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Journal of Molecular Catalysis A: Chemical 180 (2002) 187–192

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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NO reduction and CO oxidation over Cu/Ce/Mg/Al mixed oxide catalyst in FCC operation

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Received 15 August 2001; accepted 26 October 2001

Abstract

Simultaneous NO reduction and CO oxidation in the presence of O_2, H_2O and SO_2 over Cu/Mg/Al/O (Cu-cat), Ce/Mg/Al/O (Ce-cat) and Cu/Ce/Mg/Al/O (CuCe-cat) were studied. At low temperatures (<340 °C), the presence of O_2 or H_2O enhanced the activity of CuCe-cat for NO and CO conversions, but significantly suppressed the activity of Cu-cat and Ce-cat. At high temperature (720 °C), the presence of O_2 or H_2O had no adverse effect on the NO and CO conversions over these catalysts. The addition of SO_2 to $NO + CO + O_2 + H_2O$ system had no effect on the reaction of $CO + O_2$ over Cu-cat, but deactivated this catalyst for $NO + CO$ and $CO + H_2O$ reactions; over Ce-cat, all of these reactions of $NO + CO$, $CO + O_2$ and $CO + H_2O$ were suppressed significantly; over CuCe-cat, $NO + CO$ and $CO + O_2$ reactions were not affected while the reaction of $CO + H_2O$ was slightly inhibited. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NO reduction; CO oxidation; FCC; H_2O and SO_2 poisoning; NO and CO co-adsorption

1. Introduction

The reduction of NO by CO is the most ideal way to remove simultaneously NO and CO from industrial effluents, and therefore, it has received particular attention [1–3]. Copper-based catalysts show a high activity in the conversion of nitrogen oxides (NO_x) to N_2 [2–4]. However, the deactivation caused by copper oxide aggregation or SO_2 poisoning is still an unsolved problem [5]. Cerium oxide has been widely used in the automotive three-way catalytic converter as an oxygen storage medium and thermal stabilizer. The addition of ceria to precious metal (Pd, Pt, Rh) can strongly improve the catalyst performance [6,7]. Several binary mixtures of transition metal and ceria have been proposed in literature [8–10].

In the regenerator of fluid catalytic cracking units (FCC, the principal gasoline-producing process in the refinery; for details see Ref. [11]), the high-temperature flue gas (650–760 °C) contains NO, NO_2, O_2, CO, CO_2, SO_2, SO_3, H_2O simultaneously. Therefore, the FCC regenerator poses a very challenging problem for controlling NO_x [12]. In the dense phase bed of the FCC regenerator, the CO concentration is much higher than the O_2 concentration [11]. A CO combustion promoter is usually used in industrial operations to control the emission of CO. However, the use of this promoter increases the

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PII: S1381-1169(01)00427-7

NO_x emissions [13]. In this paper, we report a cerium-promoted Cu/Ce/Mg/Al/O mixed oxide catalyst which displays high activity for simultaneous removal of NO and CO in the presence of O_2, H_2O and SO_2 under the conditions similar to those found in the dense phase bed of FCC.

2. Experimental

Cu/Ce/Mg/Al/O was prepared by co-precipitation of an aqueous solution of $Cu(NO_3)_2\cdot 6H_2O$, $Ce(NO_3)_3\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ (total cation concentration of 1 M) with an aqueous solution of NaOH and Na_2CO_3 ($CO_3{}^{2-}$-to-Al molar ratio of 0.5). The detailed procedure is described elsewhere [14–17]. The precipitate was filtered, washed with water and dried at 120 °C for 12 h, and then calcined in air at 750 °C for 3 h. The resulting product was designated as CuCe-cat. Cu-cat or Ce-cat catalyst was prepared using the same procedure except $Ce(NO_3)_3\cdot 6H_2O$ or $Cu(NO_3)_2\cdot 6H_2O$, respectively, which was not included.

