Catalysis Today 61 (2000) 187–195

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Characterization and reactivity of MoO_3/SiO_2 catalysts in the selective catalytic oxidation of ammonia to N_2

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Abstract

Silica-supported MoO_3 catalysts with MoO_3 loadings up to 21% w/w were prepared, characterized and tested in the selective catalytic oxidation (SCO) of ammonia to N_2 under dilute conditions. It is found that the catalysts are active and selective in the reaction, and that the catalytic performance increases on increasing the Mo loading. Crystalline MoO_3, detected over the silica support, is supposed to be the active species in the reaction. The reactivity of the catalysts is depressed by water addition to the feed at low temperatures and is enhanced by the presence of selected promoters, like Bi and Pb. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: MoO_3/SiO_2 catalysts; Selective catalytic oxidation; Ammonia oxidation

1. Introduction

The abatement of ammonia from gaseous waste streams is becoming an important issue due to the increasing environmental concerns. Ammonia can be eliminated in several ways, including biological treatments, absorption, thermal incineration, catalytic oxidation: among these methods, the selective catalytic oxidation (SCO) of ammonia to innocuous nitrogen and water according to the following stoichiometry:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$

is of potential interest since it would be suitable for a wide range of applications. A technology for NH_3 removal under oxidizing conditions is also of interest for the control of ammonia slip in SCR units ($4NH_3+4NO+O_2\rightarrow 4N_2+6H_2O$), that accordingly could be operated at higher NH_3/NO ratios thus improving the NO_x removal efficiency.

Several catalysts were proposed for the NH_3 oxidation to molecular nitrogen, including supported oxides (e.g. V/TiO_2 [1], MoO_3/SiO_2 [2–5], Cu–Mn/TiO_2 [6]) and noble metal based catalysts (Pt, Pd and Rh supported on Al_2O_3 and ZSM-5 [7]). Among these, MoO_3 based catalysts investigated in earlier works [2–5] showed interesting activity and selectivity characteristics in reaction (1). For this reason, in this work the reactivity of silica-supported MoO_3 catalysts in the selective oxidation of ammonia to nitrogen was investigated. Catalysts having different Mo content were prepared, characterized and tested in the SCO reaction. The effect of the operating conditions and of the

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PII: S0920-5861(00)00369-2

addition of promoters on the catalyst activity and selectivity have also been addressed.

2. Experimental

2.1. Catalyst preparation

MoO_3/SiO_2 catalysts with molybdenum content of 6, 12, 16 and 21% w/w were prepared by incipient wetness impregnation of an Aerosil 200 SiO_2 support with an aqueous solution of ammonium heptamolydate complexated with citric acid. The resulting precursors were dried at 383 K overnight and calcinated at 823 K for 3 h.

Pb-, Te- and Bi-doped MoO_3/SiO_2 samples were obtained starting from a dried MoO_3/SiO_2 catalyst precursor (MoO_3=16% w/w) by further impregnation with aqueous solutions of $Pb(NO_3)_2$, H_6TeO_6 and $Bi(NO_3)_3 \cdot 5H_2O$, respectively. In all cases, a nominal Mo/Me (Me=Pb, Te, Bi) atomic ratio=1/20 was selected. After impregnation, the catalysts were dried and calcined at 823 K for 4 h.

2.2. Catalysts characterization

Surface area and pore size distribution measurements, XRD, FT-IR, Laser-Raman and NH_3-TPD analyses were performed as reported elsewhere [8].

2.3. Reactivity measurements

Catalytic activity measurements were performed in a quartz tubular fixed-bed microreactor (i.d.=7 mm) operating at atmospheric pressure. In a typical SCO run, 128 mg of catalyst (100–150 mesh) were used and a stream of NH_3 (960 ppm)+O_2 (9000 ppm)+Ar (1500 ppm, internal standard) in He (total flow rate=120 cm^3/min (STP)) was fed to the reactor maintained at a desired temperature value for at least 2 h. In selected experiments, NO (960 ppm) was also present in the feed stream. The effect of water vapor on the catalyst reactivity was investigated by feeding a wet feed (H_2O=0.5 and 1% v/v) by saturating the He stream with a saturator. Analysis of reaction products was performed by using a mass spectrometer (Balzers QMS 200) and a gas chromatograph (HP 6890). Further details on the experimental setup and procedure can be found elsewhere [8].

