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Journal of Catalysis 236 (2005) 172–175

JOURNAL OF CATALYSIS

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Research Note

Catalytic carbon oxidation over Ag/Al_2O_3

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Received 30 June 2005; revised 8 September 2005; accepted 16 September 2005

Available online 17 October 2005

Abstract

The potential of silver on alumina (Ag/Al_2O_3) catalyst for the oxidation of carbon particles in simulated lean combustion gas was explored. At low temperatures in the presence of NO_x, oxygen, and water, the silver of the catalyst is transformed into silver nitrate. On heating, finely dispersed silver metal is formed that catalyzes the oxidation of NO into NO_2. The carbon oxidation rates in loose mixtures of carbon black and nitrated Ag/Al_2O_3 catalyst were determined gravimetrically using a magnetic suspension balance and gas mixture comprising nitric oxide, oxygen, and water. The temperature for achieving carbon oxidation was lower with nitrated Ag/Al_2O_3 than with Pt/Al_2O_3. The finely dispersed metallic state of the silver required for efficient NO oxidation can be regenerated in cycles involving cooling and heating in the presence of NO_x.

Keywords: Ag/Al_2O_3; Carbon oxidation; Surface nitrates; Particulate trap regeneration

1. Introduction

Diesel engines are energy-efficient power sources for vehicles and are environmentally acceptable when provided with efficient exhaust gas after-treatment systems for eliminating air pollutants. A popular approach for removing soot from diesel engine exhaust involves trapping the particles on a filter. Regeneration of soot filters is a critical issue. In the continuously regenerated particulate trap (CRT) [1–3], a platinum-based catalyst positioned upstream of the filter catalyzes oxidation of NO into the more powerful NO_2 oxidant, such that the light-off temperature of soot combustion is significantly decreased. In the soot oxidation process, NO_2 is reduced back to NO [4,5]. The realization of an NO into NO_2 oxidation function in the soot filter itself presents a significant advantage, because it enables multiple oxidation and reuse of the NO_x molecules [6,7]. An associated difficulty is the realization of efficient catalytic coatings.

Ag/Al_2O_3 is known for its catalytic activity in selective catalytic reduction of NO_x with hydrocarbons [8–19]. Below ca. 250 °C, the Ag/Al_2O_3 catalyst exhibits low activity, because of nitrate formation through reaction of the silver with NO_2 [12,16,20,21]. When exposed to NO-bearing gas mixtures on heating, the alumina-supported silver nitrate decomposes into a mixture of finely dispersed metallic silver particles and cationic silver according to the following reaction stoichiometries [22]:

$$AgNO_3 + NO \rightarrow 2NO_2 + Ag^0 \tag{1}$$

and

$$2AgNO_3 + NO \rightarrow 3NO_2 + Ag_2O. \tag{2}$$

Both of these reactions generate NO_2. The transformation of $AgNO_3$ into Ag_2O and Ag^0 through the reaction of NO into NO_2 is thermodynamically favored at elevated temperatures (Fig. 1). On the Ag/Al_2O_3 surface, reduced silver is present in the form of partially charged clusters composed of up to eight Ag atoms [23]. Reduced silver is an effective NO oxidation catalyst, whereas cationic silver is inactive [12,24]. In this work we report the unique activity of the finely dispersed silver metal obtained through nitrate decomposition for oxidation of carbon particles.

