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Co/Al_2O_3 Lean NO_x Reduction Catalyst

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Certain Co/Al_2O_3 catalysts are active and stable for the selective catalytic reduction (SCR) of NO_x by propene or propane. The addition of 30 ppm SO_2 to the feed only mildly affects the catalytic performance. The effectiveness of Co/Al_2O_3 in the SCR process depends strongly on the Co loading, the calcination temperature, and the source of alumina. Characterization of the catalysts with UV-vis spectroscopy under ambient conditions, temperature-programmed reduction by H_2 (H_2-TPR), XRD, iodometric titration, and BET surface area measurements led to the proposal that there exist four different Co species: Co^{2+} ions in $CoAl_2O_4$, small Co_3O_4 particles that interact strongly with Al_2O_3, large Co_3O_4 particles, and dispersed surface Co^{2+} ions in octahedral coordination. The latter Co^{2+} species are likely the catalytically most active species. Their propensity to interact with NO_x is reminiscent of that of Co ions in ZSM-5. © **1997 Academic Press**

I. INTRODUCTION

Selective catalytic reduction (SCR) of NO_x under lean conditions, in which NO_x is reduced to N_2 with hydrocarbon in the presence of an excess of oxygen, has recently received extensive attention because of its potential for commercial applications. Most of the active catalysts known to date are zeolite-based. However, these catalysts have hydrothermal stability problems (1–5), and it is of interest to explore alternative supports that may be potentially more stable. Supported alumina catalysts such as Ag/Al_2O_3 (6), Au/Al_2O_3 (7, 8), and Co/Al_2O_3 (9) show fairly high effectiveness for NO_x reduction. Their activities depend strongly on the preparation procedure and the metal loading. For example, Co/Al_2O_3 catalysts prepared from $Co(NO_3)_2$ or $Co(OAc)_2$ differ dramatically in NO_x reduction activity (9): samples prepared from the nitrate precursor are inactive, but samples made from the acetate show moderate NO_x reduction activity. In order to explore the potential of Co/Al_2O_3 as a practical catalyst, elucidation of the active site is necessary to relate the structural and catalytic properties of the catalyst to the preparation variables. In this study, Co/Al_2O_3 catalysts of different Co loading and pretreated differently were characterized in an attempt to identify the active Co species.

II. EXPERIMENTAL

II.1. Catalyst Preparation

The γ-Al_2O_3 support, denoted as Al_2O_3(H), was prepared by a complexing agent-assisted sol–gel method, modified from Masuda *et al.* (10). Aluminum isopropoxide (99.99+%, Aldrich Chemicals) was first dissolved in 2-methylpentane-2,4-diol (complexing reagent, 99%, Aldrich Chemicals). After stirring for 4 h at 125°C, H_2O was added and a white precipitate was formed. The precipitate was aged at 80°C for 15 h, filtered, and washed with isopropanol, then dried in air at 105°C overnight. Calcination was carried out in a tubular reactor with air flowing through it and with the following schedule:

$$25^\circ C \xrightarrow[\text{air}]{1^\circ C/\text{min}} 450^\circ C \xrightarrow[2\%\ H_2O/\text{air}]{1^\circ C/\text{min}} 700^\circ C \xrightarrow[6\%\ H_2O/\text{air}]{2\ \text{h}} 700^\circ C \xrightarrow[\text{air}]{} 25^\circ C.$$

The resulting Al_2O_3 had a higher surface area and was thermally more stable than other commercial aluminas (10, 11). For comparison, γ-Al_2O_3 samples purchased from Aldrich Chemicals (Al_2O_3(A)) and Alfa-aesar Chemicals (Al_2O_3(B)) were also used. The surface areas of these samples were: Al_2O_3(H), 273 m^2/g; Al_2O_3(A), 155 m^2/g; and Al_2O_3(B), 86 m^2/g.

Co/Al_2O_3 samples were prepared by three different methods: (1) deposition–precipitation, using solution $Co(OAc)_2$ and $Mg(C_6H_6O_7)$, similar to the preparation of supported Au catalyst (12). $Co(OAc)_2$ (Johnson–Matthey) was dissolved in H_2O at 0°C and added to γ-Al_2O_3. The mixture was stirred vigorously at 0°C for 1 h. $Mg(C_6H_6O_7)$ (Johnson–Matthey) was added and the mixture was stirred for another hour, filtered, and rinsed with cold H_2O. The solid was then suspended in water at 55°C and stirred for 5 min, filtered, rinsed with warm water, and dried overnight in an oven at 105°C. It was suggested that this method produces very highly dispersed samples (12).

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(2) Incipient-wetness impregnation of $Co(NO_3)_2$ (Aldrich) on Al_2O_3. (3) Incipient-wetness impregnation of cobalt citrate ($Co(C_6H_6O_7)$ (Strem Chemicals)) on Al_2O_3. The Co/Al_2O_3 samples were calcined in air at 350°C for 2 h to decompose the organic or nitrate ligands. Some specified samples were further calcined at 800°C for 2 h.

Unsupported Co_3O_4 was prepared by oxidative decomposition of $CoCO_3$ at 500°C. $CoCO_3$ was made by precipitation of $CO(NO_3)_2$ (Aldrich) with Na_2CO_3 (Aldrich). The surface area of Co_3O_4 was 52 m^2/g; 1.24 wt% Co/ZSM-5-17 and 2.4 wt% Cu/ZSM-5-17 were prepared by the ion-exchange method using Na/ZSM-5 (UOP) and $Co(OAc)_2$ (Aldrich).

II.2. Catalytic Evaluation

The catalytic activities were evaluated using a 13-mm OD fused quartz U-tube microreactor. The temperature was measured with a thermocouple placed adjacent to the catalyst outside the reactor. Normally, 0.5-g catalyst was used. The standard reaction feed was 100 ml/min of 0.095% NO, 0.1% C_3H_6, 5% O_2, and 1.7% H_2O, balanced with He. The catalyst was pretreated in the reaction feed at 450°C for 2 h, 500°C for 1 h, and at the highest reaction temperature (550°C) until there were no changes in their conversions within 1 h. The reaction data were then collected. In the catalyst stability test, 10% H_2O was used, and the flow rate was 500 ml/min. A gas-chromatograph with a TCD detector, sometimes in combination with a NO_x analyzer, were used to analyze the reaction products. In all experiments reported here, N_2 was the only nitrogen product detected. Thus, the %NO conversion equaled the %N_2 yield.

