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Catalysis by Supported Metal Crystallites from Carbonyl Clusters. I. Catalytic Methanol Synthesis under Mild Conditions over Supported Rhodium, Platinum, and Iridium Crystallites Prepared from Rh, Pt, and Ir Carbonyl Cluster Compounds Deposited on ZnO and MgO

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Methanol synthesis by the catalytic hydrogenation of carbon monoxide proceeded under atmospheric pressure and at 150—250 °C over rhodium, platinum and iridium crystallite catalysts, prepared from well-defined Rh, Pt, and Ir carbonyl cluster compounds highly dispersed on ZnO and MgO. The activity and selectivity of methanol formation depended considerably on the kind of metal carbonyl clusters and metal oxides employed as inorganic carriers. The catalysts prepared by the pyrolysis of smaller Rh, Pt, and Ir carbonyl clusters on ZnO, MgO, CaO, and BeO exhibited a higher selectivity of methanol synthesis. A small amount of ethanol was also produced besides methanol in CO–H_2 reaction over the pyrolysed catalysts of Rh carbonyl clusters on MgO, CaO, and BeO. Other metal oxides such as SiO_2 gel, γ-Al_2O_3, SnO_2, and WO_2 were employed for preparation of the dispersed Rh catalysts from carbonyl clusters, which catalysed mainly formation of methane and higher hydrocarbons with negligible selectivity of the oxygenated products under the reaction conditions.

The dispersion of metal plays, in many cases, an important role in exhibiting high activity and selectivity of metal supported catalysts. The proportion and fraction of metal atoms in the dispersed metal aggregates present on surface depend on the system and conditions of catalyst preparation. Various devices have been proposed for the preparation of highly dispersed metal, such as in the conventional impregnation methods and ion exchange methods.[1] In some cases, molecular metallic cluster compounds have been used as specific precursors for the generation of dispersed metal aggregates.[2] The pyrolysed Pt_3–Pt_{15} carbonyl clusters deposited on γ-Al_2O_3 or silica gel catalyse the selective dehydrocyclization of hexane, the particle size of which being conventionally estimated to be down to 10 Å.[3]

The work has been extended to rhodium, platinum and iridium crystallites similarly prepared on ZnO and MgO from the corresponding carbonyl clusters which catalysed selective methanol synthesis from CO and H_2 under atmospheric pressure. The rates and selectivity of methanol formation have been measured by changing the reaction conditions and preparation of the catalysts uning various carbonyl clusters and metal oxides as inorganic carriers.

Experimental and Procedures

The catalyst preparation and reaction of CO and H_2 were carried out in a closed circulating glass reactor (total volume 420 ml) operating in a continuous circulating flow mode. Analysis of the 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) columns for alcohol and water, alumina–DMF (38 wt%) 4 m (0 °C He carrier) for C_2—C_5 hydrocarbons and active carbon 1 m (25 °C) for CH_4, CO, and H_2 in the gas phase. Highly pure hydrogen and CO were used from the respective cylinders. Alcohols and water produced were separately obtained at the cooling part equipped with a Dry Ice trap in the circulating reaction systems. $Rh_4(CO)_{12}$ was synthesized by the method of Chini and Matinengo[4] and identified by the IR carbonyl absorption of its hexane solution and by mass spectrometry. $Rh_2(\pi$-$C_5H_5)_2(CO)_3$ was prepared from $Rh(\pi$-$C_5H_5)(CO)_2$ by prolonged UV illumination (with a high pressure Hg lamp) of hexane solution at 25 °C under N_2 atmosphere, and purified by recrystallization.[5] The deep-red crystal was identified with with $Rh_2(\pi$-$C_5H_5)_2(CO)_3$ from its IR spectra in solid and solution, and by mass spectrometry. $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ (Strem Chem. Co.,) were used without purification. The trigonal prismatic carbonyl cluster salts $[Pt_3(\mu_2\text{-}CO)_3(CO)_3]_n$ $2NR_4$ (n=3, 4, and 5, R=C_2H_5 and n-C_4H_9) were separately obtained by the reaction with alkaline–methanol solution of $PtCl_6^{2-}$ under CO atmosphere in a similar way to that described[3] and isolated as tetra-alkylamine salts, which were stored under inert atmosphere in ampoules. $Rh_{13}(CO)_{23}H_{2-3}2N(C_4H_9)_4$ was synthesized by the method of Albano *et al.*[6] by the reaction with $Rh_{12}(CO)_{30}2N(C_4H_9)_4$ under hydrogen atmosphere and identified by IR carbonyl absorption of is tetrahydrofuran solution. The carbonyl clusters were deposited in high dispersion from the solution onto the metal oxides such as ZnO, MgO, CaO, BeO, SiO_2 gel and γ-Al_2O_3 powders. The entire procedure was performed in a vacuum or inert atmosphere of He and N_2. Pyrolysis of each dispersed metal carbonyl cluster compound on various oxides proceeded in a vacuum or hydrogen atmosphere by raising the temperature up to 180—200 °C in order to remove CO and the pyrolysed organic residues. The infrared spectra of the Rh and Pt carbonyl clusters on metal oxides were recorded in the range 2200—1600 cm^{-1} with a Hitachi EPI-G3 grating spectrometer.

