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Letter

Selective catalytic reduction of NO with methane over Ag-alumina catalysts

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Abstract

Silver-alumina catalysts prepared by a single-step co-gelation technique are reported in this letter as highly active and stable for the selective catalytic reduction of NO with methane (CH_4–SCR). This type catalyst is active over a wide-temperature range (450–650°C), and for a relatively wide range of Ag loading (1–7 wt.%). Excess O_2 in the feed gas favors the SCR reaction. Catalysts capable of high conversions of NO_x by CH_4 in excess O_2-containing gas streams would be an attractive alternative to high temperature NH_3–SCR, which is commercially practised for NO_x reduction in gas turbine exhausts at >500°C. The structural stability of Ag was studied in reduction-oxidation cycles from 25–600°C by UV–VIS diffuse reflectance spectroscopy. Totally reversible structures were observed. The catalyst is active both for CH_4–SCR as well as for the complete oxidation of CH_4. This bifunctionality appears to be related to the coexistence of highly dispersed silver clusters and silver nanoparticles in the alumina matrix. The catalyst activity/stability remained high under demanding reaction conditions; namely in 10%O_2, 30 ppm SO_2 and 10%H_2O and high space velocities. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Lean NO_x reduction; Silver catalyst; Methane oxidation; Alumina; SO_2; H_2O

1. Introduction

The selective catalytic reduction (SCR) of NO_x by hydrocarbons is under investigation worldwide as the most attractive technique for NO_x reduction to N_2 in exhaust gas streams from both mobile and stationary sources. For the latter application, the hydrocarbon of interest is methane, the chief component of natural gas. This is also true for natural gas-fueled vehicles. Since the 1992 disclosure by Li and Armor [1] of SCR of NO_x with CH_4 over cobalt zeolites, a large number of studies using cobalt and various other metals and zeolite hosts has been reported. Methane is hard to activate. The light-off temperature of methane is higher than 300°C on the most active catalysts under industrial conditions. The challenges for SCR are to successfully react CH_4 with ($NO+O_2$), rather than oxygen only, to the preferred reduction product N_2, with adequate resistance to water vapor and sulfur and over a wide temperature window. Catalysts capable of high conversions of NO_x by CH_4 in excess O_2-containing

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gas streams would be an attractive alternative to high temperature NH_3–SCR, which is commercially practised for NO_x reduction in gas turbine exhausts at >500°C [2].

Several metals (Co, Pd, Ag, Ni, Mn, Fe, In) [3–12] in atomic dispersion, i.e. as ions stabilized in zeolites, have been found to possess high selectivity for the reduction of NO_x to nitrogen with CH_4 in the presence of excess oxygen. However, these catalysts are limited by a narrow operating temperature window and low hydrothermal stability, mainly in connection with the metastable zeolite host matrix. In many systems, hydrated metal ion migration and agglomeration to metal particles is also a problem [13]. On open supports, such as alumina, zirconia and sulfated zirconia, the activity and selectivity of the same metals are limited by structural effects, especially low dispersion, which renders the catalyst more active for CH_4 combustion than for the SCR of NO. Yet, open supports are more attractive than zeolites because of their superior hydrothermal stability.

In this paper, we report on the CH_4–SCR activity of Ag-alumina catalysts, prepared by a single step co-gelation. Although Ag/Al_2O_3 has been reported as an active HC–SCR catalyst with good resistance to H_2O and SO_2, only reductants other than methane, such as propene or ethanol were found practical [14–20]. The conventional preparation of Ag-alumina in the literature is by impregnation of commercial alumina or of one prepared by a sol–gel technique. To our knowledge, this is the first report of a highly stable and active Ag-alumina system for the SCR of NO by methane in excess O_2-containing gases.

2. Experimental

Bulk alumina and Ag-alumina catalysts with a varying content of silver were prepared by a co-gelation procedure reported earlier for the preparation of transition metal — the zirconia systems [21]. Briefly, stoichiometric amounts of aluminum nitrate (Fluka, 99%) and silver nitrate (Aldrich, 99.9%) were dissolved completely in deionized water and an aqueous solution of tetra-methylammonium hydroxide (25%) was quickly added to the nitrate solution under constant stirring to an end point pH=8–9. The resultant pale yellow/grey-colored gelatinous precipitate was aged for 8–10 h at room temperature, filtered and washed several times with deionized water, dried under vacuum at 100°C for 8 h, followed by calcination at 650 and 800°C (in two parts) for 10 h (heating rate: 2°C/min). The solid density was ~0.5 g/ml. Elemental analysis was performed by inductively coupled plasma (ICP) atomic emission spectrometry (Perkin Elmer Plasma 40) by dissolving the samples in HF and HNO_3 and diluting with deionized water.