II.3. Catalysts Characterization

UV-vis spectra were collected in air with a Cary 5 spectrometer. Iodometric titration was carried out using a standard method (13). A HF/HCl solution was used to dissolve the Co/Al_2O_3 samples before titration, and a physical mixture of $Co_3O_4 + Al_2O_3$ to yield 5 wt% Co was used for calibration. BET surface areas were determined with a OmniSorp 360 analyzer using static adsorption measurement with N_2. Temperature-programmed reduction by H_2 (H_2-TPR) and XRD analyses were conducted as previously described (4).

III. RESULTS

III.1. Catalytic Activities of 2 wt% Co/Al_2O_3 and Its Stability

Figure 1 compares the NO_x conversion by C_3H_6 and C_3H_8 over a 2 wt% Co/Al_2O_3 prepared by impregnating Al_2O_3(H) with a $Co(NO_3)_2$ precursor followed by a 800°C calcination. It was observed that both reductants were highly effective in the conversion of NO to N_2. A maximum of 76% NO conversion to N_2 was observed, which was equivalent to a NO reduction rate of 6.4 μmol/g · min.

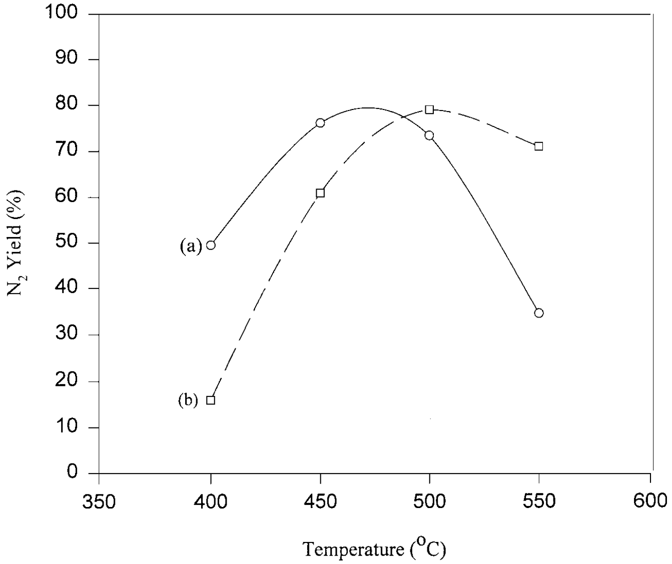

FIG. 1. NO reduction to N_2 by (a) C_3H_6 and (b) C_3H_8 over 800°C calcined 2 wt% Co/Al_2O_3(H).

The long term stability of the catalyst was evaluated with respect to its hydrothermal stability and its tolerance to SO_2. The hydrothermal stability of the catalyst was tested by subjecting the catalyst to a SCR feed containing 10% H_2O at 550°C for 124 h. Figure 2 shows that the catalytic performance was constant over the test period. After the test, the activity evaluated with the standard reaction feed and 450–600°C was the same as that of the fresh sample. In contrast, the NO conversion of a Cu/ZSM-5-17-102 catalyst with 102% nominal exchange level of Cu evaluated with the standard reaction feed was found to have decreased from 33 to 25% at 350°C after a treatment of 104 h at 500°C in the same feed.

The tolerance of Co/Al_2O_3(H) towards SO_2 is shown by the data in Table 1. Within experimental error, there was no decrease of NO reduction activity in a feed containing 30 ppm SO_2 for 6.5 h at 450°C, but the propene conversion was suppressed. The amount of SO_2 that had passed over

TABLE 1

Effect of SO_2 on the Activity of 2 wt% Co/Al_2O_3(H)[a]

Reaction time (h)	SO_2 concentration (ppm)	NO conversion (%)	C_3H_6 conversion (%)
0	0	63	78
1.5	30	64	74
5.5	30	64	69
6.5	30	62	67

[a] Feed: NO (0.095%)/C_3H_6 (0.1%)/O_2 (5%)/H_2O (1.5%)/He; flow rate = 250 ml/min; reaction temperature = 450°C; 1.25 g catalyst.

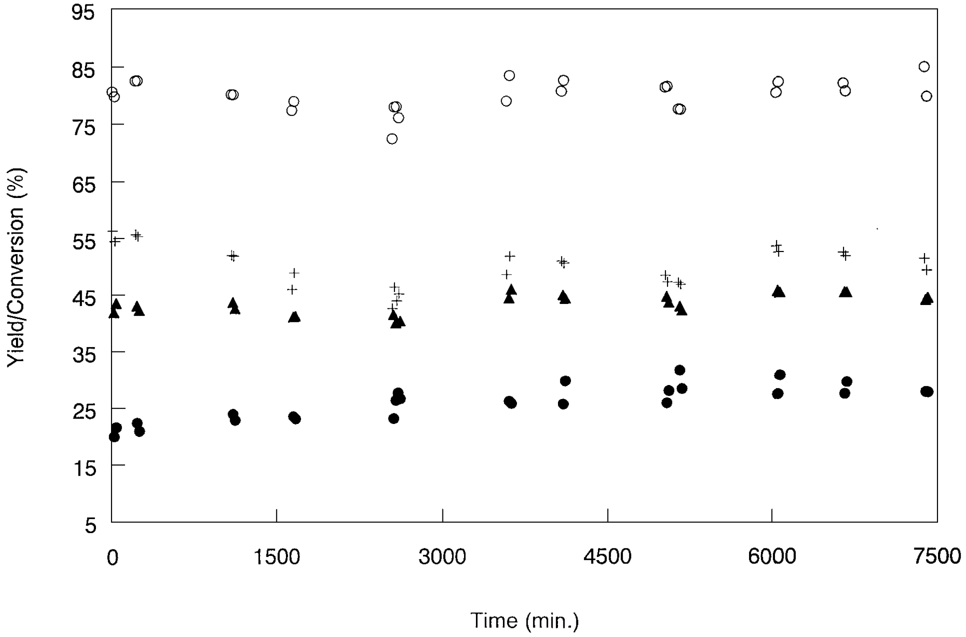

FIG. 2. NO reduction by C_3H_6 vs reaction time over 2 wt% Co/Al_2O_3: (▲) N_2 yield; (○) C_3H_6 conversion; (+) CO_2 yield; (●) CO yield. Temp. = 550°C; flow rate = 500 ml/min; 0.5 g catalyst; feed: NO (0.095%)/C_3H_6 (0.1%)/O_2 (5%)/H_2O (10%)/He.

the catalyst after 6.5 h was about 30% of the amount of Co in the catalyst (mole ratio). Since only a small fraction of the Co was active catalytically, as will be discussed later, this result showed that the Co/Al_2O_3(H) catalyst was not sensitive to sulfur poisoning. In contrast, Iwamoto *et al.* (14) reported that SO_2 suppresses NO conversion over Cu/ZSM-5. Thus, Co/Al_2O_3 appears to have a higher SO_2 tolerance than Cu/ZSM-5.

