Investigation on catalytic reduction of NO with methane over metal catalysts

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Catalytic reduction of NO with methane over Pt/MgO, Pd/Al₂O₃, Co/MgO and Pt/Al₂O₃ catalysts has been studied using a closed circulation apparatus. The reaction activities of catalysts are: Pd/MgO > Pd/Al₂O₃ > Pt/Al₂O₃ > Co/MgO. The mol. ratio of CO₂ and Nz in the products is near 1/2, which indicates that the reaction can be described as 4NO + CH₄ = 2N₂ + CO₂ + 2H₂O. With N₂O as an intermediate, the reaction mechanism can be described as NO + NzO = N₂ + CO₂. The values of k₁ and k₂ for the catalysts used are related as follows: Co/MgO catalyst, k₁ << k₂ at 600°C; Pd/MgO catalyst, k₁ ≈ k₂ at 420°C; and Pd/Al₂O₃ catalyst, k₁ > k₂ at 420°C. Methane can be used as reductant to remove the nitric oxide under mild reaction condition. CO is detected when NO + CH₄ reacts on Pd/Al₂O₃. It is assumed that the excess CH₄ would react further with the reduction product CO₂ to produce CO.

Emission of NOₓ is a global environmental problem. Conventional process used ammonia to reduce NOₓ emission from stationary sources. However, a new process using an alternative reductant such as hydrocarbon is required because of the difficulty in handling ammonia. Recently, several types of catalysts, such as Cu-ion exchanged ZSM-5 (ref. 1), Al₂O₃ and acidic catalysts²,³, have been proposed. In these cases, it is expected that NOₓ will be reduced to nitrogen with simultaneous production of carbon dioxide in the presence of hydrocarbon. Some attempts, such as, using nitrogen oxides (NO and N₂O) instead of O₂ (refs 4, 5) and CO₂ (refs 6, 7) as oxidant to oxidize methane and other small hydrocarbon molecules into oxygen-containing organic compounds, have also been made⁸. In this note, we report some novel catalyst systems, Pt/support, Pd/support and Co/MgO, for catalytic reduction of NO with methane, and some interesting results obtained.

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Experimental

Catalyst preparation

All the metal supported catalysts were prepared by impregnating supports with aqueous H₂PtCl₆ or H₂PtCl₄ followed by drying at room temperature and then calcining at 120°C for 4 h, and calcining at 600°C for 4 h. The supports used in this work were Al₂O₃ (Wenzhou Al₂O₃ Chemical factory, P.R. China) and MgO (UBE of Japan). Al₂O₃ was calcined for 5 h at 1000°C. BET surface areas of the supports were 135 and 30 m²/g, respectively. The content of metal was always 1 wt. %.

The Co/MgO catalyst was prepared by thoroughly mixing finely ground pure magnesium carbonate and cobalt nitrate in the desired proportions and calcining in air at 700°C for 4 h.

Apparatus and analysis

The performance of catalytic-reduction of NO was carried out in a closed circulation apparatus with a U tubular quartz reactor. The catalyst (50 mg) was reduced by circulating H₂ (30 KPa) at 500°C for one and a half hours, then evacuated for 30 min before reaction. The mixture of CH₄ and NO (4 KPa total pressure) with 1.5/1 mol. ratio was introduced into the apparatus. NO (99.5%) and CH₄ (99.99%) (Wuxi gas Company, P.R. China) were further purified by liquid nitrogen cold trap. The analyses of the reactor effluent were performed with an on-line sp-2304A model gas chromatograph. The separation of NO, CO, CH₄ and NzO from main components occurred on a stainless steel column containing Porapak Q at room temperature, and the separation of N₂ and CO from main components occurred on a stainless steel column containing TDX-01 at the same temperature.

