Formation of C(2)-Oxygenated Compounds from the Reaction of CO and H_2 over Alkali-metal Doped Rhodium Catalysts under Mild Conditions

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Novel rhodium catalysts, prepared from M_3RhCl_6 (M = alkali metal), give C(2)-oxygenated compounds with good selectivity from a CO–H_2 mixture below atmospheric pressure; the nature of the active sites in the formation of the oxygenated compounds is discussed.

Rhodium metal is an excellent catalyst for the formation of C(2)-oxygenated compounds, *e.g.* acetaldehyde, ethanol, and ethylene glycol, from a CO–H_2 mixture under high pressures.[1] However only methane and other hydrocarbons are produced under atmospheric pressure.[2] Recently it was reported that rhodium catalysts supported on La_2O_3, Nd_2O_3, or ZrO_2 produce ethanol selectively from a CO–H_2 mixture under atmospheric pressure.[3] On the other hand, we reported recently that palladium catalysts, prepared from M_2PdCl_4 (M = alkali metals), produce methanol selectively from CO–H_2 below atmospheric pressure.[4] This demonstrates the important role of sodium and lithium cations in the formation of the active sites, which stabilize the formate ions; the intermediates in methanol formation.

In order to extend this concept, we examined the effect of alkali metal addition to rhodium catalysts and found that the selective formation of acetaldehyde and ethanol from a CO–H_2 mixture below atmospheric pressure was considerably improved. The catalysts were prepared by impregnating aqueous solutions of M_3RhCl_6 (M = Na, K, or NH_4) onto alumina. After impregnation, the catalysts (5 wt% Rh) were dried by air circulation at room temperature with a liquid nitrogen cold trap for 20 h. The catalysts were then reduced with hydrogen at 473—773 K [$P(H_2)$ 40 kPa and P(CO)

Table 1. CO–H_2 reaction over M_3RhCl_6-derived (M = Na, K, and NH_4) alumina-supported catalysts.[a]

Catalysts	H_2 Reduction temperature/K	H_2 Adsorption/ ml-S.T.P. g-cat.$^{-1}$	Product formation rates[b]/10^2 ml-S.T.P. g-cat.$^{-1}$ h^{-1}						Selectivity of C(2) oxygenation compounds (%)
			MeOH	AcH	EtOH	CH_4	$C_{>2}$[e]	CO_2	
Rh–Na/Al_2O_3	473[c]	1.8	2.3	4.3	1.8	—[d]	29.4	0.2	—
	773	1.3	20.1	27.0	21.6	30.9	39.0	2.9	34.4
Rh–K/Al_2O_3	473	1.9	0.2	1.5	0.0	6.3	6.0	0.8	10.6
	773	1.5	2.1	2.9	0.1	2.9	4.2	0.6	23.6
Rh/Al_2O_3	473	0.7	0.0	0.0	0.0	24.6	36.0	6.1	0.0
	773	1.2	3.1	0.1	0.1	14.5	46.5	0.5	0.2

[a] $P(H_2)$ 40 kPa, P(CO) 20 kPa, reaction temperature 453 K. [b] Calculated by counting the total number of carbon atoms in the product. [c] $P(H_2)$ 27 kPa, P(CO) 13.5 kPa. [d] Not analysed. [e] $C_{>2}$ Represents hydrocarbons with more than two carbon atoms.

20 kPa] in a closed circulation system with a liquid nitrogen cold trap and the products were analysed by gas chromatography. In the case of experiments with labelled isotopes, the products were separated into components by gas chromatography before mass spectroscopic analysis.

Table 1 shows the effect of hydrogen pretreatments at various temperatures upon the activity of the CO–H_2 reaction at 453 K over M_3RhCl_6-derived (M = Na, K, or NH_4) alumina-supported catalysts. As the reduction temperature of the catalyst was raised from 473 to 773 K, the activity of the formation of oxygenated compounds increased considerably, but the activity of methane and other hydrocarbon formation and the 'metal' surface area, estimated from the amount of H_2 adsorbed, remained almost unchanged. These phenomena are quite similar to those observed for Pd catalysts, and they may be due to the formation of active sites for oxygenated compounds on hydrogen reduction at higher temperature. The activity of formation of methane and other hydrocarbons was similar on non-doped and sodium-doped catalysts, but the activity of formation of oxygenated compounds was one order of magnitude higher in the latter case. These results suggest that the active sites for the formation of oxygenated compounds are different from those for methane and other hydrocarbons. With a potassium-doped catalyst, the activities of all the product formations decreased considerably in spite of its similar surface area compared to the sodium-doped catalyst. In this case the alkane/alkene and alcohol/aldehyde ratios of reaction products were quite small compared to those with the sodium-doped catalyst, suggesting the electronic state of rhodium has been modified by doping with potassium cations, causing a decrease in the hydrogenation activity in the CO–H_2 reaction.

Table 2. Effect of the addition of $^{13}CH_3OH$ to the ^{12}CO–H_2 reaction over Rh–Na/Al_2O_3 at 453 K.

Products	V_a/V_b[a]	Isotope distribution ratio $^{13}C/^{12}C$
CH_4	1.32	0.21
$C_{>2}$[b]	1.28	0.24
EtOH	1.20	0.05

[a] V_a is the rate after the addition of $^{13}CH_3OH$. V_b is the rate before the addition of $^{13}CH_3OH$. [b] See footnote e, Table 1.

To examine the reaction mechanism of C–C bond formation in C(2)-oxygenated compounds, dissociative carbon-13 was deposited on a freshly reduced sodium-doped catalyst by the disproportionation of ^{13}CO, and the ^{12}CO–H_2 reaction was then carried out at 453 K. The hydrocarbons produced initially contained considerable amounts of ^{13}C, indicating the incorporation of the dissociative carbon in the formation of hydrocarbons over the rhodium surface. However, the role of this dissociative carbon in the formation of C(2)-oxygenated compounds was not clear owing to the induction period in the formation of these products. To examine these points more clearly, $^{13}CH_3OH$ was added during the steady-state period of the ^{12}CO–H_2 reaction at 453 K over a sodium-doped catalyst, and the isotope distribution of the products was analysed by mass spectrometry. As summarized in Table 2, all the rates of product formation increased 20—30% on addition of $^{13}CH_3OH$. The methane and other hydrocarbons produced contained appreciable amounts of ^{13}C, indicating the incorporation of a methyl radical in the reaction pathway of product formation. The ethanol produced, however, contained a very small amount of ^{13}C, which indicates that the methyl radicals formed on the rhodium surface are not used directly for C–C bond formation of C(2)-oxygenated compounds. These results support the conclusion that the active sites for the formation of the oxygenated compounds are different from those for methane and other hydrocarbon formation. By analogy with palladium catalysts,[4] these active sites may be located in the vicinity of the rhodium metal and the support, and they are modified by the addition of sodium cations.

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References

1 M. M. Bhasin, W. J. Bartley, P. C. Ellgen, and T. P. Wilson, *J. Catal.*, 1978, **54**, 120.
2 M. A. Vannice, *J. Catal.*, 1975, **37**, 449.
3 M. Ichikawa and K. Shikakura, Proc. VII Inter. Congr. Catal., Tokyo, 1980, B17.
4 Y. Kikuzono, S. Kagami, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, 1981, 1249; *Faraday Discuss. Chem. Soc.*, 1982, 135.