III.2. Effect of Co Loading and Calcination Temperature

Table 2 compares the catalytic activity of Co/Al_2O_3 with different Co loadings and calcination temperatures. The 2 wt% sample was a more effective catalyst than the 5 wt% sample calcination at the same temperature. Calcination at 800°C led to higher N_2 yields than calcination at 350°C for both the 2 and 5 wt% samples. The difference was greater for the 5 wt% sample. The high temperature treatment also improved the C_3H_6 conversion for the 5 wt% sample. Interestingly, it retarded the hydrocarbon oxidation activity of the 2 wt% sample.

III.3. Characterization of Co/Al_2O_3 Catalysts

III.3.1. UV-vis spectroscopy. The UV-vis spectra of Co/Al_2O_3 samples of different Co loading and the calcination temperature are shown in Fig. 3. (spectra a–e). Since the UV-vis spectra were collected under ambient conditions, surface exposed cations are expected to adsorb gas molecules to complete their coordination sphere. The spectrum of the 350°C calcined, 2 wt% sample (spectrum 3a) showed a triplet at 540, 580, and 625 nm, indicative of

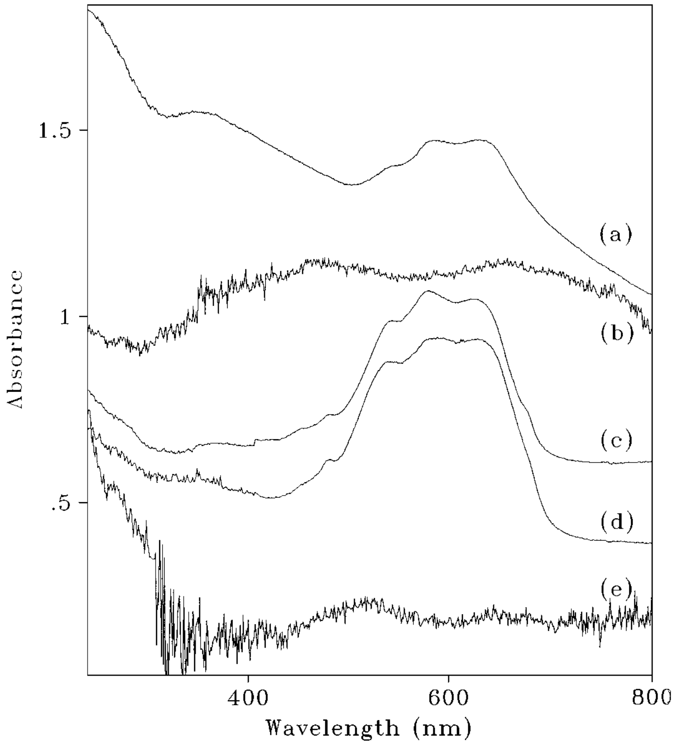

FIG. 3. UV-vis spectra of 350°C calcined (a) 2 wt% and (b) 5 wt% Co/Al_2O_3(H); 800°C calcined (c) 2 wt%, (d) 5 wt% Co/Al_2O_3(H); (e) 1.24 wt% Co/ZSM-5-17-53.5.

TABLE 2

Effect of Cobalt Loading and Calcination Temperature on the NO Reduction Activity of Co/Al_2O_3(H) Catalysts[a]

Sample	Co wt%	Calcine/ pretreat temp.[b]	Rxn temp. (°C)	N_2 yield[c] (%)	C_3H_6 conversion to CO_2 (%)	C_3H_6 conversion to CO (%)	NO C.F.[d] (%)
1a	2	350/550	350	29	10	5	16
			400	59	51	8	11
			450	66	87	5	8
			500	60	98	2	6
			550	32	100	0	3
1b	2	800/550	400	50	14	16	19
			450	76	54	24	11
			500	73	87	12	8
			550	35	96	4	3
2a	5	350/550	400	24	8	9	12
			450	38	27	17	9
			500	35	26	27	8
			550	21	94	6	2
2b	5	800/550	400	31	18	8	12
			450	50	49	16	9
			475	61	64	17	9
			500	54	77	12	7
			550	17	96	4	2

[a] Samples prepared by incipient-wetness with $Co(NO_3)_2$ precursor.

[b] Samples were calcined in air at 350°C or 800°C and pretreated in the reaction mixture at the highest reaction temperature (550°C) before testing. See text for details.

[c] Feed: NO (0.095%)/C_3H_6 (0.1%)/O_2 (5%)/H_2O (1.7%)/He; flow rate = 100 ml/min; 0.5 g catalysts.

[d] NO competitiveness factor $= [N_2]*2/(([C_3H_6]_{in} - [C_3H_6]_{out})*9\text{-}[CO])*100\%$.

tetrahedral Co^{2+} ions (15), as found in the compound $CoAl_2O_4$. After calcining at 800°C, the sample (spectrum 3c) showed an increase in the triplet intensity and the emergence of a small but distinct shoulder at 480 nm that could be assigned to octahedral Co^{2+} ions (16). The spectrum of the 5 wt% sample calcined at 350°C (spectrum 3b) differed substantially from that of the 2 wt% sample. The triplet corresponding to tetrahedral Co^{2+} was practically undetectable. Instead, there were broad peaks at 380 and 650 nm. The spectrum of Co_3O_4 was characterized by broad bands at 670 and 380 nm peaks (15, 17). Thus, the 650 nm peak might be a combination of the 670 nm peak of Co_3O_4 and the 625 nm peak of the tetrahedral Co^{2+}. Upon calcining at 800°C (spectrum 3d), the triplet, characteristic of tetrahedral Co^{2+}, became very intense at the expense of the 380 and 680 nm peaks, indicating that the high temperature treatment promoted the dispersion of Co_3O_4 clusters and resulted in the formation of $CoAl_2O_4$. However, dispersion of the Co_3O_4 particles was still incomplete as evidenced by a weak broad band at 380 nm and the still distorted band shape of the triplet adsorption. The 480 nm peak of octahedral Co^{2+} also became easily identifiable. An accurate determination of the ratio of octahedral to tetrahedral Co^{2+} ions is difficult, because the 480 nm peak ($^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition) is almost two orders of magnitude weaker than the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition of the 540, 580, and 625 nm triplet (18).

