrast to all other reducing agents, such as H_2, CO, and CH_4, only ammonia has been found to be selective in the reduction of NO_x in gas flows containing an excess of oxygen.

From the catalyst systems investigated for SCR (*2–6*), WO_3 on TiO_2 (*5*) and especially V_2O_5 on TiO_2 (*6*) have proved to be promising. Also, the V_2O_5 on SiO_2 catalyst we have developed (*7, 8*) exhibits an attractive activity in SCR, although its high selectivity decreases somewhat at temperatures above 300°C. Most procedures to prepare V_2O_5 on TiO_2 start from TiO_2 as the support onto which pentavalent vanadium oxide is deposited by impregnation or adsorption. Impregnation agents like ammonium metavanadate (*9, 10*) and vanadium or vanadyl chlorides (*11, 12*) have been described. Using the adsorption method (*13*), vanadyl acetylacetonate (*14, 15*) and vanadyl triisobutoxide have been reported (*16*).

Opinion about the use of bulk TiO_2 as a support is not unequivocally favorable. Commercial TiO_2 is expensive, difficult to process to mechanically strong bodies, and has a relatively low specific surface area. Since multimolecular adsorption of a precursor of the active component generally does not occur, an adsorption procedure usually leads to a low loading. Impregnation, especially at higher loadings, results mainly in inhomogeneous distribution of the active component, which exhibits a broad particle size distribution.

To avoid these deficiencies, some investigators have proposed the application of silica as a support for the active components. Shikada *et al.* (*17*) and Odenbrand *et al.* (*18*) thus prepared silica-based catalysts by first producing a SiO_2–TiO_2 coprecipitate by homogeneously raising the pH of an acidified solution of Na_2SiO_3 and $TiCl_4$ by means of hydrolysis of urea. Shikada *et al.* (*19*) also proposed a procedure in which a silica support was consecutively impregnated with a solution of titanic sulfate and a solution of vanadium oxide in oxalic acid. However, both procedures suffer from the disadvantages of coprecipitation and impregnation. The porous structure is difficult

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to control with coprecipitation, and the distribution of the active components is not homogeneous with impregnation.

To produce better titania–vanadia catalysts for the SCR we therefore developed a preparation technique, based on the deposition–precipitation procedure described by van Dillen *et al.* (*20*) and Geus (*21*). In this procedure a cheap support of a high, thermostable surface area and good mechanical properties with a titania surface is prepared by the application of TiO_2 onto silica. In a previous paper the preparation of a vanadia on silica catalyst was described (*7*). In that paper it was shown that vanadium(III) ions dissolved in water are much more basic than vanadium(V) ions. As a result the V(III) ions exhibit a stronger interaction with the Brønsted acid sites of the silica surface. The V_2O_3 deposited onto the silica was subsequently oxidized to V_2O_5. The thus obtained V_2O_5 on SiO_2 catalyst showed a high activity in the selective reduction of NO with NH_3 in the presence of oxygen.

In the present work attention is focused on the improvement of this V_2O_5 on silica catalyst by introduction of a layer of titanium oxide between the silica support and the vanadium oxide moieties. Addition of a uniform interlayer of titania was achieved by the subsequent precipitation of hydrated titanium(III) and vanadium(III) oxides onto silica. Both deposition–precipitations were performed from a homogeneous solution of titanium(III) and vanadium(III), respectively.

After drying and calcination, the loaded carrier was characterized with temperature-programmed reduction (TPR), BET surface area measurement (N_2, 77 K), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), and high-temperature X-ray diffraction (HTXRD). The interaction of the different oxidic phases in the catalyst was assessed by measurement of the kinetic parameters in the oxidation of carbon monoxide. The catalytic performance of the V_2O_5/TiO_2 on SiO_2 catalyst was measured in the SCR of NO with NH_3. Selectivity data were obtained using labeled molecules such as ^{15}NO and $^{15}NH_3$.