Supported Ag/Al_2O_3 was prepared by incipient wetness impregnation of a high surface area γ-Al_2O_3 (Condea Puralox, S.A.~200 m^2/g). An aqueous solution of silver nitrate at the desired amount was added dropwise to the fine support powder. The impregnated samples were then dried at 100°C for 12 h and calcined in air at 650°C for 2 h.

Ag-ZSM-5 was prepared by ion-exchange of a Na-ZSM-5 (Si/Al=13.8, Davison), using 0.01 M aqueous silver nitrate solution at room temperature for 24 h in the dark [9]. The samples were filtered, washed and dried at 100°C for 8 h, then heated in air at 500°C for 2 h.

The BET specific surface area of the alumina-based samples was measured by single-point N_2 adsorption/desorption on a Micromeritics Pulse Chemisorb 2705 instrument. Silver dispersion was measured by oxygen pulse chemisorption in the same instrument. Each sample was heated at 300°C for 30 min under He flow; cooled to 170°C and reduced at this temperature in a flow of 10%H_2/He for 1h, then purged in He at 300°C for 1.5 h. Oxygen uptake was then measured at 170°C by injecting pulses of a 20%O_2/He gas mixture. Ag dispersion was calculated based on O:Ag=1:1 stoichiometry [22].

X-ray powder diffraction (XRD) analyses were performed on a Rigaku 300 X-ray diffractometer. Cu K_α radiation was used. The tube voltage was 60 kV, and the current was 300 mA. UV–VIS diffuse reflectance spectra were collected with a Hewlett Packard 8052A diode array spectrophotometer (2 nm spectral resolution) equipped with a diffuse reflectance attachment (DRA) (Harrick). Samples could be heated to 600°C in various gas mixtures for in situ studies. MgO powder (99.99%, Aldrich) was used as reference.

Catalyst tests for the selective reduction of NO to N_2 were carried out in a packed-bed flow microreactor (1 cm I.D., quartz tube) operated isothermally. Baseline tests were performed in a gas mixture consisting

of oxygen (5%), methane (2%) and NO (0.25%) in helium at a gas hourly space velocity of 9000 h^{-1} (NTP), 0.4 g sample loading and 100 ml/min flow rate. The catalysts, in powder form (<150 μm size), were tested in the temperature range 300–700°C in 50°C-steps. At each temperature, data were collected for a period of 1–1.5 h after steady-state had been established. Only steady-state data are reported here. Following the ascending-temperature tests, several tests were run at lower temperatures to check for possible catalyst deactivation. The product gas stream was analyzed by a gas chromatograph (HP 5890) equipped with a 5Å molecular sieve column and a thermal conductivity detector. The production of N_2 and consumption of CH_4 were followed to calculate conversions. Methane was typically converted to CO_2 only. Selected catalysts were tested at higher space velocities and in the presence of 10% O_2. The catalyst resistance to SO_2 and water vapor was examined in long term operation at 550 and 600°C.

3. Results and discussion

The BET surface area and percent of Ag dispersion of the 650 and 800°C calcined Ag-alumina samples, denoted by AlAg-1A, AlAg-2A, etc., are presented in Table 1, where the numbers 1, 2, etc. indicate the nominal silver loading expressed as atomic percent (Ag/(Ag+Al)×100). The actual wt.% Ag loadings of the samples are listed in Column 3. The specific surface area of the CG alumina, prepared by the same gelation procedure as the silver-loaded one, was 190 m^2/g after the 650°C calcination step. The surface area of the low Ag-content samples (650°C-calcined) is in the range 175–185 m^2/g, decreasing only at silver loadings >6 wt.%. The properties of the Ag supported on the Condea alumina are also shown in Table 1. After impregnation, the surface area of the samples is 10–15% lower than that of the support.