The spectrum for Co/ZSM-5-17-53.5 (1.24 wt% Co) is also shown for comparison (spectrum 3e). The broad hump at 440–560 nm may be assigned to the same octahedrally coordinated Co^{2+} ions (18), as the 480 nm peak in Co/Al_2O_3(H). This absorption band was very weak, consistent with the low absorption coefficient associated with this species. After use in the lean NO_x reduction reaction and cooling in a dry O_2/He flow, the color of this Co/ZSM-5 sample was light purple, but quickly turned to white after exposure to air. This could be interpreted as conversion of tetrahedrally coordinate Co^{2+} ions to octahedrally coordinated Co^{2+} ions through adsorption of H_2O.

III.3.2. Temperature-programmed reduction by H_2. Figure 4 compares the TPR profiles of different Co/Al_2O_3(H) samples and Co-ZSM-5. For the 2 wt% sample (curve a), the total H_2 consumption up to 800°C was equivalent to 0.04 H/Co. In contrast, large reduction peaks at 530 and 700°C, and a small peak at 260°C were observed in the postreaction 5 wt% sample (profile b), The corresponding H_2 consumptions for these peaks were 0.9, 0.5, and 0.02 H/Co, respectively. After calcination in air at 800°C for 2 h (profile c), the Co ions became much less

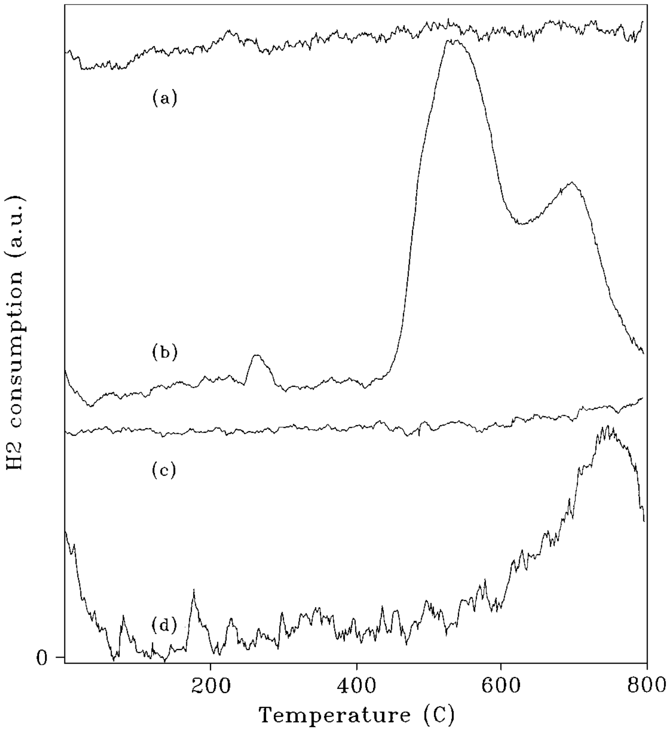

FIG. 4. H_2-TPR profiles of (a) 800°C calcined 2 wt% Co/Al_2O_3(H); (b) postreaction 5 wt% Co/Al_2O_3(H); (c) 800°C calcined 5 wt% Co/Al_2O_3(H); (d) postreaction 1.24 wt% Co/ZSM-5-17-53.5.

reducible (H/Co is 0.09), and the TPR profile resembled that of the 2 wt% sample.

For comparison, the H_2-TPR profile of a postreaction Co/ZSM-5 catalyst (profile d) showed only one H_2 consumption peak at 750°C, which continued above 800°C. The amount of H_2 consumed up to 800°C corresponded to a H/Co ratio of 1.0.

III.3.3. Iodometric titration. Iodometric titration of a 5 wt% Co/Al_2O_3(H) sample calcined at 350°C showed that up to 33% of the Co was present as Co^{3+}. This corresponded to 50% of the Co being present as Co_3O_4. After calcination at 800°C, the amount of Co^{3+} dropped to 10%.

III.3.4. XRD. XRD patterns of a postreaction 5 wt% Co/Al_2O_3(H) calcined at 350 and 800°C are shown in Fig. 5. For the 350°C calcined sample, small diffraction peaks due to Co_3O_4 crystallites (peaks at 45.3° and 65.7° 2θ) were detected (pattern 5a). However, the 800°C calcined sample showed only diffractions of γ-Al_2O_3 (pattern 5b).

III.3.5. BET surface area. The BET surface area of Al_2O_3(H) was $273 \pm 14\,m^2/g$. For the low Co loading (0.65%) catalyst, no discernible change in surface area was observed for the 350°C calcined sample. However, the 5 wt% Co/Al_2O_3(H) had a surface area of only 192 m^2/g after calcination at 350°C, which further decreased to 140 m^2/g after calcination at 800°C. The surface area of the 0.65 wt% Co sample also decreased to 200 m^2/g after calcination at 800°C.

III.4. Role of NO_2

Over Co-ZSM-5, the mechanism of NO SCR has been proposed to proceed through reaction of the hydrocarbon with a surface nitrito group (19). Here, the role of adsorbed NO_2 on Co/Al_2O_3 was investigated. Table 3 shows that the addition of 1000 ppm of NO to a feed of O_2 and C_3H_6 greatly enhanced the hydrocarbon oxidation activity. Figure 6 compares the reduction of NO_2 by C_3H_6 over Al_2O_3(H) and 2 wt% Co/Al_2O_3(H), and with the reduction of NO by C_3H_6 over the same 2 wt% Co/Al_2O_3(H). Over Co/Al_2O_3(H) at temperatures below 460°C, the reduction of NO_2 to N_2 by C_3H_6 was more effective than the reduction of NO. Under the same conditions, Al_2O_3(H) was very active in the selective reduction of NO_2 by C_3H_6.

