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NO decomposition over sodium-promoted cobalt oxide

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Abstract

The catalytic decomposition of NO over cobalt oxide was significantly enhanced by the addition of alkali promoters. The promotional effect was the highest with Na and the optimal Na/Co atomic ratio was 0.015. The reaction rate increased with increasing temperature up to 650°C. At 550°C, the rate measured at low conversions for the most active catalyst was 0.28 μmol N_2/g s. In contrast, very low decomposition rate was observed when Na was added to ZrO_2. This suggests that both Na^+ and Co_3O_4 are necessary for the high NO decomposition activity. In ^{15}NO temperature programmed desorption, the presence of Na in the sample resulted in the appearance of desorption peaks of NO, O_2 and N_2 at temperatures higher than 450°C. X-ray diffraction of a post-reaction sample detected a $NaNO_3$ phase. It was proposed that the presence of Na facilitated the desorption of oxygen from Co^{3+} to form Co^{2+} via the formation and decomposition of $NaNO_3$, and Co^{2+} was the active site for NO decomposition.

Keywords: NO decomposition; Co_3O_4; Na promotion; TPD; XRD

1. Introduction

Direct catalytic decomposition of NO is the most attractive as well as the most challenging NO_x abatement process. A large number of metal oxides [1,2] have been examined for NO decomposition, but none has an activity that approaches practical application. In many of the studies, kinetic measurements [1–3] indicate that oxygen suppression plays an important role in the catalytic activity. In particular, for Co_3O_4, Amirnazmi et al. [3] found that the kinetics follows the equation:

$$\text{Rate} = k[\text{NO}]/(1 + K[\text{O}_2]), \quad (1)$$

where k is the rate constant for NO decomposition and K is the equilibrium constant for O_2 adsorption. For the more active catalysts, such as Co_3O_4, CuO and MnO_2, the ΔH of vaporization of O_2 is relatively low, between 75 and 85 kJ/mol [4].

In recent years, new catalysts have been discovered that have much higher activities than the simple metal oxides. The most notable example is the Cu-ZSM-5 catalyst [5]. It has been suggested that the active site responsible for the high catalytic activity is an unique dimeric Cu which is stabilized by the zeolitic framework [6–8]. Adsorption of NO on this dimeric species to form a cuprous hyponitrite that decomposes to form N_2 is proposed to be a possible reaction mechanism [9]. Xie et al. [10] have reported high activities on Ba/MgO. NO decomposes on barium oxide via a barium-nitro phase that subsequently decomposes to N_2 and O_2. Chuang and Tan [11] have observed that the formation of a Tb-nitrate intermediate may be impor-

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tant in NO decomposition over Tb promoted Pt catalyst.

Co_3O_4 is one of the most active, single component, metal oxides for NO decomposition [12]. Its activity can be enhanced by addition of Ag, presumably by modifying the extent of oxygen suppression [13]. Thus, it might be possible to further improve the catalytic activity of Co_3O_4 using other promoters. In this paper, we report on the modification of Co_3O_4 by alkali metals ions, in particular Na. Results of catalyst characterization by temperature programmed desorption (TPD) and X-ray diffraction (XRD) are reported, and a proposed scheme for the promotional effect is described.

2. Experimental

2.1. Catalyst preparation

Cobalt oxide was prepared by precipitation of $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98+%) as the hydroxy carbonate with Na_2CO_3 (Fisher Scientific, certified ACS). For the Cs promoted sample, Cs_2CO_3 (Aldrich, 99%) was the precipitation agent. The precipitate was thoroughly washed with deionized water, dried in air at 100°C for 24 h and subsequently calcined in air at 400°C for 4 h before the introduction of promoters. The residual Na content in the parent Co_3O_4 was 0.1 wt%. Alkali metals were introduced in the form of nitrate or carbonate to the Co_3O_4 by incipient wetness impregnation. The alkali metal M/Co atomic ratio varied from 0 to 0.091 in the M/Co_3O_4 series of catalysts and the catalysts were labeled "M(#)" where M is the alkali metal and # is the M/Co atomic ratio. The promoted and parent Co_3O_4 were calcined in air at 575°C for 16 h. One sample of Na(0.030) was also calcined at 700°C. ZrO_2 was prepared by precipitating the nitrate salt of Zr (Aldrich Chemical 99.99% $ZrO(NO_3)_2$) with urea at about 100°C. It was calcined at 575°C for 6 h before the introduction of Na. It was subsequently calcined at 575°C for 12 h.