Table 1 shows a comparison of the fractional conversion of NO to N_2 and of CH_4 to CO_2 at 550°C over the listed catalysts tested under the baseline operating conditions. For the high silver-content samples there is a trend of decreasing conversion of NO to N_2 with the amount of silver loading. The dispersion of silver also drops with the metal loading. However, the most active catalysts, namely AlAg-1A and AlAg-2A, do not show a corresponding higher dispersion of silver. We may attribute this to the presence of hard-to-reduce silver ions in the aluminum oxide matrix [17]. Thus, we may have underestimated

Table 1
Physical properties and catalytic activities of Ag-alumina

Samples[a]	Calcination temperature (°C)	Wt. % Ag[b]	Surface area (used) (m^2/g)	D^c (used) (%)	% NO[d] converted to N_2 at 550°C	% CH_4[d] converted to CO_2 at 550°C
AlAg-1A	650	1.5	172 (131)	32.6 (34)	90.3	76.0
AlAg-2A	650	3.6	184 (137)	26.8	87.1	81.5
AlAg-3A	650	5.5	187	30.9 (17.5)	64.2	66.9
AlAg-5A	650	7.3	176 (137)	26.4	45.0	94.3
AlAg-10A	650	19.2	143 (106)	15.7 (11)	26.3	96.0
AlAg-20A	650	30.4	91	12.9	9.2	100
Al_2O_3 (CG)	650	0	190	–	10.0	20
1at.%Ag/Al_2O_3 (Condea)	650	2.08	160 (145)	44.4 (11)	75.7	65.7
2at.%Ag/Al_2O_3 (Condea)	650	4.13	167 (155)	37.7 (5)	68.3	67.7
5at.%Ag/Al_2O_3 (Condea)	650	10.01	154 (147)	31.9 (13.7)	15.1	52.4
Al_2O_3 (Condea)	as received		184	–	17.1	48.1
AlAg-1B	800	1.5	91		55	38
AlAg-3B	800	5.5	95		16.6	40.5

[a] Samples prepared by co-gelation are denoted by AlAg-*x*A or AlAg-*x*B, where *x* is the nominal at.% Ag; A denotes samples calcined at 650°C and B is for 800°C calcination; Al_2O_3 (CG) is prepared by hydrolysis of aluminum nitrate with tetramethylammonium hydroxide.

[b] Bulk composition of co-gel samples was analyzed by ICP; the silver loading of supported samples is based on the amounts of reagents used in impregnation.

[c] % dispersion, *D*, is calculated from O_2 pulse chemisorption assuming a stoichiometry of Ag:O=1:1 [22].

[d] Measured in a feed gas with 0.25%NO, 2%CH_4, 5%O_2, bal. He, S.V.=9000/h.

the dispersion of silver in the AlAg-1A and AlAg-2A samples. In their study of supported Ag/alumina, Hoost et al. [17] have similarly explained their finding of increasing silver dispersion with the temperature of the H_2 reduction step prior to oxygen chemisorption. Here we have checked the reducibility of the silver structures by UV–VIS spectroscopy (see further). The CG and Condea alumina supports have very low SCR activity. The surface area of samples calcined at 800°C was decreased nearly by half, and the conversion of both NO and CH_4 was reduced appreciably. The silver dispersion was not estimated in these samples, because it was not known what fraction of silver was potentially bound with the alumina in the form of bulk aluminate after the high-temperature calcination.

In Fig. 1a, the conversion of NO to N_2 over Ag-alumina catalysts prepared by co-gelation is shown as a function of temperature. First, a wide-temperature window of activity is observed (450–650°C). Also, there is a shift of the peak temperature from ~575°C for the low Ag-content (1.5–3 wt.%) catalysts to 500°C for the two highly-loaded AlAg-10A and AlAg-20A samples. More importantly, there is a continuous decline of conversion of NO to N_2 over the whole range of temperature as the loading of silver increased above ~3.5 wt.%. In contrast, as shown in Fig. 1b, the methane combustion activity is increased with the silver loading.