Figure 7 compares both the NO oxidation and NO_2 decomposition activity over a 2 wt% Co/Al_2O_3(H) calcined at 800°C. It can be seen that only above 550°C, the activity was sufficiently high such that equilibrium NO_x composition was obtained. Thus, although Al_2O_3(H) was very effective in catalyzing NO_2 reduction by propene, migration of NO_2 from Co center to Al_2O_3 support, and its participation in SCR process are insignificant below 550°C. Since very low concentration of gas phase NO_2 could be produced by the NO oxidation over Co/Al_2O_3(H).

TABLE 3

Effect of NO on Hydrocarbon Oxidation[a]

Catalyst	Reaction temp., °C	C_3H_6 conversion % Without NO	 With NO
2 wt% Co/Al_2O_3	450	14	79
	500	37	93
5 wt% Co/Al_2O_3	450	10	45
	500	28	70

[a] Feed: NO (0.095%)/C_3H_6(0.1%)/O_2(5%)/H_2O (1.7%)/He; flow rate = 100 ml/min; 0.5 g catalysts.

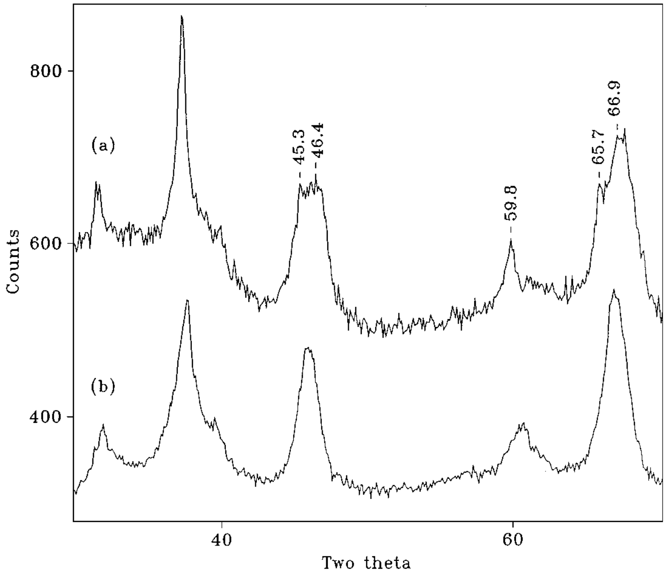

FIG. 5. XRD spectra of (a) 350°C; (b) 800°C calcined postreaction 5 wt% Co/Al_2O_3(H).

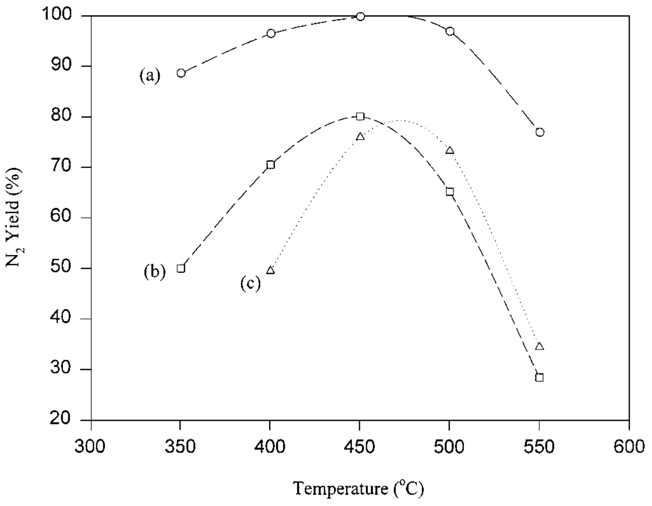

FIG. 6. NO_2 reduction by C_3H_6 over (a) γ-Al_2O_3(H); (b) 800°C calcined 2 wt% Co/Al_2O_3(H); (c) NO reduction by C_3H_6 over 800°C calcined 2 wt% Co/Al_2O_3(H).

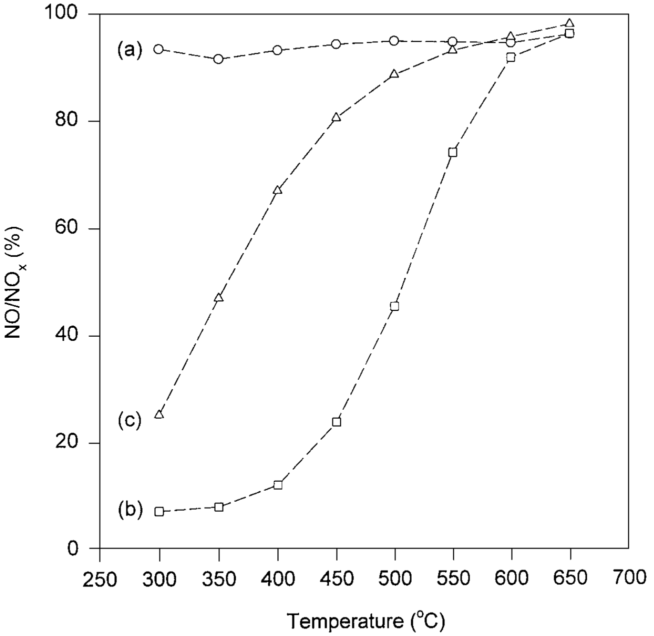

FIG. 7. The ratio of NO/NO_x ($NO_x = NO + NO_2$) in the exit gas in (a) NO oxidation and (b) NO_2 decomposition over a 800°C calcined 2 wt% Co/Al_2O_3(H); (c) equilibrium NO/NO_x ratio. Feed: [NO] or $[NO_2] = 0.095\%$, $[O_2] = 2\%$. Baseline (bypassing reactor): NO/O_2 feed, 97%; NO_2/O_2 feed, 7%.