EXPERIMENTAL

Preparation of Catalysts

An aqueous solution of NH_4VO_3 was electrochemically reduced according to the procedure described before (*7*). A suitable amount of this solution was added to an acidified suspension (pH about 0.5) of the support material, Degussa Aerosil 200V (BET surface area 187 $m^2\ g^{-1}$). The suspension was present in a precipitation vessel equipped with baffles to ensure a good homogeneity of the suspension during agitation. To the suspension, an appropriate amount of a solution of $TiCl_3$ (Merck, 15% $TiCl_3$ in HCl) was added.

The pH of the suspension was raised homogeneously by the slow injection of a NaOH solution (injection rate 0.1 mmol $OH^-\ min^{-1}$) into the vigorously agitated solution. At a pH of about 8, injection was stopped. The catalytic properties, to be dealt with later, will show that this preparation procedure leads to the deposition of the hydrated titanium(III) oxide first, and subsequently to the decomposition of the hydrated vanadium(III) oxide.

The precipitate was collected, washed thoroughly with deionized water, and subsequently dried at 120°C in air for 24 h. The dried product was finally calcined at 350°C in air for at least 24 h.

Four samples of various compositions of vanadium and titanium were prepared using this procedure. The vanadium content of the samples was between 5 and 10 wt%. The titania loading was varied to provide a range of coverages of the surface of the silica support. One catalyst was prepared with a TiO_2 loading far above that required for monolayer coverage, a second catalyst was prepared with a TiO_2 loading just sufficient to cover the silica surface with a monolayer, and a third sample was prepared with a TiO_2 loading far below the amount corresponding to a monolayer.

Monolayer coverage is defined here as complete coverage of the silica surface with a layer of TiO_2 with a thickness of 0.38 nm, the largest cell axis for rutile. The catalytic properties of the V_2O_5 on SiO_2 catalyst without TiO_2 described before (*7*) was also tested. A V_2O_5 on TiO_2 catalyst prepared by the so-called monolayer adsorption of vanadyl acetylacetonate (*6*) was used as a reference.

Characterization

The elemental composition of the catalyst samples was established using atomic absorption spectrometry (AAS). Samples were destroyed following the procedure described in our previous paper (*22*). The V_2O_5 content was also determined with TPR, yielding composition in agreement with the AAS results. BET surface areas were measured on a Carlo Erba Sorptomatic 1800. XRD spectra of the samples were recorded in order to establish the particle size distribution and to assess the titania modification (anatase or rutile). A high-temperature Guinier camera was used at temperatures 800°C in order to investigate phase transitions. The use of DRIFT on a Perkin–Elmer 1800 FTIR in order to establish the surface coverage was described previously (*22*). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed with a Philips EM 420 microscope. The sample preparation techniques have been described elsewhere (*22*).

The kinetic parameters of the catalysts in the oxidation of carbon monoxide were used to establish whether the active component is supported by either TiO_2 or SiO_2. The activation energies of supported vanadium oxide depend on the supporting material (*22*).

The activity for the CO oxidation was tested in a fully automated microreactor setup described previously (*22*). Approximately 500 mg of catalyst was used in these experiments. CO and O_2 partial pressures were 1 kPa, balanced with helium. Space velocities were typically of the order of 3000 h^{-1}.

NO Reduction Activity

${}^{15}NH_3$ and ${}^{15}NO$ were obtained from MSD Isotopes (Canada) and were used without further purification. Gas mixtures of these labeled compounds with helium to 10 MPa with concentrations of 2000–3000 ppm were prepared by conventional static gravimetric methods.

Gas mixtures of 2000 ppm ${}^{14}NH_3$ in helium, 2000 ppm ${}^{14}NO$ in helium, and 25% O_2 in helium were purchased from Air Products (Belgium) and were used without further purification.

A steady-state plug–flow reactor, described in detail elsewhere (*4*), was used to determine the activity of the catalysts. All experiments were carried out with about 50 mg catalyst, particle size 0.25–0.50 mm, with a total flow of 100 cm^3 min^{-1} of a gas mixture of 500 ppm of NO, 500 ppm of NH_3, and 2 vol% O_2. Helium was used as balance, and the space velocity was 60,000 h^{-1}. The reactor was coupled via an adjustable leak valve to a sector mass spectrometer. Another apparatus was used to study the influence of SO_2 on the reduction reaction over the catalyst C (see Table 1 for nomenclature). This was done in a conventional fixed bed reactor (space velocity 70,000 h^{-1}). A vertical quartz tube (inner diameter 4.4 mm) containing about 400 mg catalyst was heated to 400°C. The flow through the reactor was 1 liter (STP) min^{-1}. The gases were heated before mixing to 200°C in order to avoid the formation of ammonium sulfate and ammonium hydrogen sulfate. Mixing of the gases was established with the aid of mass flow controllers. The inlet and outlet gas compositions were measured using a quadrupole mass spectrometer.