The XRD analyses did not show any silver or silver compound reflections in the low Ag-content (1.5–.5 wt.%) samples; only γ-Al_2O_3 reflections were found. Metallic silver was present only in the highly-loaded silver/alumina samples. Since highly dispersed silver is not detectable by wide-angle XRD [23,24], electron microscopy (STEM and HRTEM) was used to identify nanoscale silver in these catalysts. Interestingly, there were only a few big (>10 nm) silver particles on the surface of the used AlAg-1A and 2A samples, while most of the silver was in the alumina matrix as clusters of <2 nm size, very hard to discern. However, on sample AlAg-5A (fresh), containing 7.3 wt.% silver, metallic silver nanoparticles were easy to identify. Fig. 2 is a HRTEM picture of this catalyst. All silver particles are <10 nm, with an average size ~4 nm. This size is close to the Ag particle size calculated from the dispersion value shown for this catalyst in Table 1.

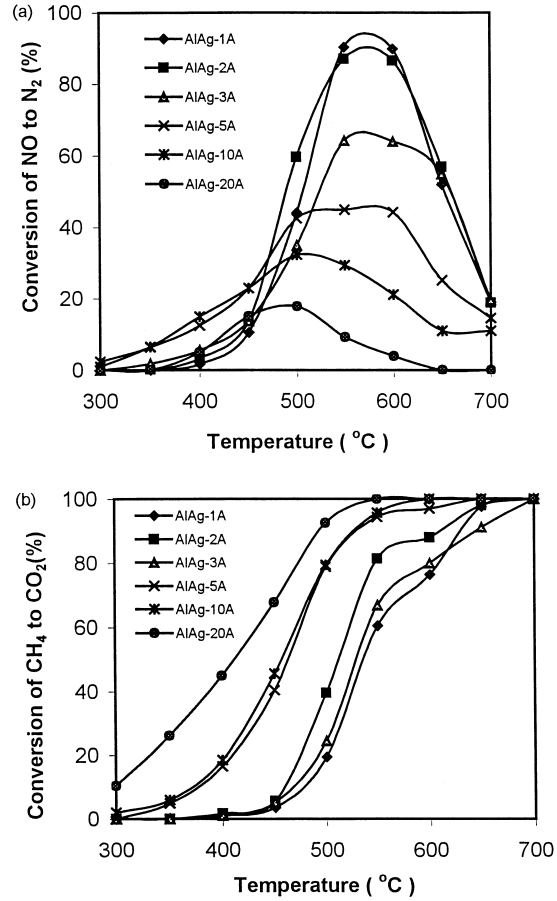

Fig. 1. CH_4–SCR of NO over Ag-Al_2O_3 catalysts prepared by co-gelation (see Table 1). (a) conversion of NO to N_2; (b) conversion of CH_4 to CO_2. Feed gas: 0.25%NO–2%CH_4–5%O_2/He; S.V.=9000/h (NTP).

The coexistence of various silver structures was further investigated by UV–VIS spectrometry. Fig. 3 shows the UV–VIS DR spectra of the co-gel samples AlAg-1A through AlAg-20A taken at room temperature in air. The absorption spectrum of the Al_2O_3 (CG) is also shown. The isolated Ag^+ ion bands at 190 and 220 nm [25,26] can not be determined due to strong absorption of Al_2O_3 at these wavelengths. With a Ag loading of 1.5 wt.%, a broad peak is seen at ~350 nm. This band weakens gradually with Ag loading up to 7.3 wt.%, and finally disappears at higher silver loadings. The band at 350 nm is assigned to oxidized Ag clusters ($Ag_n^{\delta+}$) [27]. Thus, in Ag-alumina samples of low Ag loading (1.5–7.3 wt.%), it appears that silver

Fig. 2. HRTEM micrograph of AlAg-5A; as prepared after 650°C calcination.

mainly exists in oxidized state. However, the oxidized Ag clusters can not be detected in the high Ag-content samples (19–30 wt.%). Also absent from these samples is the metallic Ag band at 420 nm [27]. This may be due to the surface of silver nanoparticles being covered by adsorbed oxygen, as was recently reported by Kundakovic and Flytzani-Stephanopoulos [23], or to the presence of silver aluminate, which is UV-silent.

