CHEMISTRY LETTERS, pp. 1935-1938, 1993.

The Role of Oxygen in the Reduction of NO with Propene over Rh/Al_2O_3 in Oxidizing Atmosphere

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Infrared spectroscopy and isotopic tracer technique with microwave spectroscopy revealed a marked change of reaction intermediates as well as reaction mechanisms by the presence of excess oxygen in NO-propene reaction over highly dispersed Rh/Al_2O_3 catalyst.

Rhodium metal is an excellent catalyst for the reduction of nitric oxide by H_2 or CO and has been used in catalytic converters to control NO_x emissions from automobiles. Detailed mechanistic study has been reported by Hecker and Bell,1) but its catalytic behavior in oxidizing atmosphere has not so far been investigated. Reduction of NO under excess oxygen has recently attracted great attention because of necessary NO_x removal from diesel engine or gas turbine exhaust. Various cation-exchanged zeolites2-4) and metallosilicates5,6) have been reported to catalyze selectively the reduction of NO with various hydrocarbons under oxidizing conditions. Interestingly only hydrocarbons are effective as reducing agents, whereas H_2 and CO are ineffective. Although many speculative mechanisms have been proposed, the role of excess oxygen is not clear at present.

In the present study we have found that also Rh metal highly dispersed on alumina exhibited enhancement due to excess oxygen in the rate of the reduction of NO with propene. Applying microwave as well as infrared spectroscopy, we clarified the intrinsic role of oxygen molecules by comparing the reaction intermediates in the presence and absence of oxygen.

Higher dispersion catalyst (D = 0.68, determined by H_2 adsorption; Rh(68)) was prepared by impregnating alumina powder (Aerosil Aluminium Oxide C, evacuated at 723 K for 2h) with a dry hexane solution of $Rh_4(CO)_{12}$ (1 wt.% Rh metal) under nitrogen atmosphere and then by reducing it with H_2 at 573 K overnight. Lower dispersion catalyst (D = 0.35;Rh(35)) was prepared by the impregnation of aqueous solution of $RhCl_3$. The reaction was carried out in a closed gas circulation system (total volume: 310 cm^3). The gas phase composition was analyzed by gas chromatography with molecular sieve and Porapak Q columns. In the C_3H_6-C_3D_6-NO and C_3H_6-C_3D_6-NO-O_2 reactions the deuterium composition in the exchanged propene was determined by mass spectroscopy. The location of the deuterium atom in monodeuteropropene (propene-d_1) was determined by microwave spectroscopy.7) In the IR measurements, the reduced catalyst was pressed into a self-supporting disk and reduced by H_2 at 573 K for several hours. Infrared spectra were recorded by a JEOL JIR-DIAMOND 20 Fourier transform infrared spectrometer.

Figure 1 shows the enhancement effect of oxygen on C_3H_6-NO reaction at 453 K. In the case of Rh(68) catalyst, the rate of N_2 and N_2O (almost 1:1) formation increased several times in the presence of oxygen molecules. The similar extent of increase in the CO_2 formation rate indicates that the direct oxidation of propene by oxygen is not fast under this condition. On the other hand, the reduction of NO was retarded somehow over Rh(35) catalyst because of the competitive oxidation of propene by oxygen.

Infrared spectra of various adsorbed species are summarized in Fig. 2. Figures 2-(a) and (b) show respectively the spectra of adsorbed NO(a) over freshly reduced Rh(35) and Rh(68) catalysts at room temperature. The bands at 1825 and 1730 cm^{-1} were assigned to linearly adsorbed Rh-NO species and the band at 1650 cm^{-1} to the bent Rh-NO^- species. Relative intensities of these three bands depended on the particle sizes of Rh metal and linear NO(a) was abundant on higher dispersion catalysts. When propene was added to this system, no changes were observed in the spectrum. Figure 2-(c) shows the spectrum during the C_3H_6-NO reaction over Rh(68) catalyst at 423 K, where the emergence of 1260 and 1230 cm^{-1} bands was noted. When propene was introduced after the evacuation of the gas phase to see the reactivity of adsorbed NO(a), the bands disappeared in 10 min. with the formation of N_2 and N_2O. The resulting spectrum is shown in Fig. 2-(d).

