Catalysis Letters 47 (1997) 189–191

Rate-determining step of NO–CH_4–O_2 reaction catalyzed by Pd / H-ZSM-5

Hidenaga Kato, Chikafumi Yokoyama and Makoto Misono*

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Hongo,
Bunkyo-ku, Tokyo 113, Japan

Received 29 April 1997; accepted 17 July 1997

The rate-determining step of the NO–CH_4–O_2 reaction over Pd / H-ZSM-5 catalyst at 623–703 K was investigated mainly by the kinetic isotope effect, that is, the relative rates of the NO–CH_4–O_2 and NO–CD_4–O_2 reactions. Based on the isotope effect and its temperature dependency as well as the relative rates of NO–CH_4–O_2 and NO_2–CH_4–O_2, it was concluded that the oxidation of NO to NO_2 and the dissociation of a C–H bond of CH_4 to form CHx are slow steps of comparable order and there is no dominant rate-determining step in the present reaction system. The relative rates of the two reactions vary depending on the reaction temperature; the oxidation of NO tends to be more rate-controlling at low temperatures. It is also probable under certain conditions that the reaction between NO_2 and CHx subsequent to the above two reaction steps becomes a slow step.

Keywords: rate-determining step, kinetic isotope effect, Pd / H-ZSM-5

1. Introduction

For the abatement of NOx from the exhaust of gas engine, the catalytic reduction of NOx by methane in the presence of oxygen is an attractive process. Methane had not been regarded an efficient reductant until Co-ZSM-5 [1] and Ga / H-ZSM-5 [2] catalysts were reported to be effective. We have previously reported that Pd ion-exchanged H-ZSM-5 (denoted by Pd / H-ZSM-5) was very active for the NO–CH_4–O_2 reaction [3] and that this reaction consists of three steps [4,5]: (1) the oxidation of NO to NO_2 on Pd and / or protonic acid; (2) the activation of CH_4 on Pd to give CHx; and (3) the reactions between NO_2 and CHx promoted probably by protonic acidity to produce N_2 and COx. In this study, we discuss the relative rates of these three steps.

$$\left.\begin{array}{l} NO \xrightarrow{O_2} NO_2 \\ CH_4 \xrightarrow{-H} CHx \end{array}\right] \longrightarrow N_2, COx \qquad (1)$$

The dissociation of a C–H bond in CH_4 was the rate-determining step in the case of a Co-ZSM-5 catalyst at 648 and 704 K for the NO–CH_4–O_2 reaction, as reported by Cowan et al. [6]. They observed that the relative rate for CH_4 and CD_4 was 2.4, which is close to the primary kinetic effect expected from the zero-point energy, and that the H–D isotopic exchange between CH_4 and CD_4 was much slower than the CH_4 (or CD_4) oxidation.

In this study, we investigated the rate-determining step of the NO–CH_4–O_2 reaction catalyzed by Pd / H-ZSM-5 by measuring the kinetic isotope effect for the NO–(CH_4 / CD_4)–O_2 and NO_2–(CH_4 / CD_4)–O_2 reactions.

2. Experimental

Pd / H-ZSM-5 was prepared as in the previous works [3–5] by ion-exchange of H-ZSM-5 ($SiO_2 / Al_2O_3 = 23.8$) in an aqueous solution of $[Pd(NH_3)_4]Cl_2$, followed by drying at 373 K and calcination in air at 773 K for 4 h. The amount of Pd loaded was approximately 1 wt% (corresponding to 15% ion-exchange level). Neither Pd nor PdO peak was observed in X-ray diffraction of Pd / H-ZSM-5 before and after the reaction, indicating that Pd was highly dispersed in ZSM-5.

NO–(CH_4 or CD_4)–O_2 and NO_2–(CH_4 or CD_4)–O_2 reactions were performed over Pd / H-ZSM-5 as described previously [3–5]. After pretreatment of the catalyst in 10% oxygen at 673 K, a gas mixture (NO or NO_2, 1000 ppm; CH_4, 2000 ppm; O_2, 2% and He; balance) was fed at a rate of 150 $cm^3\ min^{-1}$. After the conversions reached a steady state, CH_4 in the feed gas was changed to CD_4. These reactions were carried out changing the amount of catalyst. The effluent gas was analyzed by a gas chromatograph (Nippon Tyran; M200) and a mass spectrometer (Balzers; Quadstar 421).

3. Results and discussion

Figure 1 shows an example of the time course of NO–CH_4–O_2 reaction over Pd / H-ZSM-5. After the introduction of the feed gas, NO–CH_4–O_2, onto Pd / H-ZSM-5 at 673 K, the conversion of NO to N_2 initially increased and showed a stationary value after about 20 min. The CH_4 oxidation exhibited a similar behavior. The temperature dependencies of the NO reduction and CH_4 oxidation for NO–CH_4–O_2 reaction at the steady state over

---

* To whom correspondence should be addressed.