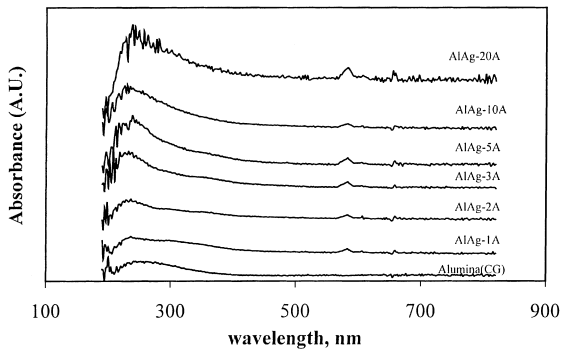

Fig. 3. UV–VIS DR spectra of alumina (CG) and Ag/Al_2O_3 samples prepared by co-gelation, 650°C-calcined; spectra at 25°C, in air.

Since the samples with low Ag loading from 1.5 to 7.3 wt.% show very good CH_4–SCR activity, it is plausible to correlate the presence of oxidized silver with the high SCR activity. This is consistent with our earlier findings for Ag,Ce-ZSM-5 catalysts [9,24]. Also, this is in agreement with Bethke and Kung [18], who reported that oxidized Ag catalyzes the SCR of NO by propene. However, these authors as well as Hoost et al. [17], have reported a limit of 2 wt.% Ag loading on the alumina support; above this loading, metallic silver was dominant, catalyzing the oxidation of the hydrocarbon rather than the SCR reaction. The co-gel Ag-alumina samples appear to be less limited by silver loading. We attribute this to a better contact of silver with the aluminum hydroxide during the co-gelation step. Calcination at 650°C in air strengthens this contact. Recently, silver aluminate was reported to be

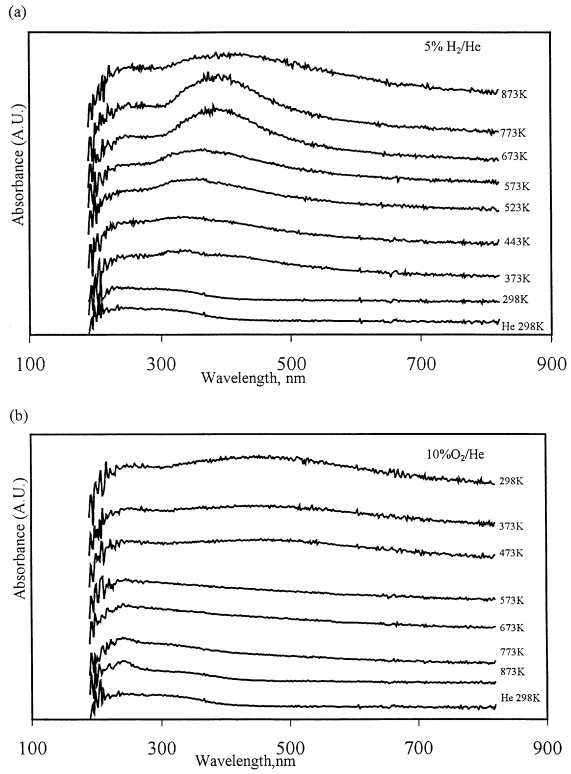

Fig. 4. UV–VIS DR spectra of AlAg-1A in (a) 5% H_2/He in ascending temperature from 298 to 873 K; (b) 10% O_2/He in ascending temperature from 298 to 873 K following the reduction in (a).

more reactive in SCR than metallic Ag on alumina [28]. Also, a Ag/alumina system prepared by the traditional sol–gel method using alcoxide precursors, was reported to have good activity for C_3H_6–SCR of NO_x up to 5 wt.% silver loading [29].

Fig. 4 presents UV–VIS DR spectra of AlAg-1A in cyclic reduction-oxidation experiments with, respectively, 5%H_2/He and 10%O_2/He at various temperatures. As stated earlier, there exists a $Ag_n^{\delta+}$ band around 350 nm in AlAg-1A which is also shown in Fig. 4a in H_2 at 25°C. Hence, oxidized $Ag_n^{\delta+}$ clusters are not reduced at this temperature. The band decreases gradually with temperature (100–600°C) and a new peak grows at ~420 nm which is assigned to metallic silver [27]. After reduction, the UV–VIS DR spectra are taken under oxidizing conditions from 25 to 600°C (Fig. 4b). The band at 420 nm still exists from 25 to 200°C. As the temperature is increased further to 300–600°C, however, this band disappears and the band around 260–350 nm (oxidized silver clusters) reappears. Hence, we observe here a remarkable reversibility of Ag structures in cyclic redox operation. The redispersion of silver in oxygen at T>300°C is noteworthy.

