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Relative rates of various steps of NO–CH_4–O_2 reaction catalyzed by Pd/H-ZSM-5

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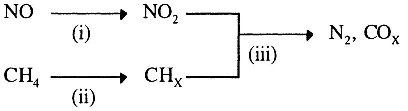
Abstract

Reaction mechanism of the reduction of nitrogen monoxide by methane in an oxygen excess atmosphere (NO–CH_4–O_2 reaction) catalyzed by Pd/H-ZSM-5 has been studied at 623–703 K in the absence of water vapor, in comparison with the mechanism for Co-ZSM-5. Kinetic isotope effect for the N_2 formation in NO–CH_4–O_2 vs. NO–CD_4–O_2 reactions was 1.65 at 673 K and decreased with a decrease in the reaction temperature. In addition, H–D isotopic exchange took place significantly in NO–(CH_4+CD_4)–O_2 reaction. These results are in marked contrast with the case of Co-ZSM-5, for which the C–H dissociation of methane is the only rate-determining step, and show that the C–H dissociation is slow but not the only rate-determining step in the case of Pd/H-ZSM-5.

A reaction scheme was proposed, in which the relative rates of the three steps ((i)–(iii) below) vary depending on the reaction conditions.



Further, in contrast to Co-ZSM-5, NO_x–CH_4–O_2 reaction was much slower than CH_4–O_2 reaction for Pd/H-ZSM-5; the presence of NO_x retards the reaction of CH_4 over the latter catalyst, while it accelerates the reaction over the former. It is suggested that CH_4 is activated directly by the Pd atoms in the case of Pd/H-ZSM-5, but by NO_2 strongly adsorbed on Co ion for Co-ZSM-5. The reaction order of the NO–CH_4–O_2 reaction with respect to NO pressure was consistent with this mechanism; 1.05 for Pd/H-ZSM-5 and 0.11 for Co-ZSM-5. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Reduction; NO; Nitrogen oxides; Palladium; ZSM-5

1. Introduction

The catalytic abatement of nitrogen oxides in the combustion exhausts is an important area of research for the environment sustainability. For the exhausts from gas engines or turbines using natural gas for fuel, the reduction of nitrogen oxides by methane in excess oxygen is a desirable reaction to be pursued. Methane was at first thought to be a nonselective reductant for nitrogen oxides, but three groups recently reported promising catalysts for the selective reduction;

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Co-ZSM-5 by Li and Armor [1], Ga-ZSM-5 by Kikuchi's group [2] and Pd/H-ZSM-5 by our group [3–6]. Recently, Kikuchi's group found that Pd/H-ZSM-5 was the most active at a very low NO concentration. The activity of Pd/H-ZSM-5 was further promoted by the addition of Rh [5] or Co [7].

What is very interesting with the Pd catalysts is that Pd dispersed in H-ZSM-5 is very active for the reduction of NO, but Pd in Na-ZSM-5 is not active at all, while both Pd catalysts show comparable activities for CH_4 oxidation which takes place concurrently [3,4]. In other words, the efficiency of CH_4 utilization for NO reduction dramatically develops by the presence of proton in ZSM-5. We proposed previously a reaction scheme in which NO_2 (adsorbed or gaseous) formed by the oxidation of NO on proton and/or Pd site reacts with CH_4 after it is activated by Pd (probably to CH_x), and concluded that the presence of proton is indispensable in the reaction between NO_2 and CH_x [4]. We further assumed from the measurements of acidity and Pd dispersion that not only the presence of proton enhances the Pd dispersion but also the proton itself participates in the key step between NO_2 and CH_x (bifunctional catalysis of Pd + proton) [4,5].

In the present study, we focused on the mechanistic aspect of the reaction on Pd/H-ZSM-5. The Pd catalyst exhibits good performance even in the presence of water vapor, if Rh or Co is added [5,7]. However, the mechanism was investigated here in the absence of water vapor for a catalyst containing only Pd, to make the system simpler. At least in the case of Co-ZSM-5, the water vapor does not change the essential aspects of the mechanism, although the activity is suppressed by water [8]. The study in the presence of water is underway.

First, the rate-determining step was investigated by measuring the isotope effect for CH_4 vs. CD_4 and the H–D exchange for NO–(CH_4+CD_4)–O_2. As for Co-ZSM-5 a large isotope effect which indicates that the C–H bond dissociation is rate-limiting was reported [8]. A reaction mechanism has already been proposed for Co-ZSM-5; which basically comprises (i) the oxidation of NO to NO_2 on Co ion, and (ii) the subsequent abstraction of hydrogen from CH_4 by adsorbed or gaseous NO_2, followed by (iii) several steps including the formation of CH_3NO_2 to form N_2 [8–10]. We previously studied the oxidative decomposition of CH_3NO_2 in relation to the reduction of NO and indicated its possible intermediary for Ce-ZSM-5 [11,12]. Further comparison was made in this study between Pd/H-ZSM-5 and Co-ZSM-5 based on the relative reactivities of several relevant reactions such as NO_2–CH_4–O_2, CH_4–O_2 and NO–O_2, as well as the reaction orders and the adsorption of NO. It has been revealed that there are several marked differences between the two catalysts with respect to the mechanism, although their catalytic performances were similar under the present reaction conditions.

