PERIODIC OPERATION EFFECTS IN SELECTIVE CATALYTIC REDUCTION OF NITROGEN MONOXIDE WITH PRO-pane OVER ALUMINA

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Selective reduction of nitrogen monoxide with propane over alumina was investigated under the periodic operation of the reactant gas concentration. As expected in advance from the mechanism reported, time-averaged conversion under periodic operation exceeded that under steady operation in the range of the period tested. The averaged conversion curve showed a maximum against the period and discussion was made on the mechanism of the appearance of the maximum. It is proposed that the appearance of the periodic operation effect in the reaction system resulted from the consecutive formation of the oxidized hydrocarbon intermediate through NO₂ and from the competitive consumption of the intermediate by NO and O₂, which is fundamentally different from those of NO-CO reaction and CO oxidation over noble metal catalysts where self-poisoning adsorption of CO was proposed as the reasons. Simplified model calculations were made and the proposed mechanism of the periodic operation effect in the case was estimated.

Introduction

Automobile catalysts are used in very wide temperature ranges and concentration ranges compared with ordinary catalytic processes. A feedback system equipped with an O₂ concentration sensor is now employed in order to control steady A/F around the theoretical value. Recently, dynamic behaviors of three-way catalysts (TWC) by using blended auto-exhaust gas mixture have been reported (Hegedus et al., 1980; Taylor and Sinkevitch, 1983; Herz and Shinouskis, 1985). The oxygen storage effect of cerium oxide (V) was attainable for the stable performance of the TWC catalysts even in the existence of the fluctuation of each component in the exhaust gas. It had been reported that supported Pt or Pd catalysts showed higher activities under periodic operation at certain frequencies than under steady operation (Muraki et al., 1985, 1986b; Muraki and Fujitani, 1986b; Matsunaga et al., 1987). They explained that the periodic operation effect was caused by the inhibition of the reaction by the self-poisoning adsorption of carbon monoxide on the metal surface under steady operation, and that suppression of the self-poisoning under periodic operation resulted in better performance. Similar discussions were formerly made on CO oxidation over supported Pt catalyst (Cutlip, 1979). Reviews concerning periodic operations in recent years have been published on automotive emission control (Silveston, 1995a) and on general catalytic reaction engineering (Silveston et al., 1995b).

Selective catalytic reduction of nitrogen monoxide with hydrocarbons (HC) reported for Cu/ZSM-5 (Held et al., 1990; Iwamoto et al., 1991) and for alumina and other oxides (Hamada et al., 1990; Kintaichi et al., 1990) is one of the promising processes for auto exhaust gas treatment from diesel engines, lean-burn engines and for Rh-free catalysts. Hamada et al. (1991) and Sasaki et al. (1992) proposed that the first step of the reaction is the oxidation of HC (hydrocarbon) to form an intermediate for Cu/ZSM-5 and Pt/Al₂O₃ and the oxidation of NO to NO₂ for H-mordenites and alumina. NO₂ is considered to oxidize HC to form another intermediate in the latter case. The intermediate reacts with both NO and O₂. That is to say, the characteristics of the mechanism are concluded in the consecutive formation and the competitive consumption of the intermediate. No report could be found for the dynamic behavior of these new reactions.

In this paper, the periodic operation of the selective NO reduction with propane over alumina was investigated. Not only the experimental observations, but also simple calculations were made. The mechanism of the periodic operation effect expected in this system is fundamentally different from either the self-poisoning mechanism in the noble metal catalysts system or the O₂ storage effect of cerium oxide. Under steady operation, it is supposed that competitive consumption of the intermediate by O₂ dominates. Under periodic operation, however, formation of the intermediate occurs during the
absence of O₂ in the gas phase. That is to say, NO₂ is formed during the lean period (rich in O₂) and it may be adsorbed on the alumina surface. The adsorbed NO₂ reacts with HC during the subsequent rich period (rich in HC). More selective and more yielding reduction of NO can be expected under periodic operation than under steady operation in the case.

