Catalysis Today 164 (2011) 480–483

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

SCR of NO by DME over Al_2O_3 based catalysts: Influence of noble metals and Ba additive on low-temperature activity

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ARTICLE INFO

Article history:
Received 1 July 2010
Received in revised form 29 October 2010
Accepted 2 November 2010
Available online 14 December 2010

Keywords:
NO-SCR
DME
Metal loaded Al_2O_3

ABSTRACT

The selective catalytic reduction (SCR) of NO by dimethyl ether (DME) has been investigated over various noble metal loaded Al_2O_3 catalysts. It was found that Ag loaded Al_2O_3 was much more active than Rh, Pd, and Pt loaded ones. Further improvement of the low-temperature performance of Ag/Al_2O_3 between 200 °C and 300 °C was attempted by the addition of various amounts of Ba species; an Al_2O_3 supported Ag (1 wt.%) catalyst promoted by 0.2 wt.% Ba was the most effective for DME-SCR. UV–vis spectra showed that Ag^+ ion played an important role in the reaction and the addition of Ba increased the amount of this active species. Furthermore, FTIR measurements indicated that the formation of such reaction intermediates as –NCO and –CN was promoted by the isolated Ag^+ ions, resulting in the higher activity for DME-SCR.

1. Introduction

Nitrogen oxides (NO, NO_2, and N_2O) are major sources of air pollutants, which bring about acid rain, photochemical smog, ozone destruction, and green house effects. Recently, the selective catalytic reduction (SCR) of NO in oxygen-rich atmosphere has been attracting extensive attention for removing NOx emitted from various engines and combustors. Hydrocarbons (HC) have been proved to act as effective reductants in SCR of NO under lean conditions [1,2], and dimethyl ether (DME) is attracting more attention as a viable alternative to diesel. The advantages of DME over conventional diesel fuels include decreased emissions of NOx, hydrocarbons and carbon monoxide and no undesired production of soot [3]. Recently, application of DME as a reducing agent in SCR of NOx in diesel-powered engines has also been suggested [4–11]. Several authors have reported that DME displays high performance for SCR of NO over γ-Al_2O_3 and promoted alumina [4,5]. The two current most promising HC-SCR catalysts, Ag/Al_2O_3 and Cu-ZSM-5, for after-treatment of diesel-exhaust, are not active for the DME-SCR in the presence of water [8,9]. However, the acidic form of zeolite ZSM-5 (H-ZSM-5) has recently been shown to be a promising catalyst for DME-SCR in the presence of water [10]. Okazaki et al. have suggested that the main working reducing agent is methanol generated from DME on alumina with surface hydroxyl groups [7]. At present, however, the detailed reaction mechanisms are still open to question. The present authors previously reported that Ir/WO_3 was highly active for NO-SCR by CO [12,13] and In and Ga loaded Al_2O_3 for NO-SCR by DME under lean-burn conditions [14].

The present work has been undertaken to further examine the effectiveness of DME for the SCR of NO using four kinds of noble metal loaded Al_2O_3 catalysts and to study the influence of metal loading and addition of an alkali metal of Ba.

2. Experimental

Various catalysts of Ag, Pd, Pt, and Rh supported on Al_2O_3 were prepared by a conventional impregnation method [14]. A high quality alumina (NST-5) produced by Nikki Universal was impregnated with such metal precursors as $RhCl_3{\bullet}3H_2O$, $Pt(NH_3)_4(NO_3)_2$, $Pd(NO_3)_2$, $AgNO_3$, $Ba(NO_3)_2$, dried in air at 110 °C for 12 h, and further calcined in air at 500 °C for 2 h. The reaction procedures used were similar to those used previously [13,14]. So, these will be described in brief in the following. The reaction was carried out in a conventional flow reactor at an SV of 10^4 h^{-1} and at 200–400 °C. The reaction data were collected at increasing temperatures by every 50 °C. The catalyst bed was heated up to the desired temperature, this temperature was held for 1 h within which the reaction became to the steady state, the outlet gases were sampled and analyzed, and the catalyst was further heated up to the next desired temperature. The reactant gases used were NO (1000 ppm), DME (3000 ppm) and O_2 (10%) balanced by He. The standard gases of DME and NO diluted by He were supplied by Sumitomo Seika. The concentrations of NO, N_2O, N_2, O_2, DME, CO, CO_2, and hydrocarbons in the outflow gas were determined using gas chromatographs, Hitachi 663-50 (Porapak Q + Porapak T) and Shimadzu GC-8A (Molecular sieve 5A), and

