Catalytic Synthesis of Ethanol from CO and H_2 under Atmospheric Pressure over Pyrolysed Rhodium Carbonyl Clusters on TiO_2, ZrO_2, and La_2O_3

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Summary C_2-oxygenated compounds composed mainly of ethanol were catalytically produced from CO and H_2 under atmospheric pressure over pyrolysed Rh carbonyl clusters dispersed on specific metal oxides such as TiO_2, ZrO_2, and La_2O_3.

The catalytic synthesis of oxygenated C_2 compounds such as ethanol directly from CO and H_2 is of great practical and theoretical interest. Recently, Muetterties and others[1] demonstrated that metal carbonyl clusters such as $Ru_3(CO)_{12}$ and $Ir_4(CO)_{12}$ catalysed methanation in the homogeneous hydrogenation of CO at 140 °C and *ca.* 2 atm pressure. Several patents[2] have also described the catalytic conversion of CO and H_2 into methanol and ethylene glycol under higher pressures (150—3000 atm) with rhodium catalysts in specific solvents. We here report that ethanol synthesis takes place from CO and H_2 with higher selectivities over pyrolysed Rh carbonyl clusters dispersed on specific metal oxides such as TiO_2, ZrO_2, and La_2O_3.

The carbonyl clusters, *e.g.* $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)_3]$, $[Rh_4(CO)_{12}]$, $[Rh_6(CO)_{16}]$, $[Rh_7(CO)_{16}][NEt_4]_3$, and $[Rh_{13}(CO)_{23}H_{2-3}][NBu_4]_2$ were synthesized and isolated by Chini's methods.[3] The precursor carbonyl clusters were deposited on various metal oxides: *e.g.* silica gel, γ-Al_2O_3, ZnO, MgO, La_2O_3, TiO_2, and ZrO_2 (99·9% purity, 10—280 m^2/g surface area) from hexane, acetone, and tetrahydrofuran solutions. Solvent was evaporated off, and

Table. Rates and product distribution in the CO–H_2 reaction over pyrolysed Rh carbonyl clusters dispersed on various metal oxides: $P(CO):P(H_2) = 20:45$ cmHg.

Catalyst (wt./g)	% Total conversion[a] of CO in 5 h	(T/°C)	Product distribution (%) (carbon efficiency for each product per CO molecule consumed)[b] MeOH	EtOH	MeCHO	AcOH[d]	C_1	C_2	C_3	C_4
$[Rh_4(CO)_{12}]$ (0·10)–TiO_2 (20)	3·9	(210)	6·5	33·4	8·4	+[e]	30·8	7·0	10·3	4·0
$[Rh_4(CO)_{12}]$ (0·11)–ZrO_2 (20)	12·1	(210)	27·4	52·7	+	+	17·4	0·3	2·3	0·2
$[Rh_4(CO)_{12}]$ (0·10)–La_2O_3 (20)	14·9	(205)	41·7	48·3	+	+	7·5	0·4	0·9	+
	36·4	(224)	20·0	61·1	1·2	+	11·9	0·8	3·2	0·3
$[Rh_4(CO)_{12}]$ (0·11)–ZnO (20)	8·8	(220)	95·5	—[e]	—	—	4·5	—	—	—
$[Rh_4(CO)_{12}]$ (0·11)–MgO (20)	13·0	(220)	90·5	1·6	—	—	7·8	+	+	—
$[Rh_2(C_5H_5)_2(CO)_3]$ (0·08)–La_2O_3 (20)	1·9	(220)	25·6	53·0	3·0	1·8	13·3	1·0	2·2	+
$[Rh_6(CO)_{16}]$ (0·10)–La_2O_3 (20)	16·4	(220)	17·7	46·6	3·6	+	18·9	3·8	4·9	3·2
$[Rh_7(CO)_{16}][NEt_4]_3$ (0·10)–La_2O_3 (20)	14·8	(220)	8·9	32·8	4·6	+	13·5	14·0	19·4	6·8
$[Rh_{13}(CO)_{23}H_{2-3}][NBu_4]_2$ (0·16)–La_2O_3 (20)	15·5	(225)	6·4	28·9	2·4	+	22·5	19·8	19·8	6·6
$[RhCl_3],3H_2O$ (0·50)–La_2O_3 (20)[c]	4·7	(220)	10·7	17·1	+	+	56·4	6·2	7·9	1·4

[a] The average rate of circulation of CO–H_2 was *ca.* 100 ml/min. [b] Carbon efficiency $= i(C_i)/(CO_{\text{consumed}}) \times 100\ \%$, where i denotes number of carbon atoms in each product molecule. $C_1 = CH_4$, $C_2 = C_2H_4 + C_2H_6$, $C_3 = C_3H_6 + C_3H_8$, $C_4 = C_4H_8 + C_4H_{10}$. [c] The impregnated $RhCl_3$ on La_2O_3 was reduced by hydrogen (1 atm) at 350° C. [d] Acetic acid was obtained as methyl and ethyl acetates. Analysis of the oxygenated products was based on gas chromatography using Porapak Q (4 m; 200 °C; He carrier) and Polyethylene glycol 1500 (2 m; 80 °C; He carrier). C_1–C_4 hydrocarbons were analysed by gas chromatography using active carbon (1 m; 25 °C) and Al_2O_3–dimethylformamide (4 m; 25 °C). [e] The + and — signs denote carbon efficiencies of the product of $<0{\cdot}1\%$ and $<0{\cdot}01\%$ (undetectable), respectively.