III.5. *Comparison of the SCR Activity of Co/Al_2O_3(H) and Co-ZSM-5*

Figure 8 compares the catalytic activity of Co-ZSM-5, a 2 wt% Co/Al_2O_3(H) prepared by a single impregnation of $Co(NO_3)_2$ onto alumina, and a 5 wt% Co/Al_2O_3 prepared by a stepwise impregnation method. In the stepwise method, the Co was introduced in five sequential steps of impregnating 1 wt% of Co each time (20). After each impregnation, the sample was calcined at 500°C overnight, the calcination after the final impregnation was at 800°C for 2 h. In comparison to a 5 wt% Co/Al_2O_3(H) prepared by a single impregnation, this sample was more effective in the SCR reaction (compare curve c in Fig. 8 with sample 2b in Table 2). These data show that the maximum NO conversions were similar for all three catalysts (Fig. 8). However, Co-ZSM-5 was the most active catalyst, it attained the maximum NO conversion at the lowest temperature (T_{max}). The data also show that the preparative procedure had a substantial effect on the catalytic performance of Co/Al_2O_3(H). The temperature window of high NO conversion was considerably broader for the 5 wt% sample prepared by the stepwise impregnation than the 2 wt% sample.

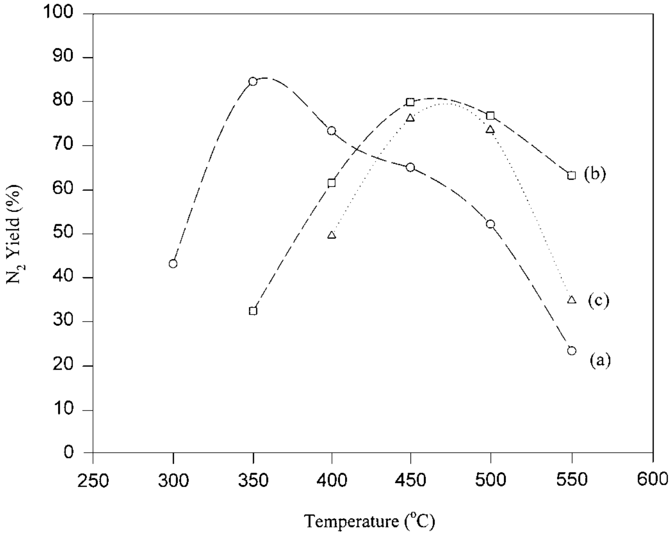

FIG. 8. NO reduction to N_2 by C_3H_6 over (a) 1.24 wt% Co/ZSM-5-17-53.5; (b) 800°C calcined 5 wt% Co/Al_2O_3(H) prepared by step-wise impregnation; (c) 800°C calcined 2 wt% Co/Al_2O_3(H) prepared by single impregnation.

III.6. *Effect of Different Cobalt Precursors and Sources of Alumina*

The catalysts discussed so far were all prepared by introducing $Co(NO_3)_2$ onto Al_2O_3(H) via incipient wetness impregnation. Although significant differences in catalytic behavior were observed upon changing calcination temperature and metal loading, even the poorest catalyst studied had moderate SCR activity. These results are in contrast with the report of Hamada *et al.* (9) who found that Co/Al_2O_3 prepared from $Co(OAc)_2$ had a moderate NO reduction activity, whereas that prepared from $Co(NO_3)_2$ was inactive. To explore this discrepancy, samples prepared by different methods and using different precursors (Table 4), and samples prepared with alumina from different sources (Table 5) were examined.

Supported Co/Al_2O_3(H) samples with comparable Co loadings prepared from different precursors showed similar SCR activities (Table 4 sample 1 vs 2 and 3 vs 4). However, the data in Table 5 show that catalysts prepared with alumina from other sources (Al_2O_3(A) and Al_2O_3(B)) after 350°C calcination were very poor SCR catalysts. Calcination at 800°C resulted in modest improvement in the catalytic performance of Co/Al_2O_3(B) but had little effect on Co/Al_2O_3(A). It appears that Al_2O_3(H) prepared from complexing agent-assisted sol–gel hydrolysis method is a much more desirable support.

IV. DISCUSSION

IV.1. *The State of Co in Co/Al_2O_3(H)*

The UV-vis spectra and TPR results reported here agree well with the literature data (20, 21). The UV-vis spectra indicate the presence of both tetrahedrally coordinated Co^{2+}($Co(T_d)$) and octahedrally coordinated Co^{2+}($Co(O_h)$). These two species are predominant in samples of low Co loadings and samples that have been calcined

TABLE 4

Effect of Preparation Method on the NO Reduction Activity of Co/Al_2O_3(H)[a]

Sample	Preparation method	Co wt%	Rxn temp. (°C)	N_2 yield[b] (%)	C_3H_6 conversion to CO_2 (%)	C_3H_6 conversion to CO (%)	NO C.F.[c] (%)
1	Deposition–precipitation Co (acetate)	0.65[d]	400	27	12	9	15
			450	60	54	12	10
			475	65	75	12	8
			500	56	92	7	7
			550	31	96	4	3
2	Incipient-wetness impregnation with Co (citrate)	0.5	450	42	20	16	15
			500	70	62	22	10
			550	32	100	5	4
3	Incipient-wetness impregnation with Co (citrate)	2	400	43	44	6	10
			450	54	78	5	7
			500	57	96	2	6
			550	42	100	0	4
4	Incipient-wetness impregnation with Co $(NO_3)_2$	2	350	29	10	5	16
			400	59	51	8	11
			450	66	87	5	8
			500	60	98	2	6
			550	32	100	0	3

[a] Sample were calcined in air at 350°C or 800°C, and were pretreated in the reaction mixture at the highest reaction temperature (550°C) before testing. See text for details.

[b] Feed: NO (0.095%)/C_3H_6 (0.1%)/O_2 (5%)/H_2O (1.7%)/He; flow rate = 100 ml/min; 0.5 g catalysts.

[c] NO competitiveness factor $= [N_2]*2/(([C_3H_6]_{in} - [C_3H_6]_{out})*9\text{-}[CO])*100\%$.