3. Results

3.1. Characterization studies

3.1.1. XRD and morphology

For all the prepared $MoO_3(x)/SiO_2$ samples, the only detected phase by XRD is crystalline MoO_3. Very weak XRD reflections were observed in the sample with the lowest Mo loading (MoO_3=6% w/w), whereas for higher MoO_3 loading the MoO_3 crystallites were well evident. The morphological characteristics of the support are moderately modified upon MoO_3 addition up to 21% w/w: the BET surface area decreases progressively from 160 m^2/g for the silica support down to 123 m^2/g for the $MoO_3(21)/SiO_2$ samples whereas the pore volume and the mean pore radius are not significantly affected by molybdena addition and are in the range 0.56–0.60 cc/g and 70–90 Å, respectively.

The addition of the Pb, Te and Bi promoters (PbO=1.3, TeO_2=0.9 and Bi_2O_3=1.3% w/w) to the $MoO_3(16)/SiO_2$ catalyst only slightly modifies its morphological features: the surface area is not affected by PbO addition whereas it drops to 123 and 85 m^2/g following the Bi_2O_3 and TeO_2 addition, respectively. No significant modification in the pore volume and pore radius was observed for the Pb- and Bi-promoted samples, whereas a slight increase of the pore radius and a corresponding decrease of the pore volume was observed in the case of the Te-doped sample, in line with the observed decrease of the surface area value. Only the crystalline MoO_3 phase was observed by XRD in all cases: the crystallite dimensions, estimated by the Scherrer method, do not differ with respect to the unpromoted samples.

3.1.2. Spectroscopic studies

Information concerning the structural and vibrational characteristics of molybdenum on the SiO_2 surface were provided by the spectroscopic analysis (FT-IR and FT-Raman). The FT-IR spectra (KBr pressed disks) of the $MoO_3(x)/SiO_2$ samples, not reported for brevity, show strong absorptions in the region 950–1250 cm^{-1}, at 808 and at 472 cm^{-1}, which are due to the silica support. In addition to these major absorptions, in the samples with the highest Mo content (i.e. 16 and 21% w/w) additional components are evident at 990, 864, 820 and 583 cm^{-1}. These bands, which can be hardly detected in the samples with MoO_3=6 and 12% w/w, can be attributed to crystalline MoO_3.

The FT-Raman spectra of all the MoO_3/SiO_2 samples show a modulation in the baseline near 800 cm^{-1}, due to the silica support, and additional bands near 990 and 820 cm^{-1} which can be associated with the presence of crystalline MoO_3 [9]. These bands, which are already visible in the sample with the lowest Mo content (6% w/w), increase in intensity on increasing the MoO_3 content. It is noteworthy that no bands were observed near 960 cm^{-1}, which are typical of the Mo=O stretching mode of molybdenil species [9].

3.1.3. Adsorption of ammonia

The interaction of the reactant (i.e. ammonia) with the catalyst surface was investigated by means of NH_3-TPD experiments and FT-IR of adsorbed ammonia. Preliminary TPD experiments performed in the case of the pure silica support showed that ammonia is not appreciably adsorbed on the support, thus pointing out a very weak NH_3–SiO_2 interaction. Fig. 1 shows the results of the ammonia TPD runs performed over the $MoO_3(16)/SiO_2$ catalyst. NH_3-TPD experiments were performed in the case of the other samples as well, and similar results were obtained. The desorption of significant amounts of NH_3 was observed, with a maximum near 150°C. Minor amounts of water also desorb in the same *T*-range where NH_3 evolution occurs, along trace amounts of N_2. The non-negligible amount of water desorbed in the TPD experiments is likely related to two distinct effects, i.e. (i) presence of water impurities in the NH_3 feed, and (ii) surface dehydroxylation. The first effect is possibly of minor importance when compared to the surface dehydroxylation, as already discussed in [8] for TiO_2-supported MoO_3. Formation of N_2 is likely associated with oxidation of surface-adsorbed ammonia.