Results and discussion

Table 1 shows the results of the reduction of NO with methane. It can be seen that the Pd/MgO catalyst exhibited very high activity, and NO was changed completely to N₂, while CH₄ was converted to carbon dioxide. On the other hand, the activity of the Co/MgO catalyst was poor under the same conditions but when the reaction temperature rose up to 600°C, the rate of NO converting to N₂ could be accelerated. The activity of Pt/Al₂O₃ was also low but a little higher than Co/MgO. N₂O was an intermediate during NO reducing to N₂ for most catalysts. It was interest-
Table 1—The results of reaction evaluation for catalytic reduction of NO with CH₄ over various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration of component, vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td>Co/MgO (2:1)</td>
<td>26.15</td>
</tr>
<tr>
<td>Co/MgO (2:1)*</td>
<td>9.30</td>
</tr>
<tr>
<td>1%Pd/MgO*</td>
<td>26.01</td>
</tr>
<tr>
<td>1%Pt/Al₂O₃</td>
<td>8.08</td>
</tr>
<tr>
<td>1%Pd/Al₂O₃*</td>
<td>19.43</td>
</tr>
</tbody>
</table>

*reaction temperature 600°C, reaction time 150 min; *500°C, 150 min; *420°C, 100 min.

Fig. 1—Profiles of reaction/product concentrations for catalytic reduction of NO with CH₄ over 1% Pd/Al₂O₃ catalyst at 420°C. (O) CH₄, (△) N₂, (△) NO, (v) N₂O, (●) CO, (○) CO₂

Fig. 2—Profiles of reaction/product concentrations for catalytic reduction of NO with CH₄ over 1% Pd/MgO catalyst at 420°C. (O) CH₄, (△) N₂, (△) NO, (v) N₂O, (●) CO, (○) CO₂

Effect of reaction time on concentration of components during the catalytic reduction of NO/CH₄ over Pd/MgO catalyst was plotted in Fig. 2. It was found that the amount of N₂O formed increased during the NO consumption. However, when the concentration of NO decreased to less than 10%, the rate of N₂O converting to N₂ was accelerated rapidly and was removed completely simultaneously with NO. But CO was not detected in the course of NO reduction over this catalyst. Comparing the profiles of Figs 1, 2, and 3, it can be seen that there were no CO and N₂O formed during the NO and CH₄ depletion when Co/MgO catalyst was employed at 600°C.

From these observations it is clear that methane instead of NH₃ can be used as reductant to remove the emission of NO under mild reaction condition, and NO can be reduced completely to N₂ over our novel catalysts. It is worth to emphasize that NO can also be used as oxidant to oxidize CH₄ into CO which is very important feedstock for F-T synthesis and methanol synthesis. In addition, the data in Table 1 shows that the mol. ratio of CO₂ and N₂ in the product is near 1/2, which indicates that the catalytic reduction can be proposed in stoichiometric Eq. (1).

\[ 4\text{NO} + \text{CH₄} \rightarrow 2\text{N₂} + \text{CO₂} + 2\text{H₂O} \]  \hspace{1cm} (1)

Reduction intermediate is N₂O. It can be described as shown in Eq. (2).

\[ \text{NO} \xrightarrow{k₁} \text{N₂O} \xrightarrow{k₂} \text{N₂} \]  \hspace{1cm} (2)

Because there is no N₂O formed over Co/MgO...
Fig. 3—Profiles of reaction/product concentrations for catalytic reduction of NO with CH₄ over Co/MgO (2:1) catalyst at 600°C. (○) CH₄, (▲) N₂, (△) NO, (●) CO₂

(Fig. 3) at 600°C, it is clear that \( k_1 \ll k_2 \). However, N₂O is removed completely simultaneously with NO over Pd/MgO (Fig. 2) at 420°C, which indicates \( k_1 = k_2 \). It can be seen that NO is removed rapidly, and N₂O concentration decreases slowly with the reaction time over Pd/Al₂O₃ (Fig. 1) at 420°C, which indicates \( k_1 > k_2 \).

Acknowledgement
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References