CHEMISTRY LETTERS, pp. 1161-1164, 1983.

IMPROVEMENT OF SELECTIVITY FOR C_2-OXYGENATED COMPOUNDS IN CO-H_2 REACTION OVER TiO_2-SUPPORTED Rh CATALYSTS BY DOPING ALKALI METAL CATIONS

Hideo ORITA, Shuichi NAITO,* and Kenzi TAMARU
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

The addition of alkali metal cations to TiO_2-supported Rh catalysts improved the selectivity for C_2-oxygenated compounds in CO-H_2 reaction under atmospheric pressure. The dependences of the reaction rates on pretreatment conditions and reaction temperatures were also examined, which suggest that the active sites or the reaction path for the formation of acetaldehyde may be different from those for ethanol as well as hydrocarbons.

The effect of potassium added to Fischer-Tropsch catalysts (Fe, Ru, Ir) has long been known to enhance the formation of longer chain as well as olefinic hydrocarbons.$^{1-3)}$ On the other hand, we have recently reported that palladium catalysts prepared from M_2PdCl_4 (M=alkali metal) type complexes produce methanol selectively from CO-H_2 under atmospheric pressure,$^{4)}$ and demonstrated the important role of sodium and lithium cations for the formation of the active sites available for methanol formation.

The supported rhodium catalysts are effective for the C_2-oxygenated compounds from CO-H_2 under high pressure,$^{5)}$ though they produce only methane and hydrocarbons under atmospheric pressure.$^{6)}$ In this communication, we have studied the effects of doped alkali metal cations on the catalytic properties of TiO_2-supported Rh catalysts and found that the selectivity for C_2-oxygenated compounds from CO-H_2 reaction is increased and the rate of hydrocarbon formation is decreased simultaneously.

The catalysts were prepared by impregnating aqueous solutions of metal chlorides ($RhCl_3$, $(NH_4)_3RhCl_6$, Na_3RhCl_6, or mixture of $RhCl_3$ and alkaline chloride) onto TiO_2 (P-25, Aerosil). After the impregnation, the catalysts (5 wt% Rh) were dried in air at 383 K for $\simeq$12 h. Then they were put in a U-shape glass reactor, which is connected to a closed gas circulation system, and treated in air at room temperature with a liquid nitrogen cold trap for $\simeq$15 h prior to the reduction by hydrogen at 473 - 723 K for several hours. The hydrogenation of CO was carried out at 393 - 493 K in the circulation system with a liquid nitrogen cold trap, and the reaction products were analyzed by gas chromatography and quadrupole mass spectrometer.

Table 1 shows the rates of the product formation from CO-H_2 reaction (CO: 12 kPa, H_2: 24 kPa) at 453 K over various rhodium catalysts supported on TiO_2. The addition of alkali metal cations increased the rate as well as selectivity of

Table 1. CO-H_2 reaction over various rhodium catalysts supported on TiO_2

Metal precursors	H_2 red. temp (K)	H/Rh[a] (%)	Product formation rates[b] (10^{-2} ml-STP/h·g-cat.)						Selectivity[d] of C_2-oxy. compounds (%)
			CO_2	MeOH	AcH	EtOH	C_2^{+}[c]	CH_4	
$RhCl_3$	573	26	84	—	—	—	5600	1090	0
	723	1	8.2	—	—	1.4	263	33.4	1
$(NH_4)_3RhCl_6$	573	4	9.2	—	2.0	6.7	1550	154	1
	723	$\simeq 0$	2.9	—	—	0.5	79.2	34.9	1
$RhCl_3$+3LiCl	573	14	8.2	—	46.3	49.1	394	82.6	28
	723	$\simeq 0$	5.8	0.6	3.3	2.3	75.2	8.8	11
Na_3RhCl_6	573	17	3.7	0.4	29.0	16.3	283	117	18
	723	$\simeq 0$	7.8	3.7	5.0	11.0	118	34	16
$RhCl_3$+3KCl	573	20	3.0	—	37.7	4.4	247	69.2	21
	723	$\simeq 0$	4.7	0.7	8.1	4.5	100	18.3	17
$RhCl_3$+3CsCl	573	9	1.3	—	16.3	2.3	278	50.1	10
	723	$\simeq 0$	1.6	0.2	3.8	0.5	60.9	9.4	10

a) Based on H_2 adsorption at room temperature.

b) Reaction temperature = 453 K, $P^{\circ}_{H_2}$ = 24 kPa, P°_{CO} = 12 kPa, the data were taken after the catalysts showed constant activities.

c) Total amounts of carbon contained in hydrocarbons which have more than two carbon atoms.

d) Selectivity of C_2-oxy. compounds (%) = $100\times2([AcH]+[EtOH])/([CO_2]+[MeOH]+2[AcH]+2[EtOH]+[C_2^{+}]+[CH_4])$.

C_2-oxygenated compounds considerably and decreased those of hydrocarbons. The formation rate ethanol was more influenced by the kinds of doped alkali metal cations than that of acetaldehyde, and decreased with decreasing the ionization potential of alkali metals, i.e., Li>Na>K>Cs. Even the doping of cesium is effective for the increase of selectivity for oxygenated compounds by one order of magnitude, which was not the case over supported Pd catalysts.$^{4)}$ Therefore, the effect of alkali metal cations are (i) the formation of active sites for C_2-oxygenated compounds and (ii) the depression of the rates of hydrocarbon formation.

As the reduction temperature was raised up to 723 K, the H/Rh values (the ratios of the amount of adsorved hydrogen atoms to rhodium metal atoms on the support) of all the catalysts dropped down to nearly zero and the rates of formation of all the products except methanol was depressed, although the selectivity stayed unchanged. Oxidation of catalysts at 723 K followed by the reduction at 573 K restored the initial properties of TiO_2-supported catalysts. These facts indicate that the catalysts reduced at 723 K are in the SMSI (Strong Metal-Support Interaction) state.