2. Experimental

2.1. Catalysts

Catalysts were prepared as described previously [3–6,8]. H-ZSM-5 was prepared by ion-exchange of Na-ZSM-5 (SiO_2/Al_2O_3=23.8) in an aqueous solution of ammonium nitrate. After the exchange the solid was washed, dried at 373 K for 12 h, and then calcined at 773 K for 4 h in air. Pd/H-ZSM-5 was prepared at room temperature by ion-exchange of H-ZSM-5 by using an aqueous solution of $[Pd(NH_3)_4]Cl_2$. The solid was washed, dried at 373 K for 12 h and calcined at 773 K for 2 h in air. The exchange level was estimated by measuring the amount of Pd in the filtrate by means of inductively coupled plasma. Co-ZSM-5 was prepared by ion-exchange of Na-ZSM-5 in an aqueous solution of cobalt acetate. The exchange level was estimated by measuring the amount of Na eluted in the filtrate by means of atomic adsorption spectroscopy. The ion-exchange levels of Pd and Co loaded were, respectively, approximately 15% (Pd 1 wt%) and 85%.

2.2. Reactions

The catalytic reactions were performed with a fixed-bed flow reactor as described previously [3–6]. In the ordinary experiments, after the treatment of the catalyst in 10% oxygen at 673 K for 1 h, a gas mixture (NO or NO_2, 1000 ppm; CH_4 or CD_4, 2000 ppm; O_2, 2% and He; balance) was fed at a rate of 150 $cm^3\ min^{-1}$. The effluent gas was analyzed by a gas chromatograph (Nippon Tyran; M200), a chemiluminescence NO_x analyzer (Yanaco; ELC-77A) and a mass spectrometer (Balzers; Quadstar 421).

NO–(CH_4/CD_4)–O_2 and NO_2–(CH_4/CD_4)–O_2 reactions were carried out for the measurements of kinetic isotope effects as described below. After the conversions reached a steady state for NO_x–CH_4–O_2 reaction, CH_4 in the feed was replaced by CD_4. These reactions were carried out changing the amount of catalyst. From the linear plots between the contact time and the conversions of NO into N_2 obtained below the 30% conversion level, the reaction rates (v_H and v_D) were calculated. The kinetic isotope effect for N_2 formation, $k_H/k_D(N_2)$, was approximated by the ratio, v_H/v_D, thus obtained. The isotope effect for CH_4 oxidation, $k_H/k_D(CO_x)$, was obtained in a similar way from the rates of CO_x (=CO+CO_2) formation.

2.3. NO adsorption

Adsorption of NO was carried out in the flow reactor. Catalysts, 0.1 g for both Pd/H-ZSM-5 and Co-ZSM-5, were pretreated at 773 K for 2 h in He and cooled down to room temperature. Then NO, 1000 ppm in He, was fed at a rate of 100 cm^3 min^{-1}. After the adsorption of NO was saturated (the amount of this adsorption is called the amount of total adsorption), the feed gas was changed to pure He and the amount of NO reversibly desorbed was measured. After NO at the outlet reached an undetectable level, the temperature of the catalysts was raised at 8 K min^{-1} to 773 K in He (temperature programmed desorption, TPD) and desorbed species were measured as well. This desorption amount is called the amount of TPD desorption. NO/M (M=Pd, Co) means the molar ratio of the amount of TPD desorption to the amount of metal loaded. NO was monitored by a chemiluminescence NO_x analyzer (Yanaco; ELC-77A). NO_2, N_2 and N_2O were checked occasionally, but these amounts were small. This is reasonable, as the material balance for nitrogen was good without taking into account the formation of NO_2, N_2 and N_2O as described later.

3. Results

3.1. NO–CH_4–O_2, NO–O_2 and NO_2–CH_4–O_2 reactions

Fig. 1 shows the temperature dependencies of the conversions of NO into N_2 for NO–CH_4–O_2 over Pd/H-ZSM-5 and Co-ZSM-5. The results are from the present study as well as from earlier reports. We reported previously [3] that Pd/H-ZSM-5 showed the highest activity when the Pd loaded was 1 wt% under these conditions, and the reaction rate increased with increasing pressure of oxygen at low temperatures. It was noted that the NO reduction proceeded considerably even in the absence of oxygen at 773 K [3]. The catalytic activity of Pd/H-ZSM-5 prepared in the present study was slightly lower than that reported previously [3–5] for the conversion of NO into N_2, but both catalysts were almost the same as for the conversion of CH_4 into CO_x. The activity and its dependency on the reaction temperature of Co-ZSM-5 prepared in this study were not much different from those of Co-ZSM-5 reported by Li and Armor [13], considering the difference in the reaction conditions. As shown in Fig. 1, the conversions of NO into N_2 and CH_4 into CO_x were similar for Pd/H-ZSM-5 and Co-ZSM-5 prepared in this study. After the introduction of the feed gas, NO+CH_4+O_2, onto Pd/H-ZSM-5, the conversion of NO into N_2 initially increased and reached a stationary value in about 20 min after