2.2. Catalyst characterization

BET surface area measurements were performed using an Omnisorp 360 automatic system (Omicron Technology). X-ray powder diffraction patterns were obtained with a Scintag XDS 2000 employing Cu K_α radiation and a solid state detector. Desorbed species in TPD of NO from Na(0.015) and Co_3O_4 were detected with a quadrupole mass spectrometer (UTI 100 C). Prior to the TPD experiment, 0.1 g of the catalyst, after use in NO decomposition reaction, was pretreated in a 100 cm^3/min flow of 10% O_2/He at 550°C for 1 h. It was then purged in He for 30 min and subsequently cooled in He to the adsorption temperature. ^{15}NO was used to avoid interference from the background gases present in the TPD system. The temperature of the sample was increased up to 600°C at a rate of 20°C/min. O_2 TPD experiment was performed using a HP 6890 gas chromatograph. After pretreatment at 550°C and cooled down to room temperature in 10% O_2/He, the reactor was purged with He for 1 h. Then the temperature was raised at a rate of 10°C/min. The ultra high purity He stream used in the desorption experiment was purified by passing through a trap filled with molecular sieve and calcium sulfate to remove water. It was then passed over manganese oxide supported on silica to remove trace amounts of O_2. The 10% O_2/He gas stream was passed through the molecular sieve-calcium sulfate trap to remove H_2O.

2.3. NO decomposition activity

Measurement of the NO decomposition activity was performed in a flow microreactor. The reactor was heated by a tube furnace with the temperature being controlled within 1°C by a K-type thermocouple and an Omega CN 2010 temperature controller. The reactant gas flow rates were controlled with Brooks 5850 mass flow controllers. The product gases were analyzed with a HP 6890 gas chromatograph equipped with a 4 ft. molecular sieve and a 6 ft. Porapak Q column. The NO decomposition reaction was investigated with a 0.976% NO/He gas mixture (Matheson, >99.99%) at a constant flow rate of 30 cm^3/min. In a reaction run, 1 g of catalyst was heated in the reaction feed from room temperature to 450°C and the first data point at 450°C was recorded 3 h after the start of heating. All activity measurements were obtained under steady-state conditions. NO conversion was calculated based on the N_2 product. No byproduct, such as N_2O, was observed. No reaction was observed

when an empty reactor was tested up to 700°C with the reaction feed.

3. Results

3.1. NO decomposition over Na promoted Co_3O_4

In the preliminary experiments, the NO decomposition activity of Co_3O_4 was observed to vary significantly for different preparations. Subsequently, this variation was correlated with the concentration of residual Na in the sample. Impregnation of thoroughly washed samples with Na showed that the rate of NO decomposition was indeed dependent on the Na/Co atomic ratio (Fig. 1), with the highest rate observed at a Na/Co atomic ratio of 0.015.

The dependence of the activity on time on stream at three temperatures is shown in Fig. 2 for sample Na(0.015) calcined at 575°C. Between 450°C and 550°C, the catalyst quickly reached a steady state with each change in temperature. After prolonged testing at 550°C, the reaction rate reexamined at 500°C remained unchanged. Thus, there was no evidence of deactivation.

At temperatures where steady state was attained, O_2 was always detected, albeit at a lower value than N_2. The lower value of O_2 was due to the reaction of O_2 with NO in the chromatography column and the extent of this reaction was more severe at lower NO conversions. For example, at a conversion of 10.8% the O_2/N_2 ratio was only about 0.09, but increased to 0.57 at a conversion of 51.6%.

Fig. 3 shows the temperature dependence of the decomposition activity for a 700°C calcined sample. The surface area of this sample (8 m^2/g) was lower than the 575°C calcined one (24 m^2/g), but its areal activity (that is, activity/m^2) was higher. In this experiment, steady-state activity was obtained in ascending temperature up to 650°C. At 700°C, a 3.7% decrease in N_2 yield was observed after 1.5 h of testing. But when the sample was cooled to 600°C and 500°C, there was no discernible change in activity from the earlier measurements. The ratios of O_2/N_2 detected at 650°C and 700°C were 0.85 and 0.88, respectively.

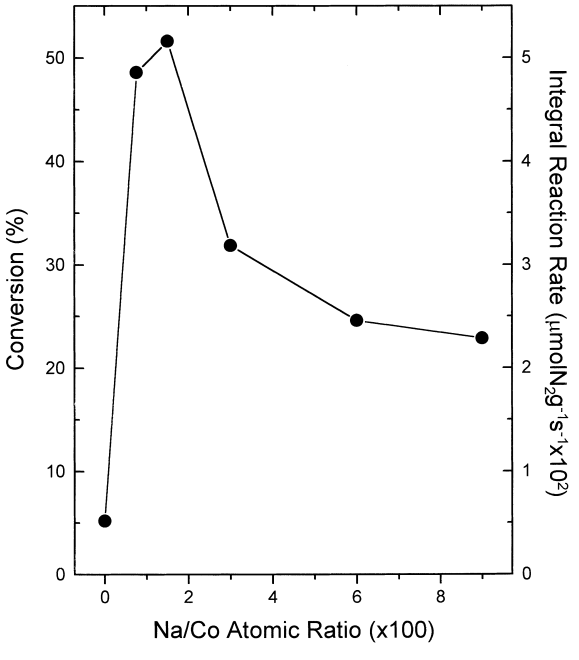

Fig. 1. NO decomposition activity over Na(0.015) catalyst as a function of Na content at 550°C.