In a recent report [30], Ag nanoparticles on a TiO_2 (110) single crystal were found to evolve into a mixture of fine clusters and bigger particles when exposed to low oxygen pressure at room temperature [30]. A quantum effect was identified in silver clusters, while the metallic character was present in nanoparticles of ~5 nm size. There is no similar report for silver on alumina. However, the co-existence of silver clusters and nanoparticles is strongly supported by the present results on alumina.

Fig. 5 presents a comparison of Ag catalysts over various support materials. The loading of silver is kept constant at ~4 wt.%. Among the co-gel AlAg-2A, impregnated Ag/Al_2O_3 and ion-exchanged Ag/ZSM-5, AlAg-2A has the best activity both for SCR of NO to N_2 and conversion of CH_4 to CO_2 over the whole temperature range. AlAg-2A reaches a maximum NO to N_2 conversion of 87% at 550°C. At high temperature (500–650°C), AlAg-2A is comparable to Ce promoted Ag-ZSM-5, which is the highest activity Ag-catalyst for CH_4–SCR [9,24,31] reported in the literature. While Ag-ZSM-5 and Ag-Ce-ZSM-5 are active over a wider operating temperature window, these catalysts are not as stable as their Ag-alumina counterparts. In fact, the zeolite-based catalysts lost 20–30% of their activity after reaction at 700°C, unlike the alumina-based samples. The Ag-Ce-ZSM-5 material, however, is superior to Ag-alumina with low CH_4/NO ratios in the feed gas [32]. Lacking a good kinetic or mechanistic explanation for this at the present time, we may attribute the activity of Ag-Ce-ZSM-5 to promotion by cerium.

The used catalysts (after reaction at 700°C) lost 10–20% of their surface area, Table 1. The dispersion of AlAg-1A remained the same after 12 h-on-stream at the conditions of Fig. 1, while the high-content Ag samples had lower Ag dispersion after use. The most dramatic loss of silver dispersion was found on the Condea alumina-supported samples (Table 1). This loss of dispersion may be overestimated, however, since we do not know if any (hard to reduce) silver aluminate had formed on these catalysts. Indeed,

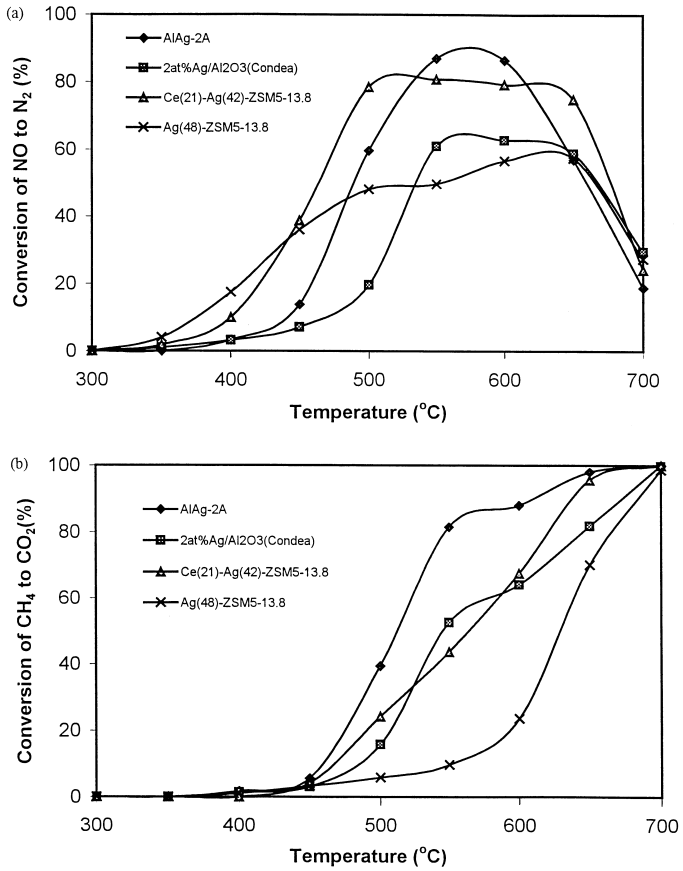

Fig. 5. CH_4–SCR of NO over various Ag-containing catalysts with similar Ag loading (3.5–4 wt.%). (a) conversion of NO to N_2; (b) conversion of CH_4 to CO_2. Feed gas: 0.25%NO–2%CH_4–5%O_2/He; S.V.=9000/h (NTP)

while the apparent dispersion of the used samples is so low, their activity remained stable.