The interaction of ammonia with the catalyst surface has been investigated by spectroscopic techniques. The FT-IR spectra recorded after adsorption of ammonia over the $MoO_3(16)/SiO_2$ sample are shown

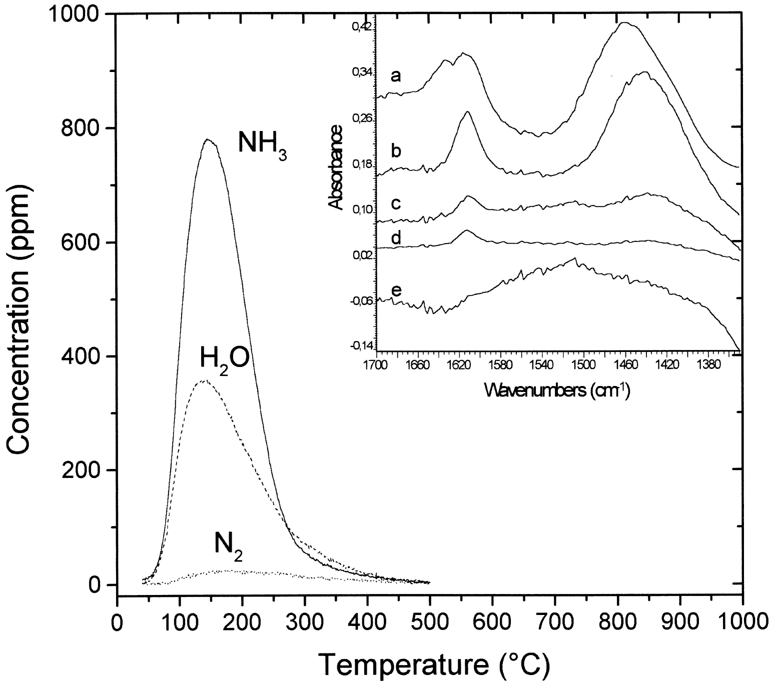

Fig. 1. NH_3-TPD experiments performed over the $MoO_3(16)/SiO_2$ sample. NH_3, H_2O and N_2 concentration traces as a function of temperature. The inset shows the results of the NH_3-FT-IR experiments performed: (a) in the presence of NH_3 (20 Torr); (b) evacuated at RT; (c) 150°C; (d) 250°C; (d) 350°C.

in the insert of Fig. 1. After contact with NH_3 gas the bands of ammonia adsorbed molecularly on Lewis acid sites (bands at 1604 and 1612 cm^{-1} ($\delta_{as}NH_3$) and the corresponding N–H stretching at 3410, 3385, 3280 and 3180 cm^{-1}, not shown) and on Brønsted acid sites (bands at 1667 ($\delta_{sym}NH_4$) and 1448 cm^{-1} ($\delta_{as}NH_4$) and the associated stretching in the region 3100–2600 cm^{-1}, not shown) are apparent. The bands of the NH_3 symmetrical bending ($\delta_{sym}NH_3$), expected in the range 1260–1150 cm^{-1}, are not shown because the spectral region is obscured by Si–O absorption. Upon outgassing at increasing temperatures, the bands associated to ammonium ions decrease in intensity and completely disappear after evacuation at 250°C, while the bands associated to ammonia on Lewis acid site are, although strongly reduced in intensity, again detectable. These bands disappear only after outgassing at 350°C, in line with TPD results showing that complete desorption of ammonia is attained in this temperature range.

3.2. Reactivity studies

3.2.1. Reactivity MoO_3/SiO_2 catalysts

The results of catalytic activity measurements performed in the SCO reaction over the investigated MoO_3/SiO_2 samples are shown in Fig. 2A and B in terms of NH_3 conversion and N_2 selectivity, respectively. In the case of the sample with the lowest MoO_3 loading (i.e. 6% w/w), appreciable NH_3 conversion is seen above 250°C. The NH_3 conversion increases with temperature and approaches 90% at 500°C. The N_2 selectivity is over 90% at 300°C but declines with increasing conversion, and is near 75% at 500°C. The decrease in the N_2 selectivity is primarily related to the formation of NO and, to a minor extent, of N_2O.