Results and Discussion

Catalytic Hydrogenation of CO over the Supported Rh Crystallites on ZnO and MgO Prepared by Pyrolysis of $Rh_4(CO)_{12}$. $Rh_4(CO)_{12}$ was deposited from hexane solution onto zinc oxide (Kadox 25 ZnO from New Jersey Co. 22 m^2/g) and magnesium oxide powders, (MgO Merck Chem. Co., 99.9%, 34 m^2/g) evacuated at 320 °C for 15 h prior to use. The solvent was removed by evaporation at room temperature. Removal of CO was accomplished by heating the material charged in a Pyrex-reactor at 160 °C for 2 h *in vacuo* (10^{-3}—10^{-4}

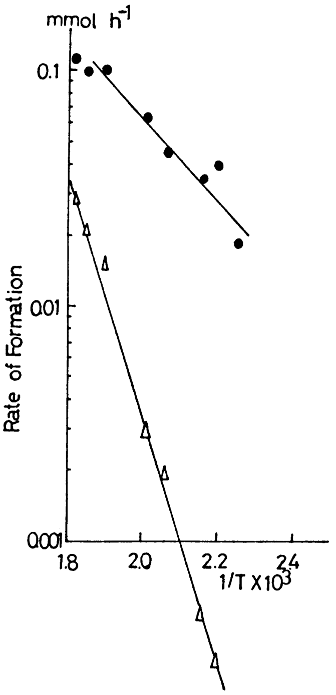

Fig. 1a. Arrhenius plots of methanol and methane formation over the pyrolysed catalyst on ZnO prepared from $Rh_4(CO)_{12}$. $Rh_4(CO)_{12}$ 0.11 g (0.15 mmol) and ZnO (Kadox 25) 20 g, 0.75% Rh wt dispersion. The volume of the reactor was 320 ml. CO: H_2=15 cmHg: 45 cmHg.
-●-: Formation of methanol (mmol/h),
-△-: formation of methane (mmol/h).

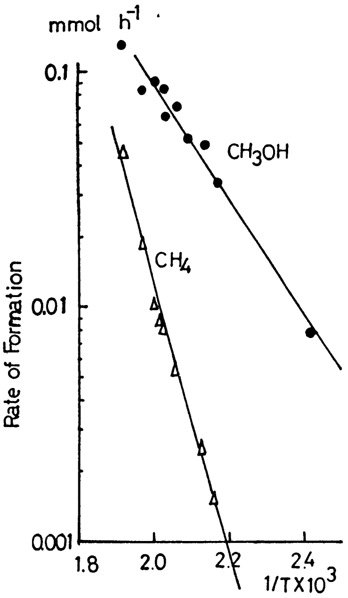

Fig. 1b. Arrhenius plots of methanol and methane formation over the pyrolysed catalyst on MgO prepared from $Rh_4(CO)_{12}$. $Rh_4(CO)_{12}$ 0.11 g (0.15 mmol) and MgO 20 g, 0.75% Rh wt dispersion. The volume of the reactor was 320 ml. CO: H_2=20 cmHg and 45 cmHg.
-●-: Formation of methanol (mmol/h),
-△-: formation of methane (mmol/h).