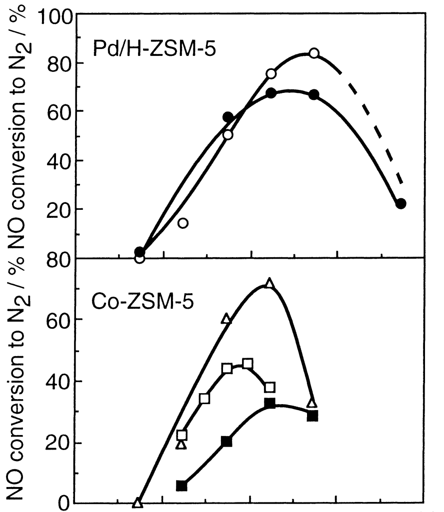


Fig. 1. The dependencies of the conversion of NO into N_2 on the reaction temperature: (○) Pd/H-ZSM-5 in this study, (●) Pd/H-ZSM-5 previously reported, and (△) Co-ZSM-5 in this study (NO 1000 ppm, CH_4 2000 ppm, O_2 2% SV=9000 h^{-1}). (□) Co-ZSM-5 (SV=7500 h^{-1}) in [13], and (■) Co-ZSM-5 (SV=30 000 h^{-1}) in [13] (NO 1600 ppm, CH_4 1025 ppm, O_2 2.5%).

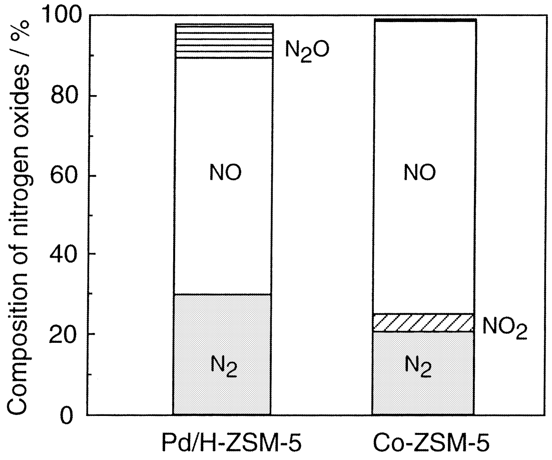


Fig. 2. Composition of nitrogen oxides at the outlet for NO–CH_4–O_2 reaction over Pd/H-ZSM-5 and Co-ZSM-5 at 673 K. NO 1000 ppm, CH_4 2000 ppm, O_2 2%, SV=45 000 h^{-1}. (□) N_2, (□) NO_2, (□) NO, and (□) N_2O.

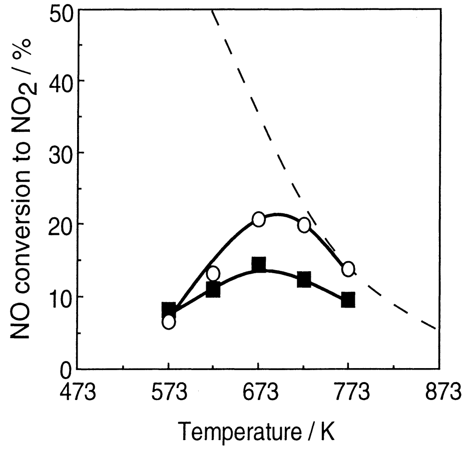


Fig. 3. The dependencies of the conversion of NO into NO_2 on the reaction temperature. NO 1000 ppm, O_2 2%, SV=9000 h^{-1}: (○) Co-ZSM-5, (■) Pd/H-ZSM-5, and (- - -) equilibrium.

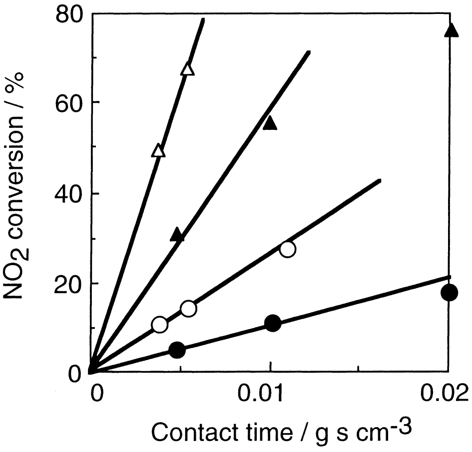


Fig. 4. The dependencies of the conversion of NO_2 to NO, N_2 and N_2O on the contact time at 673 K. NO_2 1000 ppm, CH_4 2000 ppm, O_2 2%. (○) The conversion of NO_2 into N_2 (over Pd/H-ZSM-5), (△) the conversion of NO_2 into N_2+NO+N_2O (over Pd/H-ZSM-5), (●) the conversion of NO_2 into N_2 (over Co-ZSM-5), and (▲) the conversion of NO_2 into N_2+NO+N_2O (over Co-ZSM-5).

passing through a maximum. The CH_4 oxidation exhibited a similar behavior. This transient behavior was not observed for NO–CH_4–O_2 over Co-ZSM-5 or NO_2–CH_4–O_2 over Pd/H-ZSM-5. It is possible that the dispersion and oxidation state of Pd changed during this initial stage. It is also noteworthy that NO_2 was detected in the gas phase for NO–CH_4–O_2 at 673 K over Co-ZSM-5, but not over Pd/H-ZSM-5 (Fig. 2). A small amount of N_2O was detected for Pd/H-ZSM-5 and a very small amount for Co-ZSM-5.