1. Experimental

1.1 Catalyst

Alumina (JRC-ALO-4, 32/60 mesh) was used as a catalyst. The catalyst was pretreated at 973 K for 1 h in a flow reactor in N₂ atmosphere before each reaction test.

1.2 Apparatus

Periodic operation tests were performed in a flow system, shown in Fig. 1, equipped with timer-controlled solenoid valves. The reactor was a U-tube made of quartz glass with 8 mm-i.d.. Quartz sand (32/42 mesh) was packed before and after the catalyst bed in 2 cm height. The system can provide alternative flow of two different gases into the reactor. A valve at the vent line was adjusted to minimize the pressure difference between the reactor line and the vent line. NOₓ (NO+NO₂) concentration was measured by NOₓ meter (Shimadzu: NOA-7000). The effluent gas from the reactor was diluted by N₂ to a flow rate of 1 liter min⁻¹ before the measurement.

1.3 Standard condition

The steady operation was conducted with the gas composition of NO: 1000 ppm, C₃H₈: 200 ppm, O₂: 1%. The standard condition for the periodic operation was summarized in Table 1. The periodic operation was performed by introducing 400 ppm of C₃H₈ or 2% of O₂ alternatively to the feed. The split of each component was constant at 0.5, which corresponds to symmetrical cycled feeding. Amplitude was adjusted at 400 ppm for C₃H₈ and at 2% for O₂. The phase lag was kept at π rad. The concentration of NO was kept steady at 1000 ppm.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Gas A</td>
</tr>
<tr>
<td>NO</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>2%</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
</tr>
<tr>
<td>Total flow rate</td>
<td>100 cm³ min⁻¹</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Split</td>
<td>0.5 (C₃H₈, O₂)</td>
</tr>
<tr>
<td>Amplitude</td>
<td>C₃H₈: 200 ppm, O₂: 1%</td>
</tr>
<tr>
<td>Phase lag</td>
<td>π rad</td>
</tr>
<tr>
<td>Variable</td>
<td>Period, Temperature</td>
</tr>
</tbody>
</table>

2. Mathematical Model

The model mechanism was assumed to be the scheme in Fig. 2. Only the mass balances within the surface species were considered for the model calculation with the differential reactor approximation. The rates of formation of the surface species were derived as Eqs. (1) – (5) from the scheme.

\[ \frac{d\theta_A}{dt} = k_{aC}C_A(1 - \theta_C) - k_{dB}\theta_A - k_{dA}\theta_A \theta_D \]  
\[ \frac{d\theta_B}{dt} = k_{aC}C_B(1 - \theta_C) - k_{dB}\theta_B - k_{dA}\theta_B\theta_C - k_{dB}\theta_B \theta_R \]  
\[ \frac{d\theta_C}{dt} = k_{aC}C_C(1 - \theta_C) - k_{dA}\theta_C - k_{dB}\theta_C - k_{dC}\theta_R \]  
\[ \frac{d\theta_D}{dt} = k_D\theta_A\theta_C - k_D\theta_A \theta_D \]  
\[ \frac{d\theta_R}{dt} = k_D\theta_A\theta_D - k_3\theta_C\theta_R - k_{dB}\theta_R \]
Table 2 Parameters used in calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{d_a} ), ( k_{d_p} ), ( k_{d_c} ) ( [\text{m}^3\text{s}^{-1}\text{mol}^{-1}] )</td>
<td>10</td>
</tr>
<tr>
<td>( k_{d_a} ), ( k_{d_p} ), ( k_{d_c} ) ( [\text{s}^{-1}] )</td>
<td>10</td>
</tr>
<tr>
<td>( k_1, k_2 ) ( [\text{s}^{-1}] )</td>
<td>1</td>
</tr>
<tr>
<td>( k_3, k_4 ) ( [\text{s}^{-1}] )</td>
<td>10</td>
</tr>
<tr>
<td>( C_A, C_B, C_C ) ( [\text{mol} \cdot \text{m}^{-3}] )</td>
<td>1</td>
</tr>
<tr>
<td>Split ( [-] )</td>
<td>0.5</td>
</tr>
<tr>
<td>Amplitude ( [\text{mol} \cdot \text{m}^{-3}] )</td>
<td>1</td>
</tr>
<tr>
<td>Phase lag ( [\text{rad}] )</td>
<td>( \pi )</td>
</tr>
</tbody>
</table>

