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RESEARCH NOTE

Improvement of SO_x-Resistance of Silver Lean-$DeNO_x$ Catalysts by Supporting on CeO_2-Containing Zirconia

N. Hickey,* P. Fornasiero,* J. Kašpar,*,[1] M. Graziani,* G. Martra,†
S. Coluccia,† S. Biella,‡ L. Prati,‡ and M. Rossi‡

**Dipartimento di Scienze Chimiche, Università di Trieste, Via Giorgieri 1, I-34127 Trieste, Italy; †Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, I-10125 Torino, Italy; and ‡Dipartimento di Chimica Inorganica, Metallorganica e Analitica—Centro CNR, Università di Milano, Via G.Venezian 21, I-20133 Milan, Italy*

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The lean-deNO$_x$ activity of Ag/Al_2O_3, $Ag/Ce_{0.16}Zr_{0.84}O_2$, and Ag/ZrO_2 was compared. The activity data showed that by supporting Ag on ZrO_2-containing supports, low-temperature deNO$_x$ activity is greatly improved compared to Ag/Al_2O_3. TEM investigation suggested that the support is at the origin of this shift of activity to low temperature rather than in the presence of large Ag particles. More important, use of $Ce_{0.16}Zr_{0.84}O_2$ and ZrO_2 as supports confers improved sulphur resistance compared to Al_2O_3-based materials in that regeneration of the SO_2-poisoned catalyst may be achieved under moderate conditions. © 2002 Elsevier Science (USA)

Key Words: **deNO$_x$ catalysts; silver catalysts; sulphur poisoning; ceria–zirconia catalysts.**

INTRODUCTION

Efficient NO_x abatement from oxygen-rich exhausts, such as those originating from lean-fuelled engines, has become one of the major challenges for environmental catalysis. Literally hundreds of catalysts have been tested (1), with transition-metal-containing zeolites and Pt/Al_2O_3 being among the most effective systems. They, however, respectively suffer from poor hydrothermal stability and a narrow range of activity (200–270°C). Ag-containing catalysts have attracted attention as inexpensive—compared to Pt catalysts—and highly active systems (2–7). However, even these catalysts suffer from some major drawbacks, showing activity only at relatively high temperatures (around 500°C) and high sensitivity to sulphur poisoning, which makes them unsuitable for typical lean-deNO$_x$ applications such as in diesel engines. Here, we show the key role of ZrO_2-based supports in modifying the catalytic properties of supported Ag. Both low-temperature lean-deNO$_x$ activity and the sulphur tolerance of the system are improved compared to that of Ag/Al_2O_3.

EXPERIMENTS AND METHODS

Ag was supported either by incipient wetness (IW) (using $AgNO_3$) or by depositing a preformed Ag sol (8) (SOL) onto the support (Ag loading, 2 wt%; $Ce_{0.16}Zr_{0.84}O_2$, 100 m^2 g^{-1}; ZrO_2, 40 m^2 g^{-1}; and γ-Al_2O_3, 100 or 180 m^2 g^{-1}). Samples were calcined at 650°C before reaction. Activity tests were performed using a reaction mixture of 1000 ppm NO, 1000 ppm C_3H_6, and 5% O_2 (balance He) and, when present, 50 ppm SO_2 and 10% H_2O; the weight/flow rate (W/F) was 0.10–0.025 g s ml^{-1}. Activity profiles were obtained either by increasing the temperature in steps of 25°C and monitoring activity for at least 40 min at each temperature, or by run-up experiments (heating rate, 10°C min^{-1}). Analysis was performed by gas chromatography (C_3H_6, CO_2, CO, O_2, N_2O, N_2) and a chemiluminescence detector (NO, NO_2). Transmission electron micrographs (TEM) were obtained with a Jeol 2000EX microscope. The samples were ultrasonically dispersed in 2-propanol and deposited on a copper grid covered with a lacey carbon film.

RESULTS AND DISCUSSION

Figure 1 compares NO_x and C_3H_6 conversion curves for Ag/Al_2O_3 (IW, 100; IW, 180) Ag/ZrO_2 (IW, 40), and $Ag/Ce_{0.16}Zr_{0.84}O_2$ (SOL, 100) as a function of temperature. There is a remarkable difference between Ag/Al_2O_3 and the zirconia-based systems, as the range of temperatures of NO_x conversion is shifted down by about 150°C for the latter catalysts. Similar shifts of activity to low temperatures have previously been reported for an Ag/ZrO_2 catalyst compared to Ag/Al_2O_3 (4) and also for highly loaded Ag/Al_2O_3 (>6 wt%) (2). Such shifts of deNO$_x$ activity were generally attributed to the presence of large Ag

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[1] To whom correspondence should be addressed. Fax: +39-040-5583960. E-mail: kaspar@units.it.