mmHg). The desorption of CO from the dispersed $Rh_4(CO)_{12}$ on ZnO and MgO proceeded sharply under He flow (1 atm 45 ml/min) in the temperature range 125—135 °C. This was confirmed by temperature-programmed technique using gas chromatography with active-carbon 1 m column. The infrared spectra of $Rh_4(CO)_{12}$ dispersed on ZnO were measured before and after the heattreatment *in vacuo*, and by introducing CO onto it. The sample wafer for infrared study was prepared by pressing the supported $Rh_4(CO)_{12}$ on Kadox 25 ZnO (1.8 Rh wt% dispersion) in a 2 cm diameter die and area force of 500 kg/cm^2. The IR spectra of the sample showed strong bands at 2050 and 1845 cm^{-1}, assigned to the terminal and bridged carbonyl absorptions, respectively, of the corresponding carbonyl cluster in solution and in crystal.[7] Both carbonyl bands completely disappeared by evacuation of the sample wafer at 120—150 °C for 1 h, probably due to desorption of CO. After evacuation 10—250 mmHg of CO was admitted at 25 °C, a broad and intense bands at 2000 and 1840—1870 cm^{-1} being observed. After pyrolysis, a mixture of CO and H_2 (molar ratio 1 : 2 under total pressure of 45—65 cmHg) was introduced onto the pyrolysed catalysts at 150—250 °C, methanol being catalytically obtained after some induction period (*ca.* 5 h) in Dry-Ice cooling part of the circulating reactor. A small amount of methane was formed in gas phase. Carbon dioxde and C_2—C_5 hydrocarbons were detected in a minute quantity in the reaction products over these catalysts. The material balance of the methanol and methane produced was confirmed by means of the total amount of consumed CO through the reaction. The rates of methanol and methane formation over the pyrolysed catalysts were found to obey approximately the first order kinetics in each run, after the stationary state of the reaction was realized. The initial rates of methanol and methane formation (mmol/h) over the pyrolysed $Rh_4(CO)_{12}$ on ZnO and MgO were plotted against the reaction temperature (Figs. 1a and 1b). The apparent activation energies of methanol and methane formation were estimated at 11—12 kcal/mol and 32—37 kcal/mol, respectively, in the given temperature range. The selectivity of methanol synthesis over the catalysts was over 90% per CO consumed at 180—220 °C. Magnesium oxide was completely inactive for methanol synthesis under the reaction conditions. A small amount of methanol and methane was only detected over ZnO powder (Kadox 25 or 99.9% purity zinc oxide from Kishida Chem. Reagent Co.) at 260 °C in 125 h when CO (20 cmHg) and H_2 (45 cmHg) was admitted onto it, after the prolonged hydrogen reduction. A small amount of ethanol besides methanol was catalytically produced in CO–H_2 reaction over the pyrolysed $Rh_4(CO)_{12}$ catalyst dispersed on MgO. At temperatures above 220 °C, methane formation proceeded considerably, the proportion of ethanol and C_2—C_4 hydrocarbons slightly increasing (Table 1). Methane and C_2—C_4 hydrocarbons were markedly suppressed by increasing the CO/H_2 molar ratio from 0.2 to 2.0 under a constant total pressure.