The rates of consumption of B and C by the reaction were expressed as the rate of uptaking of the species on the surface from the gas phase in the dimension of the rates of the coverage change as Eqs. (6) and (7). The time-average rates were calculated by Eqs. (8) and (9) by using the data which are obtained in the stable cycling results.

\[
\dot{r}_B = k_{d_a} C_B (1 - \theta_i) - k_{d_p} \theta_B \quad (6)
\]

\[
\dot{r}_C = k_{d_a} C_C (1 - \theta_i) - k_{d_p} \theta_C \quad (7)
\]

\[
\overline{\dot{r}_B} = \frac{1}{\tau} \int_{t}^{t+\tau} \dot{r}_B \, dt \quad (8)
\]

\[
\overline{\dot{r}_C} = \frac{1}{\tau} \int_{t}^{t+\tau} \dot{r}_C \, dt \quad (9)
\]

Equations (1) – (9) were numerically integrated by using the parameters shown in Table 2. The alphabetically-named compound C was assumed to be fed with a constant concentration, while A or B were alternatively introduced by a rectangular wave.

3. Results and Discussion

3.1 Steady operation

Results for the NO-C\textsubscript{3}H\textsubscript{8} (HC)-O\textsubscript{2} reaction are shown in Fig. 3. The reaction proceeded above 773 K and the conversion of NO showed a maximum around 873 K. The result agrees well with that reported by Kintaichi et al. (1990). They suggested that the decrease in NO conversion at high temperature is due to the consumption of HC by O\textsubscript{2}. Figure 3 also shows the activity curve obtained for the reaction of NO and C\textsubscript{3}H\textsubscript{8} without O\textsubscript{2} feeding. A higher temperature gave higher NO conversion in this case.

The result indicates that NO can be directly reduced by C\textsubscript{3}H\textsubscript{8}, although the presence of O\textsubscript{2} lowered the reaction temperature by about 100 K. The results obtained under steady operation were also employed as the data for the periodic operation at \( \tau = 0 \) because the periodic condition becomes steady in the actual case when \( \tau \rightarrow 0 \) due to mixing and diffusion of the gases.

3.2 Periodic operation

Real-time conversions of NO under periodic operation were shown in Figs. 4, 5 and 6 at 823, 873 and 973 K, respectively. The figures show the stable cycling results. The conversions were calculated from the real-time concentration curve recorded by the NO\textsubscript{X} meter used. NO conversions periodically changed with the same frequencies of the feed gas fluctuation. In Figs. 4, 5 and 6a, the curves showed two maxima within one cycle. Based on the mechanism reported (Sasaki et al., 1992), the introduction of O\textsubscript{2} likely produces NO\textsubscript{2} adsorbed on the surface with continuously fed NO and then the conversion of NO increases (region I in Fig. 4a). When the surface is saturated by adsorbed NO\textsubscript{2}, the consumption of NO is terminated and then the conversion of NO decreases (region II in Fig. 4a). NO conversion again increases by the change of the feed from O\textsubscript{2} to C\textsubscript{3}H\textsubscript{8} probably due to the formation of the intermediates by the reaction of C\textsubscript{3}H\textsubscript{8} and adsorbed NO\textsubscript{2} (region III in Fig. 4a).

When the adsorbed NO\textsubscript{2} is used up, C\textsubscript{3}H\textsubscript{8} can no longer form the intermediate and then the conversion of NO decreases (region IV in Fig. 4a). At 973 K, only a maximum appeared for \( \tau = 60 \) s in one cycle. Direct reduction of NO by C\textsubscript{3}H\textsubscript{8} can occur in parallel (Fig. 3) under the condition so that the region IV was not clearly observed during the short period as 60 s. These results are consistent with the assumed mechanism of the consecutive formation and competitive consumption of the intermediate.