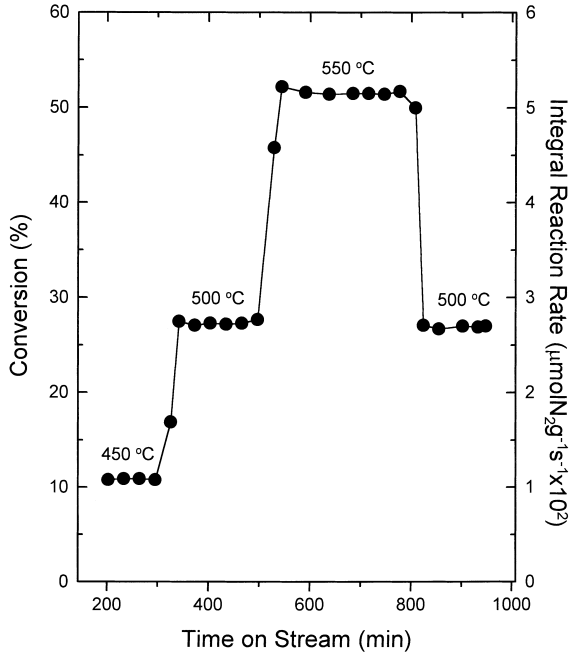

Fig. 2. NO decomposition activity over Na(0.015) catalyst as a function of time on stream.

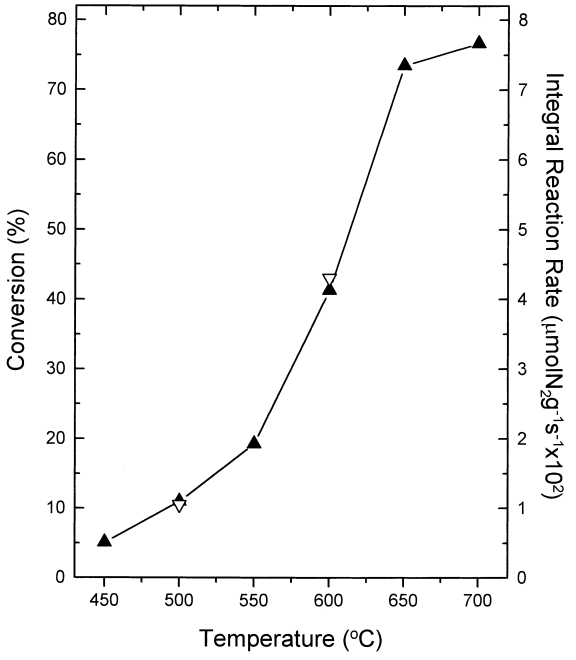

Fig. 3. NO decomposition activity over Na(0.030) calcined at 700°C for 16 h as a function of reaction temperature: (▲) ascending temperature and (▽) descending temperature.

3.2. Differential NO decomposition rates over Co_3O_4 and Na/Co_3O_4

Differential reaction rates were calculated using data of <3.3% conversion. Table 1 compares these rates over Co_3O_4 and Na(0.015) catalysts with the reported values for other cobalt oxide catalysts as well as that for Cu-ZSM-5 [14]. The literature values tabulated by Yamashita and Vannice [14] were extrapolated to our reaction condition of 0.962% NO by assuming a first order dependence on NO concentration. The reaction rates for Co_3O_4 and Na(0.015) were 0.014 and 0.28 μmol N_2/g s, respectively.

3.3. Alkali metal promoted Co_3O_4

Promotional effect in NO decomposition was also observed with other alkali metals (Fig. 4). In this series of experiments, the M/Co atomic ratio was 0.015. Except for Li, this value was close to the optimal ratio for all alkali metals. The promotional effect varied for different metals, with Li being the most ineffective. For Li, the NO decomposition rate increased with Li loading up to a Li/Co ratio of 0.075, beyond which there was little change.

3.4. Catalyst characterization

Extensive characterization of the catalysts were performed in order to understand the differences in catalytic activity with different alkali metals as well as with changes in metal loadings. Table 2 lists the BET surface areas of the different catalysts. With the exception of Li, the addition of a small amount of alkali metals impeded the sintering of Co_3O_4, and the

Table 1
NO decomposition activity over oxide catalysts

Catalyst	Temperature (°C)	Activity		References[d]
		10^{-4} μmol N_2/g s	10^{-5} μmol N_2/m^2 s	
Co_3O_4	500	63	77	[21]
Co_3O_4	500	100	—	[13]
$AgCo_3O_4$	500	500	—	[13]
Cu-ZSM-5	500	29 000	—	[16]
Co_3O_4	600	—	240	[3]
Co_3O_4[a]	550	140	100	This study
Na(0.015)[b]	550	2800	1400	This study
Na(0.015)/ZrO_2[c]	600	8	3	This study
Na(1.07)/ZrO_2[c]	600	5	11	This study