Most remarkable was the stability of the co-gel samples. Fig. 6 shows that over the AlAg-2A sample, the NO conversion to N_2 and CH_4 to CO_2 remained unchanged during 24 h-on-stream at 550°C in the presence of H_2O (~3%) produced by the reaction. We also found that the SCR activity was increased in the presence of higher O_2-content in the feed gas [32]. Fig. 7 presents data on the activity of AlAg-1A under more demanding conditions. The catalyst was first used in long tests (for 80 h) with SO_2 and H_2O present in the feed gas at the conditions of Fig. 8 (see further). The tests in Fig. 7 were conducted with 10% O_2 in the feed gas and at space velocities in the range 38,000–106,000/h. The catalyst retains good activity and stability at these conditions.

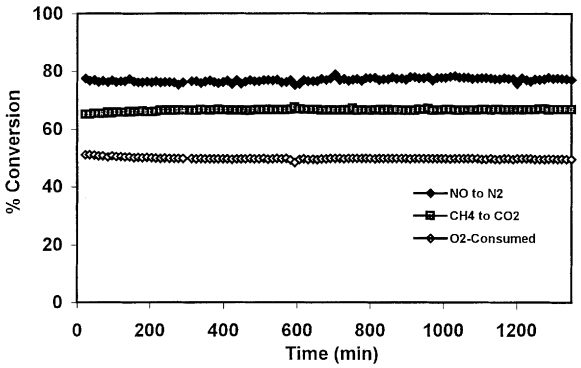

Fig. 6. Conversion of NO to N_2, CH_4 to CO_2 and consumption of O_2 with time-on-stream at 550°C over AlAg-2A. Feed gas: 0.25%NO–2%CH_4–5%O_2/He; S.V.=9000/h (NTP)

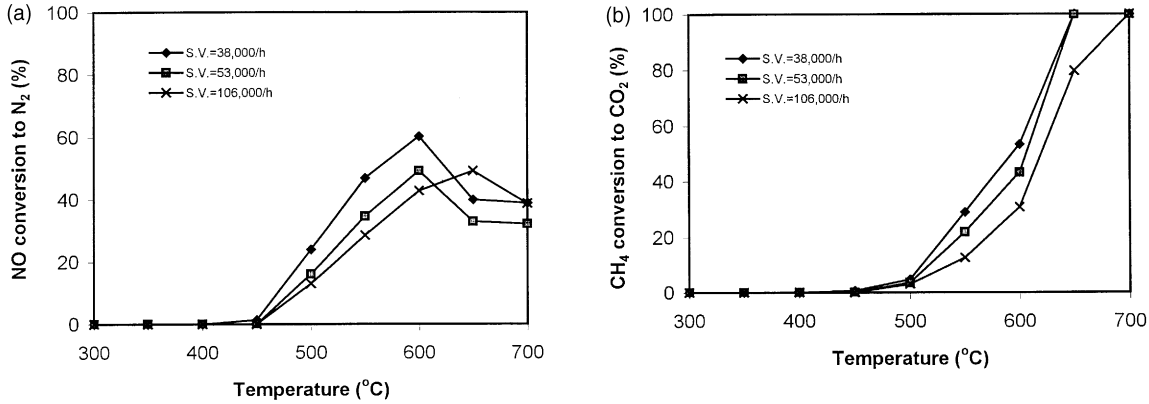

Fig. 7. CH_4–SCR of NO over aged AlAg-1A at various space velocities. (a) conversion of NO to N_2; (b) conversion of CH_4 to CO_2. Feed gas: 0.25%NO–2%CH_4–10%O_2/He.