The catalytic reaction tests were carried out in a fixed bed quartz reactor with a porous frit in flow conditions. The quartz reactor was loaded with 150 mg (particulate size: 0.45–0.90 mm) of catalyst. The composition of the feed gas was regulated by mass flow controllers (Brooks 5058). A typical feed contained 600 ppm NO, 1.4 vol.% CO and 0.5% O_2 (similar to the conditions in the dense phase bed of the FCC regenerator) with ultra-high purity He as diluent. When desired, 1% H_2O was added to the feed using a H_2O saturator. The effect of SO_2 was examined by introducing 500 ppm SO_2 into the reaction system. The total flow rate was 400 ml/min. The experiments were carried out under atmospheric pressure. A cold trap connected at the outlet of the reactor was used to remove the water from the effluent gas. The composition of the feed or effluent gas was analyzed on-line with QGS-08B infrared analyzers (for NO) and a GC-8APT gas chromatograph with two columns (GDX303 for SO_2 and CO_2; 13X for CO, O_2, N_2) and a TCD detector. NO and CO conversions were calculated from the formation of N_2 and CO_2, respectively. The products were also monitored on-line by mass spectrometry (Balzers Oministar, Quadrupole) in some runs.

3. Results and discussion

The catalysts used in this work are listed in Table 1.

Fig. 1 shows the NO conversions as a function of temperature over Cu-cat and CuCe-cat in the absence and presence of O_2. It can be seen that for the NO+CO system, in the low temperature region (lower than 340 °C), CuCe-cat has a higher NO reduction activity (reaching 100% conversion at 315 °C) than Cu-cat, and the difference increases with temperature within that region. At high temperatures, NO conversions over both catalysts reach 100%. The addition of O_2 to the feed produces a completely different effect on the NO conversion over Cu-cat and CuCe-cat. The presence of O_2 enhances the activity of CuCe-cat while it decreases the activity of Cu-cat. The activity of Ce-cat for NO conversion (not shown in Fig. 1) is much lower than that of CuCe-cat or Cu-cat under the same conditions. The presence of O_2 reduces the activity of Ce-cat.

In order to clarify the effect of O_2 on the reaction of NO + CO over these catalysts, the co-adsorption of NO and CO and the influence of O_2 on the adsorption of NO and CO were investigated by IR spectroscopy. Fig. 2 shows the IR spectra of NO and CO co-adsorption on CuCe-cat at room temperature. There is an intense band at 2118 cm^{-1} with several

Table 1
The physico-chemical properties of samples[a]

Catalyst	Composition (wt.%)				S_{BET} ($m^2\,g^{-1}$)	Pore volume ($ml\,g^{-1}$)
	MgO	Al_2O_3	CuO	CeO_2		
Cu-cat	62.0	29.3	8.4		184	0.68
Ce-cat	60.0	29.0		9.1	160	0.59
CuCe-cat	56.0	26.0	7.2	8.7	169	0.93

[a] Mg to Al atomic ratio is about 2.7 for all samples.

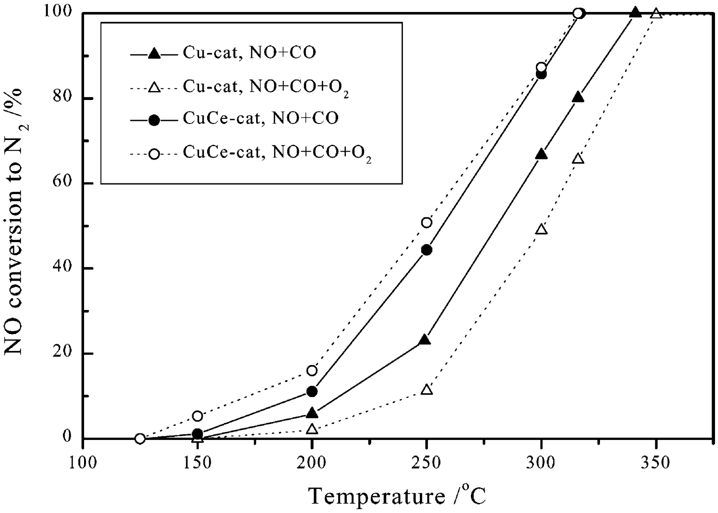

Fig. 1. NO conversions as a function of temperature over Cu-cat and CuCe-cat catalysts in the absence and presence of O_2. Reaction conditions: 600 ppm NO, 1.4% CO, 0.5% O_2; total flow rate: 400 ml/min.