The effect of the period on the time-averaged NO conversion is shown in Fig. 7 at varied temperatures. The maxima appeared for all the curve shown in Fig. 7. At 873 K, the highest time-averaged conversion of
Fig. 4  Fluctuation of real-time conversion of NO as function of time on stream at 823 K

Fig. 5  Fluctuation of real-time conversion of NO as function of time on stream at 873 K

Fig. 6  Fluctuation of real-time conversion of NO as function of time on stream at 973 K

Fig. 7  Effect of period on time-averaged conversion of NO under periodic operation of NO-HC-O\textsubscript{2} reaction at varied temperatures. Results under steady operation were plotted at $\tau=0$ s

NO was obtained as 44% at $\tau=5$ s, showing a distinct maximum. And the time-averaged NO conversion decreased inversely to the period for $\tau>5$ s. It is considered that the adsorption amounts of NO\textsubscript{2} and/
or the intermediate in one cycle increased with extending the period up to 5 s. For \( \tau > 5 \) s, the adsorption of NO\(_2\) may be saturated before the switching to C\(_3\)H\(_8\) or the intermediate may be used up before O\(_2\) injection so that the averaged conversion decreased. On the other hand, the averaged conversions slightly decreased by extending the period up to 30 s at 923 and 973 K, showing indistinct maxima at around 10 s. At these high temperatures, not only the reaction between NO and the intermediate, but also the direct reduction of NO by C\(_3\)H\(_8\) occurs (Fig. 3) so that the high NO conversion was kept even for long periods.

Figure 8 shows the reaction temperature dependence of the averaged NO conversion with varied period. At higher temperatures than 873 K, the periodic operation effect was apparent. Periodic operations at \( \tau = 5 \) and 10 s gave higher averaged conversions than steady operations in all temperature ranges tested. Interesting findings are that the maximum observed in Fig. 3 disappeared at \( \tau = 10 \) and 120 s and that the higher temperature prefers the longer period of operation. Both are caused by the side reaction of direct reduction of NO by C\(_3\)H\(_8\). From these results, better performance of the catalyst system can be expected by operating a feedback system with short response time while the catalyst temperature is still low. On the other hand, the system should be controlled with longer response time at higher catalyst temperature. The tendency is different from the one reported on NO-CO reaction over supported noble metal catalysts (Muraki et al., 1986a). In the latter case, the periodic operation effect was more remarkable at lower temperatures.

They noted that CO was more strongly adsorbed on the surface at lower temperatures so that the adsorbed CO inhibited the reaction more under the steady operation. Our case is fundamentally different from the latter case from the viewpoint of the periodic operation effect.

3.3 The model calculation

A very simplified model was employed for the calculation as described in the mathematical model. Our objective to employ the model calculation at this stage is to reproduce the major characteristics of the experimental results obtained. Here, hypothetical compounds A, B, C, D and R represent C\(_3\)H\(_8\), O\(_2\), NO, NO\(_2\) and the intermediate, respectively. The stoichiometric ratios of each reactant of each step were assumed to be 1/1 as shown in Fig. 2. The kinetic parameters in Table 1 were chosen considering only that the surface reaction is the rate controlling step under steady operation. Discussions were made by using the rate of consumption of NO in terms of the rates of the coverage change with the differential reactor approximation. For further discussions, more detailed and more estimated calculation should be done as Nowobilski and Takoudis (1986) suggested that better evaluation can be made by considering the mass balance not only within the surface species but also between the surface and the gas phase in order to determine which is advantageous, either steady operation or periodic operation.