[a]Reaction rate determined at 2.1% conversion using 0.96% NO, 200 cm^3/min and 1 g sample.
[b]Reaction rate determined at 3.3% conversion using 0.96% NO, 150 cm^3/min and 0.058 g sample.
[c]Reaction rate determined at <1% conversion using 0.96% NO, 30 cm^3/min and 1 g sample.
[d]Reaction rates obtained from Table 4 in [14]. Data extrapolated to 0.96% NO by using first order dependence for NO.

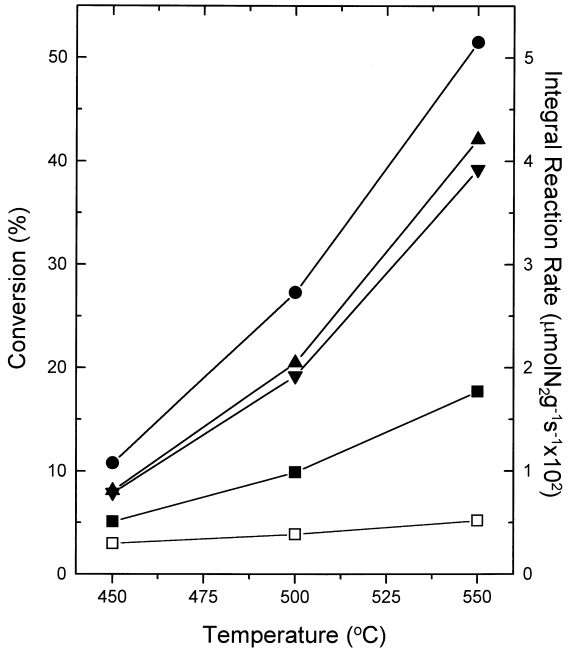

Fig. 4. NO decomposition activity over alkali metal promoted Co_3O_4 catalysts (M/Co atomic ratio=0.015): (●) Na, (▲) K, (▼) Cs, (■) Li and (□) Co_3O_4.

surface area stabilization increased with the size of the alkali metal. The XRD patterns of Na/Co_3O_4 before and after reaction are shown in Fig. 5(a) and (b), respectively. XRD patterns of fresh catalysts with $Na/Co \leq 0.015$ showed only lines characteristic of Co_3O_4. For samples with $Na/Co \geq 0.03$, peaks characteristic of β-$Na_{0.6}CoO_2$ were observed. The intensities of the β-$Na_{0.6}CoO_2$ peaks increased with increasing Na content. In addition, $NaNO_3$ peaks were detected in the post reaction catalysts with $Na/Co \geq 0.03$.

3.5. Temperature programmed desorption

TPD of O_2 and NO were performed to better understand their roles in the decomposition process. Fig. 6 shows the oxygen desorption profiles for Co_3O_4 and the different Na/Co_3O_4 catalysts. The total amount of O_2 desorbed and the amount of O_2 desorbed at the temperatures of interest (between 400°C and 600°C) all increased with Na loading.

The desorption profiles for room temperature adsorption of ^{15}NO on Co_3O_4 and Na(0.015) catalysts are shown in Fig. 7(a) and (b). For the Co_3O_4 sample, the gas phase species detected were ^{15}NO, $^{15}N_2$ and O_2. The ^{15}NO desorption peak, with a shoulder around 160°C and a peak at 250°C, was very broad. Low levels of N_2 were detected over a wide range of temperatures; the highest concentration detected was between 250°C and 350°C. O_2 desorption showed a peak at 350°C. Above 450°C, O_2 desorption increased with increasing temperature.

For the Na(0.015) sample, ^{15}NO and $^{15}N_2$ and O_2 were also the desorption products from room tem-

Table 2
BET surface area of M/Co_3O_4 and Na/ZrO_2 catalysts

Catalyst	wt% M	Calcination temperature (°C)	Surface area (m^2/g)	
			Fresh	Used
Co_3O_4	—	575	14	14
Na(0.0075)	0.22	575	30	28
Na(0.015)	0.43	575	27	20
Na(0.030)	0.86	575	32	24
Na(0.030)	0.86	700	8	8
Na(0.061)	1.7	575	32	19
Na(0.091)	2.5	575	23	15
Li(0.015)	0.13	575	14	14
K(0.015)	0.73	575	30	31
Cs(0.015)	2.45	575	51	44
$Na(0.015)/ZrO_2$[a]	0.29	575	—	30
$Na(1.07)/ZrO_2$[a]	20	575	—	5

[a]Numbers are Na/Zr atomic ratio.