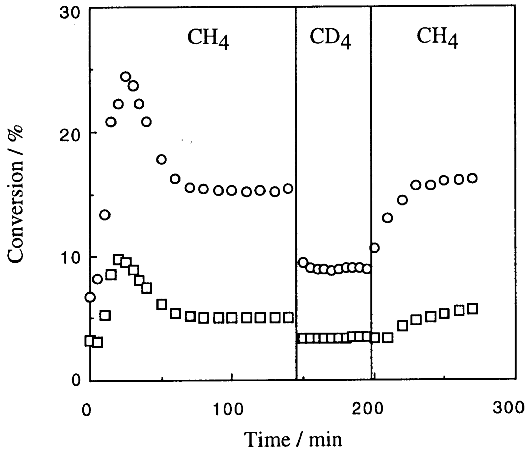

Figure 1. Time course of NO–$CH_4(CD_4)$–O_2 reaction over Pd/H-ZSM-5 at 673 K. (○) Conversion of NO into N_2; (□) conversion of $CH_4(CD_4)$ into COx.

Pd/H-ZSM-5 were the same as reported previously [3–5]. Upon the replacement of CH_4 by CD_4 in the feed, the formation of N_2 and COx (mostly CO_2) decreased rapidly, and when CD_4 was changed to CH_4, those rates recovered.

Figure 2 shows the dependencies of the conversions 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 K. The rates of N_2 formation were calculated from the slopes of the straight lines from the origin. Here, considering the rather low conversions, the rates may be approximated to be proportional to the rate constants. Then, the kinetic isotope effect for N_2 formation, $k_H/k_D(N_2)$, was estimated by the ratio of the two slopes for the NO–CH_4–O_2 and NO–CD_4–O_2 reactions. The ratio of the rate of COx $(= CO + CO_2)$ formation, $k_H/k_D(COx)$, was obtained in a similar way.

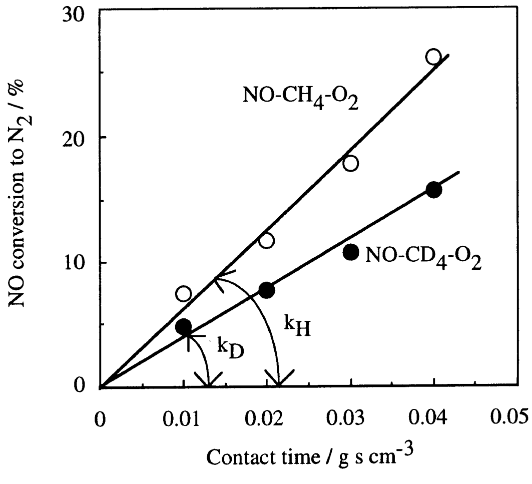

Figure 2. The dependences of the conversion of NO to N_2 on the contact time for NO–CH_4–O_2 and NO–CD_4–O_2 reactions over Pd/H-ZSM-5 at 673 K.

Table 1 summarizes the values of $k_H/k_D(N_2)$ and $k_H/k_D(COx)$ obtained at several reaction temperatures. As for the NO–(CH_4/CD_4)–O_2 reaction at 673 and 703 K, the kinetic isotope effects, $k_H/k_D(N_2)$, were 1.65 and 1.59, respectively. These values indicate that the dissociation of a C–H bond in CH_4 is the slow step of NO–CH_4–O_2 reaction. However, the values were smaller than the values reported in the case of Co-ZSM-5 [6], for which the authors claimed that the dissociation of C–H was rate-determining. This suggests that there are other slow steps in the present system, in addition to the C–H dissociation.

In this respect, it is noteworthy that $k_H/k_D(N_2)$ for the NO–(CH_4/CD_4)–O_2 reaction tended to decrease at lower reaction temperatures (below 673 K). If the C–H dissociation were rate-determining, the ratio should increase with a decrease in the temperature. Therefore, this fact clearly indicates that there are other steps which are as slow as the CH_4 dissociation and become relatively slower at lower temperatures.

Here, it is interesting to note that the $k_H/k_D(N_2)$ values for the $\underline{NO_2}$–(CH_4/CD_4)–O_2 reaction were greater than those for the $\underline{NO}$–(CH_4/CD_4)–O_2 reaction. Since the reaction proceeds by the oxidation of NO to NO_2 followed by the reaction between NO_2 and CHx (cf. eq. (1)) [3–5], these results demonstrate that the oxidation of NO is not fast enough to make the CH_4 dissociation dominantly rate-determining. In accordance with this idea, N_2 formation for the $\underline{NO_2}$–CH_4–O_2 reaction was several times faster than for the $\underline{NO}$–CH_4–O_2 reaction.

