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Cationic Rh-catalyzed CO insertion into surface carbonaceous species formed by the decomposition of methane in the presence of nitric oxide

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Acetaldehyde was successfully formed by means of CO-TPR from the surface carbonaceous species, which was accumulated by the homologation of methane over Rh/SiO_2 catalysts after NO preadsorption. Infrared spectroscopic study revealed that cationic rhodium atoms were formed by the function of negatively charged preadsorbed NO and its dissociation, which facilitated CO insertion into surface methyl groups by weakening Rh–C bond, followed by the formation of acetaldehyde.

KEY WORDS: acetaldehyde formation; CO insertion; cationic rhodium metals.

1. Introduction

Recently, the catalytic conversion of methane has attracted great attention, both as a topic of academic interest in activating stable starting materials and as a practical substitute for petroleum. Various studies have been reported concerning the conversion of methane such as steam or dry reforming to form syngas, partial oxidation toward methanol and formaldehyde, and aromatization into benzene and toluene under nonoxidative condition. However, very few successful studies have been reported on the carbonylation of methane with carbon monoxide, which is still one of the most challenging targets in the field of catalytic chemistry.

Sen *et al*. succeeded in the homogeneous carbonylation of methane with CO in the presence of O_2 using $RhCl_3$ as a catalyst in aqueous solutions, and reported the formation of acetic acid in the yields of 0.012% [1]. Fujiwara *et al*. also reported that acetic acid was synthesized in the CH_4-CO reaction catalyzed by $Co(OAc)_2$ or $Pd(OAc)_2$ in the presence of potassium peroxodisulfate ($K_2S_2O_8$) or O_2 as an oxidant and trifluoroacetic acid in THF solution [2,3]. However, the carbonylation of methane to acetaldehyde has rarely been reported, except for the study by Sakakura *et al*., which showed that CO insertion occurred by the irradiation of ultraviolet light under dense CO_2 conditions (300 atm) using $RhCl(CO)(PMe_3)_2$ as a catalyst [4]. They concluded that the formation of acetaldehyde proceeded via the oxidative addition of methane to $RhCl(CO)(PMe_3)_2$, and the resulting methyl-rhodium complex underwent CO insertion to form acetaldehyde.

For several years, we have been studying a novel reaction mechanism of selective benzene formation in CH_4-CO reaction over supported group VIII metal catalysts [5,6]. We found a marked role of adsorbed CO, which facilitated C–C bond formation from surface carbonaceous species accumulated by the decomposition of methane and resulted in the formation of various higher hydrocarbons [7]. In the following study, we have discovered the formation of acetaldehyde from the surface carbonaceous species in the presence of adsorbed NO by means of CO-TPR (temperature-programmed reaction) technique. Here, we report the successful catalytic synthesis of acetaldehyde by the carbonylation of methane with carbon monoxide over silica-supported rhodium catalysts in the presence of nitric oxide.

2. Experimental

Rh/SiO_2 (5 wt%) catalyst was prepared by impregnating an aqueous solution of $RhCl_3 3H_2O$ into silica, which was put in a quartz reactor (0.5 g) connected to a closed gas circulation system and reduced by H_2 at 673 K for 6 h. In all the reaction procedures, a liquid N_2 cold trap was employed to gather reaction products and to shift the reaction equilibrium. He-TPD (temperature-programmed desorption) and CO-TPR were carried out as follows: 1.3 kPa of CH_4 was first exposed onto the freshly reduced catalyst at 523 K for 1 h and then 1.3 kPa of NO was adsorbed at 298 K in the case of NO-present experiments. Then, NO in the gas phase was substituted by 1.3 kPa of helium or CO, and the temperature was raised slowly with a ramp speed of 1.7 K/min. The products formed during TPD or TPR

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processes were analyzed by TCD (molecular sieve column) and FID (Porapak N column) gas chromatography and GC-MS. Fourier-transform infrared spectroscopy was employed to observe the adsorbed species during this procedure.

