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Unusual activity enhancement of NO conversion over Ag/Al_2O_3 by using a mixed NH_3/H_2 reductant under lean conditions

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Addition of H_2 to a $NO/NH_3/O_2/H_2O$ feed for selective catalytic reduction of nitrogen oxide over Ag/Al_2O_3 catalysts causes an unusual enhancement of activity, e.g., the marginal activity (< 10%) of 1 wt% Ag impregnated on γ-Al_2O_3 or mesoporous Al_2O_3 modifications is boosted to nearly 100% over a broad temperature range from 200 to 550 °C at a space velocity of 30,000 $cm^3\ g^{-1}\ h^{-1}$). Contrary, silver on SiO_2 or α-Al_2O_3 shows no improvement of activity in the presence of H_2. The effect is tentatively attributed to a higher percentage of intermediary nano-sized Ag clusters on high-surface area Al_2O_3 in the presence of hydrogen. This promotes oxygen activation and hence NO oxidation to reactive intermediate nitrite species. The required dispersion of Ag cannot be stabilized on SiO_2 or α-Al_2O_3.

KEY WORDS: SCR of NO_x by NH_3; Ag-based catalysts; activity enhancement; hydrogen admixture.

1. Introduction

The selective catalytic reduction (SCR) of NO/NO_2 (NO_x) by ammonia over V/TiO_2 catalysts is a versatile technology for exhaust cleaning of gas- and oil-fired boilers, waste incineration plants, chemicals plants (e.g., for nitric acid production), gas turbines and Diesel-fuelled stationary combustion engines [1]. Recently, the application concentrates on the removal of NO_x from exhaust gas of Diesel-fuelled cars [2]. A modified ammonia-assisted SCR of NO_x is reported to be in use for heavy duty vehicles [3], where ammonia is produced by decomposition of urea on board. One drawback of the V/TiO_2 catalyst system is the decline of activity whenever temperatures fall beneath 250 °C. Therefore, the catalyst cannot guarantee sufficient NO_x conversion during any start-up and idle engine operation mode. Several catalyst formulations have been proposed for substitution of the V/TiO_2 system such as Fe-modified zeolites [4], CeO_2/zeolite composite catalysts [5] or Fe–Mn-based catalysts [6], however, without any commercial breakthrough so far. Silver-based catalysts are only marginally active for the NH_3-SCR of NO_x within the temperature window of operation. On the other side, the Ag/Al_2O_3 catalyst system is promising for NO_x removal with other reductants like alkenes, alkanes, alcohols and ethers [7]. Nevertheless, activities are disappointing as well at low temperatures, especially with wet exhaust feed. Recently, it has been reported [8,9] that the hydrocarbon-assisted SCR of NO_x over Ag/Al_2O_3 catalysts can be promoted by additionally mixing hydrogen to the feed, although hydrogen per se is an unsuitable reductant for conversion of NO_x to N_2 in O_2 excess [7]. The question not addressed so far is, whether this "H_2 effect" also appears in case of non-hydrocarbon reductants, e.g. ammonia. If indeed the use of a ammonia/hydrogen mixed reducing agent would enable higher activities of silver-based catalysts, this approach could open a competitive alternative to the V/TiO_2 catalyst system.

Thus, we investigated the SCR of NO_x over a series of supported Ag catalysts by using NH_3 and NH_3/H_2 for reduction.

2. Experimental

2.1. Catalyst preparation

Samples Ag/α-Al_2O_3 and Ag/γ-Al_2O_3 were prepared by incipient wetness impregnation of commercial α-Al_2O_3 and γ-Al_2O_3 (CONDEA), respectively, with $AgNO_3$ solution to yield the desired loading. For preparation of Ag/Al_2O_3 by a sol–gel (sg) process, a water dispersible alumina hydrate (Disperal P2 (CONDEA)) was used with average colloidal particle sizes of about 10 nm in the resulting sol. After re-dispersion, a 1 M $AgNO_3$ solution was added to the sol to give the desired Ag contents of 1 and 5 wt%, leading to immediate gel formation. The gel was filtered, dried at 120 °C for 2 h, and calcined at 550 °C in air. The silver loading was 0.95 and 4.61 wt% as determined by ICP-OES.