weak bands at 1888, 1875, and 2355 cm^{-1}, respectively (Fig. 2A). The band at 2118 cm^{-1} is ascribed to CO ligated to Cu^+ sites [18] and the band at 1888 cm^{-1} corresponds to the adsorption of NO on Cu^{2+} [19]. The 1875 cm^{-1} band is attributed to gaseous NO and the 2355 cm^{-1} band is tentatively attributed to the adsorption of N_2O [20]. After subsequent evacuation up to 10^{-2} Pa at room temperature, the 2118 cm^{-1} band decreases and shifts to a lower frequency of 2102 cm^{-1} while the bands at 1888 and

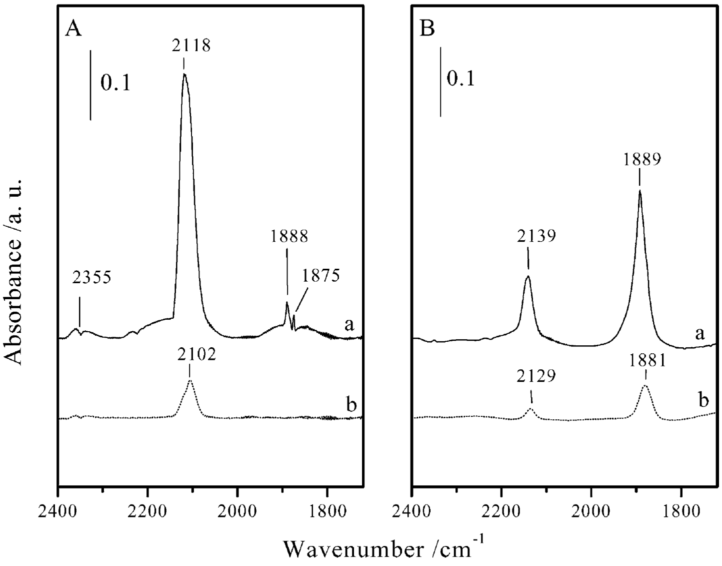

Fig. 2. IR spectra of NO and CO co-adsorption on CuCe-cat at room temperature. A: $P_{NO+CO} = 4.0$ kPa, P_{NO}:P_{CO} = 1:2; B: $P_{NO+CO+O_2} = 4$ kPa, P_{NO}:P_{CO}:P_{O_2} = 1:3:1 (a): after 25 min adsorption at the conditions of A or B; (b): followed by evacuation to 10^{-2} Pa.

Table 2
Influences of the addition of water vapor and SO_2 on the NO conversions over the three catalysts

Catalyst	NO conversion (%)[a]								
	250 °C		300 °C		550 °C		720 °C		
	1	2	1	2	1	2	1	2	3
Cu-cat	11.3	0	49.0	1.6	97.8	98.5	98.7	100	31.4
Ce-cat	0	0	0	0	51.6	52.1	100	100	16.2
CuCe-cat	50.8	100	86.9	100	100	100	100	100	100

[a] 1: $NO + CO + O_2$; 2: $NO + CO + O_2 + H_2O$; 3: $NO + CO + O_2 + H_2O + SO_2$. 1 and 2: after the reactions reach steady state; 3: after 40 min reaction.