On increasing the MoO_3 loading from 6 to 12% w/w, an increase in the catalyst activity is observed. Ammonia is converted starting from 250°C, and complete NH_3 conversion is achieved at 450–480°C. The N_2 selectivity is higher with respect to the $MoO_3(6)/SiO_2$ sample at low temperatures but rapidly decreases at high temperature, where complete ammonia conversion is reached. For further increases of the MoO_3 loading, a leveling off in the catalyst activity is observed, but a significant increase in the N_2 selectivity is also evident. Notably, N_2 yields near 90% were attained at 500°C in the case of the sample with the highest MoO_3 loading (i.e. 21% w/w).

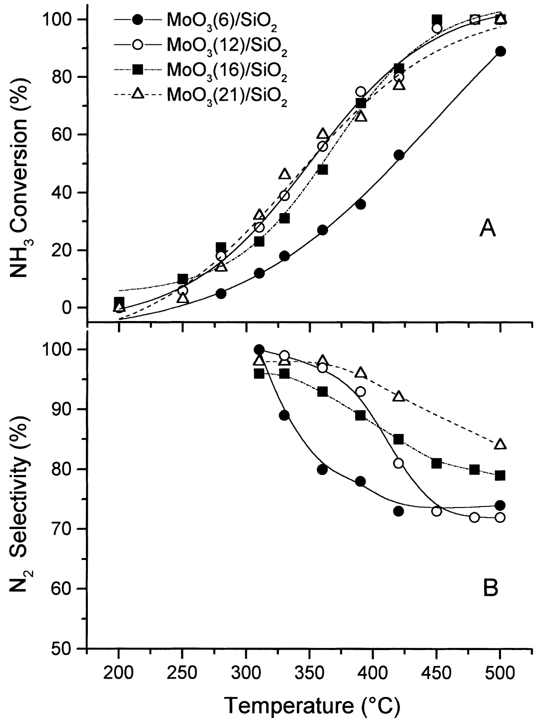

Fig. 2. Catalytic activity data of the $MoO_3(x)/SiO_2$ samples in the catalytic oxidation of ammonia.

3.2.2. Effect of the NH_3 inlet concentration

The effect of the NH_3 inlet concentration on the catalytic performances was investigated. The data were collected in this case under temperature programming, i.e. by heating the catalyst at 15°C/min while continuously monitoring the gases exiting the reactor. Fig. 3 shows, in the case of the $MoO_3(16)/SiO_2$ sample taken as example, the outlet product concentrations monitored as a function of temperature upon feeding 960, 430, 180 and 70 ppm of ammonia (curves *a*, *b*, *c* and *d*, respectively). The estimated N_2 selectivity values have also been reported, along with the corresponding values obtained under steady state conditions obtained with NH_3=960 ppm (filled squares). From Fig. 3 it appears that the temperature threshold for the occurrence of the SCO reaction, monitored by the formation of N_2, is apparently not affected by the inlet NH_3 concentration in the investigated range, being in all