Sample Ag/SiO_2 represents a MCM-41-like mesoporous structure synthesized from tetraethyl ortho silicate and hexadecyl trimethlyammonium bromide as template according to well-known routines [10]. Obtained powders were compacted to tablets first and crushed subsequently to granules with mesh sizes (ASTM) of 42–24 (0.35–0.71 mm).

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Surface areas and pore volumes of the catalyst samples were determined by N_2 adsorption using a ASAP 2010 (Micromeritics) unit. The samples were kept at 400 °C under vacuum (0.13 Pa) for 4 h before starting N_2 adsorption at liquid nitrogen temperature. Average pore diameters were determined from the desorption branch of the isotherms according to the Barrett–Joyner–Halenda approach [11].

2.2. Catalytic measurements

Before catalytic tests, all catalysts were pretreated ex situ at 550 °C in air for 2 h. Catalytic tests were carried out in a flow reactor at 300 °C with a feed composed of 1000 ppm NO, 1000 ppm NH_3, 6% O_2, 7% H_2O and 750–10,000 ppm H_2. Analysis of product composition corresponds to the experimental details given elsewhere [12]. Conversion of NO is defined as $X_{NO} = 100([NO]_0-[NO])/[NO]_0$ (%) where $[NO]_0$ and [NO] are the concentration of NO at the reactor inlet and outlet, respectively. The selectivity of the process S_{N2} is expressed as $100[N_2]/([N_2]+[N_2O])$ (%).

3. Results and Discussion

Textural data of the catalysts and values of X_{NO} and S_{N2} at a reaction temperature of 300 °C are summarized in table 1. It can be seen, that Ag on α-Al_2O_3 and SiO_2 show no positive response to feed modification by H_2 addition. The initial NO conversion of sample Ag/SiO_2 could not be reproduced after returning from H_2-containing feed to H_2-free feed. Instead, activity has dropped to near zero. Obviously, reaction with H_2-containing feed led to irreversible modification of the Ag surface phase. Therefore, it can be concluded that, actually, sample Ag/SiO_2 has no activity at all. Sample Ag/α-Al_2O_3 is comparatively active (ca. 50% NO conversion at 300 °C), but, the reaction leads to mainly N_2O (N_2 selectivity ca. 30%). Both, activity and selectivity are only marginally influenced by the additional presence of H_2 in the feed.

However, catalyst samples on γ-Al_2O_3 or mesoporous Al_2O_3 (sg) supports respond in a pronounced way to co-fed H_2. The activity is boosted from values less than 10 – 100% at 300 °C, even in the presence of 7% H_2O, with N_2 selectivities always higher than 95%.

The activity temperature profile of the most promising catalyst samples, prepared by sg transformation is shown in figure 1. Without H_2 addition, the $deNO_x$ activity is negligibly low within the temperature range from 150 to 450 °C. A NO_x conversion of approximately 30% at maximum is achieved at 550 °C. The N_2 selectivity is relatively low due to the percentage of N_2O formed (cf. table 1). Upon addition of 1% H_2, the NO_x conversion is enhanced to nearly 100% over a wide temperature range. The onset of activity lies beneath a temperature of 150 °C. For example, the low-temperature activity of 5% Ag/Al_2O_3 (sg) is as high as 60% at 150 °C. Remarkably, a high N_2 selectivity is retained over the broad temperature range of operation, contrary to other low temperature NH_3-SCR catalyst formulations [13], where NO_x reduction is shifted to undesired N_2O formation at higher reaction temperatures.