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doi:10.1016/j.cattod.2010.11.008

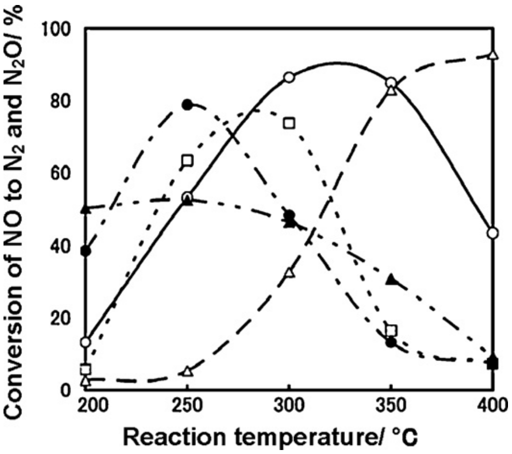

Fig. 1. The conversion of NO to N_2 and N_2O in SCR by DME at different temperatures obtained over 1 wt.% metal loaded Al_2O_3 catalysts and Al_2O_3 alone. ○: Ag/Al_2O_3, ●: Pd/Al_2O_3, □: Rh/Al_2O_3, ▲: Pt/Al_2O_3, and △: Al_2O_3 alone.

UV spectrophotometer (Shimadzu UV-1600). Diffuse reflectance UV–vis spectra were recorded by a Shimadzu UV-3100PC spectrophotometer with a diffuse reflectance attachment. XRD patterns were measured using a JEOL JDX-8020 instrument (Cu-Kα). The specific surface area was measured by means of a Yuasa Ionics NOVA 1000 instrument. Fourier transform-infrared spectrometry (Nihon Bunko FT-IR5M) was used to examine the surface species formed on the catalysts during SCR of NO by DME.

3. Results and discussion

3.1. DME-SCR activity

Fig. 1 shows the NO conversion in SCR by DME at different temperatures for four 1 wt.% noble metal loaded Al_2O_3 catalysts and Al_2O_3 alone. The values of NO conversion to N_2 and N_2O obtained in the reactions over 5 catalysts are summarized in Table 1. The support itself was active at high temperatures above 350 °C. Compared with the support, Ag/Al_2O_3 was more active at these high temperatures and the conversion of NO to N_2 obtained at 300 °C and 350 °C were 87% and 85%, respectively, but the other catalysts were less active. At low temperatures below 300 °C, Pd, Rh and Ag catalysts were more effective and 60–80% total conversions of NO to N_2 and N_2O were obtained but considerable amounts of N_2O were produced over Pd and Rh loaded Al_2O_3. In the case of Pt catalyst, a maximum conversion was observed at 200 °C, while the total conversions observed at 200–400 °C were around 50% with considerable amounts of N_2O produced. Each metal loaded Al_2O_3 catalyst showed a maximum activity for SCR at a different temperature. The reductant DME could be consumed through the reduction of NOx and the reaction with coexisting oxygen. The former target reaction should be superior to the latter undesired one at low temperatures but *vice versa* at high temperatures, resulting in the maximum in the SCR activity. Since Ag and Rh loaded catalysts showed good DME-SCR performance, the influence of metal loading was further investigated for these Ag and Rh catalysts.

Table 1
NO conversion to N_2 and N_2O over various metal supported Al_2O_3.

Metal (wt.%)	200 °C		250 °C		300 °C		350 °C		400 °C	
	N_2	N_2O	N_2	N_2O	N_2	N_2O	N_2	N_2O	N_2	N_2O
None	3	0	5	0	32	0	83	0	93	0
Ag(1)	13	0	53	0	87	0	85	0	43	0
Rh(1)	6	0	53	10	45	29	14	2	7	0
Pd(1)	10	28	26	53	21	28	9	4	7	0
Pt(1)	4	46	7	46	10	37	10	20	8	2
Ag(0.1)	4	0	10	0	55	0	81	0	70	0
Ag(0.5)	10	0	26	0	73	0	96	0	63	0
Ag(2)	5	16	9	24	20	7	24	1	11	0
Rh(0.1)	5	0	11	0	73	13	40	0	9	0
Rh(0.5)	7	0	16	0	73	18	24	11	9	0
Rh(2)	8	6	75	7	48	18	17	3	10	0

DME, 3000 ppm; NO, 1000 ppm; O_2, 10%; SV, 6000 h^{-1}.