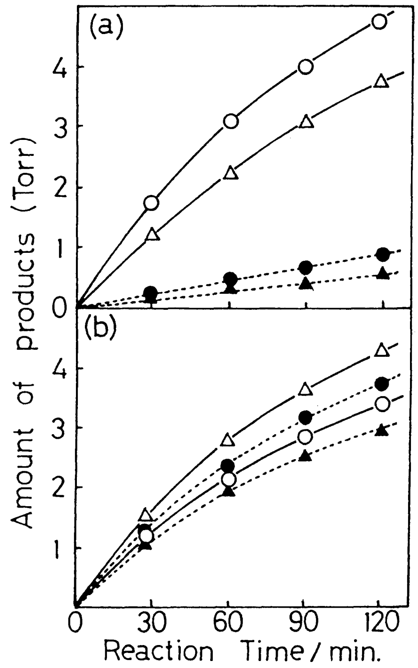

Fig.1. NO-C_3H_6(········) and NO-C_3H_6-O_2(———) reactions on (a) Rh(68) and (b) Rh(35) at 453 K(0.2 g Cat.), $P(O_2)$=5 Torr, P(NO)=$P(C_3H_6)$=50 Torr. ○ ● ; N_2+N_2O, △ ▲; CO_2

The situation was completely different when NO was introduced onto the oxygen preadsorbed Rh(68) surface at room temperature. Figure 2-(e) shows strong bands at 1620, 1590, 1560, 1290 and 1265 cm^{-1}, which were assigned to the adsorbed NO_2(a) or NO_3(a) species.$^{8)}$ Very weak band at around 1900 cm^{-1} may be assigned to the Rh-NO $^{\delta+}$ species. After evacuating the gas phase NO, only propene was introduced at room temperature, Fig. 2-(f), and the temperature was raised slowly. The above bands were very stable and gradually decreased only above 500 K as shown in Fig. 2-(g), suggesting the existence of these species at the vicinity of alumina support.

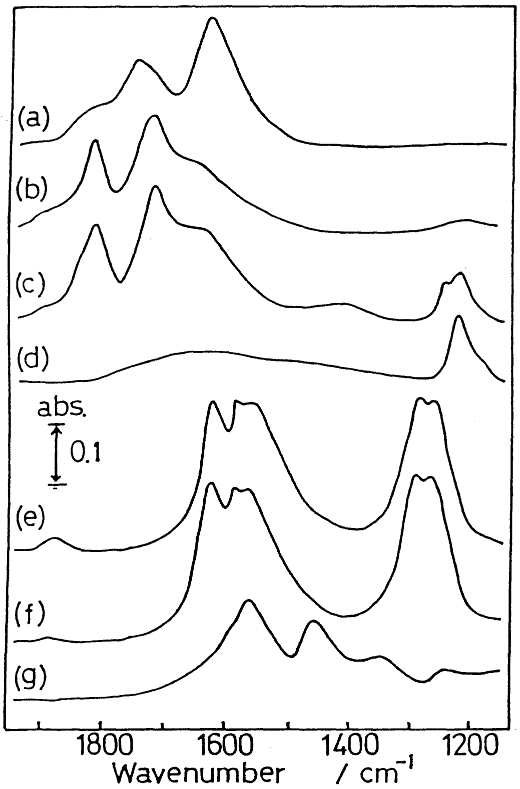

Fig.2. Infrared spectra of adsorbed species at R.T. for (a)-(g); see the text.