Table 2 shows the activation energies of product formation from the CO-H_2 reaction over $RhCl_3$+3LiCl/TiO_2, which is the most active catalyst for the formation of oxygenated products. The activation energies for the SMSI state catalyst were not very different from those for the non-SMSI state one, which suggests that the SMSI only reduces the number of active sites but may not change the reaction paths. It is noteworthy that the activation energy of acetaldehyde formation is larger than that of ethanol, and rather resembles to that of hydrocarbon formation.

Table 2. Activation energies of product formation from CO-H_2 reaction over $RhCl_3$+3LiCl/TiO_2 catalyst

H_2 red.	H/Rh$^{a)}$	Activation energies$^{b)}$ (kcal/mol)				
temp (K)	(%)	CO_2	AcH	EtOH	CH_4	C_2^+
573	14	31	30	21	28	25
723	$\simeq$0	24	29	23	28	27

a) Based on H_2 adsorption at room temperature.

b) $P^\circ_{H_2}$ = 24 kPa, P°_{CO} = 12 kPa, reaction temperature = 393 - 493 K.

The typical time courses of the CO-H_2 reaction is shown in Fig. 1. The induction period was observed for the formation of ethanol and methanol, but not for hydrocarbons and acetaldehyde. Even when the reaction was carried out without the liquid nitrogen cold trap, the similar induction period existed for the formation of ethanol and methanol, and the amount of acetaldehyde formed was very small. Furthermore, the addition of acetaldehyde to the CO-H_2 reaction under steady state condition did not increase the formation of ethanol, but the

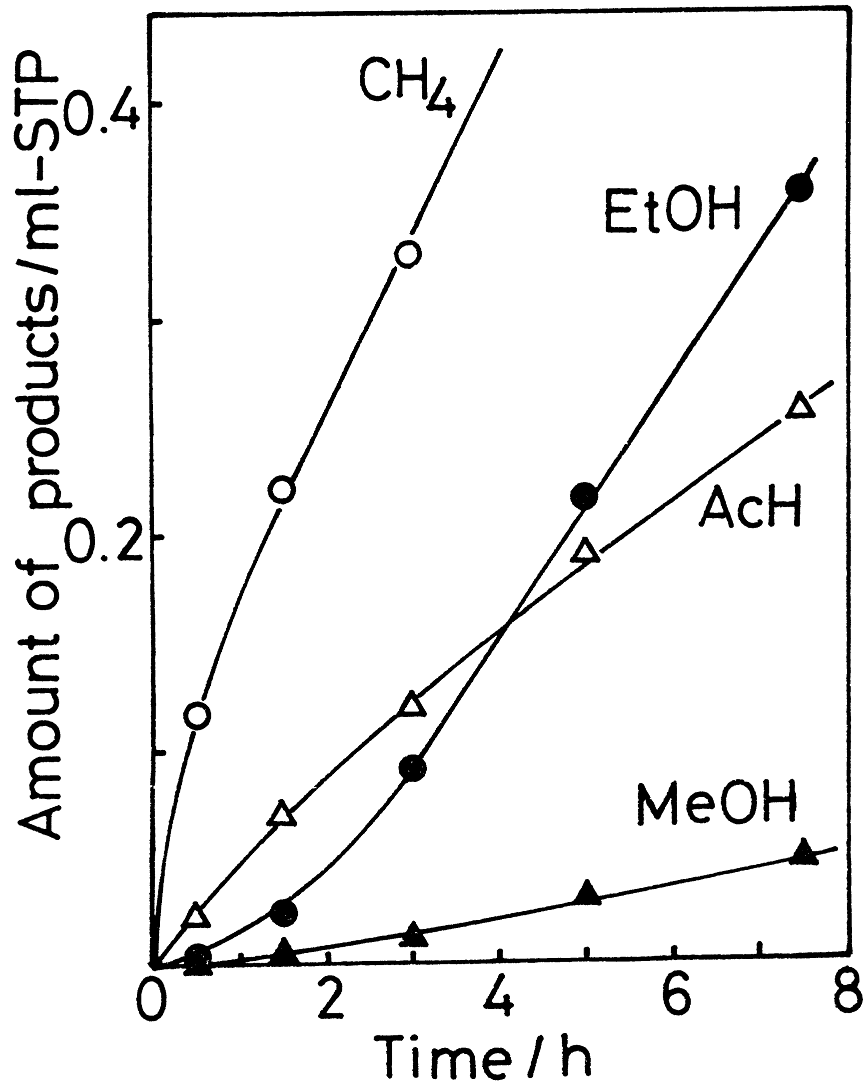

Fig. 1. Time courses of the CO-H_2 reaction at 433 K with a liquid nitrogen cold trap over $RhCl_3$+3LiCl/TiO_2. CO_2 and C_2^+ are not shown in the figure.

decomposition of acetaldehyde was observed. These results may suggest that the route of acetaldehyde formation would be different from that of ethanol.

References
1) R.B. Anderson, "Catalysis," Reinhold, New York (1956), Vol. 4, pp. 29 - 443.
2) G.B. McVicker and M.A. Vannice, J. Catal., 63, 25, (1980).
3) R.D. Gonzalez and H. Miura, J. Catal., 77, 338, (1982).
4) Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, Chem. Lett., 1981, 1249; Faraday Discuss. Chem. Soc., 72, 135, (1981).
5) M.M. Bhasin, W.J. Bartley, P.C. Ellgen, and T.P. Wilson, J. Catal., 54, 120, (1978).
6) M. A. Vannice, J. Catal., 37, 449, (1975).

(Received May 4, 1983)