A study on N₂O catalytic decomposition over Co/MgO catalysts

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ABSTRACT

Different oxide supported cobalt catalysts were prepared by co-precipitation method and tested for the decomposition of nitrous oxide. Co/MgO with cobalt loading of 15% showed the best activity and a 100% N₂O conversion was obtained at temperatures higher than 700 K. The active phase of cobalt species in Co/MgO catalysts was Co₃O₄ highly dispersed in the matrices of MgO, based on XRD and XPS results as well as the kinetic analysis. The existence of NO, O₂ and H₂O in reaction system showed different negative effects on N₂O decomposition. Nevertheless, a 100% N₂O conversion could be achieved at 800 K under simulated conditions of tail gas from nitric acid plant. Moreover, Co/MgO catalyst exhibited quite good durability and no obvious activity loss was observed in the 100 h stability test.

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1. Introduction

For a long time, nitrous oxide (N₂O) had been considered as a relatively harmless gas and not received much attention from the viewpoint of environmental pollutants. However, since the last decade, N₂O has been recognized as a strong greenhouse gas and also severely destructs the ozone in the stratosphere [1]. N₂O has a very long atmospheric lifetime (~120 years), the global warming potential (GWP) of nitrous oxide (N₂O) is about 310 times of carbon dioxide (CO₂) [2]. Anthropogenic N₂O emissions mainly come from chemical industries, e.g. the production of nitric acid and organic synthesis employing nitric oxidation process (production of adipic acid and glyoxal). Several end-of-pipe technologies have been developed to mitigate N₂O emission from above anthropogenic sources and amongst these different technologies, the catalytic decomposition is proposed as the most economical method. However, for N₂O catalytic decomposition, catalysts should possess a sufficient activity and durability.

Various types of catalysts, e.g. supported noble metals [3–5], mixed oxides with different structure [6–10], iron zeolites [11–15], have been investigated for N₂O decomposition. Supported cobalt catalysts have received considerable attention due to high activity [16–26]. da Cruz et al. [16] reported the studies of N₂O decomposition on Co-ZSM-5 prepared with different methods and claimed that isolated Co²⁺ ions showed high activity. Kannan and Swamy

[18] studied N₂O decomposition over calcined cobalt aluminum catalyst and found that the activity increased with the increasing cobalt concentration. Chellam et al. [19] and Yan et al. [20] reported that Co₃O₄ spinel with the addition of another kind of transition metal (M_xCo_{1-x}Co₂O₄, M = Ni, Mg) were very active for N₂O decomposition, even at reaction temperatures below 400 °C. However, the high activity of catalysts seems to depend much on the preparation parameters [19]. Recently, MgCo₂O₄ was reported to have the best activity for N₂O decomposition by Russo et al. [21]. A 100% N₂O conversion was achieved on the MgCo₂O₄ (spinel-type AB₂O₄) catalyst at higher than 500 °C in the absence of oxygen. Obalová et al. [22,23] presented a detailed study on N₂O decomposition over spinel catalysts prepared from Co/Mg–Mn/Al hydrotalcite-like compounds and found Mn/Al ratio played a key role on the activity. For most studies on supported cobalt catalysts for N₂O decomposition, the high activity of catalysts was severely affected by the addition of oxygen and water vapor to the feed gas. [24].

However, to-date, the active phase for N₂O decomposition in the Co/MgO catalyst is not adequately understood. And the activity under simulated conditions at the typical nitric acid plant has not been presented yet considering the future application. During our research on potential catalyst for N₂O decomposition, we also found that Co/MgO samples prepared by simple co-precipitation method showed remarkably activity. In this work, a detailed study is presented concerning the following aspects: (i) characterization of active phase of cobalt species in Co/MgO for N₂O decomposition; (ii) the activity and durability of Co/MgO catalysts for N₂O decomposition under different reaction conditions.

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2. Experimental

2.1. Catalyst preparation

The Co-based catalysts were prepared with co-precipitation method. In a typical synthesis, cobalt nitrate and magnesium (or zinc, manganese, aluminum, cerium) nitrate were mixed with various metal mole ratio (fixing the cobalt loading) in 200 mL distilled water. The precipitator (1 M Na₂CO₃ solution) was added drop-wise into the as-prepared mixed-metal nitrate aqueous solution under vigorous magnetic stirring with 180 rpm until the pH of mother liquor reached about 9.0. After aging in the suspension for 2 h under stirring at room temperature, precipitates were collected by filtration and thoroughly washed with distilled water. The cake was dried at 353 K overnight and then calcined in air at 773 K for 6 h to derive the corresponding oxides. The cobalt loadings in Co/ZnO, Co/Mn_xO_y, Co/Al₂O₃ and Co/CeO₂ were designed to be 10%, which were confirmed by ICP analysis. For Co/MgO, samples with different cobalt loadings were prepared, which were denoted as Co/MgO-5%, Co/MgO-10%, Co/MgO-15% and Co/MgO-20%.