To obtain information on the adsorbed state of propene we applied microwave spectroscopy to analyze monodeuteropropene formed through the hydrogen exchange process in a mixture of C_3H_6 and C_3D_6. Figure 3-(a) shows the isotopic distribution pattern of monodeuteropropene formed over Rh(68) catalyst at 220 K. The main products at the initial stage were propene-1-d_1($HDC=CH-CH_3$) and 2-d_1($H_2C=CD-CH_3$). Since hydrogen exchange in the C_3H_6-D_2 reaction proceeded more than one order of magnitude faster than this reaction, hydrogen exchange in the C_3H_6-C_3D_6 reaction was considered to take place through the dissociative mechanism. From the distribution pattern we conclude that only the hydrogens attached to double bond carbons can be dissociated on this catalyst through n-propenyl and s-propenyl intermediates. Gradual increase of propene-3-d_1($H_2C=CH-CH_2D$) may be explained by the independent intramolecular hydrogen shift.$^{7)}$

By adding NO, the isotopic distribution as well as exchange rate changed drastically as shown in Fig. 3-(b). Now, the reaction began to proceed only at around room temperature and the main product was propene-3-d_1, indicating the change of the reaction intermediate from propenyl species to σ-allyl species by the interaction with NO(a). The same isotopic distribution pattern was obtained at such higher temperatures as 423 K. On the other hand, in the C_3H_6-C_3D_6-NO-O_2 reaction, the exchange rate decreased one order of magnitude and the distribution pattern changed completely, as seen in Fig. 3-(c). The pattern is similar to that of the C_3H_6-C_3D_6-O_2 reaction in Fig. 3-(d), although the exchange rate itself was much slower than in the latter reaction. The lower exchange rate may be explained by the fast removal of adsorbed hydrogen by NO_2(a) or NO_3(a), which causes a shift of the adsorption equilibrium of propene toward the dissociation side. Over Rh(35) catalyst, we observed no hydrogen exchange in the C_3H_6-C_3D_6-O_2 or C_3H_6-C_3D_6-NO-O_2 reaction, which can similarly be explained by the fast oxidation of propene by oxygen molecules.

We conclude thus that excess oxygen in C_3H_6-NO reaction modifies the Rh(68) catalyst surface to an oxidative one, where NO_2(a) or NO_3(a) species formed may promote the dissociation of propene by the fast removal of hydrogen to leave irreversibly adsorbed propenyl species. N_2 and N_2O may be formed by the reaction of weakly adsorbed Rh-NO $^{\delta+}$ species with these propenyl species.

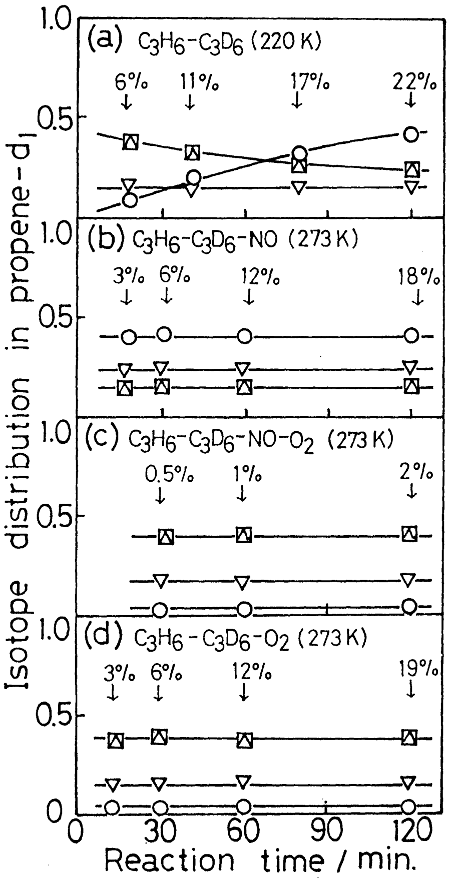

Fig.3. Time courses of isotope distribution in propene-d_1 on Rh(68) catalysts (0.2 g). "%";mean D content in propene $=100\sum_{i=0}^{6} id_i/6$,

□ ; cis-1-d_1
Δ ; trans-1-d_1
∇ ; 2-d_1
○ ; 3-d_1

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(Received July 14,1993)