Fig. 3 shows the temperature dependencies of the conversions of NO into NO_2 for the NO–O_2 reaction catalyzed by Pd/H-ZSM-5 and Co-ZSM-5. The reaction rate over Co-ZSM-5 was higher than that over Pd/H-ZSM-5. The conversion to NO_2 reached equilibrium above 723 K for Co-ZSM-5, but not for Pd/H-ZSM-5. At 673 K, the rate for Co-ZSM-5 was about 1.5 times that for Pd/H-ZSM-5.

Fig. 4 shows the dependencies of the conversion of NO_2 in NO_2–CH_4–O_2 at 673 K on the contact time for Pd/H-ZSM-5 and Co-ZSM-5. Both the rates of the formations of N_2 and N_2+NO+N_2O (=total conversion of NO_2) over Pd/H-ZSM-5 were about twice those over Co-ZSM-5. The selectivities of N_2 formation from NO_2 (the ratio of N_2/(N_2+NO+N_2O)) were approximately equal; 0.24 and 0.23 for Pd/H-ZSM-5 and Co-ZSM-5, respectively. The rate of NO–CH_4–O_2 was also proportional to the contact time as described later (Fig. 5).

Table 1 summarizes the reaction orders of the N_2 and CO_x formations for NO–CH_4–O_2 over Pd/H-ZSM-5 at 673 K. The ranges of the partial pressure were, NO: 250–2300 ppm, CH_4: 250–3800 ppm, and O_2: 6500 ppm–6.5%. The reaction orders of the N_2

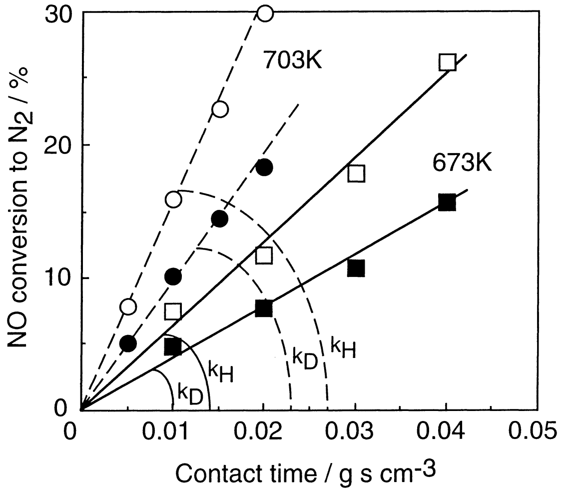


Fig. 5. The dependencies of the conversion of NO to N_2 on the contact time for $NO–CH_4–O_2$ and $NO–CD_4–O_2$ reactions over Pd/H-ZSM-5 at 673 and 703 K. Reaction conditions are the same as in Fig. 2. (○) $NO–CH_4–O_2$ reaction at 703 K, (●) $NO–CD_4–O_2$ reaction at 703 K, (□) $NO–CH_4–O_2$ reaction at 673 K, and (■) $NO–CD_4–O_2$ reaction at 673 K.

Table 1
Reaction orders of $NO–CH_4–O_2$ reaction over Pd/H-ZSM-5 and Co-ZSM-5

	Catalyst	x^a	y^a	z^a
NO conv. to N_2 (%)	Pd/H-ZSM-5[b]	1.05	0.66	−0.26
	Co-ZSM-5[c]	0.11	0.68	0.18
CH_4 conv. to CO_x (%)	Pd/H-ZSM-5[b]	0.22	0.52	0.02
	Co-ZSM-5[c]	−0.06	0.70	0.27

[a] $r=k[NO]^x[CH_4]^y[O_2]^z$.

[b] NO: 250–2300 ppm, CH_4: 250–3800 ppm, O_2: 0.65–5.6%, at 673 K, catalyst weight 0.05 g.

[c] NO: 900–2350 ppm, CH_4: 500–1300 ppm, O_2: 0.4–4%, at 633 K, catalyst weight 0.4 g [7].

formation were 1.05 in NO, 0.66 in CH_4 and −0.26 in O_2 for Pd/H-ZSM-5. The reaction orders of the N_2 formation were reported to be 0.11 in NO, 0.68 in CH_4 and 0.18 in O_2 over Co-ZSM-5 as given also in Table 1[8].

3.2. *Kinetic isotope effect for $NO(NO_2)–CH_4–O_2$ reactions over Pd/H-ZSM-5 [6]*

When CH_4 in the feed gas was replaced by CD_4 after the stationary state was reached for $NO–CH_4–O_2$ over Pd/H-ZSM-5, the conversions of NO into N_2 and CH_4 into CO_x decreased rapidly, and when CD_4 was changed to CH_4 again, those conversions recovered. This result shows the presence of the kinetic hydrogen isotope effect of C–H dissociation. In Fig. 5 the stationary conversions of NO into N_2 for $NO–CH_4–O_2$ and $NO–CD_4–O_2$ are plotted against the contact time for 673 and 703 K. In these experiments, the maximum space velocity was 3.6×10^5 h^{-1} at 703 K. It was 4.5×10^5 h^{-1} at 673 K for $NO_2–CH_4–O_2$ (Fig. 4).