3. Results and discussion

The results of He-TPD and CO-TPR experiments over CH_4-decomposed surface in the absence of adsorbed NO are displayed in figure 1(a) and (b). Although only methane was released in the He-TPD step, various hydrocarbons were obtained in the CO-TPR step. In particular, benzene was selectively formed at higher temperatures, suggesting that adsorbed CO facilitates C–C bond formation and can be a framework for benzene formation. On the contrary, in the case of NO preadsorbed surface, small amounts of HCN and acetonitrile were formed even in the TPD step (figure 2(a)). Moreover, CO-TPR provided considerable amounts of acetaldehyde and acetonitrile together with various hydrocarbons as shown in figure 2(b). At the same time, substantial amounts of N_2 and CO_2 were formed by the NO-CO reaction (not plotted in the figure). These results indicate that the adsorbed NO plays some specific role affecting the surface active sites or adsorbed species.

Infrared spectroscopic study was carried out to elucidate the effect of adsorbed NO on the formation of acetaldehyde and acetonitrile during CO-TPR on NO preadsorbed surface. The bottom spectrum in figure 3 represents the adsorbed species when CO was introduced at 303 K over CH_4-decomposed and then NO preadsorbed surface. The infrared bands at 2070 and 1667 cm^{-1} can be assigned to linearly adsorbed CO and negatively charged adsorbed NO ($Rh\text{-}NO^-$) on the reduced rhodium surface, respectively. As the temperature was raised (473 K), the latter band decreased considerably, indicating the decomposition of adsorbed NO. Simultaneously, three CO bands emerged at 2033, 2091 and 2104 cm^{-1}, which can be assigned to $Rh^+\text{-}(CO)_2$ (gem-dicarbonyl) and $Rh^{2+}\text{-}CO$ species, respectively. At the same time, a broad band appeared at 2177 cm^{-1}, which can be assigned to Rh-CN species formed by the reaction between surface carbonaceous species with adsorbed NO.

As mentioned already, considerable amounts of acetaldehyde and acetonitrile were released in the gas phase during this CO-TPR (figure 2(b)). Accordingly, the formation of cationic surface rhodium atoms via NO adsorption and/or decomposition may facilitate the CO-insertion process into the surface methyl groups by weakening the Rh–C bond. The resulting acetyl species may be eliminated reductively to form acetaldehyde. At the same time, associative desorption of surface methyl groups with adsorbed cyanide groups may produce acetonitrile. On the contrary, few amounts of these products were released in the gas phase when only helium was introduced as a substitute for CO. This is a new reaction pathway for the accumulated surface carbonaceous species in the two-step sequence reaction of methane, and we succeeded in the formation of acetaldehyde and acetonitrile for the first time. As the