The stability of AlAg-1A under the combined effect of SO_2 and H_2O is also reported here. Fig. 8 shows the conversion of NO and CH_4 over AlAg-1A in the presence or absence of SO_2 and H_2O at SV=38,000/h. At 600°C, 30 ppm SO_2 in the feed gas has no effect on the NO conversion to N_2, although it causes a small, but measurable drop in CH_4 conversion. This is totally reversible when SO_2 is removed. Adding 10% H_2O and 30 ppm SO_2, at 600°C, caused a drop in NO conversion (from 78 to 50%) and increased the CH_4 conversion (from 68 to 90%). However, this increase was found to be due to carbon monoxide produced from CH_4 (20%). After aging in H_2O and SO_2 for 16 h, H_2O and SO_2 were switched off and the NO conversion increased to 70%, while CH_4 conversion decreased back to 80%. The combined H_2O and SO_2 effect was also

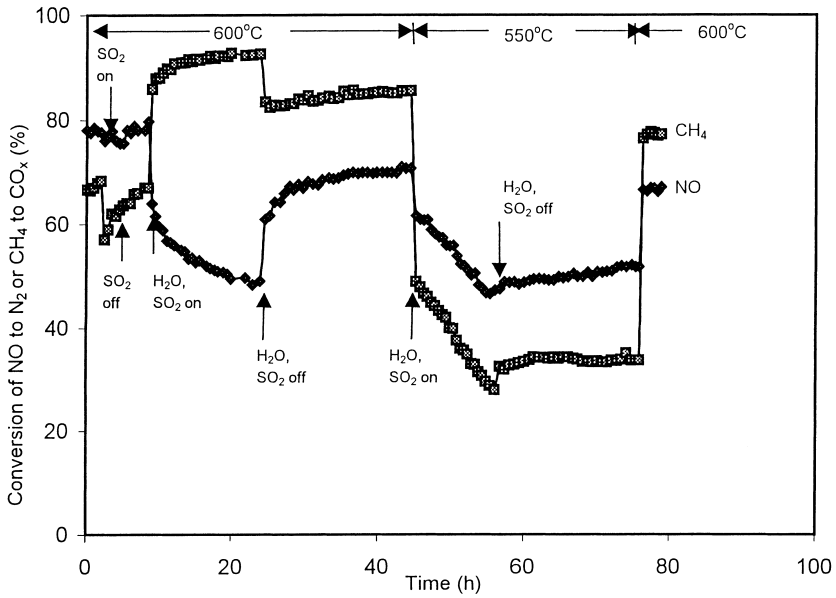

Fig. 8. Effect of SO_2 and H_2O on CH_4–SCR of NO over AlAg-1A; S.V.=38,000/h (NTP) Feed gas : 0.25%NO–2%CH_4–10%O_2–(0 or 30 ppm) SO_2–(0 or 10%) H_2O/He.

tested at 550°C. Both NO and CH_4 conversion decreased gradually for 11 h. Upon switching off the SO_2 and H_2O, only partial recovery was observed. After 16 more hours, the temperature was raised to 600°C, and the NO and CH_4 conversion were increased to 70 and 75%, respectively. Thus, the Ag-alumina system shows promise for SCR of NO with CH_4 even in the presence of SO_2 and excess water, as long as the temperature is kept above 550°C. These results are very promising for further development of the Ag-alumina catalysts as bifunctional catalysts for the SCR of NO_x and the combustion of excess methane in gas turbine, CNG engine and other exhaust gas streams.

4. Conclusions

Silver-alumina catalysts with high activity for the SCR of NO with methane were demonstrated in this work. The catalysts were synthesized by a single-step co-gelation technique which was superior to impregnation methods. The resulting Ag structure is active for SCR of NO by CH_4 over the temperature range 450–700°C. A remarkable activity and performance stability is exhibited by this type catalyst. This may derive from small clusters of oxidized silver and even embedded Ag ions in the alumina matrix which have high activity for CH_4–SCR, but low CH_4 combustion activity. However, the latter reaction also occurs on other sites of the silver catalyst. Thus, in the temperature range of 550–600°C, the Ag-alumina catalyst is effectively bifunctional, i.e. similarly active for both reactions. Development of catalysts capable of high conversions of NO_x by CH_4 in excess O_2-containing gas streams would offer an attractive alternative to high temperature NH_3–SCR, which is commercially practised for NO_x reduction in gas turbine exhausts at >500°C. Kinetic studies are currently underway to further correlate the SCR activity with the silver-structure. This may be relevant not only to CH_4–SCR, but to SCR of NO_x by other hydrocarbons as well as oxygenates.

Acknowledgements

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