2. Experimental

Ag/Al_2O_3 with 2 wt% Ag loading was prepared at Åbo Akademi University by impregnation of a commercial Al_2O_3 support (LaRoche Industries). The support material was ground

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2005.09.018

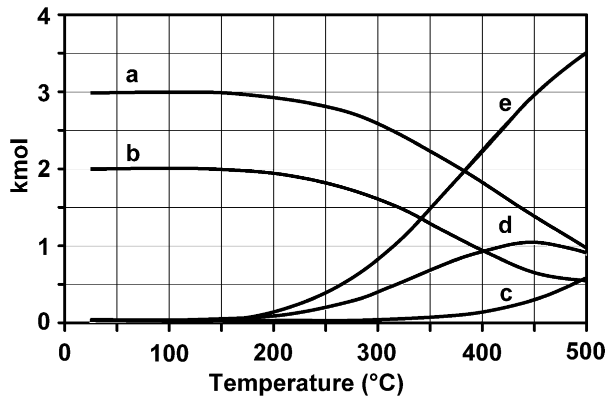

Fig. 1. Thermodynamic equilibrium of the conversion of $AgNO_3$ (a) and NO (b) into Ag_2O (c), Ag metal (d), and NO_2 (e) at 0.1 MPa pressure (computed using HSC Chemistry® 4.0, Outokumpu).

to a particle size of <250 μm and mixed with a 0.022 M $AgNO_3$ solution, followed by drying and calcination at 550 °C for 3 h [13]. The Ag/Al_2O_3 powder was compressed into pellets with diameters of 0.25–0.5 mm. The formation and reactivity of nitrates on Ag/Al_2O_3 catalyst were investigated in a fixed-bed tubular quartz reactor. A total of 400 mg of catalyst pellets, representing a bed volume of 0.6 ml, was held in position between two quartz wool plugs. Gases were fed from cylinders and hydrated using a thermostatted saturator. Helium was used as an inert gas. The contact time of the gas with the catalyst on volume basis was 15,000 h^{-1}. NO and NO_2 concentrations in the outlet of the reactor were analyzed using an internally heated chemiluminescence detector (Ecophysics 700 EL ht). The Ag/Al_2O_3 catalyst was loaded with nitrate in the following manner. The catalyst was pretreated at 400 °C in a gas stream comprising 6% oxygen and 12% water. The temperature was decreased to 150 °C, and the gas mixture was spiked with 500 ppm NO_2 for 2 h. Such treatment, according to our earlier experience, leads to saturation of the catalyst with nitrates [22].

Pt/Al_2O_3 with 0.5 wt% Pt loading was prepared by the incipient impregnation method using an aqueous solution of $Pt(NH_3)_4Cl_2 \cdot H_2O$ (Alfa Aesar). For impregnating 1 g of support, 9 mg of $Pt(NH_3)_4Cl_2 \cdot H_2O$ was dissolved in about 1 ml of water. The impregnated material was dried at 60 °C. Calcination was done at 400 °C for 1 h under a stream of oxygen gas. The catalyst was reduced under hydrogen flow at 400 °C for 1 h.

Carbon oxidation was investigated gravimetrically using a Rubotherm magnetic suspension balance. The carbon black sample selected was Printex-U (Degussa AG), which has combustion properties similar to those of diesel soot [25]. Catalysts were loosely mixed with carbon, using a spatula to obtain realistic contact conditions [26]. The catalyst:carbon ratio was 2:1 by weight. An aliquot of ethanol was added to obtain a paste, which was dried at 60 °C for 2 h and crushed to obtain small fragments. Then 270 mg of the catalyst/carbon mixture was loaded into the suspended, perforated, stainless steel mini basket. A heating rate of 5 °C/min and a total flow rate of 150 ml/min of 10% O_2, 1000 ppm NO, and 5% H_2O in helium were used.