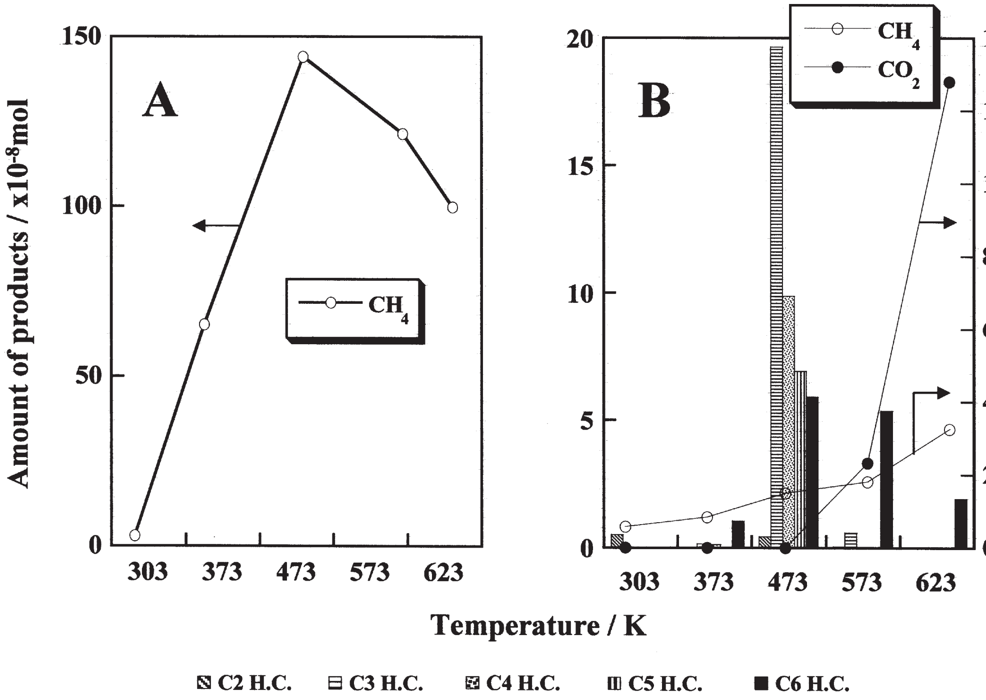

Figure 1. The distribution of products in (A) He-TPD; and (B) CO-TPR; over 5 wt% Rh/SiO_2 after the decomposition of CH_4 at 523 K for 1 h.

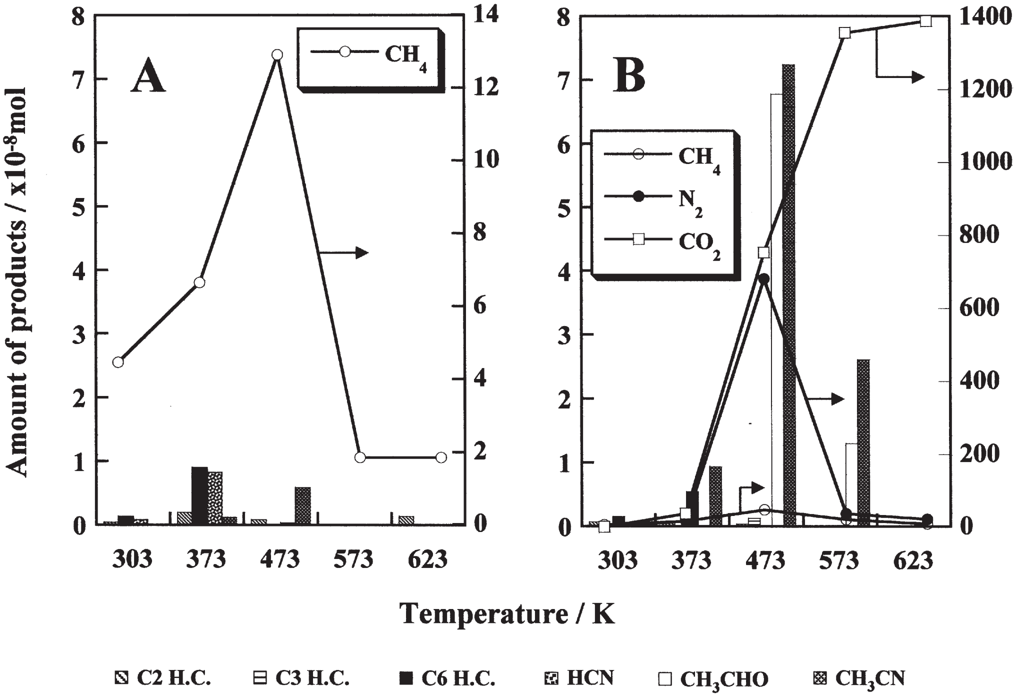

Figure 2. The distribution of products in (A) He-TPD; and (B) CO-TPR; over 5 wt% Rh/SiO_2 after the decomposition of CH_4 at 523 K for 1 h and the preadsorption of NO at 298 K.

TPR temperature was raised further as shown in figure 3 (until 623 K), the intensities of these positively charged Rh-CO bands decreased again, while the linearly adsorbed CO band increased significantly, indicating the cleaning up of the surface carbonaceous species.

The role of adsorbed CO may be summarized as follows. On the CO-free surface after CH_4 decomposition and NO adsorption, there are many vacant sites that facilitate the dehydrogenation of accumulated carbonaceous species. Accordingly, following He-TPD process gives H_2 and CH_4 by the dehydrogenation of carbonaceous species, accompanied by the formation of H-deficient hydrocarbons and inactive carbons. In the case of CO-present surface, the saturated adsorption of CO may suppress the dissociation of hydrogen atoms from the carbonaceous species, and realize the CO insertion into the stabilized methyl groups to form acetaldehyde. The formation of acetonitrile may also be realized through the associative desorption of stabilized methyl group with adsorbed cyanide.