Selectivity of Methanol Synthesis over the Rh Crystallite

Table 1. Product distribution in CO–H_2 reaction over pyrolysed catalysts on MgO prepared from $Rh_4(CO)_{12}$

CO	H_2 (cmHg)	T (°C)	CO conv. in 10 h (%)	Product distribution (mmol in 10 h)[a]							Methanol[b] select. (%)
				CH_3OH	C_2H_5OH	O.P.	CH_4	C_2	C_3	C_4	
20	45	195	18.9	0.69	0.002	—	0.026	—	—	—	95.8
20	45	220	25.7	0.88	0.008	—	0.076	+	+	—	91.7
20	45	235	32.9	0.98	0.023	—	0.18	0.008	0.006	0.001	78.4
20	45	245	49.7	1.3	0.035	—	0.45	0.01	0.008	0.002	69.5
30	38	220	20.9	1.1	0.006	—	0.045	—	—	—	96.0
40	22	220	5.7	0.40	0.003	—	0.025	—	—	—	94.1
10	35	220	57.4	0.96	0.010	—	0.12	+	+	—	89.0

a) O.P.: other oxygenated products. $C_2=C_2H_4+C_2H_6$, $C_3=C_3H_6+C_3H_8$, $C_4=C_4H_8+C_4H_{10}$ (+) less than 0.001 mmol (—) negligible. b) (Methanol)/(CO consumed) × 100 (%).

Catalysts Prepared from Various Rh Carbonyl Clusters Deposited on ZnO. Rhodium carbonyl clusters such as $Rh_2(\pi\text{-}C_5H_5)_2CO)_3$, $Rh_6(CO)_{16}$ and $Rh_{13}(CO)_{23}H_{2-3}$-$2N(C_4H_9)_4$ were employed instead of $Rh_4(CO)_{12}$ to disperse Rh crystallite on ZnO. $Rh_2(\pi\text{-}C_5H_5)_2(CO)_3$ (0.10 g) was deposited from a hexane solution on ZnO (20 g from Kishida Chem. Reagent Co.,) and pyrolysed under hydrogen atmosphere at 180 °C for 2 h in order to remove CO and cyclopentadiene residue. $Rh_6(CO)_{16}$ and $Rh_{13}(CO)_{23}H_{2-3}2N(C_4H_9)_4$ were dispersed from tetrahydrofuran solutions onto ZnO powders (Kadox 25 and Kishida Chem. Reagent Co.,) and pyrolysed *in vacuo* by raising the temperature up to 180 °C and treated with hydrogen at 200 °C for 2 h. When a CO–H_2 mixture reactant was admitted onto the pyrolysed catalysts, methanol was catalytically produced with a small amount of methane at 180 and 250 °C. The rates and selectivity of methanol formation over the Rh crystallite catalysts prepared from various Rh carbonyl clusters were measured in the stationary state of reaction. The results are summarized in Table 2. The optimal yield of methanol was obtained over the catalysts by pyrolysis of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. The relative activity of methanol formation (mmol/h·g_{Rh}, g_{Rh}=Rh weight) varied with the kind of rhodium carbony cluster employed:

$$Rh_3(\pi\text{-}C_5H_5)_2(CO)_3 < Rh_4(CO)_{12} < Rh_6(CO)_{16} < Rh_{13}(CO)_{23}H_{2-3}2N(C_4H_9)_4$$

For comparison, the conventional Rh metal catalyst was prepared from impregnated $RhCl_33H_2O$ on ZnO (Kadox 25) in 1.0 and 2.5 Rh wt% loading followed by hydrogen reduction (1 atm 350 °C 10 h). The resulting Rh catalyst catalysed mainly methane formation with less than 15% selectivity.

Catalytic Hydrogenation of CO over the Rh Crystallites Deposited on Various Metal Oxides. A number of metal oxides were found to act as alternative carriers such as BeO and CaO. $Rh_4(CO)_{12}$ was deposited from a hexane solution over BeO (Merck Co., 99.99% purity) and CaO powders, (Merck Co., 99.9%) which were preheated *in vacuo* at 320 °C for 15 h. After pyrolysis of the substance *in vacuo* at 160 °C, the CO–H_2 reaction was carried out in the circulating reactor. Methanol was selectively, obtained but with lower CO conversion, over the pyrolysed catalyst on CaO at 200—260 °C. Over the Rh crystallites on BeO, methanol and a trace of ethanol were formed but with lower methanol selectivity. Typical results of catalytic hydrogenation of CO over the catalysts on CaO, and BeO are summarized in Table 3. For comparison, other metal oxides such as SiO_2 gel (AEROSIL-300, Yokohama Aerosil Co., 300 m²/g), γ-Al_2O_3 (A-11, Harshaw Co.,