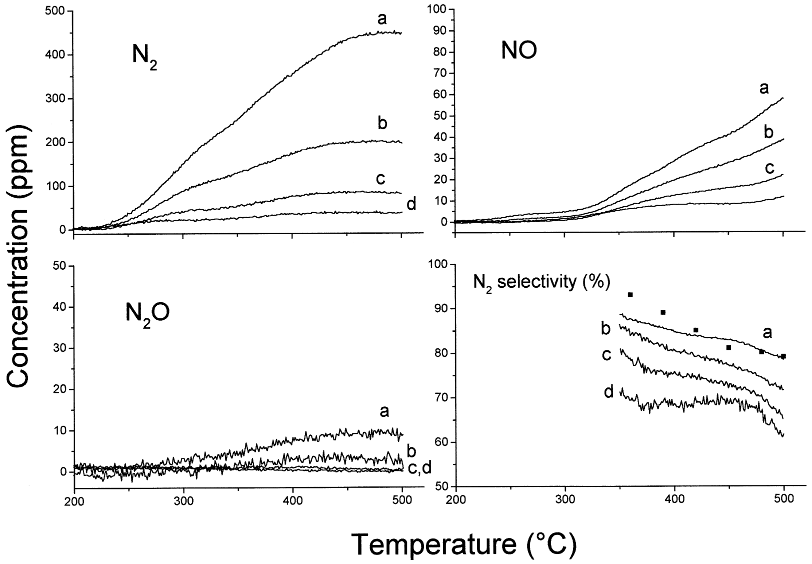

Fig. 3. Effect of the NH_3 inlet concentration on the catalytic performances of the MoO_3(16)/SiO_2 sample in the catalytic oxidation of ammonia. NH_3 inlet concentration: (a) 960 ppm; (b) 430 ppm; (c) 180 ppm; (d) 70 ppm.

cases near 250°C. The N_2 production decreases upon decreasing the ammonia concentration, as expected, along with that of NO and N_2O by-products. The decrease in the N_2 formation is however more strongly affected by the inlet ammonia concentration with respect to NO, so that the N_2 selectivity decreases upon decreasing the ammonia inlet concentration. Similar results (not reported for the sake of brevity) were also obtained over the other MoO_3/SiO_2 samples as well.

3.2.3. *Effect of water addition*

The effect of the presence of H_2O in the feed (0.5 and 1% v/v) was also investigated. Fig. 4 compares the catalytic activity data obtained with a dry feed

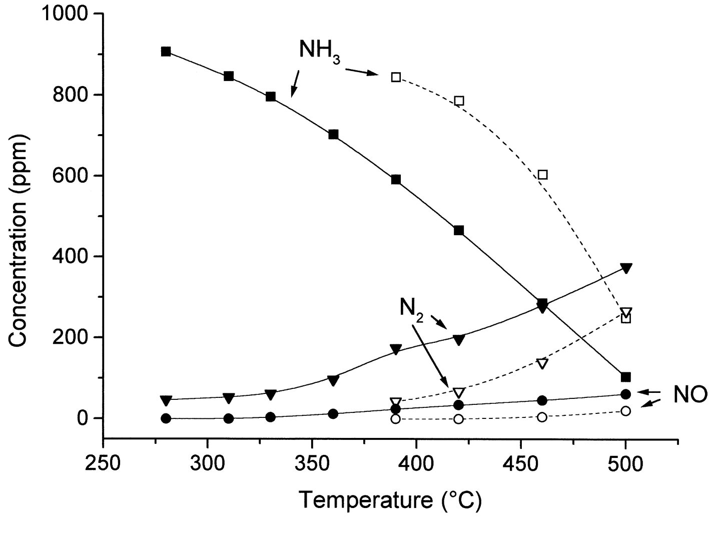

Fig. 4. Effect of water on the catalytic performances of the MoO_3(6)/SiO_2 sample in the catalytic oxidation of ammonia. H_2O inlet concentration: 0.5% v/v.

(solid symbols) with those obtained in the case of a wet feed (H_2O=0.5% v/v, empty symbols) over the $MoO_3(6)/SiO_2$ sample. It clearly appears that even for low water contents (0.5%) the reactivity of the catalyst is strongly reduced, since the NH_3 conversion curve is shifted some 50°C towards higher temperatures. Similar results have also been obtained with higher water contents, i.e. 1% v/v (not reported). This apparently indicates that the H_2O inhibition tends to level off at high H_2O concentrations. Selectivity values estimated from the data reported in Fig. 4 also showed that the presence of water reduces the formation of N_2O and NO by-products with respect to N_2, i.e. increases the N_2 selectivity.

3.2.4. *Effect of NO addition*

The NH_3 oxidation reaction was carried out over selected MoO_3/SiO_2 samples also in the presence of NO, i.e. under typical SCR conditions (960 ppm NH_3+960 ppm NO+1% v/v O_2 in He). The results obtained in this case, not reported for the sake of brevity, indicated that the NH_3 consumption is not appreciably modified by the presence of NO (i.e. the ammonia conversion closely resemble that shown in Fig. 2). On the other hand, a limited NO consumption (less than 100 ppm) was observed above 300°C. Among the reaction products, the formation of N_2 has not been affected, whereas that of N_2O is significantly increased in the temperature range where NO is converted. Hence the data clearly indicate that the MoO_3/SiO_2 catalysts do not show any appreciable activity in the SCR reaction under the investigated experimental conditions, and that NO is likely involved in N_2O formation.

