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Nitrous oxide reduction with ammonia over Co–MgO catalyst and the influence of excess oxygen

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Abstract

N_2O decomposition on Co–MgO was studied under high (6.67 kPa) and low (75 Pa) N_2O pressure and the effect of reductant (C_2H_6, NH_3) was studied. The activity decays because of the strong adsorption of oxygen produced, while the reductant removed the adsorbed oxygen giving a steady catalysis. The reaction between NH_3 and excess amount of O_2 produced N_2O as a main product. Although N_2O gives the same intermediate (O) as O_2 does, the former decomposition seems to proceed faster than the latter on Co–MgO. The reaction mechanism studied here was compared with the SCR (NO–NH_3 in O_2) reaction on V_2O_5–TiO_2. Since NH_3, N_2O and O_2 gives only N_2 and water, Co–MgO can be a possible catalyst used in the boiler exhaust to reduce N_2O concentration by adding ammonia.

Keywords: Co–MgO catalyst; N_2O decomposition

1. Introduction

N_2O in the upper atmosphere is destroying the ozone layer and is also known to be responsible for the green house effect. Among NO_x, NO, which is the main product in the boiler exhaust, is now controlled in the civilized area by the catalytic decomposition (SCR), while N_2O is not done. N_2O decomposition must be the next target of the technology. N_2O has been known to be decomposed catalytically over Co–MgO [1] and this material has been tested in the adipic acid production exhaust stream [2]. The authors have also studied this reaction under ambient pressures [3]. Since Co^{2+} cation size is almost same as that of Mg^{2+} cation, the Co–MgO system makes a solid solution [3]. Co^{2+} cation is believed to be atomically distributed among MgO media. If N_2O dissociation needs one active site and O_2 dissociation needs a pair of sites, Co–MgO must be a selective decomposition catalyst under O_2 atmosphere. Here, we again studied N_2O decomposition under low pressure, the boiler exhaust gas conditions, and the effects of ammonia and oxygen were also studied. Finally, the reaction mechanism proposed was compared with NO–NH_3 reaction on V_2O_5–TiO_2 (SCR).

2. Experimental

MgO was impregnated with $Co(NO_3)_2 \cdot 6H_2O$ in water. Partly dried slurry-sample was extruded from a syringe, dried and baked at 1173 K for 24 h in order to distribute Co^{2+} ion

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in the MgO matrix. BET surface areas measured after the evacuation were 64 m^2 g^{-1} for MgO, 162 m^2 g^{-1} for 0.02% Co^{2+}–MgO, 220 m^2 g^{-1} for 0.2% Co^{2+}–MgO and 150 m^2 g^{-1} (for the weight measured before the evacuation) for 2% Co^{2+}–MgO, respectively. The surface area of MgO increases when Co^{2+} ions are added with a maximum at 0.2% of additions. During the decomposition of cobalt nitrate, NO$_x$ evolved is thought to create a fine structure of MgO. Co^{2+} contents are represented by molar percentages against MgO. The reaction was performed in a closed circulation system. For high pressure experiments, initial amounts of the reactants (N_2O and C_2H_6) were ca. 6.67 kPa (1 kPa = 7.50 Torr). Most of the reactions were carried out at 473 K. The weight of the sample used decreased from 2.0 to 1.3 g during evacuation at 1173 K. Low pressure experiments were carried out with 0.2 g of catalyst (2% Co–MgO) under 75 kPa of total pressure containing 1000 ppm of N_2O (and/or 1000 ppm NH_3 and/or 0.5% of O_2) and He. The sample was treated with NH_3 at 723 K followed by evacuation and reactions were carried out at 573 K mostly.

3. Results and discussion

3.1. N_2O decomposition

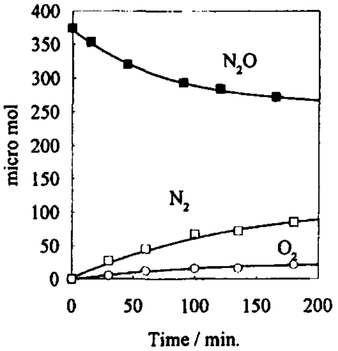


Fig. 1. Time course of high pressure (6.67 kPa) N_2O decomposition at 473 K on 0.2% Co–MgO (2 g).