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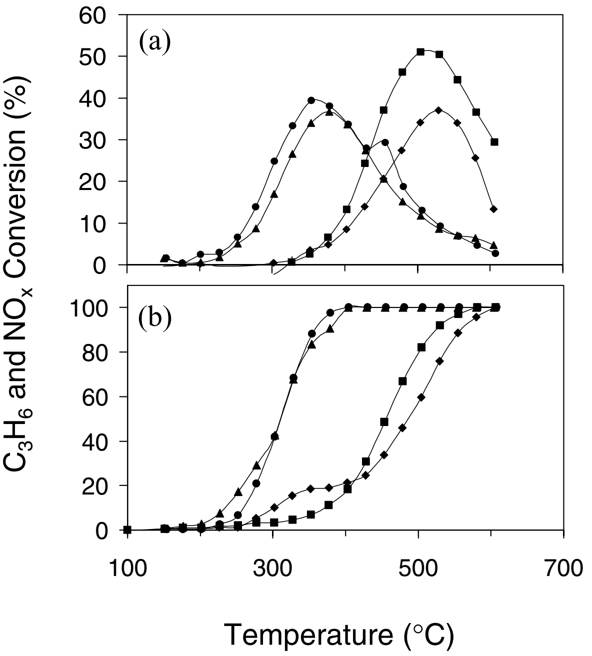

FIG. 1. (a) NO_x and (b) C_3H_6 conversions measured as a function of temperature over (●) $Ag/Ce_{0.16}Zr_{0.84}O_2$ (SOL, 100), (■) Ag/Al_2O_3 (IW, 180), (▲) Ag/ZrO_2 (IW, 40), and (◆) Ag/Al_2O_3 (IW, 100) catalysts. $W/F = 0.05$ g s ml^{-1}.

metallic particles under reaction conditions, which are selective towards N_2O formation, e.g., 27% of the NO fed was reduced to N_2O at a total NO conversion of 43% over 6 wt% Ag/Al_2O_3 (2). More dispersed oxidised Ag species are active at high temperatures and form almost exclusively N_2 (2). The product distributions obtained over the present Ag/Al_2O_3 samples are comparable to those reported in the literature; for example, less then 1% of N_2O is formed at a NO conversion of 51% over Ag/Al_2O_3 (IW, 180). At T_{max} (Table 1) 9 and 12% N_2O was observed over, respectively, $Ag/Ce_{0.16}Zr_{0.84}O_2$ and Ag/ZrO_2. With regard to the conversion levels achieved, direct comparison of data obtained in different laboratories is difficult, with space velocity, Ag loading, concentration of reductant, concentration of O_2, and preparation method all reported to be significant factors in the conversions achieved. Rates at 450°C of 1.8×10^{-7} mol of $NO_{x\text{ converted}}$ g^{-1} s^{-1} and 3.3×10^{-7} mol of $NO_{x\text{ converted}}$ g^{-1} s^{-1} were measured for Ag/Al_2O_3 (IW, 100) and Ag/Al_2O_3 (IW, 180), respectively. These compare well with the values of 3.1×10^{-7} mol of $NO_{x\text{ converted}}$ g^{-1} s^{-1} at 440°C and 2.5×10^{-7} mol of $NO_{x\text{ converted}}$ g^{-1} s^{-1} at 450°C for the same reaction under similar reaction conditions, calculated from the data reported in Refs. (4, 2), respectively. The presence of a "plateau" in the C_3H_6 conversion curve for Ag/Al_2O_3 (IW, 100) is an unexpected feature. We believe that this may be attributed to the inhomogeneous Ag particle distribution of this sample (see Table 1). As has been suggested in previous reports (2, 4), the presence of large Ag particles should promote unselective combustion at lower temperatures. As such unselective combustion occurs at the expense of the deNO_x activity, this would also contribute to the difference in deNO_x activities of the two alumina-based materials.

TABLE 1

DeNO_x Activity and Effects of SO_2 Addition to the Feed/H_2 Regeneration on Steady-State DeNO_x Activity at 450°C[a]

				DeNO_x activity					
					Maximum DeNO_x activity		DeNO_x activity at 450°C (%)		
Sample	Preparation method	BET surface area (m^2 g^{-1})	Ag particle size (nm)	Activity range (°C)	T_{max} (°C)	Conv. (%)	SO_2-free	$+SO_2$	After H_2
$Ag/Ce_{0.16}Zr_{0.84}O_2$	IW	100	See note[b]	200–600	375	13	—	—	—
	SOL	100	25 ± 5	200–600	350	39	26	6	23
							28[c]	15[c]	28[c]
Ag/ZrO_2	IW	40	4 ± 2.5	250–600	375	36	17	0	22
Ag/Al_2O_3	IW	100	8 ± 4.0[d]	325–600	510	35	21	6	9
	IW	180	11 ± 7.5[e]	325–600	500	51	50[f]	25[f]	31[f]
	SOL	100	13 ± 8[g]	400–600	540	18	20	6	14

[a] Reaction conditions as reported in the text. $W/F = 0.05$ g s ml^{-1}. H_2 regeneration at 450°C in flow of H_2 (5% in Ar) for 10 min. DeNO_x activity: conversion of NO_x ($NO + NO_2$). Three other $Ag/Ce_{0.16}Zr_{0.84}O_2$ and Ag/ZrO_2 catalysts were tested, giving analogous activity results (data not reported).