RESULTS

Characterization

Some of the characteristics of the samples are presented in Table 1. XRD mea-

TABLE 1

Characteristics of the Catalyst Samples

Sample	V_2O_5 AAS (wt%)	TiO_2 AAS (wt%)	V_2O_5 TPR (a.u.)	BET surface area (m^2 g^{-1})
A1 (SiO_2)	0	0	0	187
A2 (TiO_2/SiO_2)	0	33	0	197
B	4.5	24	42	240
C	6	33	52	235
D	9.5	6	95	141
E	44	0	—	80
F[a]	3.6	96.4	17	45

[a] Prepared by monolayer adsorption of vanadyl acetylacetonate onto TiO_2 (68% anatase, 32% rutile).

surements performed on samples B and D show that at titania loadings at or below the theoretical monolayer coverage no crystalline phases appear after calcining at 350°C. Upon heating of samples B and D, low-intensity peaks of anatase are found to appear above temperatures of about 650°C. Neither rutile lines nor V_2O_5 lines were found in the XRD patterns upon heating to 800°C. The sample C, containing 33 wt% TiO_2, shows different behavior. Already at the starting temperature the most intense anatase line at $d = 3.52$ Å can be observed, albeit very weak, and very broad. When heating the sample, the complete anatase pattern emerges at about 615°C. At about 690°C, lines belonging to rutile are found. The drop in intensity in the anatase pattern, and the simultaneous rise in the rutile pattern indicate a phase transition of the anatase into the rutile modification. Again, however, no V_2O_5 lines are observed in the temperature range 20 to 800°C.

In the DRIFT spectra of samples B and C no peak was observed at 3750 cm^{-1} (the band at this wavenumber is assigned to the O–H stretching vibration of silica), indicating a complete coverage of the silica surface. This observation was supported by the TEM images. From the micrographs shown in Fig. 1, it is obvious that the TiO_2 and V_2O_5 are well spread over the support. Furthermore, at higher Ti loadings (samples B and C), no $\nu_{O\text{-}H}$ of silica was observed.

Table 2 lists the kinetic parameters for the CO oxidation reaction for the samples used in this study. These results will be used to establish whether or not the silica surface is completely covered by titania.

NO_x Reduction

The results of the activity measurements of the catalysts of Table 1 are shown in Figs. 2 and 3. Catalyst C (Fig. 2) shows a very high activity and a very high selectivity at 400°C with respect to nitrogen formation. The behavior of catalyst D (Fig. 3) differs from that of catalyst C. The ratios of the amounts of V_2O_5 and TiO_2 in catalysts B and C are equal but the total amount of V_2O_5 and TiO_2 in catalyst C is less. Nevertheless, the catalysts B and C show the same conversion profiles. Comparing Figs. 2 and 3, it can be concluded that the selectivity remains constant up to 300°C, although the conversion of NO over catalyst D is about one-half of the conversion over catalyst (B and C) at 300°C.

The activity presented in Fig. 3 resembles that found for catalyst E, which was dealt with in a previous paper (*7*). The behavior of catalyst D in the SCR is comparable with that of the V_2O_5 on SiO_2 catalyst. Above 300°C the selectivity of the reaction changes over catalyst D and ammonia is oxidized into N_2, NO, and N_2O. In Table 3 the

TABLE 2

Kinetic Parameters for CO Oxidation

Catalyst	E_a (kJ mol^{-1})	k_0 (s^{-1} m^{-2} V_2O_5)
B	71 ± 2	2×10^3
C	73 ± 2	4×10^3
D	86 ± 2	3×10^3
E	92 ± 4	3×10^3
F	71 ± 2	5×10^3

Note. $300°C < T < 500°C$, 1% CO and 1% O_2 in He, space velocity 3000 h^{-1}.