Table 2
Kinetic isotope effects observed for $NO–(CH_4/CD_4)–O_2$ and $NO_2–(CH_4/CD_4)–O_2$ reactions over Pd/H-ZSM-5 catalyst

Temperature (K)	$NO–(CH_4/CD_4)–O_2$		$NO_2–(CH_4/CD_4)–O_2$	
	k_H/k_D (N_2)	k_H/k_D (CO_x)	k_H/k_D (N_2)	k_H/k_D (CO_x)
623	1.22	1.10	1.49	1.37
648	1.40	1.31	1.49	1.32
673	1.65	1.56	1.82	1.78
703	1.59	1.41	–	–

Table 2 summarizes the values of $k_H/k_D(N_2)$ and $k_H/k_D(CO_x)$ obtained as in Fig. 5 at several reaction temperatures. Table 2 also lists the results for $NO_2–CH_4–O_2$, in which NO_2 was used in place of NO. As for the $NO–(CH_4/CD_4)–O_2$ at 673 K, the kinetic isotope effect, $k_H/k_D(N_2)$, was 1.65. It is remarkable that the $k_H/k_D(N_2)$ value tended to be smaller with a decrease in the reaction temperatures; 1.40 at 648 K and 1.22 at 623 K. The $k_H/k_D(N_2)$ value for $NO_2–(CH_4/CD_4)–O_2$ at 673 K was 1.82 and also decreased with decreasing temperature, the value being always greater than for $NO–(CH_4/CD_4)–O_2$.

3.3. *H–D isotopic exchange during $NO–(CH_4+CD_4)–O_2$ reaction over Pd/H-ZSM-5 [6]*

Fig. 6 shows the time course of $NO–CH_4(1000\ ppm)+CD_4(1000\ ppm)–O_2$ over Pd/H-ZSM-5 at 673 K. The changes in the initial 10 min are due to the unsteady concentration of the feed gas. It is notable that a significant amount of CHD_3 was detected. The CHD_3/CD_4 at the outlet was 0.13 after 90 min. Since the distribution for the complete isotopic mixing is $CH_4:CH_3D:CH_2D_2:CHD_3:CD_4=1.0:4.0:6.0:4.0:1.0$ ($CHD_3/CD_4=4$), the H–D exchange of methane evidently took place, but to a

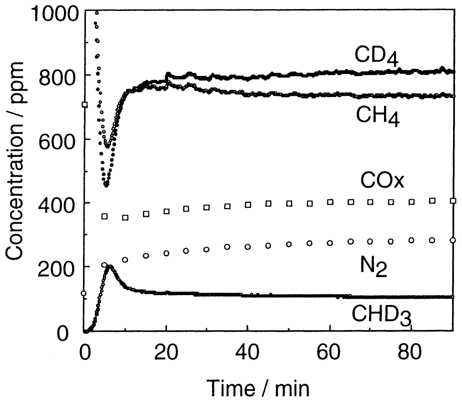


Fig. 6. Changes in the representative components at the outlet gas of NO–(CH_4+CD_4)–O_2 reaction over Pd/H-ZSM-5 at 673 K. NO 1000 ppm, CH_4 and CD_4 1000 ppm, O_2 2%, SV=9000 h^{-1}.

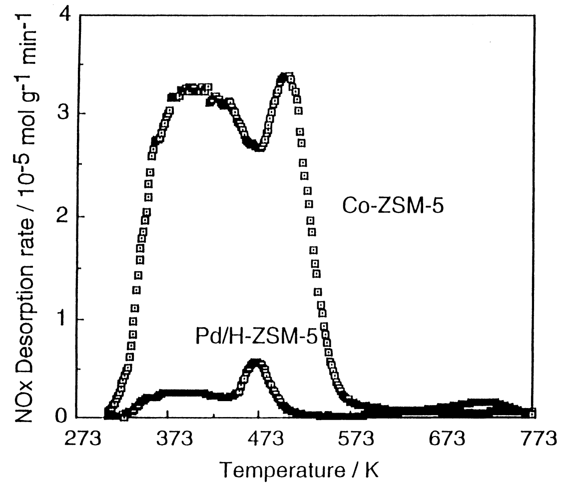


Fig. 7. TPD profiles of NO from Co-ZSM-5 and Pd/H-ZSM-5.

moderate extent. It was not possible to determine the other isotopically exchanged species such as CH_3D due to the presence of fragment mass peaks coming from water.

3.4. *Comparison of NO–CH_4–O_2, NO_2–CH_4–O_2 and CH_4–O_2 reactions over Pd/H-ZSM-5*

It was reported previously [10] that the CO_x formation for NO–CH_4–O_2 was faster than that for CH_4–O_2 reaction over Co-ZSM-5. As listed in Table 3, the rate of CO_x formation for NO–CH_4–O_2 is 10 times faster than for CH_4–O_2 at 673 K.