If the CH_4 dissociation is not the dominant rate-determining step (or the rate-determining step in a strict sense, where the other steps are much faster and in equilibrium) as discussed above, the reverse step of the C–H dissociation, that is, the H–D exchange between CH_4 and CD_4, would be observed when the NO–$(CH_4 + CD_4)$–O_2 reaction is carried out (cf. eq. (1)). Figure 3 shows the results of the NO–(CH_4(1000 ppm) + CD_4(1000 ppm))–O_2 reaction followed by the mass spectrometer. The changes in the concentrations of CH_4, CD_4 and CHD_3 after the reaction started are presented. It was not possible to determine the other isotopically exchanged species such as CH_3D due to the

Table 1

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 [a]		NO_2–(CH_4/CD_4)–O_2 [a]	
	$k_H/k_D(N_2)$	$k_H/k_D(COx)$	$k_H/k_D(N_2)$	$k_H/k_D(COx)$
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	–	–

[a] NO or NO_2, 1000 ppm; CH_4 or CD_4, 2000 ppm; O_2, 2%. $k_H/k_D(N_2)$ and $k_H/k_D(COx)$: see text.

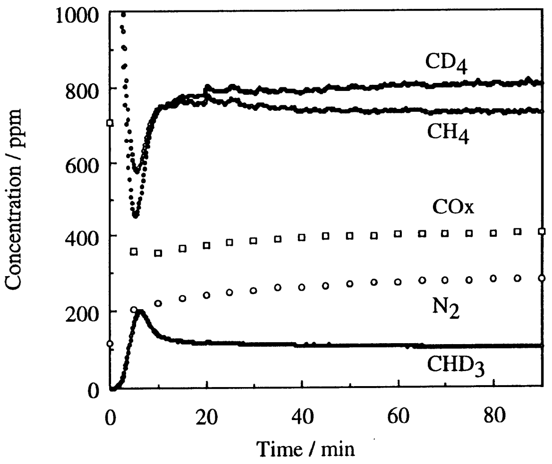

Figure 3. Changes in the representative components in the outlet gas of NO–(CH_4 + CD_4)–O_2 reaction over Pd/H-ZSM-5 at 673 K.

presence of fragment mass peaks coming from water. As expected, a significant amount of CHD_3 was observed. This result supports the mechanism described above, in which the dissociation of a C–H bond is not the dominant rate-determining step.

As discussed above, it is understandable that $k_H/k_D(N_2)$ for the NO_2–CH_4–O_2 reaction was greater than $k_H/k_D(N_2)$ for the NO–CH_4–O_2 reaction, if one assumes that the oxidation of NO was also slow. But, the result that $k_H/k_D(N_2)$ for the NO_2–CH_4–O_2 reaction also tended to decrease at lower temperatures needs an additional explanation. That is, the result indicates that at lower temperatures the subsequent step, i.e., the reaction between NO_2 and CHx, is a slow step and/or that the reduction of NO_2 to NO in the presence of CH_4 is rapid.

The isotopic effects observed for the COx formation were slightly smaller than those for the N_2 formation (table 1). This suggests that the reaction steps subsequent to the CHx–NO_2 reaction, e.g., reactions of organic nitro- or nitrite compounds with NOx and O_2 in which the C–H dissociation is not the key step [7], proceed at comparable rates.

It was notable at 623 K that the stoichiometry of the NO–CH_4–O_2 reaction nearly agreed with that of $CH_4 + 2NO + O_2 \rightarrow N_2 + CO_2 + 2H_2O$. This indicates that the reaction proceeded at a low temperature by $2NO + O_2 \rightarrow 2NO_2$, followed by $CH_4 + 2NO_2 \rightarrow N_2 + CO_2 + 2H_2O$, and that the reaction, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, was negligible.

In summary, both the rates of the oxidation of NO to NO_2 and the dissociation of a C–H bond are of comparable order in the temperature range studied and the relative rates of these two reactions are dependent on the temperature. The NO oxidation relative to the CH_4 dissociation tends to be slower at lower temperatures. In some cases at lower temperatures the reaction between NO_2 and CHx could also be a slow step.

The present result observed for Pd/H-ZSM-5 is different from that claimed for Co-ZSM-5 [6], where the C–H bond dissociation was the dominant rate-determining step. The present results combined with the earlier data demonstrate that the relative rates of the several steps involved in this reaction system very much depend on the reaction conditions and catalysts.

Acknowledgement

We acknowledge the helpful discussion with Professor N.W. Cant, Macquarie University.

References

[1] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L31.
[2] K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, Chem. Lett. (1993) 229.
[3] Y. Nishizaka and M. Misono, Chem. Lett. (1993) 1295.
[4] Y. Nishizaka and M. Misono, Chem. Lett. (1994) 2237.
[5] M. Misono, Y. Nishizaka, M. Kawamoto and H. Kato, in: *Proc. 11th Int. Zeolite Conf.*, Seoul 1996, Stud. Surf. Sci. Catal., Vol. 105 (Elsevier, Amsterdam, 1996) p. 1501.
[6] A.D. Cowan, R. Dümpelmann and N.W. Cant, J. Catal. 151 (1995) 356.
[7] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9;
C. Yokoyama, H. Yasuda and M. Misono, Shokubai 35 (1993) 122.