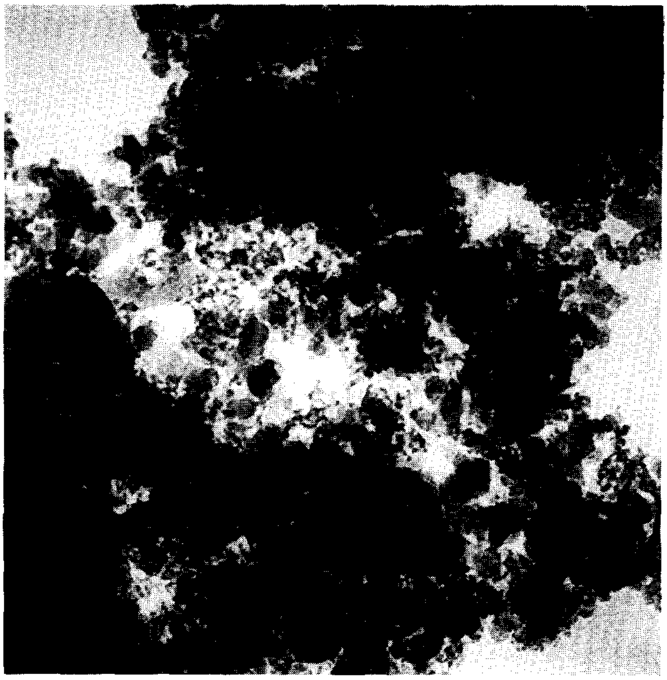

FIG. 1. Transmission electron micrograph of catalyst C, after oxidation at 350°C. Magnification 120,000×. The grayish background particles are the support material, SiO_2; the smaller dots are the oxidic material deposits. No distinction can be made between V_2O_5 and TiO_2 particles. Some larger scaly aggregates can be observed and are supposed to be TiO_2.

catalysts are compared according to their selectivities. It can be seen that by increasing the amount of titania in the catalyst, the selectivity of the ammonia oxidation changes to nitrogen formation at 400°C. The numbers 1–5 in Table 3 refer to the

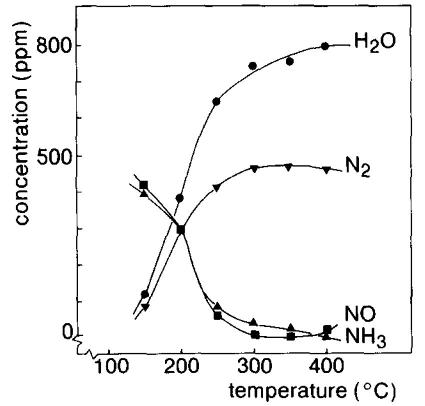

FIG. 2. The activity of catalyst C in the reaction of NO, NH_3, and O_2. The catalyst was previously calcined in air at 350°C. Initial concentrations: $[NO]_i$ = $[NH_3]_i$ = 500 ppm, $[O_2]_i$ = 2%, balance helium. Space velocity: 60,000 h^{-1}.

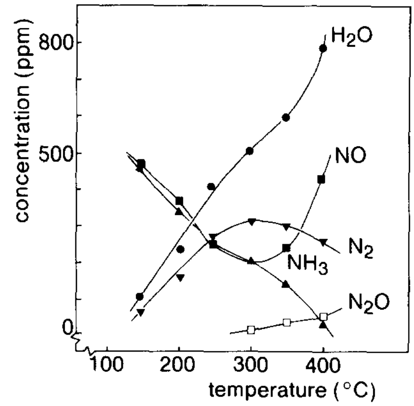

FIG. 3. The activity of catalyst D in the reaction of NO, NH_3, and O_2. The catalyst was previously calcined in air at 350°C. Initial concentrations: $[NO]_i$ = $[NH_3]_i$ = 500 ppm, $[O_2]_i$ = 2%, balance helium. Space velocity: 60,000 h^{-1}.