1875 cm^{-1} disappear completely. The shift of the 2118 cm^{-1} band upon evacuation is attributed to the decrease of surface coverage of CO. Fig. 2B shows the effect of O_2 on the NO and CO adsorption. After introducing O_2 into the system, the band corresponding to the CO adsorption on Cu^+ decreases significantly in intensity (by a factor of 4). However, it is interesting to note that the band assigned to NO adsorption on Cu^{2+} increases by a factor larger than 5. This indicates that the addition of a small amount of O_2 enhances the adsorption of NO. After evacuation, both bands shift to a slightly lower frequency while they decrease in intensity. As reported in our previous paper [14], a large number of Cu^+ ions—active for CO adsorption—are formed during the calcination of CuCe-cat as a result of the strong synergistic effect between copper and cerium ions. The presence of O_2 oxidizes some Cu^+ ions into Cu^{2+} ions, which are not active for CO adsorption but are active for NO adsorption [19]. This explains the corresponding decreased intensity of the band at 2118 cm^{-1} and the increased intensity of the band at 1888 cm^{-1}. Over Cu-cat, most of the copper ions are present as Cu^{2+} ions [14]. Over Ce-cat, no NO and CO adsorption are detected by IR spectroscopy (not shown here). The exact ν_{CO} band position is considered to be dependent on the environment of the Cu^+ ion to which CO is bound. The shift from 2118 to 2139 cm^{-1} with the addition of O_2 is due to a greater concentration of Cu^{2+} ions in positions surrounding the Cu^+ adsorption site [21].

The influences of the addition of water vapor and SO_2 on the NO conversions over these three catalysts were examined and the results are presented in Table 2. When 1% H_2O is introduced into the feed, Cu-cat loses its activity completely at 250 °C; the activity at 300 °C also drops drastically. However, at the same conditions (250 or 300 °C), it is interesting to note that the addition of H_2O enhances the activity of CuCe-cat significantly. At high temperatures, the presence of H_2O has no significant effect on the NO conversion. At 720 °C, the addition of SO_2 results in a drastic decline of NO conversion, from 100 to 31.4% for Cu-cat and from 100 to 16.2% for Ce-cat during the first 40 min. These data indicate that both catalysts are rapidly poisoned by SO_2. However, the presence of SO_2 in the feed has no adverse effect on the NO conversion over CuCe-cat which maintains 100% conversion. Even after a 24 h run, no decline in conversion is observed.

Table 3
CO conversions under different reaction conditions

Catalyst	CO conversion (%)[a]						
	250 °C		550 °C		720 °C		
	1	2	1	2	1	2	3
Cu-cat	60.9	30.8	75.7	93.7	75.7	95.3	74.4
Ce-cat	12.0	0	73.6	76.2	75.6	86.8	46.1
CuCe-cat	73.5	85.6	75.7	95.1	75.7	95.8	96.1

[a] 1: $CO + O_2 + NO$; 2: $CO + O_2 + H_2O + NO$; 3: $CO + O_2 + H_2O + NO + SO_2$. 1 and 2: after the reactions reach steady state; 3: after 40 min reaction.