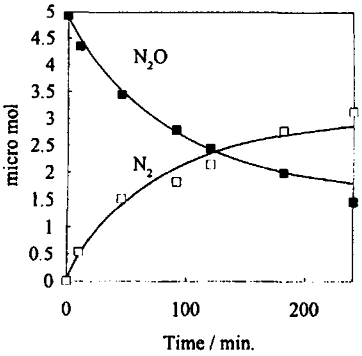


Fig. 2. Time course of low pressure (75 Pa) N_2O decomposition at 573 K on 2% Co–MgO (0.2 g).

Time courses of N_2O decomposition are shown in Figs. 1 and 2. The runs were done under high pressure (6670 Pa of N_2O on 0.2% Co–MgO at 473 K) and low pressure (75 Pa of N_2O on 2% Co–MgO at 573 K). The rate of decomposition decreases gradually due to the strong adsorption of oxygen left on the active site [3]. The produced gases were N_2 (Fig. 2) or mixture of N_2 and O_2 (O_2 was smaller than the stoichiometry) (Fig. 1). The following mechanism has been proposed [3].

$$N_2O + * \rightarrow N_2O(a) \quad (1)$$

$$N_2O(a) \rightarrow N_2 + O(a) \quad (2)$$

$$O(a) \rightarrow \tfrac{1}{2}O_2 + * \quad (3)$$

The rate of (1) seems to be fast and the amount of $N_2O(a)$ is much smaller than O(a) judging from the results of Figs. 1 and 2. Thus, the decomposition reaction is eventually controlled by step (2) and (3).

The initial rates of N_2O decomposition (6670 Pa) at 473 K were plotted as a function of surface Co number (assumed homogeneous distribution of Co^{2+} ion in MgO matrix) in Fig. 3. The rate is proportional to Co content, suggesting the Co^{2+} ion is a center of the active site.

3.2. N_2O decomposition with an aid of ethane

Since the surface oxygen is strongly adsorbed, the reaction rate might be very slow under the steady state. To eliminate the oxygen retarding the reaction, the reaction temperature should be increased [4] or some reductant should

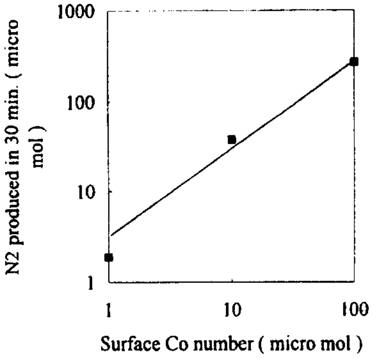


Fig. 3. Activity of N_2O decomposition at 473 K on Co–MgO as a function of "Surface Co-number".

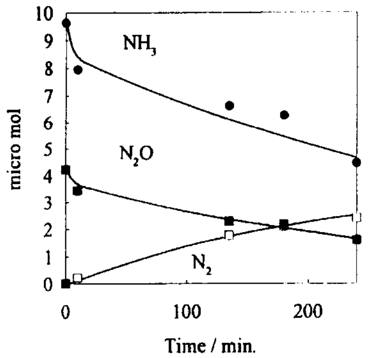


Fig. 5. N_2O (75 Pa) reduction by NH_3 (75 Pa) on 2% Co–MgO (0.2 g) at 573 K.

be introduced [3]. During N_2O (6670 Pa) decomposition on 0.02% Co–MgO, ethane (6670 Pa) was introduced (Fig. 4). The decomposition rate was recovered almost to the initial level and the oxygen evolvement stopped. About 60% of the reacted ethane was turned to ethene. Ethane is believed to remove surface oxygen. Since the rate did not surpass that of simple decomposition, the rate-determining step must be still step (2). The reductant did not seem to create another route for N_2O decomposition.