TABLE 3

Relative Occurrence of ^{14}N Atoms of NH_3 in the Reaction Products of the Five Reactions Mentioned in the Text, Using ^{15}NO and $^{14}NH_3$ in the Presence of Oxygen

Catalyst (w/w, %) $V_2O_5/TiO_2/SiO_2$	Temp. (°C)	NO reduction		NH₃ oxidation		
		1 N_2	2 N_2O	3 NO	4 N_2O	5 N_2
E	400	0.35	0.31	0.14	0.05	0.15
44/—/56	300	1.00	0	0	0	0
D	400	0.31	0.02	0.21	0.04	0.37
9.5/5/85.5	300	0.95	0	0	0	0.05
B,C	400	0.72	0.01	0	0.01	0.26
6/33/61	300	0.97	0	0	0	0.03
F	400	0.81	0.09	0	0	0.10
3.6/96.4/—						

Note. The relative occurrence is defined as the ratio of the concentration of ^{14}N atoms from ammonia in one of the products to the sum of the ^{14}N atoms in the products. The relative occurrence of reaction 5, for instance, thus becomes $2[^{14}N_2]/[^{14}N^{15}N] + [^{14}N^{15}NO] + [^{14}NO] + 2[^{14}N_2O] + 2[^{14}N_2]$. When a mixture of $^{15}NH_3$ and ^{14}NO was used (catalyst E) the relative occurrence of ^{15}N from ammonia is presented.

overall reactions

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (1)$$

$$4\,NO + 4\,NH_3 + 3\,O_2 \rightarrow 4\,N_2O + 6\,H_2O \qquad (2)$$

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \qquad (3)$$

$$2\,NH_3 + 2\,O_2 \rightarrow N_2O + 3\,H_2O \qquad (4)$$

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \qquad (5)$$

The reactions were established by the use of the reaction mixtures NO, $^{15}NH_3$, and O_2 and ^{15}NO, NH_3, and O_2 for the catalysts V_2O_5 on SiO_2 and V_2O_5/TiO_2 on SiO_2, respectively.

The catalysts in Table 3 can be divided into two groups with respect to their conversion of NO into N_2. In contrast with the results obtained with catalysts C and F, catalysts D and E produce large amounts of the oxidation products of ammonia. The activity and selectivity of these catalysts appear to rise with increasing amounts of TiO_2 in the catalyst.

The values found for catalyst B, not explicitly mentioned, closely resemble those found for catalyst C. Finally, the catalytic performance of catalyst C remains constant in the presence of NO, NH_3, O_2, and SO_2 for up to 170 h.

DISCUSSION

The behavior of catalysts B and C in the high-temperature XRD experiments appears to be in reasonable agreement with results reported by other authors. Bond *et al.* (*23*) reported on a phase transition of TiO_2 (anatase) in the presence of V_2O_5 to rutile. Other reports (*24–26*) mention a loss of oxygen in V_2O_5 mixed with TiO_2 (anatase). Both procedures appear to be activated by the remarkable fit of the crystal lattices of V_2O_5 and TiO_2 (*25*). Reportedly, the oxygen loss of V_2O_5 results in the transition of the anatase to rutile at temperatures of about 650°C, thus stabilizing a number of oxygen vacancies in the vanadium oxide. The range of V_2O_5/anatase weight ratios optimal for the transition is described to be 0.15 to 0.25 (*24*), which happens to resemble the ratio in our catalysts.

The stabilization of oxygen defects may greatly enhance the oxidation activity. The formation of the rutile can be observed only in the sample with the highest TiO_2 loading. In the samples with monolayer coverage of TiO_2 or less, rutile either cannot be observed or is truly absent, which could be caused by the small layer thickness preventing formation of the rutile lattice. The anatase crystallization observed at higher temperatures is probably caused by dehydration of the surface TiOH species.