The rates of CO_x formation were measured for relevant reactions with Pd/H-ZSM-5, as summarized in Table 3. The rate of CO_x formation for CH_4–O_2 was much faster than that for NO_2–CH_4–O_2 and NO–CH_4–O_2 at each reaction temperature. This trend for Pd/H-ZSM-5 was in marked contrast to that for Co-ZSM-5. The reaction of CH_4 was retarded by co-existing NO_x for Pd/H-ZSM-5, while it was accelerated in the case of Co-ZSM-5.

It is also noteworthy that the rate of N_2 formation for NO_2–CH_4–O_2 was about 3.6 (at 673 K) and 3.5 (at 623 K) times faster than that for NO–CH_4–O_2 in the case of Pd/H-ZSM-5.

3.5. *NO adsorption*

Fig. 7 shows the TPD profiles of NO adsorbed on Pd/H-ZSM-5 and Co-ZSM-5. Table 4 summarizes the data. Two peaks were observed in TPD for Co-ZSM-5; a broad peak from 373 to 448 K and another peak at 503 K (Fig. 7). The ratio of the two peaks was approximately 4. According to [14], both peaks belong to two kinds of $Co(NO)_2$ having different bond

Table 3
The rates of $CO_x(N_2)$ formation for NO–CH_4–O_2, NO_2–CH_4–O_2 and CH_4–O_2 reactions over Pd/H-ZSM-5 (10^{-6} mol g^{-1} min^{-1})

Reaction temperature (K)	Catalyst	NO–CH_4–O_2	NO_2–CH_4–O_2	CH_4–O_2
623	Pd/H-ZSM-5[a]	1.99 (1.92)	21.0 (6.71)	71.0
	Co-ZSM-5[b]	3.9 (6.4)	–	0.3
673	Pd/H-ZSM-5[a]	10.9 (8.40)	77.6 (30.1)	215
	Co-ZSM-5[b]	18 (27)	–	1.8

[a] NO or NO_2 1000 ppm, CH_4 2000 ppm, O_2 2%, total flow rate 150 cm^3/min.
[b] NO 0.21%, CH_4 0.28%, O_2 2.6%, total flow rate 75 cm^3/min.

Table 4
Amounts of NO adsorbed on Pd/H-ZSM-5 and Co-ZSM-5

Catalyst	Total NO[a] (10^{-5} mol g^{-1})	Rev. NO[b] (10^{-5} mol g^{-1})	NO TPD[c] (10^{-5} mol g^{-1})	NB[d] (%)	NO/M
Pd/H-ZSM-5	10.0	1.1	9.3	104	0.99
Co-ZSM-5	86.9	11.5	76.4	101	1.50

M=Pd,Co.

[a] The amount of NO adsorbed at room temperature.

[b] The amount of NO reversibly desorbed in He at room temperature.

[c] The amount of NO desorbed during TPD in He up to 773 K.

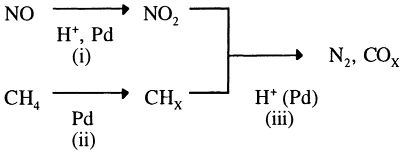
[d] NB (nitrogen balance)=100×(Rev. NO+NO TPD)/total NO.

angles between two nitrosyls. No desorption peak was observed above 623 K for Co-ZSM-5. On the other hand, three peaks were observed at 400, 473 and 723 K for Pd/H-ZSM-5. The ratio of the three peaks of the latter catalyst was about 2:1:1. Most of the adsorbed NO desorbed below about 600 K for Co-ZSM-5 and below 500 K for Pd/H-ZSM-5. The amounts of total adsorption, reversible adsorption and TPD desorption on Co-ZSM-5 were, respectively, about 8–10 times larger than those on Pd/H-ZSM-5. The NO/Co value, 1.50, was also larger than NO/Pd, 0.99.

4. Discussion

4.1. Reaction scheme for NO–CH_4–O_2 reaction over Pd/H-ZSM-5

The reaction scheme as in Scheme 1 has already been proposed for this reaction on the basis of the following experimental facts [3–6]. First, the rates of N_2 formation was in the order NO_2–CH_4–O_2≈NO_2–CH_4>NO–CH_4–O_2≫NO–CH_4. This indicates that NO is oxidized to NO_2 in the first step, and followed by the reaction between NO_2 and CH_x to form N_2. The oxidation of NO may be catalyzed by proton and/or Pd, since the order of the rates of NO_2 formation in NO–O_2 was H-ZSM-5>Pd/H-ZSM-5≈Pd/Na-ZSM-5>Na-ZSM-5. Secondly, the order of the catalytic activities for the N_2 formation in NO–CH_4–O_2 was Pd/H-ZSM-5≫H-ZSM-5≫Pd/Na-ZSM-5, Na-ZSM-5=0, and the activities for CO_x formation were Pd/H-ZSM-5=Pd/Na-ZSM-5≫H-ZSM-5, Na-ZSM-5. This indicates that Pd is necessary for the activation of CH_4. In the reaction between NO_2 and CH_4, Pd/H-ZSM-5 showed a high activity, but Pd/Na-ZSM-5 was inactive. Therefore, the presence of proton is necessary for the reaction between CH_4 (probably CH_x) and NO_2 to give N_2. As for the roles of protons we previously suggested that protons not only indirectly promoted the reaction by maintaining the high dispersion of Pd but also directly participated in the reaction between NO_2 and CH_4 or CH_x [4,5].