[d] Also contains 0.14 wt% Mg.

at 800°C. The Co(T_d) ions are probably in a $CoAl_2O_4$ phase formed in the near surface region of Al_2O_3 (20). Since the formation of $CoAl_2O_4$ involves migration of Co^{2+} ions into the Al_2O_3 lattice, it is facilitated at high temperature. The Co(O_h) ions probably exist as highly dispersed, small clusters of CoO interacting strongly with the Al_2O_3, as suggested by Chung *et al.* (20). Due to its low absorption coefficient, its presence is difficult to detect, but after 800°C calcination its concentration is sufficiently high to be observed as a small but distinct absorption at 480 nm. Co(T_d) ions in $CoAl_2O_4$ phase are not reducible below 800°C (21). TPR data suggest that the majority of Co is present as Co(T_d) in the samples calcined at 800°C.

When the Co loading is increased to 5 wt%, Co_3O_4 formation is confirmed by iodometric titration, XRD, UV-vis spectroscopy and H_2-TPR. The TPR experiment suggests that there may be two different populations of Co_3O_4. A small fraction of the Co_3O_4 has redox property similar to the bulk oxide and is reduced at 260°C (22, 23). The majority of the Co_3O_4 is reduced at much higher temperatures. A 530°C reduction peak corresponding to 0.9 H/Co and a 700°C peak corresponding to 0.5 H/Co were observed. The area ratio of these two peaks (i.e., the H/Co values) is very different from that expected for the two-step reduction of Co_3O_4 to CoO and then CoO to Co metal, as proposed by Van Steen *et al.* for unsupported Co_3O_4 (22). The area ratio of the reduction peaks would be 1 : 3 for this two-step process. Without additional evidence, we tentatively assign these reduction peaks to small Co_3O_4 particles of different sizes, as proposed by Okamoto *et al.* (23). Alternatively, these peaks might be due to the reduction to Co^0 of surface Co_3O_4 and surface CoO, respectively. After 800°C calcination, the UV-vis spectrum (spectrum 3d) indicates that most of the Co_3O_4 had reacted with Al_2O_3 to form $CoAl_2O_4$. Most of the Co ions were no longer reducible and very little Co^{3+} was detected by iodometric titration. The change in color of the samples from dark green to bright blue after high temperature calcination also indicates the conversion of surface Co_3O_4 to $CoAl_2O_4$.

IV.2. Active Sites of Co/Al_2O_3 Catalysts for NO_x Reduction

From the data presented, it is concluded that dispersed Co(O_h) and Co(T_d) ions, large and small particles of Co_3O_4 are present in Co/Al_2O_3. Their distribution varies with Co loading and calcination temperature. By comparing the catalytic activities with the distribution of different Co species in the various samples, conclusions can be drawn regarding to the catalytic properties of these Co ions.

TABLE 5

Co/Al_2O_3 Prepared by $Co(NO_3)_2$ Impregnation onto Different γ-Al_2O_3[a]

Sample	Rxn temp. (°C) Conversion (%)	350 NO	350 HC	400 NO	400 HC	450 NO	450 HC	500 NO	500 HC	550 NO	550 HC
Co/Al_2O_3(H)	350°C calcined	29	20	57	59	66	91	60	100	32	100
2 wt%	800°C calcined	—	—	50	33	76	79	73	100	35	100
Co/Al_2O_3(A)	350°C calcined	—	—	23	18	28	70	31	70	18	100
2 wt%	800°C calcined	—	—	22	28	30	83	30	83	16	100
Co/Al_2O_3(B)	350°C calcined	—	—	—	—	9	67	16	67	19	100
2 wt%	800°C calcined	—	—	19	18	42	73	64	73	34	100

[a] Feed: NO (0.095%)/C_3H_6 (0.1%)/O_2 (5%)/H_2O (1.7%)/He; flow rate = 100 ml/min; 0.5 g catalysts.

The $Co(T_d)$ ions in the surface aluminate phase is probably not the active site. In the spinel structure, the tetrahedral cations are shielded from the gas molecules by oxygen anions (24, 25) and thus are unable to adsorb gas molecules (26, 27). This is probably the reason that Chung *et al.* (20) found that $Co(T_d)$ on Co/Al_2O_3 could not be sulfided. On the other hand, surface $Co(O_h)$ on Al_2O_3 can be made coordinatively unsaturated by desorption of adsorbed water or oxygen at elevated temperatures and becomes available to adsorb gases. On a 2 wt% Co/Al_2O_3 catalyst, Topsøe *et al.* (27) observed IR absorption that can be attributed to both mononitrosyl and dinitrosyl species on $Co(O_h)$ ions. These $Co(O_h)$ ions are present on the surface of active samples, such as the 2 wt% $Co/Al_2O_3(H)$ and 5 wt% $Co/Al_2O_3(H)$ calcined at 800°C. Thus, we propose that the active species in $Co/Al_2O_3(H)$ for the SCR reaction are the $Co(O_h)$ ions that are responsible for the 480 nm absorption in the UV-vis spectra.

Not only the 480 nm peak for $Co(O_h)$ on $Co/Al_2O_3(H)$ samples that had been calcined at different temperatures correlate with the NO reduction activity. A similar correlation appears to exist for $Co(O_h)$ peak and the SCR activity of samples prepared with aluminas of different sources. Figure 9 shows the UV-vis spectra of the 800°C calcined 2 wt% Co/Al_2O_3 samples prepared with different Al_2O_3 supports. Their catalytic activities are reported in Table 5. The 480 nm peak is much more clearly observed on $Co/Al_2O_3(H)$ and $Co/Al_2O_3(B)$ than on $Co/Al_2O_3(A)$, and their NO reduction activities are much higher than the latter catalyst.

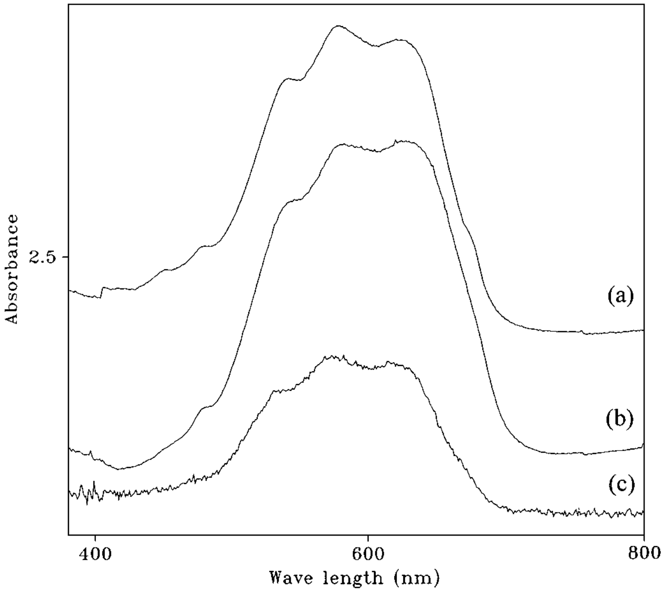

FIG. 9. UV-vis spectra of 800°C calcined 2 wt% Co/Al_2O_3 samples with different sources of alumina supports: (a) $Co/Al_2O_3(H)$; (b) $Co/Al_2O_3(B)$; (c) $Co/Al_2O_3(A)$.