[b] Due to poor contrast with the support no Ag particle could be detected at the various magnifications employed. The presence of Ag was analytically detected by the TEM/EDS technique, which suggests that Ag should be highly dispersed with particles <1 nm, even though the presence of some very large particles undetectable by TEM cannot be discounted.

[c] 10% of water was added to the feed.

[d] Inhomogeneous particle distribution was observed with a few large particles, at 24–25, 29–31, and 35 nm, accounting for about 60 mass%.

[e] Bimodal particle distribution was observed with about 8 mass% of particles both at 21 and at 27 nm.

[f] Reaction temperature, 500°C, the temperature of maximum deNO_x activity.

[g] Bimodal particle distribution was observed with about 50 mass% of particles at 32 ± 3 nm.

In an attempt to clarify the origin of this high activity at low temperatures of the zirconia-based catalysts, a number of different catalysts were tested (Table 1). The differences in preparation were intended to create variations in the Ag particle size. It can be seen that, irrespective of the synthesis method or surface area of the support, the temperatures where the deNO$_x$ activity is observed over the zirconia-containing materials is always lower by ca. 150°C compared to Ag/Al_2O_3. It should also be noted that under ramped reaction conditions (10°C min^{-1}), no differences in the activity ranges of Ag/Al_2O_3 (IW, 100) and Ag/$Ce_{0.16}Zr_{0.84}O_2$ (SOL, 100) were observed upon varying W/F by a factor of four. Attempts to detect the Ag particle size by XRD failed; likewise, the reducible nature of the $Ce_{0.16}Zr_{0.84}O_2$ precluded the use of O_2 or N_2O chemisorption. Therefore, TEM data for selected samples were obtained (Table 1). The particle size distributions measured suggests that the presence of large Ag particles is not the major factor responsible for the observed behaviour of the zirconia-based materials. Rather, an interaction between the support and the Ag particles appears at the origin of the high activity at low temperatures.

Knowledge of the ability to withstand the poisoning effects of sulphur is an important factor in the assessment of any material with potential deNO$_x$ application. Here, the effects of addition of SO_2 to the feed on the deNO$_x$ activity were compared at 450°C, where all the systems show appreciable activity (Fig. 2). All catalysts suffer from a significant deactivation as 50 ppm SO_2 is added to the feed. However, the response of the catalysts to SO_2 poisoning/catalysts regeneration is fundamentally different. A remarkably good recovery of the deNO$_x$ activity could be achieved in the case of zirconia-based materials by exposure to 5% H_2 at 450°C for 10 min at a flow rate of 60 ml min^{-1} (Fig. 2). Effective catalyst regeneration could be achieved for several deactivation/regeneration cycles. It is very important that even milder regeneration procedures were quite effective: 50–80% of the initial activity of Ag/$Ce_{0.16}Zr_{0.84}O_2$ could be recovered, for example, by pulsing 1 ml of H_2 over the catalyst, or even by simply removing the SO_2 from the feed at 450°C. In contrast, only limited regeneration of the Ag/Al_2O_3 catalysts could be achieved under the same gas-phase composition and time of reduction for temperatures as high as 600°C. This is also true for the most active Ag/Al_2O_3 (IW, 180), where the effect of SO_2 addition was tested at 500°C, i.e., at the temperature of maximum deNO$_x$ activity. For comparison, a significant degree of regeneration of SO_x-poisoned Ag/Al_2O_3 could be achieved only by employing rather severe conditions (9). The noticeably slow deactivation of Ag/$Ce_{0.16}Zr_{0.84}O_2$ (SOL, 100)—the activity halves after 140 min—upon SO_2 addition deserves some comment: immediately after the addition of SO_2 to the feed, very slow deactivation of the deNO$_x$ activity is observed as long as NO_2 is produced over the catalyst. Once production of NO_2 is totally suppressed, a constant conversion of 22% is observed for about 20 min; the activity then dropped to 6%. In contrast, over both Ag/ZrO_2 and Ag/Al_2O_3 deactivation due to SO_x poisoning started almost immediately after the SO_2 addition to the feed, with the activity halving, respectively, after 25 and 45 min. Note that differences in BET area of the support cannot account for the different activity decay. Upon regeneration of the poisoned catalysts with H_2 at 450°C, NO_2 formation is irreversibly suppressed in the case of Ag/$Ce_{0.16}Zr_{0.84}O_2$, whereas it is reversible in the case of Ag/ZrO_2. No significant amount of NO_2 is observed over Ag/Al_2O_3, due to the fact that the reaction temperature of 450°C is below the region where NO_2 is observed in the gaseous phase over this catalyst.