3.2.5. *Effects of additives on the SCO reaction*

Biermann and Janssen [2–4] have reported that the presence of Pb impurities in silica supported MoO_3 samples increase the reactivity in the SCO reaction. Accordingly, the effect of Pb doping on the activity and selectivity of the MoO_3/SiO_2 samples was investigated, along with that of other additives (Bi, Te) in view of their well known effects on the activity and selectivity of MoO_3-based catalysts in selective oxidation reactions [10].

Fig. 5 compares the results obtained in the SCO reaction over the undoped $MoO_3(16)/SiO_2$ sample with those obtained in the case of the Pb-, Bi- and Te-doped catalysts. It appears that for the Pb- and Te-doped samples the NH_3 conversion is only marginally affected by the presence of the promoters, whereas in the case of the Bi-doped sample a significant increase in the catalyst activity in the high temperature region (above 350°C) is observed. Notably, the presence of the additives, and particularly of Pb and Bi, significantly increases the N_2 selectivity with respect to the undoped $MoO_3(16)/SiO_2$ sample. As a matter of fact, N_2 yields approaching 100% at 400°C can be obtained under the investigated operating conditions in the case of the Bi-doped sample.

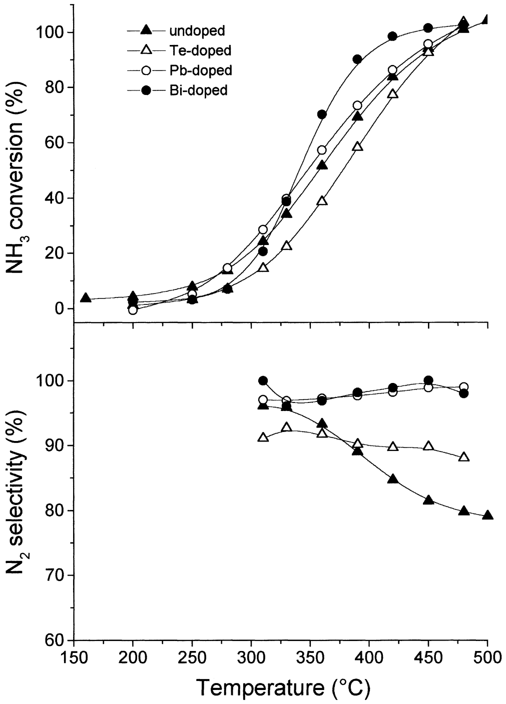

Fig. 5. Catalytic activity data of the Bi-, Pb- and Te-promoted $MoO_3(16)/SiO_2$ sample in the catalytic oxidation of ammonia.

4. Discussion

The results presented so far clearly indicate that silica-supported MoO_3 catalysts are active and selective in the oxidation of ammonia to molecular nitrogen. XRD, FT-IR and Laser-Raman have indicated that the catalysts are constituted by crystalline MoO_3 which is supported over the silica support.

The presence of crystalline MoO_3 was pointed out by XRD and Laser-Raman already in the sample with the lowest molybdena content, and is well evident for the samples with higher Mo content. The presence of other supported oxide species, e.g. isolated mono-oxo molybdenil species, has not been pointed out in our study but cannot be ruled out. The presence of crystallite MoO_3 already at low loadings, below the theoretical monolayer capacity of the support, is however not surprising in view of the low dispersing capacity of the silica support with respect to other oxide supports [11].