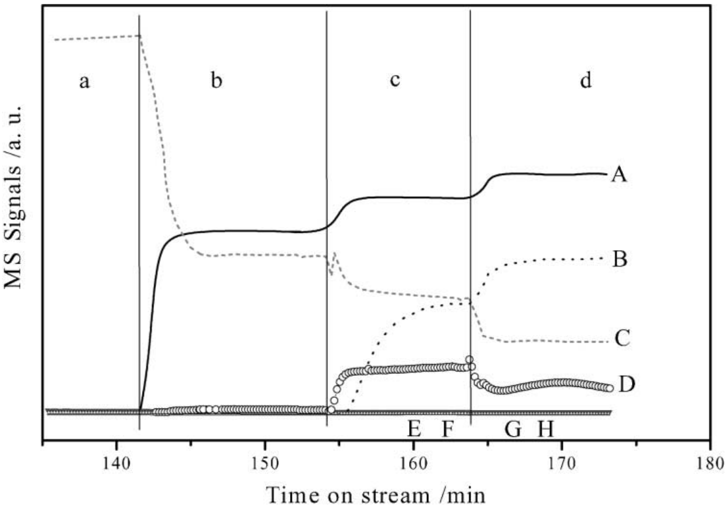

Fig. 3. Effects of the addition in sequence of O_2, H_2O and SO_2 on NO and CO conversions over CuCe-cat at 720 °C. (a): NO (600 ppm) + CO (1.4%) system; (b): introducing 0.5% O_2 into (a) system; (c): introducing 1% H_2O into (b) system; (d): introducing 500 ppm SO_2 into (c) system. A: CO_2; B: H_2O; C: CO; D: H_2; E: O_2; F: NO; G: H_2S; H: COS.

Table 3 gives CO conversions under different reaction conditions. At 250 °C, CuCe-cat and Cu-cat have much higher CO oxidation activity than Ce-cat. The presence of H_2O increases CO conversion over CuCe-cat while drastically reducing it over Cu-cat or Ce-cat. At 720 °C, the addition of H_2O promotes CO conversion over all the three catalysts. The presence of SO_2 in the $NO + CO + O_2 + H_2O$ system has no effect on the reaction between CO and O_2 over Cu-cat, but deactivates this catalyst completely for the reaction of $CO + H_2O$ (this is also confirmed by MS data; not shown here). For Ce-cat, both the reactions of $CO + O_2$ and $CO + H_2O$ are suppressed significantly. However, the CO conversion over CuCe-cat increases slightly with the addition of SO_2. The effects of O_2, H_2O and SO_2 on the CO and NO conversions over CuCe-cat can be seen in detail in Fig. 3. When 0.5% O_2 is introduced into the system, it is consumed completely by CO, concomitant with the formation of CO_2. With the addition of water vapor, the signal of CO decreases and that of CO_2 increases. Meanwhile, H_2 is detected. The addition of SO_2 has no effect on the reaction of $CO + O_2$, but slightly inhibits the reaction of $CO + H_2O$. The increase of the CO_2 signal is derived from the reaction of $CO + SO_2 \rightarrow CO_2 + S$, as evidenced by the condensate of sulfur in the reactor outlet. No undesirable COS and H_2S are detected in the whole experiment.

4. Remarks

From the preceding results, it can been seen that CuCe-cat shows higher catalytic activity and stability than Cu-cat and Ce-cat for the simultaneous removal of NO and CO in the presence of O_2, H_2O and SO_2. The addition of O_2 increases NO conversion over CuCe-cat because it oxidizes some Cu^+ ions to Cu^{2+} ions which are active for NO adsorption. The different influence of H_2O on NO and CO conversion derives from the different activities of the catalysts for the water-gas shift reaction (WGSR, $CO + H_2O \rightarrow CO_2 + H_2$). With many more Cu^+ sites for CO adsorption, CuCe-cat exhibits a high WGSR activity at low temperature while Cu-cat and Ce-cat require high temperature [22]. At low temperature, the strong adsorption of H_2O on Cu^{2+} or Cu^+ sites will inhibit the adsorption of NO or CO over Cu-cat; however, for CuCe-cat, WGSR leads to the increase of CO conversion and the formation of H_2 which is active for NO reduction at low temperature. The presence of SO_2 increases the CO conversion and has no adverse effect on NO conversion over CuCe-cat at 720 °C; however, it significantly decreases both NO and CO conversions over Cu-cat and Ce-cat. All of these promoted performances of CuCe-cat result from the strong interaction of copper and cerium which gives rise to a large number of Cu^+ ions [14]. SO_2 cannot block CO adsorption on Cu^+ ions [23]. Further work is underway to elucidate the reaction mechanism in detail.

Acknowledgements

Support for this work from the Research Institute of Petroleum Processing is gratefully acknowledged. The authors thank Dr. Jiaqing Song for helpful discussion.

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