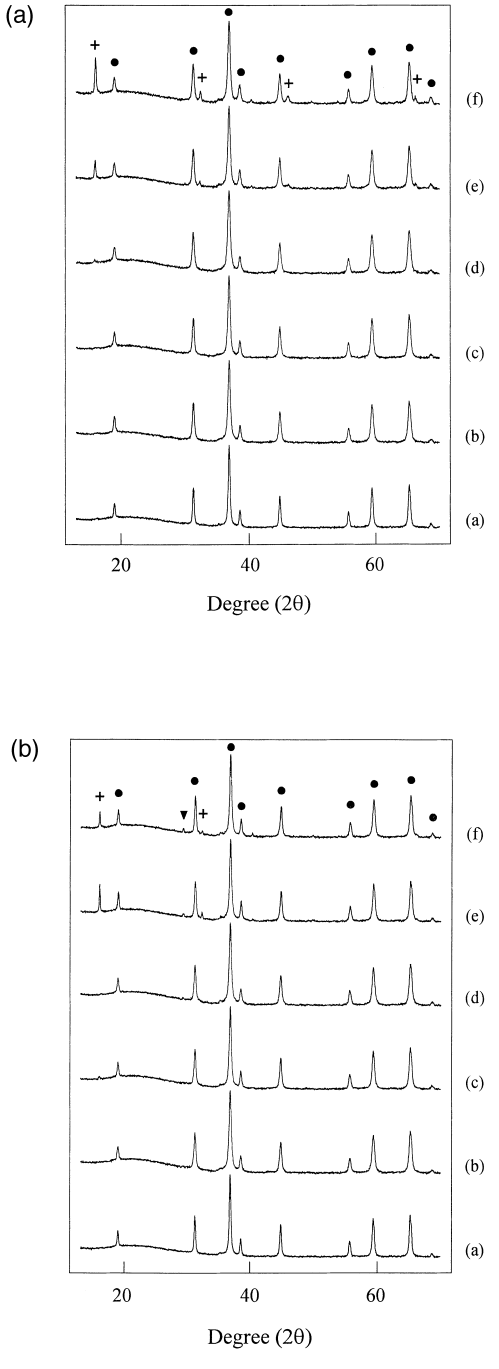

Fig. 5. (a) XRD patterns of fresh Na/Co_3O_4 catalysts (a) Na(0), (b) Na(0.0075), (c) Na(0.015), (d) Na(0.030), (e) Na(0.061) and (f) Na(0.091); (●) Co_3O_4 and (+) β-$Na_{0.6}CoO_2$. (b) XRD patterns of post reaction Na/Co_3O_4 catalysts (a) Na(0), (b) Na(0.0075), (c) Na(0.015), (d) Na(0.030), (e) Na(0.061) and (f) Na(0.091); (●) Co_3O_4, (+) β-$Na_{0.6}CoO_2$ and (▼) $NaNO_3$.

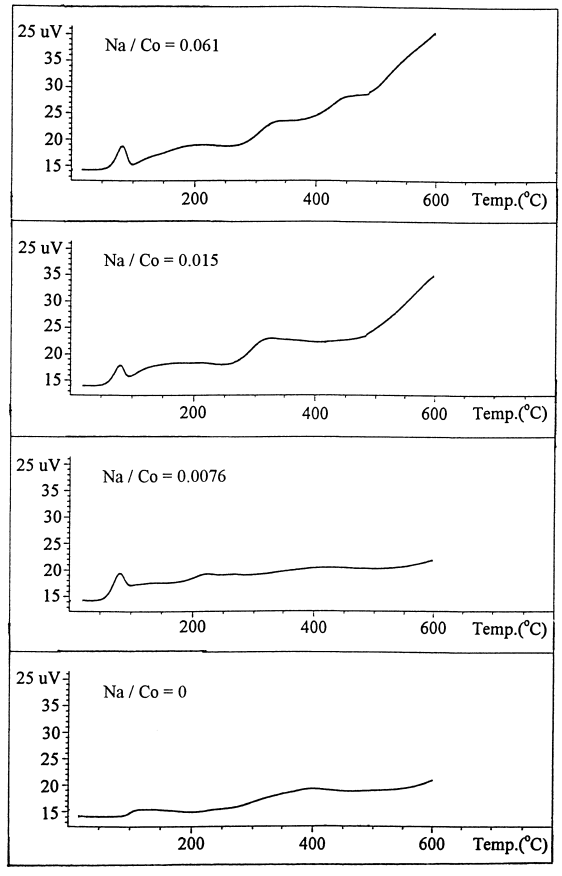

Fig. 6. O_2 TPD profiles for Na/Co_3O_4 catalysts.

perature adsorption of NO (Fig. 7(b)). Compared to the desorption profile of Co_3O_4, the 350°C O_2 peak disappeared and a new one appeared at 540°C. New ^{15}NO and $^{15}N_2$ desorption peaks also appeared at 575°C and about 600°C, respectively. Thus, these desorption peaks were associated with the presence of Na. The NO adsorption process appeared to be an activated one. Adsorption of ^{15}NO at 350°C instead of room temperature resulted in $^{15}N_2$, ^{15}NO and O_2 desorption peaks about twice as intense as those from room temperature adsorption (Fig. 7(b) and (c)).