3.3. N_2O decomposition with an aid of ammonia

Both N_2O (75 Pa) and NH_3 (75 Pa) were introduced at 573 K on 2% Co–MgO (Fig. 5). Although the initial decomposition rate was rather lower than that without ammonia due to ammonia adsorption, the rate after 120 min was promoted about 2 times with addition of ammonia. The rate ratio around at 100 min are −3 (N_2O): − 3(NH_3):4(N_2), suggesting Eq. (4) and excess ammonia adsorption (5).

$$3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O \qquad (4)$$

$$NH_3 \rightarrow NH_3(a) \qquad (5)$$

3.4. N_2O and ammonia reaction under excess amount of oxygen

A reference run between NH_3 and O_2 gave mainly N_2O with a small amount of N_2 on Co–MgO.

$$2O_2 + 2NH_3 \rightarrow N_2O + 3H_2O \qquad (6)$$

Both N_2O (75 Pa) and NH_3 (75 Pa) were introduced together with O_2 (375 Pa) at 573 K on 2% Co–MgO (Fig. 6). N_2O was proved to

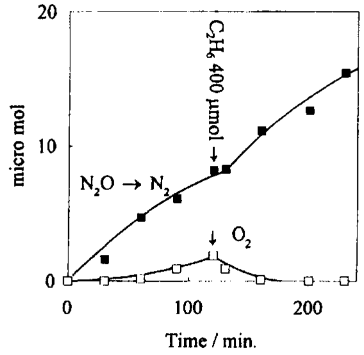


Fig. 4. C_2H_6 effect on high pressure N_2O decomposition at 473 K on 0.02% Co–MgO (2 g).

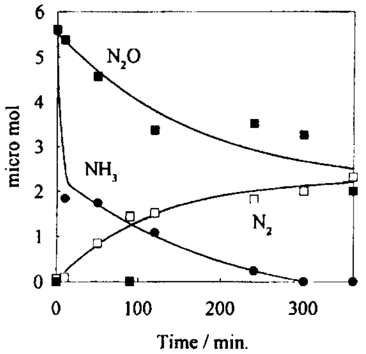


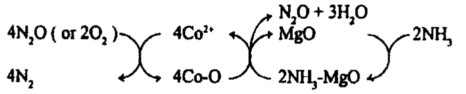
Fig. 6. N_2O (75 Pa) reduction by NH_3 (75 Pa) under the presence of O_2 (375 Pa) on 2% Co–MgO (0.2 g) at 573 K.

react with ammonia even under the presence of excess oxygen.

In the case of the three reactants, the initial decrease of N_2O was about half the increase of N_2, suggesting even contributions of reactions (4) and (6) although O_2 pressure is 5 times higher than N_2O pressure. Totalling reaction (4) and (6) gives reaction (7).

$$N_2O + O_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \qquad (7)$$

A sudden decrease of ammonia at the initial stage may be due to a strong adsorption of ammonia to MgO. These results suggested that N_2O (75 Pa) and O_2 (375 Pa) compete to supply active surface oxygen which can be eliminated with ammonia. N_2O was proved to be removed under the presence of excess (5 times) O_2 because of the higher reactivity of N_2O than of O_2. The reaction mechanisms of $N_2O + NH_3$ and $O_2 + NH_3$ on Co–MgO were tentatively proposed as follows:

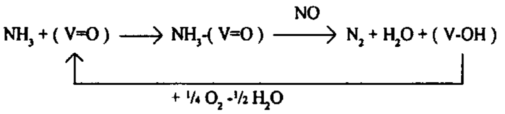


(8)

3.5. *Comparison of N_2O reduction and NO reduction*

The mechanism of selective catalytic reduction (SCR) of NO has been studied [Eq. (9)]. It has been proposed that ammonia is adsorbed on V_2O_5 surface and that ammonia intermediate favors the NO molecule rather than O_2 [5,6]. The selectivity must be determined by the reactivity of adsorbed ammonia towards the NO molecule. That might not be so convenient for N_2O against O_2 on V_2O_5–TiO_2.

In the N_2O–O_2 system, used here, the role of reductant is shown to remove surface oxygen from the active site (Co^{2+}). In this sense, the competitive activation between N_2O and O_2 must be important, thus, the selective reduction of N_2O seems not to depend on the reductant used (C_2H_6, NH_3) but much on the nature of the catalyst (Co–MgO). Of course, NH_3 is a preferable reductant because it completely decomposes to N_2 and H_2O.



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