2.2. Catalyst characterizations

The cobalt loadings of supported cobalt catalysts were determined by ICP-AES using an Optima 2000 spectrometer. Low temperature N₂ adsorption/desorption experiments of catalysts samples were carried out in a Quantachrome NOVA-1200 gas absorption analyzer, and the specific surface area was calculated with BET equation.

The X-ray diffraction (XRD) patterns of samples were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 5-80^\circ$.

Transmission electron microscopy images of sample were acquired on a JEOL 3010 transmission electron microscope at an accelerate voltage of 300 kV. A few droplets of the sample suspended in alcohol were placed on a carbon-coated copper grid followed by evaporation at ambient conditions.

XPS (X-ray photoelectron spectroscopy) measurement of selected catalysts was carried out in a VG-Microtech Multilab electron spectrometer using Mg K α (1253.6 eV) radiation source. The analysis chamber was maintained at 5×10^{-10} mbar and the binding energy was adjusted by setting the C 1s transition at 284.6 eV.

2.3. Activity evaluation and kinetics studies

N₂O decomposition experiments were performed in a fixed-bed flow microreactor at atmospheric pressure. For each run, 0.1 g catalyst (sieve fraction, 0.25–0.5 mm) was placed into a quartz reactor (4 mm i.d.) and pretreated in He at 773 K for 1 h. After the reactor was cooled to 473 K, the reactant gas mixture was fed into the reactor. The total flowing rate of inlet gas was set at 60 mL min⁻¹, corresponding to GHSV = 30 000 h⁻¹. The gas composition was analyzed on-line using a gas chromatograph (Agilent 6820 series) equipped with a TCD detector and two serial columns (a Porapak Q column served for the separation of N₂O and the mixture of N₂/O₂, and a molecular sieve 5A column for the separation of N₂ and O₂). The steady-state activity data were recorded every 25 K at ascending temperature from 473 K to 773 K (for activity test) or at a constant temperature (for durability test).

Furthermore, the first-order rate constant (k), the activation energy (E_a) were calculated. Based on the assumption of first-order reaction for N₂O decomposition, the rate of N₂O decomposition can be recognized as

$$r = kP_{\text{N}_2\text{O}} = A e^{-E_a/RT} P_{\text{N}_2\text{O}}$$

Pseudo-first-order rate constants were calculated using the formula [27]:

$$k = -\frac{\ln(1-x)F}{m_{\text{cat}}P}$$

Where x is the N₂O conversion, F is the total flow through the reactor, P is the total pressure, m_{cat} is the amount of the catalyst, T is the temperature. The plot of $\ln(k)$ versus $1/T$ was drawn according to the data collected from steady-state reaction. The slope of this plot represents the apparent activation energy, and the intercept represents associated pre-exponential factor.

3. Results and discussion

3.1. Characterization results

The XRD patterns of supported cobalt catalysts, with the same cobalt loading of 10%, are displayed in Fig. 1. It is seen that a mixture of unitary metal oxides or binary metal oxides phases are observed in the XRD patterns except the Co/MgO catalyst. For example, Co₃O₄ and CeO₂ are observed for Co/CeO₂ sample, CoAl₂O₄ and Al₂O₃ for Co/Al₂O₃, CoMnO₃ and Mn₂O₃ for Co/Mn_xO_y, Zn_xCo_{1-x}Co₂O₄ and ZnO for Co/ZnO. The main diffraction peaks are identified (Fig. 1), and diffraction peaks corresponding to other structures are not discussed here due to their low intensity. While in the XRD pattern of Co/MgO, only (Co/Mg)O phase (JCPDS 02-1201) are observed and no other diffraction peaks corresponding to other species are found.

Fig. 2 shows the XRD pattern for the Co/MgO catalysts with different cobalt loading. Only (Co/Mg)O phase are observed for Co/MgO with cobalt loading below 15%. As for Co/MgO-20%, besides the (Co/Mg)O phase, diffraction peaks corresponding to cobalt oxides (marked with *) appear.

The BET surface areas of supported cobalt catalysts are listed in Table 1. It is seen that Co/MgO shows much higher surface (179.5 m²/g) than other Co-based samples (22.6–53.5 m²/g) with similar cobalt loadings of 10%. Considering the XRD results, it is concluded the formation of bulk cobalt oxides or composite oxides leads to distinct decrease in surface area. The surface area

Fig. 1. XRD patterns of Co-based catalysts. (□)- CeO₂; (▼)- Co₃O₄; (▲)- CoAl₂O₄; (□)- Al₂O₃; (○)- Mn₂O₃; (■)- CoMnO₃; (□)- ZnO; (●)- Zn_xCo_{1-x}Co₂O₄; (#)- (Co,Mg)O.