The results of the model calculation at \( \tau = 10 \) s is shown in Fig. 9 as an example. The curve of the rate of consumption of NO had two maxima in one cycle. The cycle of \( r_{NO} \) fluctuated can be divided into four regions corresponding to the regions in Fig. 4a. In this case, however, a decrease of \( r_{NO} \) in region II is caused by saturation of the surface by adsorbed oxygen, not by adsorbed NO\(_2\). \( k_1 \) is responsible for which surface species is dominant for the saturation.

Figure 10 shows the results at varied periods. Only a maximum of \( r_{NO} \) appeared at the short periods of 1 and 2 s, although two maxima were observed at \( \tau = 5 \) and 10 s. In Fig. 9, \( \theta_{int} \) showed the maximum about 1 s after changing the feed gas from oxygen to propane. And then \( r_{NO} \) reached the maximum about 1 s behind \( \theta_{int} \). The reason of the disappearance of the maximum between region III and IV is the shorter period of operation adopted than the time constant of the intermediate formation in region III. This is different from the case in Fig. 6b where the parallel reaction path was responsible for the disappearance of the maximum between region III and IV but rather similar to Fig. 4b where the maxima between region III and IV was weakly observed. Figure 11 shows the effect of the period on the time averaged rates of consumption of oxygen and NO. A maximum appeared for \( r_{NO} \) against the period, while \( r_{O2} \) monotonously decreased with the increase of the
Fig. 9 Calculated rate of consumption of NO and surface coverages as function of normalized time on stream under periodic operation of NO-C₃H₈-O₂ reaction at \( \tau = 10 \) s.

Fig. 10 Calculated rates of consumption of NO as function of normalized time on stream under periodic operation of NO-C₃H₈-O₂ reaction at varied periods.

Fig. 11 Effect of periods on rates of consumption of NO and O₂ under periodic operation of NO-C₃H₈-O₂ reaction. Results under steady operation were plotted at \( \tau = 0 \) s.

**Conclusion**

Periodic operation of the selective NO reduction with propane over alumina has been investigated. It was found that the time-averaged conversion of NO under the periodic operation exceeded that under the steady operations under several experimental conditions. The appearance of the periodic operation effect was explained with relation to the reaction mechanism, that is the consecutive formation and the competitive consumption of the intermediate. The model calculation results agreed with the explanation, giving information on the behaviors of the adsorbed species. For further research work, not only the periodic operation of the reactant gas concentration but also that of the reactant gas flow rate and the reactant gas temperature should be investigated to develop an up-dated catalytic system for auto exhaust gas treatment.

**Nomenclature**

- \( C \) = concentration of gases [mol m\(^{-3}\)]
- \( \bar{C} \) = time averaged concentration of gases [mol m\(^{-3}\)]
- \( k \) = rate constants [s\(^{-1}\)]
- \( k_a \) = adsorption rate constant [mol m\(^{-3}\) s\(^{-1}\) mol\(^{-1}\)]
- \( k_d \) = desorption rate constant [s\(^{-1}\)]
- \( r \) = rate of consumption [s\(^{-1}\)]
- \( \bar{r} \) = time-averaged rate of consumption [s\(^{-1}\)]
- \( T \) = reaction temperature [K]
- \( t \) = time on stream [s]
- \( \chi \) = conversion of NO [-]
- \( \bar{\chi} \) = time-averaged conversion of NO [-]
- \( \theta \) = surface coverage [-]
- \( \theta_t \) = total surface coverage [-]
- \( \tau \) = period [s]

<subscript>
- 1 = reaction step 1 in Fig. 2
</subscript>
2 = reaction step 2 in Fig. 2
3 = reaction step 3 in Fig. 2
4 = reaction step 4 in Fig. 2
A = hypothetical compound as a representative of propane
B = hypothetical compound as a representative of oxygen
C = hypothetical compound as a representative of nitrogen monoxide
D = hypothetical compound as a representative of nitrogen dioxide
HC = propane
Int = the intermediate
NO = nitrogen monoxide
NO2 = nitrogen dioxide
O2 = oxygen
R = hypothetical compound as a representative of the intermediate

Literature Cited