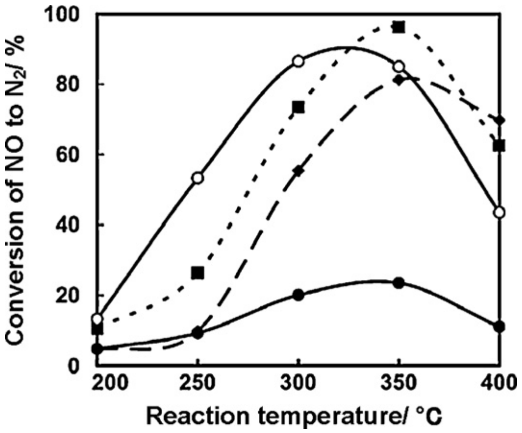

Fig. 2. The conversion of NO to N_2 in SCR by DME at different temperatures obtained over Ag/Al_2O_3 with various metal loadings. ●: $Ag(2)/Al_2O_3$, ○: $Ag(1)/Al_2O_3$, ■: $Ag(0.5)/Al_2O_3$, and ♦: $Ag(0.1)/Al_2O_3$.

Fig. 2 shows NO conversion to N_2 obtained over Ag/Al_2O_3 with various metal loadings (shown in parentheses). The highest activity for DME-SCR was obtained over Ag(0.5) at 350 °C. At lower temperatures between 200 °C and 300 °C, Ag(1) was the most effective. The Ag(2) catalyst was less active than those of lower metal loadings and produced N_2O in a larger quantity compared to N_2.

Fig. 3 shows NO conversion to N_2 obtained over Rh/Al_2O_3 with various metal loadings. At lower temperatures between 200 °C and 300 °C, the DME-SCR activity increased with an increase in Rh loading and the conversion of NO to N_2 observed over Rh(2) at 250 °C and 300 °C were 75% and 48%, respectively. The Rh(0.1) and Rh(0.5) catalysts had similar conversions of NO to N_2 of about 73% at 300 °C but smaller conversions <16% at 250 °C or below. The maximum activity was found to appear at the lower temperature for Rh compared to the other noble metals but considerable amounts of N_2O were produced over the Rh catalysts.

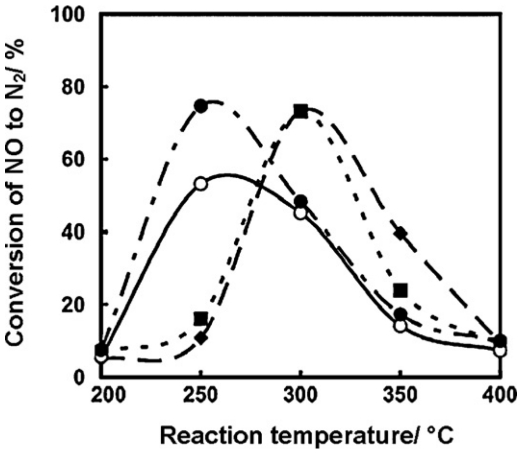

Fig. 3. The conversion of NO to N_2 in SCR by DME at different temperatures obtained over Rh/Al_2O_3 with various metal loadings. ●: $Rh(2)/Al_2O_3$, ○: $Rh(1)/Al_2O_3$, ■: $Rh(0.5)/Al_2O_3$, and ♦: $Rh(0.1)/Al_2O_3$.

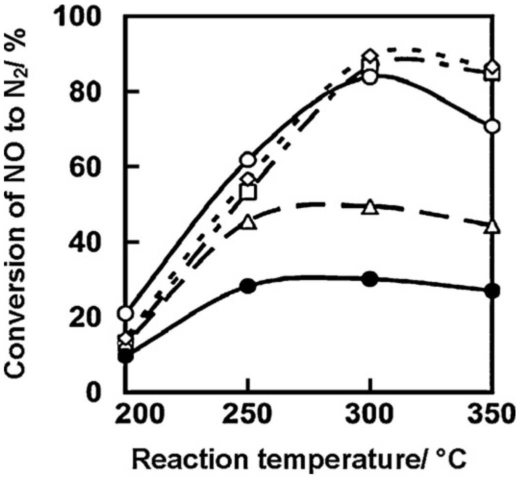

Fig. 4. The conversion of NO to N_2 in SCR by DME at different temperatures over Ba-modified Ag(1)/Al_2O_3 catalysts. ●: Ba(1 wt.%), △: Ba(0.5 wt.%), ○: Ba(0.2 wt.%), ◇: Ba(0.1 wt.%), and □: Ba(0 wt.%).