carbonyl cluster dispersed on the metal oxide (0·1—0·5 Rh wt % loading) was placed in a closed circulating glass reactor (*ca.* 420 ml), and heated at 120—180 °C for 1—2 h *in vacuo* to remove CO.† When the CO–H_2 reactant mixture (molar ratio 1 : 1—3 under a total pressure of 45—65 cmHg) was circulated over, for example, pyrolysed $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ deposited on La_2O_3 powder, at 120—230 °C, oxygenated products containing ethanol (mainly), methanol, and a small amount of acetaldehyde and acetate were obtained in a trap at −80 °C. Methane and a small amount of C_2–C_4 hydrocarbons were also detected in gas phase. The carbon efficiencies of the oxygen-containing compounds per CO consumed in the reaction amounted to 60—90% under the optimum conditions. At lower temperatures, the methanol content in the oxygenated products was relatively high, and ethanol yields increased markedly at >200 °C. The apparent activation energies of methanol, ethanol, and methane formation were 12, 20, and 32 kcal/mol, respectively, over the $[Rh_4(CO)_{12}]$ on La_2O_3 (0·5 Rh wt%) catalyst.

The activities and product distribution in the CO–H_2 reaction for each pyrolysed Rh carbonyl cluster deposited on the various metal oxides‡ are summarized in the Table. The product distribution depends markedly on the supporting metal oxides as well as on the precursor cluster using in catalyst preparation. Pyrolysed Rh clusters on the strong basic oxides ZnO and MgO selectively catalysed methanol formation from CO and H_2. A number of basic oxides having weak acidity, such as La_2O_3, CeO_2, TiO_2, ZrO_2, and ThO_2, acted as promoters for formation of ethanol and other C_2-oxygenated products when used as carriers for dispersing the Rh cluster. In contrast, the pyrolysed Rh clusters deposited on acidic oxides such as silica gel, γ-Al_2O_3, silica–alumina, V_2O_5, SnO_2, and WO_3 preferentially produced methane and higher hydrocarbons§ and were essentially inactive for formation of oxygenated products under these conditions.

The results suggest that the formation of C_2-oxygenated compounds such as ethanol is enhanced by appropriate surface acidity which controls dehydration and dehydrogenation of a half-hydrogenated CO intermediate catalysed by rhodium crystallites. For the carbonyl clusters, pyrolysed catalysts with smaller Rh clusters such as Rh_2–Rh_6 showed relatively higher specific conversion into ethanol. In contrast, the catalysts derived from pyrolysed Rh_7–Rh_{13} clusters produced methane and C_2–C_4 hydrocarbons. The specific yields of ethanol yields per unit Rh weight over pyrolysed Rh clusters deposited on La_2O_3 varied in the following order: $[Rh_2(C_5H_5)_2(CO)_3] < [Rh_4(CO)_{12}] > [Rh_6(CO)_{16}] > [Rh_7(CO)_{16}][NEt_4]_3 > [Rh_{13}(CO)_{23}H_{2-3}][NBu_4]_2$. For comparison, a conventional Rh metal catalyst was prepared by impregnation of $RhCl_3$ on TiO_2, ZrO_2, and La_2O_3 (1—2·5 Rh wt% loading) followed by reduction with hydrogen in the temperature range 250—350 °C.¶ The apparent activity and product distribution for these catalysts in the CO–H_2 reaction are also in the Table. Although the oxygenated products methanol and ethanol were obtained over these $RhCl_3$-derived catalysts, the specific yields of ethanol were considerably smaller than those over the Rh cluster-derived catalysts, and methanation proceeded preferentially under similar conditions. These results suggest that the smaller Rh crystallites prepared from carbonyl clusters might be more effective for selective conversion of CO and H_2 into C_2-oxygenated products.

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† The terminal and bridging carbonyl i.r. absorptions for $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ almost completely disappeared when the dispersed ZnO, TiO_2, and γ-Al_2O_3 discs were evacuated at 120—180 °C for 0·5 h.

‡ With the exception of ZnO, all the metal oxides employed were almost inactive for the CO–H_2 reaction under atmospheric pressure at 150—300 °C. A small amount of methanol (with methane) was produced in 125 h at 280 °C when CO (20 cmHg) and H_2 (45 cmHg) were circulated over ZnO (20 g, Kadox 25) powder.

§ The distributions of hydrocarbons (C_1–C_4) over the pyrolysed Rh cluster on silica and alumina were almost same as those reported for the Rh–Al_2O_3 catalyst (M. A. Vannice, *J. Catalysis*, 1975, **37**, 462).

¶ Tauster *et al.* recently reported (*J. Amer. Chem. Soc.*, 1978, **100**, 170) that noble metal catalysts supported on TiO_2 chemisorbed both H_2 and CO when reduced below 200 °C, but not when reduced at 500 °C. Presumably the activity of the supported Rh catalysts in the CO–H_2 reaction might be influenced by the temperature of the hydrogen reduction. By using $RhCl_3$-derived catalyst reduced below 200 °C, a realistic comparison between the activities in the CO–H_2 reaction of the Rh cluster- and $RhCl_3$-derived catalysts is now being studied.

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[2] U.S. P. 3,878,214, 3,878,290 and 3,878,292 (1975).
[3] S. Martinengo and P. Chini, *Gazzetta*, 1972, **102**, 344; V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W. M. Anker, *J.C.S. Chem. Comm.*, 1975, 895.