NH_3-TPD data indicate that ammonia, i.e. the reaction reactant, is not appreciably adsorbed on the bare SiO_2 support but is significantly held on the catalyst surface when Mo oxide is present. FT-IR analysis indicates that in this case ammonia is present as both molecularly adsorbed ammonia on Lewis acid sites and as NH_4^+ ions on Brønsted acid. The spectra are strongly different with respect to those recorded on the bare SiO_2 support [12], where only bands due to weakly adsorbed ammonia on surface silanols are observed, in line with the results of NH_3-TPD experiments. Accordingly these data show, in line with literature data, that molybdenum addition on SiO_2 causes the formation of new Brønsted and Lewis acid sites [13]. Ammonia adsorbed over Lewis acid sites is thermally more stable than NH_3 adsorbed over Brønsted acid sites.

The activity of the catalysts in the ammonia selective oxidation increases on increasing the molybdenum loading, but a leveling off is apparent for MoO_3 loading above 12% w/w. On the other hand, it is noteworthy that the N_2 selectivity monotonically increases with the MoO_3 loading in the investigated composition range, so that N_2 yields near 90% could be attained at 500°C in the case of the sample with the highest MoO_3 loading (i.e. 21% w/w). In this respect our results appear to be at variance with those previously reported by Biermann and Janssen [2–4], indicating that silica-supported MoO_3 catalysts are active in the NH_3 oxidation to N_2 only for MoO_3 loadings above 15% w/w. These differences can be likely ascribed to the different catalyst preparation method employed in our work and in [2–4], i.e. impregnation vs. deposition–precipitation, possibly leading to Mo supported oxide species having different characteristics.

On the basis of the characterization data, the active sites for the ammonia oxidation reaction are likely associated with crystalline MoO_3, in line with previous suggestions indicating that the reactivity in the SCO reaction is due to “combined” Mo species in MoO_3 crystallites [2–4]. According to Biermann and Janssen [2–4], these “combined” sites provide two adjacent ammonia reaction sites on which NH_x species are formed by H-abstraction from adsorbed ammonia; N_2 and water are then formed upon recombination of two adjacent NH_x species followed by decomposition of the intermediate surface species [4]. According to de Boer et al. [5], NO is formed upon oxidation of an adsorbed NH_x species by lattice oxygen, whereas the most likely mechanism for nitrous oxide formation likely involve the reaction of an in-situ generated NO molecule with an adsorbed NH_x species (“sequential mechanism”). This mechanism may also be responsible for N_2 production. It is hence argued that N_2 selectivity can be enhanced by (i) increasing the site density where NH_x species form, and (ii) by “tuning” the catalyst oxidizing properties so that lattice oxygen does not readily react with NH_x.

Our data basically agree with such a picture. As a matter of fact, on either increasing the MoO_3 loading or the ammonia inlet concentration, a beneficial effect on the N_2 selectivity was observed. In line with previous suggestions, the increase of the Mo loading would result in an increase of the “combined” Mo sites in the MoO_3 crystallites (i.e. the site density), whereas the increase in the ammonia partial pressure would increase the recombination probability of two adsorbed NH_x species, i.e. would favor the N_2 formation instead of that of NO by-product.

Notably, the addition of NO to the reacting system does not significantly alter neither the NH_3 consumption, nor the N_2 formation. This may suggest that NO does not readily react with adsorbed ammonia according to the SCR reaction, in contrast with data collected over TiO_2-supported MoO_3 catalyst samples [8]. This apparently rules out the hypothesis of an “internal” SCR mechanism for N_2 formation over silica-supported MoO_3 catalysts, i.e. a sequential mechanism involving the formation of intermediate NO followed by its reaction with adsorbed NH_x species leading to N_2. On the other hand, the presence of NO increases the N_2O production, and this may indicate that such species originates via reaction of NO with a surface intermediate NH_x species, in line with previous hypothesis [5]. Alternatively, nitrous oxide may be formed upon reoxidation by NO of the reduced catalyst active sites ($2NO+2e^{-}\rightarrow O^{2-}+N_2O$), even if reoxidation by gas-phase oxygen is expected to be much faster.

The negligible activity of the silica-supported MoO_3 samples in the NH_3+NO reaction parallels previous results reported by Biermann and Janssen [2–4] over similar catalytic systems. Notably, data reported by some of us [8] showed that MoO_3, when supported over TiO_2, is quite active in the SCR reaction. This apparently points out the different reactivities of the Mo oxide species supported over SiO_2 and TiO_2, e.g. crystalline MoO_3 (possibly the active species in the ammonia oxidation reaction and in the formation of N_2O in the presence of NO as well) vs. dispersed Mo species (active species in the SCR reaction [8]).