In Fig. 4, a number of possible arrangements of the components of the various ca-

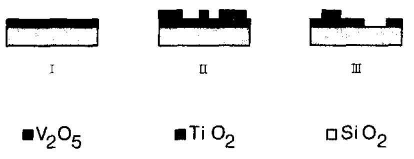

FIG. 4. Possible arrangements of the materials constituting the catalysts after preparation. The figure schematically presents: **I**, a layer of TiO_2 covering silica; **II**, V_2O_5 particles on this TiO_2 layer; **III**, V_2O_5 particles partially supported on TiO_2 and partially on SiO_2.

talysis are presented. During the first step of the deposition precipitation a monolayer of the TiO_2 precursor is formed (species **I**). In the resulting catalyst (sample A2 of Table 1) this layer shows no catalytic activity in the reaction of NO, NH_3, and O_2. The silica surface is completely covered at TiO_2 loadings above 23 wt%. In the presence of both trivalent titanium and vanadium species, texture **II** or **III** may be formed at high and low TiO_2 loadings, respectively.

From the absence of V_2O_5 in the XRD pattern and the electron micrographs we conclude that the vanadium oxide is homogeneously dispersed on both TiO_2 and SiO_2. The configurations **II** and **III** in Fig. 4 can therefore be assigned to catalysts C and D, respectively. Support for this suggestion is found in the kinetic parameters of the CO oxidation (Table 2), in the selectivity data calculated from the SCR experiments (Table 3), and in the DRIFT data.

In previous work (*22*) we concluded that the kinetic parameters in the oxidation of CO on various V_2O_5-based catalysts are strongly dependent on the support used. The apparent activation energy found for Al_2O_3- and TiO_2-supported V_2O_5 was 71–73 kJ mol^{-1}. A silica-supported V_2O_5 catalyst prepared by our deposition technique exhibited an activation energy of 90–94 kJ mol^{-1}, whereas for unsupported, well-annealed V_2O_5 an activation energy of 110–120 kJ mol^{-1} was measured. We concluded therefore that the activation energy in the CO oxidation is a good analytical device for the identification of interactions between the active species and the support.

The values presented in Table 2 thus indicate that in samples B and C, having high TiO_2 loadings, the vanadium oxide is supported on a layer of TiO_2 covering the silica surface. Sample D shows an activation energy which is intermediate between those found for titania- and silica-supported vanadium oxide. From the CO oxidation results of this and the previous work (*22*) we conclude that in this case the vanadium is supported partially on bare silica and partially on the less abundant TiO_2.

Diagnostic results from the SCR experiments were obtained when the reaction was carried out at 400°C. Catalysts D and E, showing a high activation energy in the oxidation of CO, exhibit poor catalytic performance (Table 3).

The close resemblance of the selectivities of samples D and E again indicates that in the case of D, which is loaded with an amount of TiO_2 insufficient for complete surface coverage, the V_2O_5 is supported on bare silica. The very good selectivities and activities of the samples in which complete coverage of the SiO_2 with TiO_2 has been established are in perfect agreement with the results from CO oxidation measurements. We thus conclude that, in the case of catalysts B and C, arrangement **II** from Fig. 4 is present. With sample D, arrangement **III** has been established. The presence of situation **I** can be definitively ruled out, since TiO_2 alone (A2) does not show SCR activity. It is therefore obvious that the TiO_2 precipitates completely before the onset of V_2O_5 precipitation.

CONCLUSIONS

1. It is feasible to replace the bulk of the TiO_2 in V_2O_5/TiO_2 catalysts by silica using our preparation technique, thereby obtaining a relatively cheap catalyst which is highly active and selective within a large operating window, and, moreover, is resistant to SO_2.
2. The catalyst, however, performs excellently only if the surface of the silica is completely covered by TiO_2, which calls for TiO_2 loadings of about 20–25 wt%, since the V(III) precursor will preferably interact with free silica surface if present, as is indicated by the results of the CO oxidation measurements.

A last remark should be made to stress the importance of the values reported for the operation of catalysts B and C at higher temperatures. Although a slight decrease in NO reduction activity is evident, the side reaction producing molecular nitrogen (*5*) dominates over the other NH_3 oxidation reactions with this catalysts. This implies that using this catalyst, operation at an excess concentration of NH_3 may become possible. The excess ammonia present after the SCR reaction could then be quantitatively converted to N_2 in a subsequent part of the reactor. Consequently the difficult process of instantaneous monitoring of the reactant concentration and the rapid response necessary upon concentration changes would become far easier.

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