3.6. NO *decomposition over* Na/ZrO_2

Na/ZrO_2 samples were not active for NO decomposition. Two Na/ZrO_2 samples with Na/Zr atomic

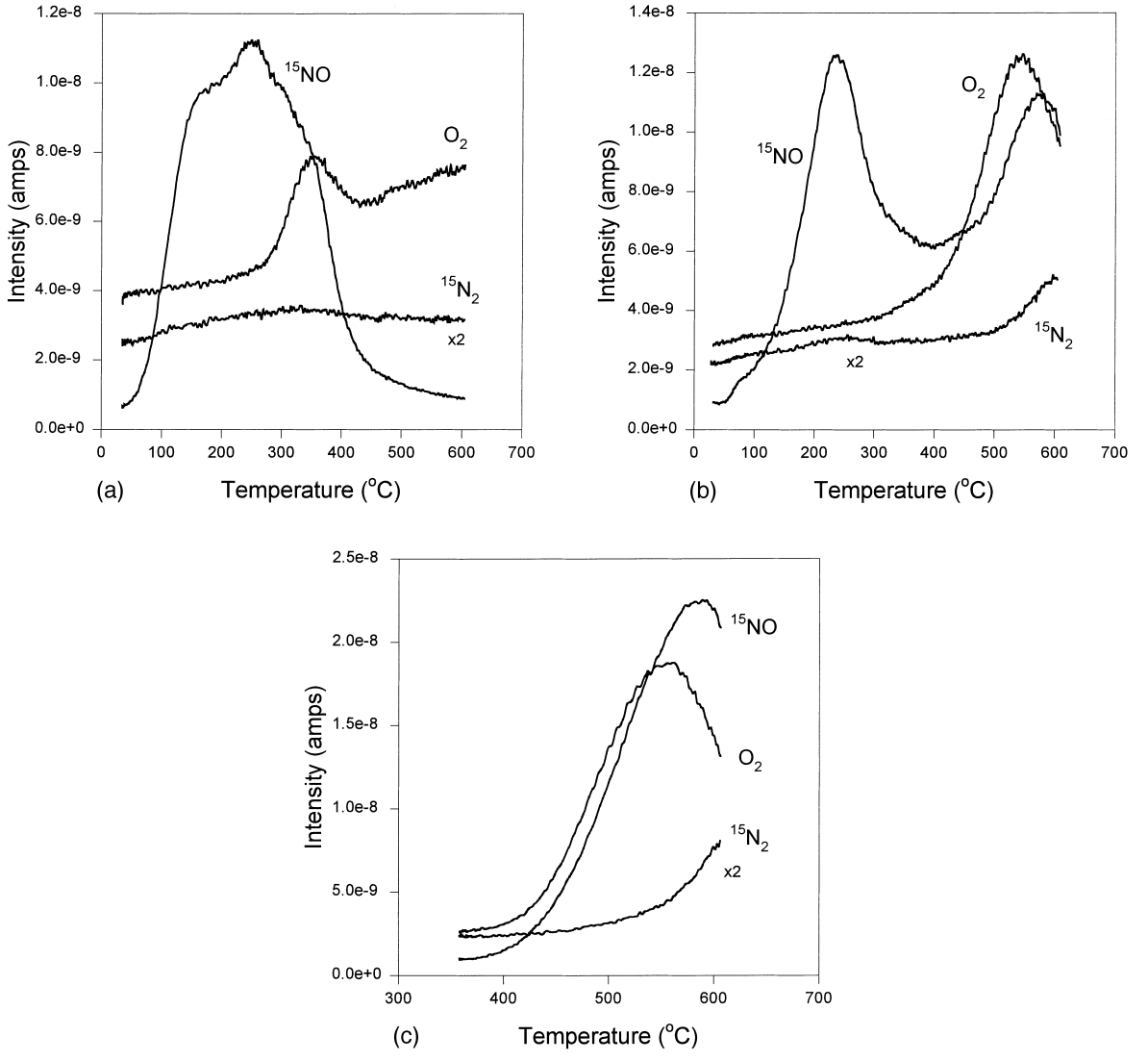

Fig. 7. TPD profiles of ^{15}NO, $^{15}N_2$, and O_2 from ^{15}NO adsorption at room temperature for (a) Co_3O_4 and (b) Na(0.015), and adsorption at 350°C for (c) Na(0.015).

ratios of 0.015 and 1.07 were tested up to 600°C. ZrO_2 was used as a support for Na as it is chemically more inert than Al_2O_3 and SiO_2 [15]. The XRD pattern of Na/ZrO_2 showed a major phase of monoclinic zirconia and a minor phase of tetragonal zirconia. No Na_2ZrO_3 compound was detected. The decomposition rates were very low (Table 1). On the per gram basis, the rate of Na/Zr(0.015) at 600°C was 350 times lower than that of Na(0.015) and 18 times lower than that of Co_3O_4 measured at 550°C.