The Co^{3+} ions present in large and small crystallites of Co_3O_4 are the least active for SCR. The 350°C calcined, 5 wt% $Co/Al_2O_3(H)$, with a high concentration of small Co_3O_4 particles, has the lowest effectiveness in NO_x conversion (Table 2). Calcination of this sample at 800°C redisperses the Co_3O_4 clusters, and an increase in the N_2 yield is observed. The SCR activity of the 800°C calcined 5 wt% Co/Al_2O_3 is still poorer than the 2 wt% sample, possibly because of incomplete dispersion of the Co_3O_4 particles.

It has been suggested that reducible transition metal cations, such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Pd^{2+} form more effective NO_x reduction catalysts if they are dispersed in a nonreducible matrix (28, 29). This is because the isolated cations are less reducible than ions in bulk oxides and they are less active in hydrocarbon combustion. Thus, by dispersing Co^{2+} ions on the surface of Al_2O_3, they become much less reducible and less active for hydrocarbon combustion.

IV.3. Comparison of Co-ZSM-5 and Co/Al_2O_3

It appears that the highly dispersed, nonreducible, coordinatively unsaturated $Co(O_h)$ ions have similar physical and chemical properties as the Co^{2+} ions in the ZSM-5 catalyst. Nitrito groups formed on the isolated Co ions in a Co/ZSM-5 catalyst have been proposed to be important in the SCR reaction as they are stronger oxidants than O_2 (19). For Co/Al_2O_3, data in Table 3 show that the presence of NO in the feed greatly enhances the rate of the oxidation of hydrocarbon. This indicates that adsorbed NO_2 facilitates the activation of hydrocarbon. These similarities of the Co ions in the two catalysts suggest that $Co/Al_2O_3(H)$ and Co/ZSM-5 could have comparable SCR properties. Indeed, the maximum NO conversions to N_2 are comparable for these two catalysts (Fig. 8).

A significant difference between the two catalysts is that Co/ZSM-5 attains the maximum N_2 yield at a much lower temperature than $Co/Al_2O_3(H)$. The activity of a catalyst is governed by the density of accessible active sites. In Co-ZSM-5, most of the Co ions are accessible to the reactants, but in $Co/Al_2O_3(H)$, due to diffusion of Co into the alumina lattice and formation of the surface $CoAl_2O_4$ phase, only a small fraction of the Co is available for reaction. An attempt was made to increase the surface concentration of dispersed Co ions in $Co/Al_2O_3(H)$ by increasing the Co loading with the stepwise impregnation method. The resultant catalyst (Fig. 8) is indeed more active than the other Co/Al_2O_3 samples prepared with a single impregnation step and also has a broader window of operation temperature.

IV.4. Effect of Different Cobalt Precursors and Alumina

It is interesting that different sources of γ-Al_2O_3 supports lead to significantly different catalytic properties of Co/Al_2O_3 (Table 5). Arnoldy *et al.* pointed out that NO_2 formed during the decomposition of $Co(NO_3)_2$ can oxidize Co^{2+} to Co^{3+} even at low calcination temperatures

(21). Once oxidized, the Co ions have a high tendency to form Co_3O_4. The ease of oxidation of the Co^{2+} ions should depend on their strength of interaction with alumina. γ-Al_2O_3(H) probably interacts very strongly with metal ions. A high dispersion of Au was reported for Au/Al_2O_3(H) (8). Similarly, high Co dispersion was achieved with impregnation of either $Co(NO_3)_2$ or Co citrate on γ-Al_2O_3(H). Al_2O_3(B) probably interacts more weakly with Co ions than Al_2O_3(H), and poorly dispersed Co/Al_2O_3(B) results when prepared with the nitrate salt and calcined at low temperatures. Indeed, the UV-vis spectrum of a 350°C calcined 2 wt% Co/Al_2O_3(B) shows very low intensities of the features assigned to Co(T_d) and Co(O_h) ions, but a high intensity of the Co_3O_4 feature. This may be the reason why Hamada *et al.* found that Co/Al_2O_3 prepared from Co nitrate is a very poor SCR catalyst (9). Redispersion of Co takes place with 800°C calcination, and then the catalytic behavior of Co/Al_2O_3(B) approaches that of Co/Al_2O_3(H). The UV-vis spectra of 2 wt% Co/Al_2O_3(B) and Co/Al_2O_3(H) are very similar after 800°C calcination (Fig. 9). However, calcination at 800°C does not improve the catalytic activities of Co/Al_2O_3(A), even though the bright blue color and the TPR profile of the catalyst suggest that the Co ions are well dispersed. Presumably, most of the Co ions in this sample are not located on the surface. Since γ-Al_2O_3(A) is not of high purity, the presence of impurity may also be a cause of the low competitiveness observed for the Co/Al_2O_3(A) sample.

V. CONCLUSION

Co/Al_2O_3 catalysts have been found to be active and stable in the NO SCR reaction. The SCR activities of these catalysts depend on the Co loading, the pretreatment conditions, particularly the calcination temperature, and the source of the alumina support. Depending on these variables, catalysts of different effectiveness for NO_x reduction are obtained, which contain different concentrations of $CoAl_2O_4$, dispersed surface Co^{2+} ions, small Co_3O_4 clusters that interact strongly with Al_2O_3, and large Co_3O_4 particles. It is suggested that dispersed surface Co^{2+} ions, which are octahedrally coordinated under ambient conditions, are responsible for the SCR activity. In contrast, particles or surface clusters of Co_3O_4 only catalyze the nonproductive combustion of hydrocarbons, and the Co^{2+} ions in $CoAl_2O_4$ are inactive.

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