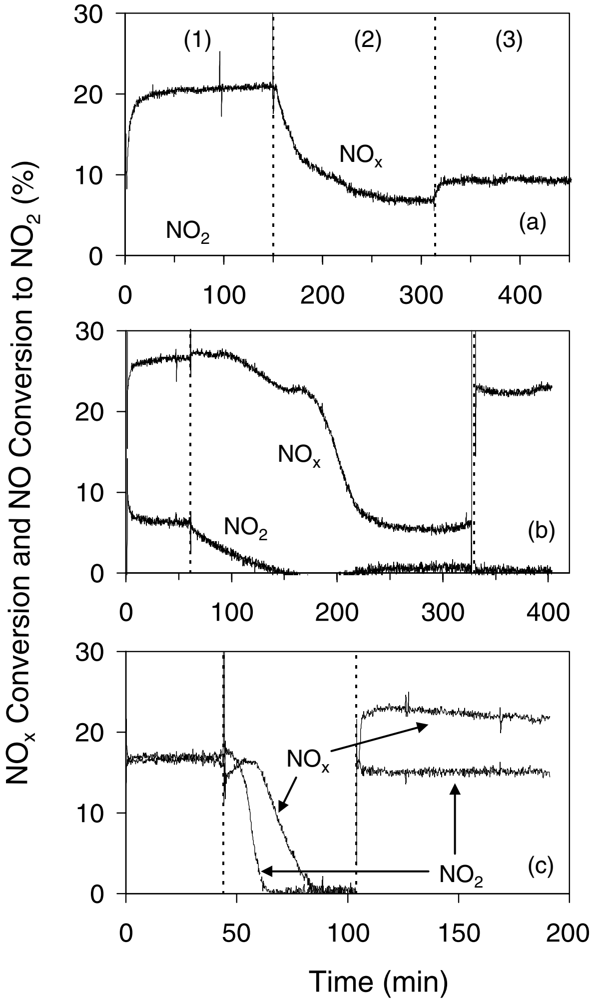

FIG. 2. DeNO$_x$ activity at 450°C: (1) activity of the fresh catalysts, (2) effect of SO_2 addition (50 ppm) to the feed on the activity, and (3) activity in the absence of SO_2 after regeneration in H_2 (5% in He for 10 min) over (a) Ag/Al_2O_3 (IW, 100) (b) Ag/$Ce_{0.16}Zr_{0.84}O_2$ (SOL, 100), and (c) Ag/ZrO_2 (IW, 40). NO$_x$, conversion of NO and NO_2 (formed in the reaction) to N_2 and N_2O; NO_2, conversion of NO to NO_2. Less then 4% of NO fed is converted to N_2O on each catalyst. Total NO conversion (not reported) is sum of NO$_x$ and NO_2 conversions. $W/F = 0.05$ g s ml^{-1}.

Experiments carried out also in the presence of water (10%) confirmed this promoting effect of the $Ce_{0.16}Zr_{0.84}O_2$

support on the Ag catalyst and the easy regeneration from SO_x poisoning (Table 1). The addition of water to the feed did not affect the catalyst activity or regeneration characteristics over the time-on-stream investigated (12 h). Finally, preliminary temperature-programmed reduction experiments carried out over the SO_2-poisoned catalysts showed that significantly higher amounts of sulphur-containing species are stored over $Ag/Ce_{0.16}Zr_{0.84}O_2$ compared to Ag/Al_2O_3. This suggests that the $Ce_{0.16}Zr_{0.84}O_2$ support may act as a sink for these species, accounting for the improved sulphur resistance.

In summary, it is shown that use of $Ce_{0.16}Zr_{0.84}O_2$ as support strongly modifies the $deNO_x$ activity of the Ag catalysts, the activity range being decreased to lower temperature. A change of Ag particle size does not appear to be a major factor responsible for this observation. However, of more importance is the observation that the sulphur tolerance is improved from the point of view that facile regeneration from SO_2 poisoning can be achieved. While the overall activity of the catalyst investigated is not sufficient to provide a practical solution to the problem, these results may provide new directions for research into lean-$deNO_x$ catalysis, as, for example, it has been demonstrated for Ag/Al_2O_3 that appropriate synthesis may result in improved activity (10).

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