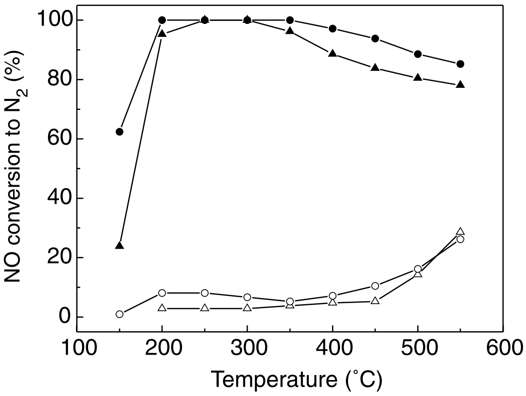

Figure 1. SCR of NO_x by NH_3 over 1% Ag/Al_2O_3 (sg) (triangles) and 5% Ag/Al_2O_3 (sg) (circles) without H_2, (open symbols) and with co-fed H_2 (1 vol%) (full symbols). Reaction conditions: 1000 ppm NO, 1000 ppm NH_3, 6 vol% O_2, 7 vol% H_2O, 0.24 g, flow rate 2 $cm^3\ s^{-1}$, space velocity 30,000 $cm^3\ g^{-1}\ h^{-1}$.

Table 1

Catalyst characteristics and catalytic properties

Sample[a]	Ag (wt%)	S_{BET} ($m^2\ g^{-1}$)	V_P ($cm^3\ g^{-1}$)	Without H_2		With H_2	
				X_{NO} (%)	S_{N2} (%)	X_{NO} (%)	S_{N2} (%)
Ag/γ–Al_2O_3	1	223	0.55	3	~0[c]	100	99
Ag/Al_2O_3 (sg)	1	235	0.43	5	75	100	99
Ag/Al_2O_3 (sg)	5	232	0.39	7	82	100	99
Ag/SiO_2	1	693	0.46	20[b]	~0[c]	~0	~0
Ag/α–Al_2O_3	1	20	0.05	46	32	49	31

[a] BET surface area (S_{BET}) and pore volumes (V_P) were determined by N_2 adsorption at −196 °C. Catalytic tests at 300 °C with 1000 ppm NO, 1000 ppm NH_3, 6% O_2, 7% H_2O ± 1% H_2, remainder He, catalyst weight 0.24 g, flow rate 2 $cm^3\ s^{-1}$, space velocity 30,000 $cm^3\ g^{-1}\ h^{-1}$.

[b] Conversion drops to near zero after returning from H_2 addition to H_2-free feed. Obviously, irreversible modification of Ag has occurred.

[c] Exclusive N_2O formation.

For comparison, a Ti/V_2O_5 standard catalyst showed no "H_2 effect". Ti/V_2O_5 needs temperatures higher by 50 K to achieve comparable NO_x conversion of Ag/Al_2O_3 (sg) samples under the reaction conditions applied.

Hydrogen consumption over Ag/Al_2O_3 (sg) samples amounts to 50–60% at 1% Ag/loading and is nearly complete at 5% Ag loading within the temperature range 200–550 °C.

From an economic viewpoint, it is desirable to limit the necessary hydrogen addition to the lowest value possible. Therefore, the influence of H_2 concentration in the feed was investigated for sample 1% Ag/Al_2O_3 (sg). At a fixed reaction temperature of 300 °C, results shown in figure 2 confirm that X_{NO} approaches 100% with only 0.25 vol% (2500 ppm) H_2 admixture. Therefore, H_2 gas phase concentrations of 1 vol% are not necessarily required. Addition of only 750–1000 ppm H_2, a concentration that lies in the range of the NO_x component concentrations, already leads to a remarkable increase in catalyst activity. With 2500 ppm H_2 admixture to the feed, the applied Ag catalysts are competitive to the commercial V/TiO_2 system that does not operate with 100% NO_x conversion at 200 °C under comparable conditions.

