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UNIQUE REACTION CHARACTERISTICS OF Rh CATALYSTS FOR THE CO HYDROGENATION BY MEANS OF PSRA

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By using PSRA, the rate constant for the formation of surface carbon species, k_{CO}, and that for its hydrogenation, k_{CHx}, were determined from dynamics of adsorbed CO and produced CH_4 in the CO hydrogenation on supported Rh catalysts. It was found that there was not much difference between these two rate constants, while k_{CHx} was extremely larger than k_{CO} on the other group VIII metal catalysts.

In the CO hydrogenation, Rh exhibits an interesting catalytic property, on which C_2-oxygenated compounds such as C_2H_5OH, CH_3CHO, and CH_3COOH are selectively produced depending on the catalyst support and the reaction conditions.[1-9] In spite of the unique selectivity of the Rh catalyst, a great deal of effort has gone into the investigation of the development of the catalyst substituted for the Rh catalyst, because of the high price of Rh and its limited production . For the development of such a catalyst, it is of primary importance that the reaction characteristics of the Rh catalyst should be clarified for the CO hydrogenation

It has generally been accepted that the surface carbon species [$(CH_x)_{ad}$] is highly reactive with H_2 and plays an important role in the CO hydrogenation.[10-13] The stability of $(CH_x)_{ad}$ on the catalyst may change from metal to metal, which may lead to the variation in the product selectivity. The PSRA (pulse surface reaction rate analysis) has been developed in order to determine the rates for the

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formation of $(CH_x)_{ad}$ and its hydrogenation to CH_4,[14-17)] where the hydrogenation of adsorbed CO $[(CO)_{ad}]$ to CH_4 is considered to proceed through $(CH_x)_{ad}$ like a kind of a consequtive reaction, viz.[10-13)]

$$(CO)_{ad} \xrightarrow{k_{CO}} (CH_x)_{ad} \xrightarrow{k_{CHx}} CH_4 \qquad (1)$$

In this study, by using the PSRA, both rate constants of k_{CO} and k_{CHx} were determined in the CO hydrogenation over supported Rh catalysts. We will report here the unique characteristics of the Rh catalysts for this reaction revealed by the PSRA.

Supported Rh catalysts were prepared by impregnating Al_2O_3 (Reference Catalyst of Catalysis Society of Japan, JRC-ALO-4), SiO_2 (Fuji-Davison, Microbeads 5D and Nikki Chemical, E96G3) or TiO_2 (Nippon Aerosil, P-25) with an aqueous solution of $RhCl_3$, followed by drying overnight and heating in flowing H_2 at 673 K for 2 h. Pd/Al_2O_3 catalyst was obtained from Nippon Engelhardt Ltd. and Pt/Al_2O_3 catalyst was a reference catalyst of Catalysis Society of Japan [JRC-A4-0.5Pt(1)]. Other transition metal catalysts were also prepared by an impregnation method. Dynamic experiments were conducted at atmospheric pressure using the PSRA apparatus, which was used in the CO hydrogenation on Ru/Al_2O_3 catalyst reported previously.[17)]

When a small amount of CO (usually 10 μl-STP) was injected to the catalyst at 328 K via the H_2 carrier gas in the PSRA apparatus,[17)] it was immediately adsorbed on the catalyst and exhibited an IR absorption band at around 2040 cm^{-1} assignable to linearly adsorbed CO. When the CO pulse was injected to the catalyst at elevated temperatures, the IR absorption band of linear CO also appeared at 2040 cm^{-1}, and its intensity gradually decreased with time due to the hydrogenation of linear CO with H_2 to selectively produce CH_4 and H_2O. Analysis of the dynamic behavior of the 2040 cm^{-1} band on the basis of the following first order rate equation led to the determination of the rate constant for the C-O bond dissociation and resultingly for the formation of $(CH_x)_{ad}$ on each active site on the catalyst (k_{CO}),

$$r(CO) = k_{CO}\ N^{o}_{CO}\ \exp(-k_{CO}t) \qquad (2)$$

where N^{o}_{CO} is the amount of CO adsorbed on the catalyst at $t = 0$.[16, 17)] The dynamics of the produced CH_4 was measured by using the flame ionization detector without any disturbance of the produced H_2O. The rate constant for the hydrogenation of $(CH_x)_{ad}$ (k_{CHx}) was also determined by using the value of k_{CO} and the rate equation for the consecutive reaction, viz.[17)]

Table 1. Rate constants of k_{CO} and k_{CHx} determined with PSRA during the CO hydrogenation on supported metal catalysts at 445 K and their ratio (k_{CHx}/k_{CO})

Catalyst	Rate constant/ks^{-1}		k_{CHx}/k_{CO}
	k_{CO}	k_{CHx}	
Rh/TiO_2	150	180	1.2
Rh/Al_2O_3	63	27	0.43
Rh/SiO_2	0.56	1.2	2.1
Fe/Al_2O_3	93	>1900	>20
Co/Al_2O_3	16	>310	
Ni/SiO_2	2.1	>42	
Ru/Al_2O_3	42	>830	
Pd/Al_2O_3	1.6	>32	
Pt/Al_2O_3	0.67	>13	

$$r(CH_4) = \frac{k_{CO}\, k_{CHx}}{k_{CHx} - k_{CO}} N^{o}_{CO}[\exp(-k_{CO}t) - \exp(-k_{CHx}t)] \qquad (3)$$

In Eqs. 2 and 3, since the reaction rate is first order with respect to the respective species, the definite value of N^{o}_{CO} is not necessary for the determination of the rate constant.

Table 1 lists the typical values of k_{CO}, k_{CHx}, and k_{CHx}/k_{CO} for supported metal catalysts. The remarkable feature of the Rh catalyst is the small difference between k_{CO} and k_{CHx}, although both rate constants greatly depend on the support. The ratios of k_{CHx}/k_{CO} on all Rh catalysts are less than 3. This is a marked contrast to the other supported metal catalysts, where the ratio of k_{CHx}/k_{CO} is larger than 20. For the latter catalysts, the ratio was so large that the exact value of k_{CHx} could not be determined. Since CH_4 is produced through the hydrogenation of $(CH_x)_{ad}$, the large ratio of k_{CHx}/k_{CO} results in the favorable condition for CH_4 production. On the other hand, the small ratio observed on the Rh catalyst leads to the further reaction of $(CH_x)_{ad}$ before its hydrogenation to CH_4, such as the polymerization of $(CH_x)_{ad}$ or the insertion of CO into the metal-carbon bond in $(CH_x)_{ad}$. Since C_2-oxygenated compounds are considered to be produced through the insertion of CO into the bond between metal and carbon atoms in $(CH_x)_{ad}$,7) the relatively slow hydrogenation of $(CH_x)_{ad}$ compared with its formation on the Rh catalyst is favorable for the production of the C_2-oxygenated compounds. High selectivity of the Rh catalyst for the production of C_2-oxygenated compounds may be ascribable to the reactivity of $(CH_x)_{ad}$ on the Rh catalyst different from that on the other group VIII metal catalysts.

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