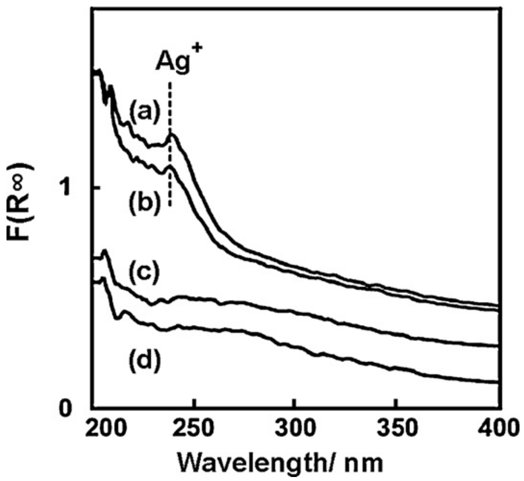

Fig. 6. UV–vis diffuse reflectance spectra of Ag(1)/Al_2O_3 with and without Ba(0.2 wt.%) additive. (a) Ag(1) + Ba(0.2)/Al_2O_3, (b) Ag(1)/Al_2O_3, (c) Ba(0.5)/Al_2O_3, and (d) Al_2O_3 alone.

Those results showed that Ag(1)/Al_2O_3 was the most effective catalyst for the conversion of NO to N_2 in DME-SCR. To improve its performance, it was modified with Ba species, which was selected as it previously showed good effects [15]. Fig. 4 shows the conversion of NO to N_2 over Ba-modified Ag(1)/Al_2O_3 catalysts. Note that the conversion obtained at 200–250 °C was improved by the addition of 0.2 wt.% Ba. Larger amounts of Ba additive (0.5, 1.0 wt.%) were less effective, decreasing the DME-SCR activity. Thus, 0.2 wt.% Ba-modified Ag(1)/Al_2O_3 was the most effective catalyst for DME-SCR of NO at low temperatures of 200–250 °C.

3.2. Catalyst characterization

The X-ray diffraction of Ag(1)/Al_2O_3 catalysts with and without Ba additive showed similar patterns assigned to γ-Al_2O_3. These two catalysts had almost the same BET surface area of $172 \pm 2\,m^2\,g^{-1}$. The difference in the activity observed between the two catalysts should be explained by other factors.

In order to examine the state of Ag over Al_2O_3, UV–vis diffuse reflectance spectra were measured, and the results obtained are shown in Fig. 5. In the literature [16,17], the band around 240 nm and the shoulder band above 260 nm are assigned to Ag^+ ion and $Ag_n^{\delta+}$ cluster, respectively. It is seen that the catalytic activity at lower temperatures is related to Ag^+ ion and the presence of $Ag_n^{\delta+}$ results in the decrease of catalytic performance (Figs. 2 and 5). For the practical use of the catalyst, it is necessary to have high activity at lower temperatures between 200 °C and 300 °C. From Table 1 and Fig. 1, Ag(1)/Al_2O_3 was considered the most effective catalyst for DME-SCR, so an additional component was introduced into the catalyst in order to improve its catalytic performance. As mentioned above, Ba was chosen as the additive since it previously showed good results [15].

Fig. 6 shows the influence of Ba with different loadings on the formation of Ag^+ ion over Ag(1)/Al_2O_3. As shown in Fig. 4, NO conversion to N_2 obtained at 200–250 °C was apparently improved by the addition of 0.2 wt.% Ba. From the results of UV–vis spectra obtained for the catalysts modified with 0.1–0.5 wt.% Ba additives, the amount of Ag^+ was shown to increase with an increase in the amount of Ba additives.