The explanation how H_2 acts has to consider the accumulated knowledge about the SCR of NO_x by C-containing reductants over Ag-based catalysts [7]. For the SCR of NO_x by propane, Satokawa *et al.* [9] and Shibata *et al.* [14] suggested that H_2 enables a higher concentration of intermediate acetate species on a 2% $Ag/\gamma\text{–}Al_2O_3$ impregnated catalyst. We could confirm by FTIR measurements of the same reaction system over 5% Ag/Al_2O_3 (sg), that the presence of H_2 leads to higher concentrations of oxidized species from propane/O_2 (acetate formation), but, moreover, to higher concentrations of nitrite and nitrate ad-species [15]. Therefore, the apparently paradoxical conclusion must be drawn, that H_2 promotes oxidative reaction steps. Taking into account the easy reduction of Ag_2O clusters by hydrogen (in absence of O_2) as revealed by temperature programmed reduction experiments [16], it is suggested that the presence of H_2 generates, on a short-term scale, zero-valent silver. Reactive O (and/or OH) species are formed via dissociative interaction of O_2 (and H_2) with these metallic silver species. Actually, these reactive oxygen atomic species should accelerate the necessary oxidative transformation of gaseous NO to adsorbed nitrite/nitrate. The fact that the "H_2 effect" works with NH_3 as well as with hydrocarbons over appropriately prepared Ag/Al_2O_3 catalysts proves that presumably the reductant activation is not the only reaction step promoted by H_2. This is corroborated by preliminary results of FTIR spectrocopic measurements on the interaction of NH_3 with the catalyst surface of sample 5% Ag/Al_2O_3 in the presence and absence of H_2 [17]. Significant concentration of intermediate surface species could not be observed in either case. Obviously, NH_3 is able to react directly from the gas phase or after activation on Lewis acid sites of the alumina support. The activation of NO seems to be of primary importance. This reaction step is influenced by the presence of H_2 in the discussed roundabout way, especially at low reaction temperatures. The interpretation is further reconcilable with the observed effect of the support. Silver species that initiates the "H_2 effect" to arise should possess an appropriate size allowing redox cycles between Ag^+/Ag^0 under reaction conditions. Stabilization of small Ag^0 clusters and re-dispersion to Ag^+ cations is known from zeolite matrices [18], based on the surface equilibrium reaction (1).

$$Ag^+ + 1/2\ H_2 \leftrightarrow Ag^0 + H^+. \qquad (1)$$

The existence of silver clusters containing three to thirteen atoms is discussed in dependence on the zeolite structure [18].

Therefore, it is assumed that $\gamma\text{-}Al_2O_3$ despite its predominant Lewis-type acidity is able to promote clustering of isolated Ag^+ cations after intermediate reduction.

Basic sites are required for storage of nitrite/nitrate intermediates. Thus, the amphoteric character of high surface area Al_2O_3 is a prerequisite for the H_2 effect to occur. Appropriate surface functions are not available for SiO_2. The α-alumina support has a low surface area. The Ag surface phase is different and the reaction proceeds along another pathway, leading predominantly to N_2O formation.

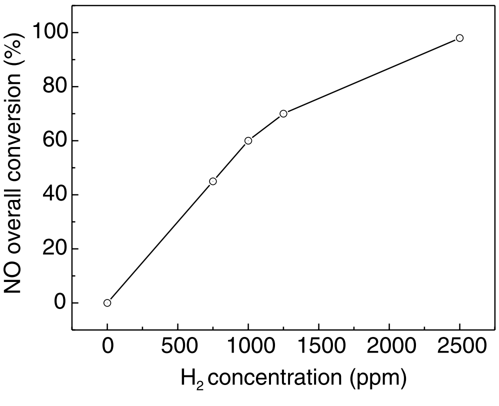

Figure 2. Influence of hydrogen on the selective catalytic reduction of NO by NH_3 at 300 °C over sample 1% Ag/Al_2O_3 (sg). Reaction conditions: 1000 ppm NO, 1000 ppm NH_3, 6 % O_2, 7 vol% H_2O, 0.24 g, flow rate 2 $cm^3\ s^{-1}$, space velocity 30,000 $cm^3 g^{-1}\ h^{-1}$.

4. Conclusions

It has been shown for the first time, that the use of a mixed NH_3/H_2 feed for selective catalytic reduction of NO_x over $Ag/\gamma\text{-}Al_2O_3$ and mesoporous Ag/Al_2O_3 leads to unusual enhancement of catalytic activity at low temperatures. This offers an elegant way to extend the operation window of appropriately prepared Ag catalysts to temperatures of 200 °C and lower, required for the NH_3-assisted catalytic NO_x removal from the exhaust of Diesel-fuelled cars [19]. The reaction occurs in a selective way to N_2 without significant formation of the undesired by-product N_2O.

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