Fig. 2. XRD patterns of Co/MgO samples with different Co loadings. (#) –(Co,Mg)O, (*) –Co₃O₄.

Fig. 3. TEM image of Co/MgO-15%.

of Co/MgO-5% sample (177.7 m²/g) is quite similar to Co/MgO-10% while the surface area of Co/MgO-20% is much lower (25.1 m²/g), due to the formation of cobalt oxides, which is also proved by the XRD results. For Co/MgO-15%, even though no other phase besides (Co/Mg)O periclase can be found in the XRD pattern, a lower surface area of 112.2 m²/g are obtained.

The TEM image for Co/MgO-15% in Fig. 3 shows the morphology of lamella. It is known that this kind of morphology is the characterized morphology of hydrotalcite [28]. The morphology of hydrotalcite-like precursor is well preserved after calcination, and cobalt oxides should evenly disperse in the MgO oxide matrices, which is consistent with the XRD results.

The surface electronic states of cobalt in Co/MgO samples were examined by means of XPS. As seen in Fig. 4, the position of Co 2p_{3/2} for all samples is 779.9 eV, while the position of Co 2p_{1/2} is 795.5 eV. It is thus confirmed that cobalt exists in the form of Co₃O₄ in matrices of MgO [29], and no difference in the electronic state with cobalt loading of 5–15%. This suggests the uniformity and good dispersion of Co species in Co/MgO. The analysis of O 1s peak in XPS spectra shows us additional information on the samples. As seen in Fig. 4, two contributions arise at 529.2 and 530.8 eV on the O 1s peak, which can be assigned to lattice oxygen in oxides and OH groups on the surface [30,31], respectively. Abundant surface OH groups exist in Co/MgO catalysts, most probably between the lamella structures.

3.2. Catalytic activities for N₂O decomposition

Fig. 5 shows the catalytic activities for N₂O decomposition over Co-based catalysts with cobalt loadings of 10%. The activity is observed as Co/MgO > Co/ZnO > Co/Mn_xO_y > Co/Al₂O₃ > Co/CeO₂. For the best Co/MgO catalyst, the reaction temperature attained 50 and 100% N₂O conversion was around 675 and 750 K, respectively. The activity is comparable with other Co-based catalysts, over which a 100% N₂O conversion was attained mostly in the temperature range of 700–773 K [19–21,25,26]. The TPR results of cobalt in different supports (not shown here) exhibit that there are no direct relationship between the redox property of cobalt and the catalytic activity. While from the distinction of appreciable activity for Co-based catalysts studied, it is clear that the supports play an important role on catalytic activity for N₂O decomposition. The alkaline MgO clearly appears to be good support for active cobalt species. We suppose that MgO as a support is propitious to the dispersion of the active cobalt species, which is proved by the XRD and BET results. Furthermore, it is well known that the initial step for N₂O decomposition is the breaking of N–O bond by filling electrons into the 3π anti-bonding orbital [32]. And MgO, as a support with strong electron donation, is favorable for the electron transformation. We suppose that during N₂O decomposition, the electrons transfer from MgO to the Co₃O₄ and thus promote the activation

Table 1
Kinetic parameters for N₂O decomposition over supported cobalt catalysts

Sample	BET area (m ² /g)	Coloading (wt%)	Activation energy (kJ/mol)	Pre-exponential factor (mol N ₂ O/s mol Co PaN ₂ O)
Co/CeO ₂ -10%	46.7	9.86	127.4	74.5
Co/Al ₂ O ₃ -10%	53.5	10.14	89.7	4.76
Co/MnO ₂ -10%	33.4	9.78	78.5	3.52
Co/ZnO-10%	22.6	9.96	76.1	1.67
Co/MgO-10%	179.5	9.86	73.1	2.41
Co/MgO-5%	177.7	4.85	73.5	1.07
Co/MgO-15%	122.2	14.64	72.9	3.68
Co/MgO-20%	35.1	19.32	77.5	5.48
Co ₃ O ₄	25.7	100	73.9	4.87

Fig. 4. XPS of Co 2p and O 1s for Co/MgO samples with different Co loadings.

of N_2O on cobalt species, similar to ammonia synthesis on Ru–Ba/C catalyst [33].