Table 3
Integral NO and NO_2 decomposition reaction rates over Na(0.015) catalyst

Temperature (°C)	Decomposition activity[a] (10^{-4} μmol N_2/g s)	
	NO	NO_2
450	108	14
500	273	90
550	515	310

[a]Reaction rate obtained at 0.976% NO or 1% NO_2 with 30 cm^3/min and 1 g sample.

3.7. NO_2 decomposition over Na(0.015)

Table 3 compares the NO and NO_2 decomposition activities over Na(0.015) catalyst. The NO_2 decomposition rate was always lower than the NO decomposition rate. The difference was more pronounced at the lower temperatures.

4. Discussion

The high NO decomposition activity, resulted from the addition of Na, is indeed catalytic as evidenced by the sustained activity over time. In the experiment depicted in Fig. 3, 5.2×10^{-3} mol of oxygen atoms would have been formed from NO decomposition, which is equivalent to 120% of the total Co^{2+} in the sample (4.2×10^{-3} mol). Since there was no detectable structural change by XRD after reaction, it can be concluded that stoichiometric reaction cannot be the primary source of N_2 production. The deviation of O_2/N_2 ratio from unity was due to the reaction of NO and O_2 in the chromatography column. The O_2/N_2 ratio increased with increasing NO conversion, and the highest ratio being 0.88 at a NO conversion of 76.7%. This phenomenon has been well documented by other workers [16].

A comparison of the Na(0.015) catalyst with Co_3O_4 (Table 1) shows that the addition of only 0.43 wt% Na is sufficient to cause a 20-fold increase in activity. The NO decomposition rate of 0.28 μmol/g s is only 10 times lower than that of Cu-ZSM-5, the most active catalyst reported to date. This activity is higher than any metal oxide catalysts reported. The activity of the Co_3O_4 used here (with a residual Na content of 0.1 wt%) is within the range of the reported values in the literature. In view of the fact that a very low level of alkali metal can significantly improve the catalytic performance of Co_3O_4, it is not surprising that there exists variations in the rates reported for Co_3O_4.

The promotional effect is not limited to Na but extends to all other alkali metals. However, the degree of promotion varies with the nature of the alkali metal and this variability is not related to the surface area of the catalyst. Li is the least effective promoter. It is a small cation and can easily diffuse into the bulk of Co_3O_4 as well as substitute for Co [17–19] to form $Li_xCo_{3-x}O_4$. These processes effectively reduce the surface density of Li and lead to the smallest observed promotional effect.

It is interesting that there exists an optimal Na/Co ratio for the NO decomposition reaction. The difference in the catalytic activity of the Na/Co_3O_4 catalysts with different Na loadings is not due to the different surface areas. Surprisingly, there is no obvious correlation between the amount of oxygen desorbed in the oxygen TPD experiment and the catalytic activities of the Na/Co_3O_4 catalysts. The total amount of oxygen desorbed as well as the amount of oxygen desorbed in the temperature region of interest (>400°C) all increase with Na loadings. One possible reason for the decline in activity at high Na loadings is the formation of a β-$Na_{0.6}CoO_2$ phase which was detected with XRD (Fig. 5) at high Na loadings. If this phase is inactive in NO decomposition, its presence would affect the overall catalytic activity. However, the existence of an optimal Na/Co ratio may best be understood with respect to the manner that Na affects the catalytic activity and will be discussed in detail in a proposed scheme later on.

Na/ZrO_2 has a very low activity compared with Na/Co_3O_4, whether compared on the basis of the amount of Na or the weight of catalyst. It has been reported that sodium oxide reacts with NO_2 to form $NaNO_3$. The subsequent thermal decomposition of the nitrate yields N_2 [20]. Thus, a possible scheme for the reaction over Na/Co_3O_4 is that NO is oxidized to NO_2 over Co_3O_4, and the latter reacts with Na_2O_2 to form sodium nitrate. However, a significant role for this scheme can be ruled out because the NO_2 decomposition rate is much lower than the NO decomposition rate at all temperatures over Na(0.015) catalyst (Table 3), and Na/ZrO_2 is much less active (Table 1).