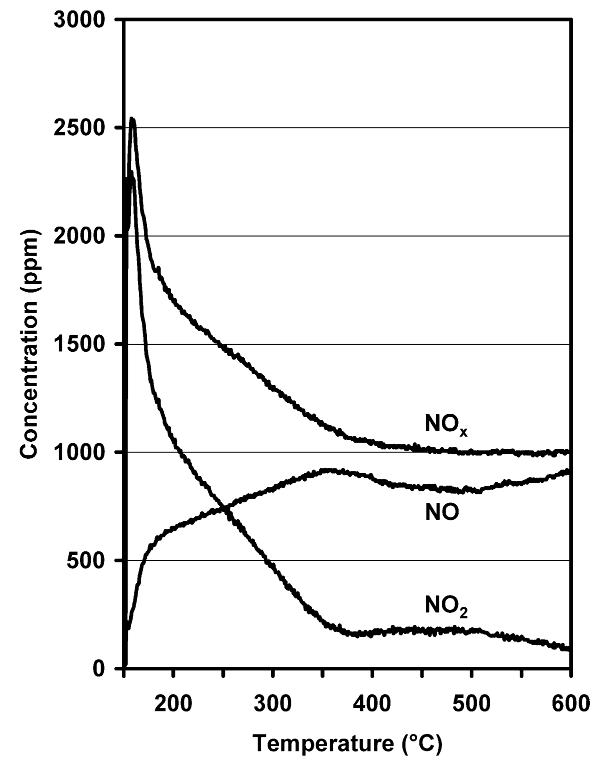

Fig. 2. NO, NO_2 and NO_x outlet concentrations during temperature ramping experiment on nitrated Ag/Al_2O_3 catalyst contacted with NO bearing gas mixture. Catalyst pretreated at 400 °C in helium with 6% O_2 and 12% H_2O; saturated at 150 °C in a gas mixture of 500 ppm NO_2, 6% O_2 and 12% H_2O in helium; temperature ramping at 5 °C/min in helium with 1000 ppm NO, 6% O_2 and 12% H_2O; VHSV = 15,000 h^{-1}.

3. Results and discussion

The evolution of NO_2 on heating of nitrated Ag/Al_2O_3 catalyst in NO atmosphere was demonstrated as follows. The catalyst temperature was raised at a rate of 5 °C/min, and 1000 ppm NO was fed in the presence of oxygen and water. The evolution of the NO, NO_2, and NO_x concentrations in the reactor outlet are shown in Fig. 2. During the heating of nitrated Ag/Al_2O_3 under an NO-bearing gas stream to 600 °C, the outlet NO concentration was always below the inlet concentration of 1000 ppm. Up to ca. 400 °C, there was a net release of NO_x from the catalyst stemming from nitrate elimination reactions [Eqs. (1) and (2)]. Termination of these nitrate decomposition reactions was marked by the outlet NO_x concentration level returning to the inlet value of 1000 ppm at around 400 °C. At higher temperatures, NO oxidation into NO_2 occurred. This NO oxidation activity was attributed to metallic silver generated via silver nitrate decomposition according to Eq. (1). This experiment demonstrates the reaction of the silver nitrate with NO leading to NO_2 formation according to Eqs. (1) and (2) to 400 °C and the NO oxidation activity of the catalyst setting in at around 400 °C.

Nitrated Ag/Al_2O_3 catalyst was prepared in the quartz reactor at 150 °C as described in the experiment of Fig. 2. The catalyst was mixed with carbon, and a carbon oxidation experiment was performed (Fig. 3, curve a). In the mixture of carbon and nitrated Ag/Al_2O_3, carbon oxidation sets in at around 400 °C,

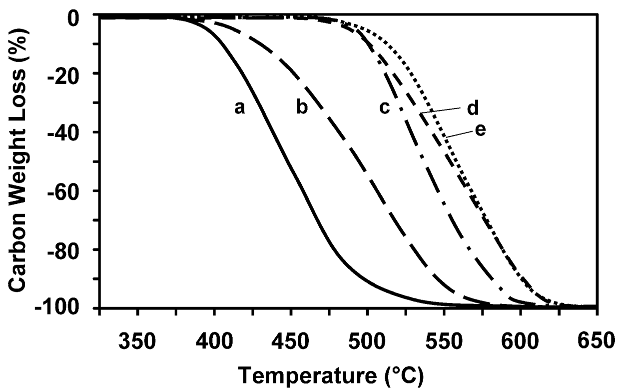

Fig. 3. Carbon oxidation against temperature: (a) nitrated Ag/Al_2O_3, (b) Pt/Al_2O_3, (c) oxidized Ag/Al_2O_3, (d) carbon without catalyst, (e) nitrated Al_2O_3. Gas composition: 10% O_2, 1000 ppm NO and 5% H_2O in He; VHSV = 15,000 h^{-1}; heating rate, 5 °C/min.