We further study the effect of cobalt loadings on the catalytic activities of Co/MgO samples. As seen in Fig. 6, Co/MgO-20% and Co/MgO-15% show similar higher activity, followed by Co/MgO-10% and then Co/MgO-5%. The activity increases with raise cobalt loadings from 5 to 15%. However, further raise in cobalt loading to 20% does not result in corresponding activity increased, probably due to the formation of new cobalt oxides phases. Moreover, the activity of pure Co_3O_4 is found to be lower than Co/MgO-10% but higher than Co/MgO-5%. The Arrhenius plots of N_2O decomposition on Co/MgO with different cobalt loadings are shown in Fig. 7. Similar apparent activation energies (72.9–73.9 kJ/mol) are obtained for pure Co_3O_4 and Co/MgO samples with cobalt loadings of 5–15% (Table 1) and accordingly their activity difference is caused by the different pre-exponential factor. In contrast, the apparent activation energy of Co/MgO-20% is much higher (77.5 kJ/mol) compared to Co/MgO samples with cobalt loadings of 5–15%. It is thus indicated that the

same active cobalt species operates during N_2O catalytic decomposition over pure Co_3O_4 and Co/MgO samples with cobalt loadings of 5–15%. Based on the XRD and XPS results, highly dispersed Co_3O_4 in the MgO matrices should be the active sites for N_2O decomposition over Co/MgO catalysts. As for pure Co_3O_4 , considering the much low BET surface ($25.7 \text{ m}^2/\text{g}$), only a small part of active sites can take part in the catalytic reaction and the activity was severely limited. As a result, the activity of pure Co_3O_4 is only a little higher than other supported catalysts (seen in Figs. 5 and 6).

In the tail gas of nitric acid plant, some typical components (i.e. O_2 , NO and H_2O) coexist with N_2O and it is very important to clarify their effects on N_2O decomposition. As seen in Fig. 8 the presence of 5% O_2 in the reaction system shows some mild negative effect on N_2O decomposition. For example, N_2O conversion was decreased by about 10% in 600–700 K. Compared to oxygen, H_2O shows more serious negative effect on N_2O decomposition. The temperature

Fig. 5. Catalytic activities for N_2O decomposition on Co-based catalysts. Reaction condition: 0.1 g catalyst, 1% N_2O and the balance He, GHSV = $30\,000 \text{ h}^{-1}$.

Fig. 6. Catalytic activities for N_2O decomposition on Co_3O_4 and Co/MgO with different cobalt loadings. Reaction conditions: 0.1 g catalyst, 1% N_2O and the balance He, GHSV = $30\,000 \text{ h}^{-1}$.

Fig. 7. Arrhenius plot of N_2O decomposition on Co/MgO with different cobalt loadings.

with 100% N_2O conversion increases at about 50 K in the presence of 2% H_2O . Similar to O_2 and H_2O , NO also shows negative activity for N_2O decomposition. The inhibition effect of other components (O_2 , H_2O and NO) on N_2O decomposition is presumably related to their competitive adsorption and reaction on cobalt sites, which reduces N_2O chemisorption and inhibits the total conversion rate. It is also seen the negative effects of O_2 , H_2O and NO may be accumulative. Under simulated conditions of tail gas from nitric acid plant (1% N_2O , 5% O_2 , 2% H_2O , and 800 ppm NO), 50% and 100% N_2O conversion can be obtained at 725 and 800 K, respectively. The high activity of Co/MgO-15% at sustainable temperature makes it promising catalyst for N_2O decomposition.

The catalyst durability is a very important criterion to be considered for its real application. Remarkably, Co/MgO-15% sample

Fig. 8. Effect of O_2 , H_2O and NO in the stream on N_2O conversion over Co/MgO-15% catalyst. Reaction conditions: 0.1 g catalyst, 1% N_2O , 0 or 5% O_2 , 0 or 2% H_2O , 0 or 800 ppm NO, balance He, GHSV = 30 000 h^{-1} .

Fig. 9. Time-on-stream behavior of Co/MgO-15% catalyst for the decomposition of N_2O at 773 K under two different conditions. Reaction conditions: 0.25 g catalyst, GHSV = 30 000 h^{-1} .

shows high durability not only under the simple condition of $\text{N}_2\text{O}/\text{He}$ but also under the simulated conditions of tail gas from nitric acid plant. As shown in Fig. 9, there is no obvious evidence of catalytic activity lost over 100 h at 773 K. The good durability of Co/MgO-15% is in sharp contrast to the case of other Co-based catalysts [24]. It is found that the structure of Co/MgO sample (XRD patterns not shown here) does not change after reaction for 100 h.

4. Conclusion

The catalytic decomposition of N_2O over a series of supported cobalt catalysts prepared by co-precipitation method was studied. The alkaline MgO, with strong electron donation effect, appears to be the best support for the active phase of cobalt species for this reaction. The optimal cobalt loading of Co/MgO is 15%, and active phase of cobalt species exists in the form of Co_3O_4 highly dispersed in the matrices of MgO, which is further confirmed to be the active sites for N_2O decomposition. Co/MgO-15% exhibits quite good N_2O decomposition activity and durability under simulated conditions of tail gas from nitric acid plant, which provides us a promising catalyst for the control of greenhouse gas N_2O from anthropogenic sources.

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