From these results, it is apparent that both Na and Co_3O_4 are necessary for the enhanced rate of NO decomposition over Na/Co_3O_4 relative to Co_3O_4. A possible mechanism for the synergistic effect between Na and Co is suggested by the ^{15}NO TPD experiments. In addition to the desorption features associated with Co_3O_4, the NO TPD profile of Na(0.015) sample shows new desorption peaks of O_2, NO and N_2 in the 500–600°C region. The O_2 and NO peaks are much more intense than the N_2 peak, and their peak maxima are slightly displaced from one another, being the lowest for O_2 and the highest for N_2. Thus, these three species are not formed from the same concerted

reaction step. The following scheme can be used to explain the high temperature features:

$$2Co^{3+}O^{-} \rightarrow 2Co^{2+} + O_2 \quad \text{(high temperature pretreatment in He)}, \tag{2}$$

$$2Co^{2+} + 2NO \rightarrow 2Co^{3+}O^{-} + N_2 \quad \text{(room temperature NO adsorption)}, \tag{3}$$

$$2Co^{3+}O^{-} + Na_2O_2 + 2NO \rightleftarrows 2Co^{2+} + 2NaNO_3 \tag{4}$$

$$2NaNO_3 \rightleftarrows Na_2O_2 + 2NO + O_2 \quad \text{(high temperature)}, \tag{5}$$

$$2Co^{2+} + 2NO \rightarrow 2Co^{2+} + N_2 + O_2 \quad \text{(high temperature)}, \tag{6}$$

$$2Co^{2+} + O_2 \rightarrow 2Co^{3+}O^{-} \tag{7}$$

In this mechanism, oxygen is desorbed from the surface Co^{3+} to produce Co^{2+} (Eq. (2)) at temperatures higher than about 350°C (the O_2 desorption peak for Co_3O_4, Fig. 7(a)). Thus, reduction of cobalt occurs during the high temperature pretreatment of the sample in He. Exposure of the sample to NO at room temperature reoxidizes the Co^{2+} to Co^{3+} (Eq. (3)). The oxygen remains adsorbed on Co^{3+} site but N_2 was desorbed immediately and purged out by He. The N_2 evolved was not monitored in the TPD experiment, but its formation was verified with GC in a separate experiment where NO was pulsed at room temperature over a sample pretreated in the same manner as the TPD experiment. The formation of $Co^{3+}O^{-}$ can be accomplished if the sample is pretreated in O_2 instead of He. Indeed, the TPD profile of such a sample is similar to those shown, except for the lower amount of desorbed NO and N_2 relative to O_2 in the high temperature desorption region.

NO also is adsorbed on Co^{3+} at room temperature and desorbed at 200–250°C. At the same time, if Na is present, the reaction of $Co^{3+}O^{-}$ with Na_2O_2 and NO can occur to form $NaNO_3$ (Eq. (4)). The occurrence of this reaction reduces the surface concentration of $Co^{3+}O^{-}$ and is manifested in the loss of the low temperature O_2 desorption peak (compare Fig. 7(a) and (b)). This is also an activated process and proceeds more rapidly when the exposure of NO is at elevated temperature (compare Fig. 7(b) and (c)).

When the sample is heated above 400°C, decomposition of $NaNO_3$ occurs (Eq. (5)). Both O_2 and NO are evolved. The latter is further decomposed on the Co^{2+} to form O_2 and N_2. The delay of the NO peak maximum relative to the O_2 peak is probably due to chromatographic effect as a result of readsorption on the catalyst surface. Since N_2 is formed from NO decomposition (Eq. (6)), its evolution lags behind that of NO. Since only a minor fraction of desorbed NO decomposes, the amount of O_2 formed is small and appears in the tail of the much larger O_2 desorption peak.

This reaction scheme can apply to the catalytic NO decomposition reaction. The formation of $NaNO_3$ was detected by XRD on samples with high Na loadings after reaction. Most likely, its concentration on the catalyst surface is determined by the gas phase NO and O_2 concentrations, and possibly, its decomposition rate is suppressed by high O_2 concentrations. The suppression of $NaNO_3$ decomposition and adsorption of O_2 on Co^{2+} at the reaction temperature are some processes that contribute to the observed negative effect of O_2 on NO decomposition. It should be noted that in this mechanism, the role of Na is depicted in reactions (4) and (5). The sum of these two reactions is the desorption of O_2 from $Co^{3+}O^{-}$ to form Co^{2+}.

5. Conclusions

Alkali metals, in particular Na, have significant promotional effect on Co_3O_4 for the NO decomposition reaction. A proposed reaction scheme suggests that the formation and decomposition of $NaNO_3$ facilitates the formation of the catalytic active site of Co^{2+}. Thus, Na and cobalt have synergistic effect for the NO decomposition reaction. On the weight basis, Na(0.015) is among the most active NO decomposition catalysts known, although its activity at 550°C is still 10 times lower than that of Cu-ZSM-5 at 500°C. However, its activity continues to increase with increasing temperature up to 650°C, whereas the activity of Cu-ZSM-5 declines at higher temperatures. Thus, the Na/Co_3O_4 system appears to be worthy of further investigation.

Acknowledgements

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