as marked by the onset of weight loss. For comparison, carbon combustion in the presence of nitrated Al_2O_3 support (Fig. 3, curve e) occurred at similar temperatures as in the absence of catalyst (Fig. 3, curve d), demonstrating that the presence of silver is essential. In another comparative example, the carbon was mixed with Ag/Al_2O_3 catalyst pretreated at 400 °C in oxidizing gas with 6% oxygen and 12% water. Oxidized silver catalyst is much less active than nitrated Ag/Al_2O_3 catalyst (Fig. 3, curve c). Nitrated Ag/Al_2O_3 oxidizes carbon at an even lower temperature than the same alumina loaded with 0.5 wt% Pt with 47% Pt dispersion (Fig. 3, curve b). The high activity of nitrated Ag/Al_2O_3 in carbon oxidation can be explained by the formation of small Ag^0 clusters around 400 °C, which oxidize NO into the NO_2 required for carbon oxidation (Fig. 1). Bogdanchikova et al. [24] demonstrated that on Ag/Al_2O_3 catalyst, reduced silver is the active phase in NO oxidation, and that oxidized silver is inactive.

After the completion of carbon oxidation at 550 °C, the catalyst was cooled to ambient temperature under a gas stream bearing 1000 ppm NO, 10% oxygen, and 5% water. The catalyst was mixed with carbon, and temperature-programmed carbon oxidation was performed. The carbon weight loss occurred in a similar way as in the first carbon oxidation (Fig. 3a), demonstrating that the reactivation was effective.

The silver system is unique as it restores a high metal dispersion on cooling and reheating in exhaust gas [22]. Each time that the catalyst is cooled, the silver is transformed into silver nitrate on reaction with NO,

$$Ag^0 + NO + O_2 \rightarrow AgNO_3. \qquad (3)$$

The conversion of Ag_2O into silver nitrate requires the presence of NO_2, which can be obtained by oxidation of NO. This oxidation function can be assumed by an oxidation catalyst upstream of the filter unit. However, it is unlikely that in soot filters conditions will occur under which all silver will be oxidized and the catalyst will be completely deactivated. Even a minute concentration of hydrocarbons or hydrogen in a net oxidizing gas stream leads to silver reduction [23,27]. Another pathway to metallic-state silver is autoreduction at elevated temperatures. The versatility of the supported silver chemistry offers a means for regeneration of the dispersed metallic state in exhaust gas depending on composition and temperature.

A potential drawback of the Ag/Al_2O_3 system is its sensitivity to poisoning by sulfur compounds [28,29]. Further work is needed to assess the sensitivity to sulfur.

4. Conclusions

Nitrated Ag/Al_2O_3 is an effective catalyst for oxidation of carbon black in a gas mixture comprising NO along with oxygen and water. This observation can be explained by the decomposition of silver nitrates at around 400 °C, resulting in the formation of very small metallic silver particles that catalyze the oxidation of NO into NO_2. Ag/Al_2O_3 shows higher catalytic activity in carbon oxidation than Pt/Al_2O_3. Ag/Al_2O_3 catalyst substantially decreases the temperature of NO_x-mediated oxidation of carbon particles and potentially can be applied in catalytic coatings of diesel particulate filters to facilitate regeneration.

Acknowledgments

The authors acknowledge the European Union for the financial support through the COMET project (contract number G3RD-CT-2002-00811). J.A.M. acknowledges the Flemish government for supporting a concerted research action on the fundamental understanding of catalytic sites (GOA). The Ag/Al_2O_3 sample was a gift from Kalle Arve from Åbo Akademi University in Finland.

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