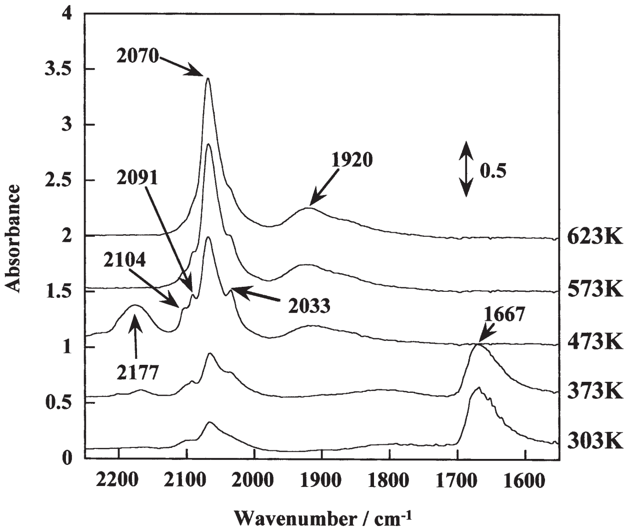

Figure 3. FT-IR spectra during CO-TPR process over 5 wt% Rh/SiO_2 after decomposition of CH_4 at 523 K for 1 h and the preadsorption of NO at 298 K.

The mechanism for the formation of acetaldehyde and acetonitrile was confirmed by employing ^{13}CO isotopic tracer experiments. After the decomposition of $^{12}CH_4$ on the reduced Rh/SiO_2 and adsorption of NO, ^{13}CO was admitted in the following CO-TPR step. The formed products were only $^{12}CH_3{}^{13}CO$ and $^{12}CH_3{}^{12}CN$. Accordingly, the methyl group in both products exclusively came from methane carbon. Formyl carbon in acetaldehyde was ^{13}C, supporting the mechanism of CO insertion into surface methyl group. On the contrary, nitrile carbon in acetonitrile came from methane, indicating the reaction between NO and surface carbonaceous species to form surface cyanide groups.

The possibility of catalytic formation of acetaldehyde and acetonitrile from CH_4-CO-NO reaction over Rh/SiO_2 catalysts was investigated at various reaction temperatures. Figure 4 represents the time courses of product formation during CH_4-CO-NO reaction ($P_{CH_4} = P_{CO} = 1.3$ kPa) over Rh/SiO_2 at 403 K. The

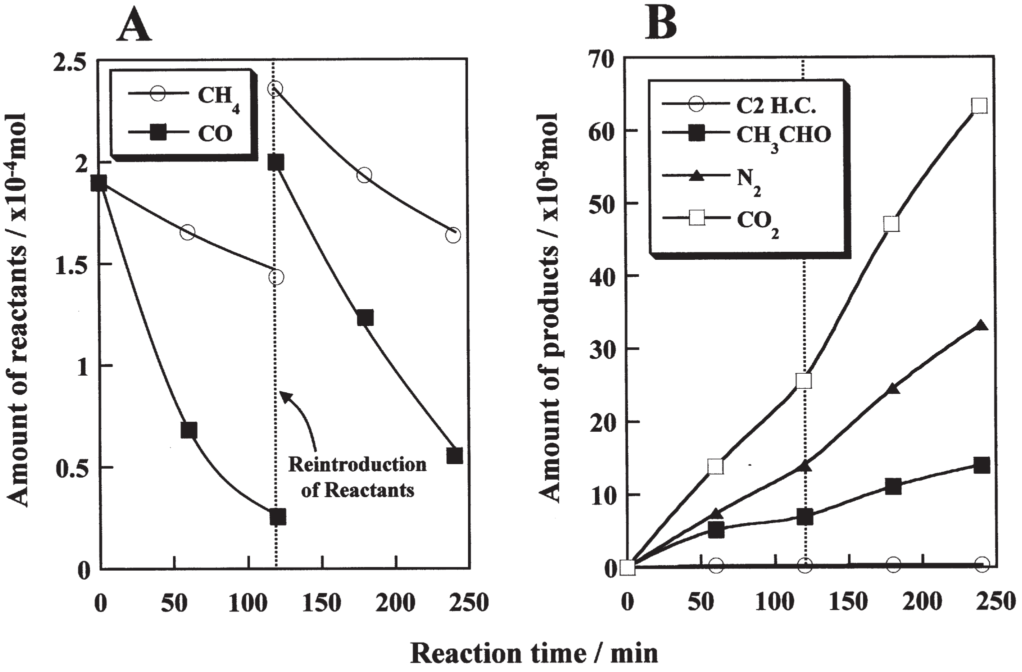

Figure 4. Time courses of (A) reactants and (B) products in CH_4-CO-NO reaction ($P_{CH_4} = P_{CO} = 1.3\,kPa$, $P_{NO} = 0.01\,kPa$) over reduced Rh/SiO_2 at 403 K.