The presence of H_2O in the feed significantly reduces the reactivity of the catalyst, and as a result the NH_3 conversion curves are shifted towards higher temperatures. However, the water effect apparently levels off at high water content and is lower at high temperature. It is likely that the observed reduction in activity is related to the competition of water on the adsorption on the active sites: accordingly, the minor effects observed at high temperatures can be associated to the stronger interaction of NH_3 with the catalyst active acid sites when compared to the less basic water molecule. It is noteworthy that the presence of water also reduces the formation of N_2O and NO by-products with respect to N_2, that is, increases the N_2 selectivity: this feature was observed in the NH_3+NO reaction over TiO_2-supported V_2O_5–MoO_3 catalysts as well [14], but the mechanisms through which H_2O exerts its inhibiting effects on N_2O and NO formation are still rather obscure.

Finally, the effects of additives (Pb, Bi and Te) on the SCO reaction was investigated. It was found that, in the range of the investigated compositions, the Pb additive increases the N_2 selectivity with respect to the undoped sample, whereas Bi increases both the activity and selectivity. Notably, in this case N_2 yields approaching 100% at 400°C could be obtained under the investigated operating conditions, making the catalytic performances of these catalysts very interesting. In the case of Pb, Biermann and Janssen [2–4] attributed the beneficial effect of the additive to the higher crystallization of the MoO_3 crystalline phase (considered the active phase in the reaction) and/or to the participation of Pb ions in the redox cycle of the reaction. In our case, XRD analysis apparently ruled out any effect of the promoters on the MoO_3 crystallinity, since the MoO_3 mean crystallite dimensions, determined by the Sherrer method, are not affected by the presence of the promoters. On the other hand, temperature programmed reduction (TPR) measurements which are currently in progress in our labs over Bi-doped MoO_3/SiO_2 samples point out a significant modification of the catalysts redox properties upon addition of the promoters. Hence, these preliminary data suggest a complex interplay between the Mo component and the various additives, particularly Bi, which likely interfere with the Mo redox properties, e.g. via a remote controlled redox process. These features are in line with the well known effects of additives (and specifically of Bi) on MoO_3-based catalysts for selective oxidation reactions, e.g. ammoxidations [10]. Work is presently in progress in order to better enlighten these aspects, specifically the role of additives (such as Bi) on the SCO reaction.

5. Conclusions

The reactivity of pure and Bi-, Te-, and Pb-doped silica-supported MoO_3 catalysts was investigated in this work. Unpromoted catalysts are made up by crystalline MoO_3, which is supported over the silica carrier. Reactant ammonia is adsorbed over the catalyst surface both in the form of molecularly adsorbed ammonia on Lewis acid sites and as NH_4^+ ions on Brønsted acid sites: these acid sites are formed upon addition of molybdenum to the silica support. The catalysts are active and selective in the oxidation of ammonia to molecular nitrogen: their activity increases on increasing the molybdenum loading, but a leveling off is apparent at high MoO_3 loadings, above 12% w/w. On the other hand, the N_2 selectivity monotonically increases with the MoO_3 loading in the investigated composition range (MoO_3 loadings up 21% w/w).

The activity of the catalysts is inhibited by the presence of H_2O in the feed. However, the water effect apparently levels off at high water contents and decreases at high temperature. Also, it is noteworthy that the presence of water reduces the formation of

N_2O and NO by-products with respect to N_2, that is, increases the N_2 selectivity.

Catalyst promotion by additives (Pb, Bi and Te) increases both the catalyst activity and selectivity, particularly in the case of Bi. Notably, in this case N_2 yields approaching 100% at 400°C could be obtained under the investigated operating conditions, making this catalytic system very promising. The observed increase in the catalyst activity and selectivity is likely related to the modification in the catalyst redox properties induced by the additive, since the catalyst structural and morphological properties are not significantly modified by the addition of the promoters. However, additional studies are needed to better clarify the role of the additives on the SCO reaction.

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