Scheme 1.

The reaction scheme deduced is summarized as follows (Scheme 1); (step (i)) the oxidation of NO to NO_2 on H^+ and/or Pd, (step (ii)) the activation of CH_4 on Pd to give CH_x, and (step (iii)) the reaction between NO_2 and CH_x promoted by proton to produce N_2 and CO_x.

The important role of NO_2 has been suggested by Hamada et al. [15] in the cases of Al_2O_3 and H-zeolites, and we also confirmed it for Ce-ZSM-5 [16,17]. The importance of highly dispersed Pd has been indicated by Loughran et al. [18].

4.2. Rate-determining steps of NO–CH_4–O_2 reaction over Pd/H-ZSM-5

The fact that $k_H/k_D(N_2)$ was 1.65 for NO–CH_4–O_2 over Pd/H-ZSM-5 at 673 K (Table 2) indicates that the C–H dissociation of CH_4 is a slow step. However, the value is considerably smaller than the effect reported for Co-ZSM-5, 2.40 at 648 K, for which the C–H dissociation of CH_4 is likely to be the only rate-determining step as reported by Cowan et al. [8].

There are two possible reasons for the small isotope effect of Pd/H-ZSM-5; (1) although the C–H dissociation of CH_4 is the only rate-determining step, the C–H bond is not loosened enough in the transition state [19], and (2) other steps are as slow as the C–H dissociation of CH_4.

It is informative here that the $k_H/k_D(N_2)$ values for NO–CH_4–O_2 over Pd/H-ZSM-5 tended to decrease with decreasing temperature (Table 2). In case (1), these values should increase with decreasing temperature. Indeed, the kinetic isotope effects for Co-ZSM-5 [8] became larger at lower temperatures as in the ordinary cases. Therefore, the second possibility must be the case for Pd/H-ZSM-5; there are other steps which are as slow as the C–H dissociation and they become slower with a decrease in the reaction temperature. Next, it is noteworthy that the $k_H/k_D(N_2)$ value was greater for NO_2–CH_4–O_2, 1.82 at 673 K, than for NO–CH_4–O_2, 1.65 and that NO_2–CH_4–O_2 itself, which does not need the oxidation of NO, was about 3.6 times faster than NO–CH_4–O_2. These facts demonstrate that the oxidation of NO to NO_2 (step (i) in Scheme 1) is a relatively slow step.

Here, it is to be noted that, even if steps (i) and (ii) are the slow steps and the relative rate of the former becomes lower at lower temperatures, the k_H/k_D values of NO_2–CH_4–O_2, which does not need the NO oxidation, should increase with decreasing temperature, and by the same reason the rate of N_2 formation for NO_2–CH_4–O_2 relative to that for NO–CH_4–O_2 should increase at lower temperatures. However, the results were opposite. The $k_H/k_D(N_2)$ values for NO_2–CH_4–O_2 were 1.49 at 648 and 623 K which are smaller than the value at 673 K, 1.82. In addition, the N_2 formation for NO_2–CH_4–O_2 was only 3.5 times faster than that for NO–CH_4–O_2 at 623 K, as compared with 3.6 times at 673 K. These results indicate that with decreasing temperature another step, that is, the reaction between NO_2 and CH_x (step (iii)), becomes slower than steps (i) and (ii). Step (iii) must comprise several reaction steps including the production of CH_3NO_2 and its oxidative decomposition.

The $k_H/k_D(CO_x)$ values, calculated from the rates of CO_x formation for NO–CH_4–O_2 and NO_2–CH_4–O_2, tended to be smaller than the $k_H/k_D(N_2)$ values. This possibly indicates that the reaction steps which do not involve the C–H dissociation as a rate-determining step such as reactions of organo-nitro species to produce N_2 were slower. Anyway, it can be concluded that NO–CH_4–O_2 over Pd/H-ZSM-5 consists of several reaction steps represented by the three steps, (i)–(iii), in Scheme 1, and the rates of these reaction are comparable and the relative magnitudes vary with the reaction conditions.

It is worthy to note here that the ratio of the consumption of NO to that of CH_4 for NO–CH_4–O_2 was 1.93 at 623 K over Pd/H-ZSM-5. This value is close to 2 which is calculated for the stoichiometric equation as described below:

$$2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad (1)$$

This indicates that this reaction proceeds almost exclusively at this low temperature. Namely, the non-selective reaction, $CH_4+O_2 \rightarrow CO_2+2H_2O$, hardly takes place.