Fig. 7 shows FTIR spectra for the Ag/Al_2O_3 catalysts after the reactions at 250 °C. Absorption bands are seen at 2253 cm^{-1} and 2177 cm^{-1}, assignable to such reaction intermediates as –NCO and –CN, respectively [11,17,18], for Ag(0.5) and Ag(1) catalysts con-

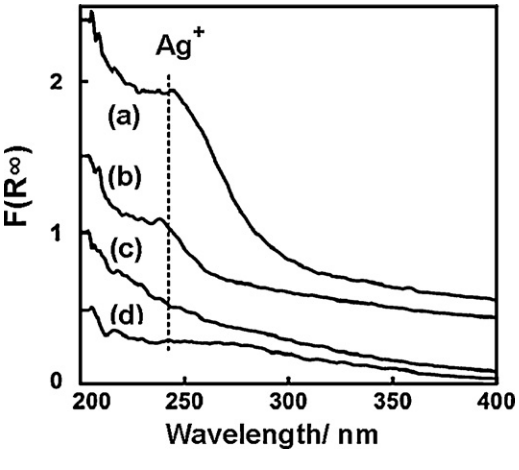

Fig. 5. UV–vis diffuse reflectance spectra of Ag/Al_2O_3 with various metal loadings. (a) Ag(2)/Al_2O_3, (b) Ag(1)/Al_2O_3, (c) Ag(0.5)/Al_2O_3, and (d) Al_2O_3 alone.

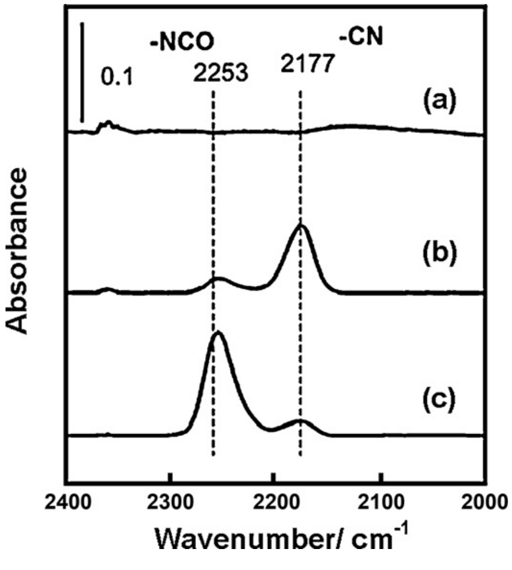

Fig. 7. FT-IR spectra of adsorbed species formed on Ag/Al_2O_3 catalysts after the reactions at 250 °C. (a) Ag(2)/Al_2O_3, (b) Ag(1)/Al_2O_3, and (c) Ag(0.5)/Al_2O_3.

taining isolated Ag^+ ions. Over Ag(1) catalyst, which shows the highest activity at 250 °C, the existence of a large quantity of –CN species is observed. In contrast to this, such reaction intermediates cannot be observed for Ag(2) catalyst having $Ag_n{}^{\delta+}$ clusters only. From these results, the catalyst having a lot of isolated Ag^+ ions beneficial for the generation of those reaction intermediates can show high DME-SCR activity.

Shimizu et al. [15] have reported that nitrates produced on Ag/Al_2O_3 by the oxidation of NO are reduced to N_2 by partially oxidized hydrocarbon species, such as acetate, via the Ag^+–NCO and –CN species, and the reaction of nitrates with partially oxidized hydrocarbon species should be a crucial step in the catalytic reduction of NO to N_2 in a steady-state. It is concluded that DME react with NOx species on Ag^+ ions that are the active site as shown above, and NOx species could be reduced to N_2 through the formation of such intermediates as –NCO and –CN. Details of the mechanism are still being examined.

4. Conclusions

The present work has been undertaken to examine the effectiveness of DME for the SCR of NO using four kinds of noble metal (Rh, Pd, Pt, Ag) loaded Al_2O_3 catalysts and to study the influence of metal loading and the addition of Ba additive. The following conclusions are drawn from the results of NO-SCR reaction and catalyst characterization (UV/vis and FTIR).

(1) Ag/Al_2O_3 catalyst is much more active than the other Rh, Pd, and Pt loaded ones.
(2) Ag (1 wt.%)/Al_2O_3 modified with 0.2 wt.% Ba is the most effective catalyst at low temperatures between 200 °C and 300 °C.
(3) Isolated Ag^+ ions play an important positive role in the reaction but the presence of $Ag_n{}^{\delta+}$ clusters results in the decrease of catalytic performance.
(4) The addition of Ba species increases the amount of the active isolated Ag^+ ions.
(5) The isolated Ag^+ ions can promote the formation of such reaction intermediates as –NCO and –CN, resulting in the higher activity for DME-SCR of NO.

Acknowledgment

The financial support from Japan Railway Construction, Transport and Technology Agency (JRTT: 2009-04) is gratefully acknowledged.

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