partial pressure of NO during the reaction was only 0.01 kPa, because liquid N_2 cold trap was put into the closed gas circulation system to gather the products. At the initial stage of the reaction, the amounts of CH_4 and CO decreased abruptly, indicating the accumulation of carbonaceous species on the surface. Gas-phase reactants were reintroduced at 120 min and the reaction was continued. Although substantial amounts of N_2 and CO_2 were formed by NO-CO reaction, the formation of acetaldehyde was recognized, accompanied with a trace amount of ethane and ethylene. On the other hand, no acetonitrile was observed under this condition, maybe because the reaction temperature was too low for acetonitrile formation. By raising the reaction temperature, the amount of acetaldehyde was decreased gradually with the increase of acetonitrile formation. However, the rates of NO-CO and NO-CH_4 processes in CH_4-CO-NO reaction were increased drastically at higher temperatures, and no products other than N_2 and CO_2 were observed at 523 K.

Figure 5 showed the changes of the infrared spectra of adsorbed species during the CH_4-CO-NO reaction at 403 K over freshly reduced Rh/SiO_2. After 1 h of the reaction, the intensity of gem-dicarbonyl (2031, 2095 cm^{-1}) and Rh^{2+}–CO (2104 cm^{-1}) was stronger than that of linear-type adsorbed CO (2070 cm^{-1}) in spectrum (a), indicating the oxidation of Rh^0 to Rh^+. As shown in spectrum (b), after 4 h of the reaction, most of the surface rhodium species may be oxidized to Rh^+. After that, only NO was removed from the gas phase and the CH_4-CO reaction was continued for 1 h. The linearly adsorbed CO band appeared again at 2070 cm^{-1}, indicating the increase of Rh^0 species on the surface. No acetaldehyde was formed under this condition. When NO was reintroduced, this linear CO band disappeared, and the formation of acetaldehyde was observed again. These results clearly indicate that the existence of Rh^+ species is necessary for acetaldehyde formation. The catalytic cycle between zero-valent Rh and Rh^+ species on the surface will be important for

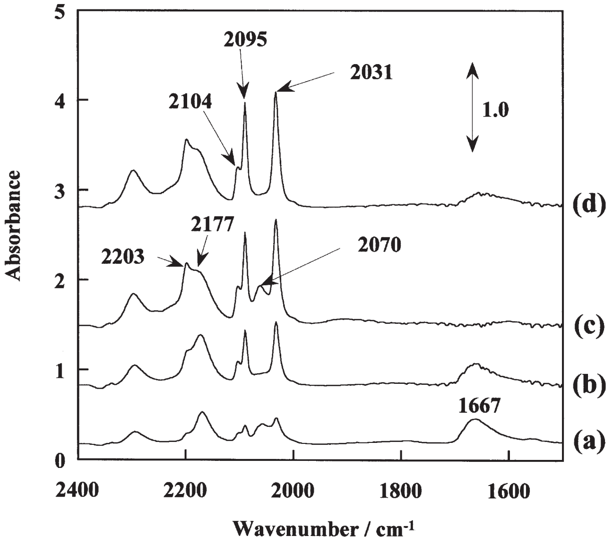

Figure 5. Changes in the FT-IR spectra of adsorbed species during sequential (a)–(d) reactions over reduced Rh/SiO_2 at 403 K. (a) for 1 h of CH_4-CO-NO reaction, (b) for 3 h after (a), (c) for 1 h of CH_4-CO reaction after (b), (d) for 1 h of CH_4-CO-NO reaction after (c).

methane activation and CO insertion, which leads to the successful synthesis of acetaldehyde.

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