The above conclusion that the C–H dissociation of CH_4 is not the ideal rate-determining step (the ideal case means that the step is the only slow step and the others are all fast and reversible) over Pd/H-ZSM-5 was confirmed by the presence of H–D exchange of methane (Fig. 6). If the C–H dissociation of CH_4 is the only rate-determining step, CH_x dissociated from CH_4 should be oxidized very rapidly to CO_x and would not exert any H–D exchange. But, in fact, CHD_3 was detected significantly, although the content of CHD_3 was far from that expected for random distribution; $CHD_3/CD_4=0.13$ observed experimentally vs. 4 for random distribution. The presence of H–D exchange of methane clearly indicates that there are slow steps other than the C–H dissociation.

4.3. Sites for methane activation

Li et al. [9] proposed a mechanism for NO–CH_4–O_2 over Co-ferrierite as described by Eqs. (2)–(5), in which CH_4 is activated by NO_2 adsorbed on Co ion. Cowan et al. [8] also indicated that NO_2 adsorbed on Co ion was the active site of CH_4 dissociation.

$$Z{-}Co + NO + 1/2\,O_2 \rightarrow Z{-}Co{-}NO_2 \qquad (2)$$

$$CH_4 + Z{-}Co{-}NO_2 \rightarrow CH_3^* + Z{-}Co{-}HNO_2 \qquad (3)$$

$$CH_3^* + Z{-}Co{-}NO_2 \rightarrow Z{-}Co{-}NO_2CH_3 \qquad (4)$$

$$2Z{-}Co{-}NO_2CH_3 + 3NO + O_2 \rightarrow\rightarrow 2N_2 + NO_2 + 3H_2O + 2CO_2 + 2Z{-}Co \qquad (5)$$

As shown in Table 3, in the case of Pd/H-ZSM-5, (c) CH_4–O_2 reaction is the fastest, and (a) NO–H_4–O_2 and (b) NO_2–H_4–O_2 are much slower. That is, the activation of CH_4 is significantly suppressed by co-existing NO_x ((c)/(a)=20–35). The trend for Co-ZSM-5 ((c)/(a)=0.1) is indeed in contrast to that for Pd/H-ZSM-5. Besides, the light-off temperature of CH_4 oxidation is also reversed. These marked differences may lead to the proposition that, although NO_2 adsorbed on Co ion abstracts hydrogen from CH_4 to form CH_3^* over Co-ZSM-5, in the case of Pd/H-ZSM-5, NO_x adsorbed on Pd is not reactive to methane but Pd itself exerts the C–H dissociation of methane.

4.4. *Kinetic aspects*

Reaction orders and the results of NO adsorption provide further information about the mechanism based on Scheme 1. The activities of Pd/H-ZSM-5 and Co-ZSM-5 were similar for NO–CH_4–O_2 under the present reaction conditions. But, during the reaction, NO_2 was detected in the gas phase for Co-ZSM-5, but not for Pd/H-ZSM-5 (Fig. 2). This indicates the oxidation of NO to NO_2 is slow as compared with the other steps over Pd/H-ZSM-5. In fact, the rate of NO oxidation to NO_2 is greater on Co-ZSM-5 than on Pd/H-ZSM-5 (Fig. 3), and the rate of reaction between NO_2 and CH_4 over Pd/H-ZSM-5 is about twice faster than that over Co-ZSM-5 (Fig. 4), though the selectivities on both catalysts are approximately the same. Besides, the amounts of NO adsorption are larger on Co-ZSM-5 than on Pd/H-ZSM-5 (Table 4). Hence, the ability of Co-ZSM-5 for NO adsorption is higher than that of Pd/H-ZSM-5, and, probably reflecting this difference, the oxidation of NO to NO_2 is faster over Co-ZSM-5 than over Pd/H-ZSM-5.

This conclusion would also be supported by the reaction orders of NO–CH_4–O_2. As reported by Cowan et al. [8], the order in NO is small for Co-ZSM-5, but that value is large for Pd/H-ZSM-5 (Table 1). Similar reaction orders have been reported by Kikuchi et al. [7] for Pd(0.4 wt%)/H-ZSM-5 to be 0.6 in NO, 0.5 in CH_4 and 0.3 in O_2. These results support the mechanism deduced above, that is, NO is strongly adsorbed on Co-ZSM-5, and oxidized rapidly to NO_2 which dissociates the C–H bond of CH_4. On the other hand, on Pd/H-ZSM-5, the C–H dissociation is accelerated by Pd itself and its rate is comparable with that of the oxidation of NO.

5. Conclusions

1. The rate-determining step(s) and mechanism of NO–CH_4–O_2 reaction are different in several respects between Pd/H-ZSM-5 and Co-ZSM-5; although the activities are similar.
2. Kinetic isotope effect, H–D exchange and kinetic analysis showed that the oxidation of NO to NO_2 and the C–H dissociation of CH_4 are the slow steps of NO–CH_4–O_2 reaction over Pd/H-ZSM-5 at about 673 K. With decreasing temperature, the oxidation of NO to NO_2 and the subsequent reaction between NO_2 and CH_4 to produce N_2 became slower than the C–H dissociation.
3. The oxidation of NO to NO_2 and the following reaction between NO_2 and CH_x to produce N_2 are common steps for Pd/H-ZSM-5 and Co-ZSM-5. But, the C–H dissociation of CH_4 presumably takes place on Pd but on NO_2 adsorbed on Co ion.

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