Table 2. Methanol synthesis over pyrolysed catalysts on ZnO prepared from various Rh carbonyl cluster compounds

Catalyst	T (°C)	Product distribution (mmol in 10 h)						CO conversion (% in 10 h)	Methanol selectivity (%)
		CH_3OH	C_2H_5OH	CH_4	C_2	C_3	C_4		
$Rh_2Cp_2(CO)_3$–ZnO(I) (0.10 g) (20 g)	220	0.23	0	0.006	0	0	0	6.2	97.4
	250	0.48	0	0.03	0	0	0	13.4	94.1
$Rh_4(CO)_{12}$–ZnO(I) (0.11 g) (20 g)	220	0.63	0	0.03	0	0	0	17.4	95.4
	250	1.12	0	0.27	0	0	0	36.5	80.6
$Rh_4(CO)_{16}$–ZnO(I) (0.10 g) (20 g)	220	0.56	0	0.006	0	0	0	14.8	98.9
	250	0.84	0	0.18	0	0	0	26.8	82.4
$Rh_6(CO)_{16}$–ZnO(II) (0.10 g) (20 g)	220	0.42	0	0.01	0	0	0	11.3	97.6
	250	0.68	0	0.15	0	0	0	21.8	81.9
$Rh_{13}(CO)_{23}H_{2-3}2NBu_4$ –ZnO(I) (0.12 g) (20 g)	220	0.25	0	0.08	0	0	0	8.7	75.7
	250	0.36	0	0.35	0	0	0	18.7	50.7

ZnO(I) Kadox 25 New Jersey Co. ZnO(II) Kishida Chem. Reagent Co. CO (20 cmHg) and H_2 (45 cmHg). The volume of the closed circulating reactor was 320 ml.

Table 3. Product distribution in CO–H_2 reaction over pyrolysed catalysts of $Rh_4(CO)_{12}$ dispersed on various metal oxides

Catalyst	T (°C)	Product distribution (mmol in 10 h)							CO conv. (% in 10h)	Methanol select. (%)
		CH_3OH	C_2H_5OH	O.P.[a]	CH_4	C_2	C_3	C_4		
$Rh_4(CO)_{12}$–BeO	225	0.36	0.01	—	0.20	—	—	—	15.4	68.3
(0.12 g) (20 g)	240	0.45	0.04	—	0.44	—	—	—	24.3	49.2
$Rh_4(CO)_{12}$–CaO	232	0.30	0.001	—	0.003	—	—	—	8.0	98.6
(0.12 g) (20 g)	250	0.51	0.003	—	0.010	—	—	—	14.2	98.1
$Rh_4(CO)_{12}$–SiO_2	220	0.005	0.023	+	0.49	0.015	0.035	0.006	23	0.6
(0.12 g) (5 g)	235	0.026	0.013	+	0.57	0.039	0.038	0.010	27	3
$Rh_4(CO)_{12}$–γ-Al_2O_3	220	0.004	0.002	—	1.18	0.16	0.13	0.053	54.6	0.2
(0.12 g) (20 g)	250	+	+	—	2.2	0.20	0.16	0.05	86	—

CO: H_2 = (15 cmHg: 50 cmHg). The volume of the reactor was 420 ml. a) A trace of CH_3CHO, C_3H_7OH, and C_4H_9OH was detected in the oxygenated products.

280 m^2/g), SnO_2 (Nakarai Chem. Co., 99.9% purity) WO_3 (Nakarai Chem. Co., 99.9%) and V_2O_5 (Kishida Chem. Reagent Co., 99.9% purity) were employed to prepare the dispersed Rh catalysts by the pyrolysis of $Rh_4(CO)_{12}$. All the pyrolysed catalysts produced mainly methane with lower CO conversion in CO–H_2 reaction. Over the catalysts on SiO_2 and γ-Al_2O_3, a trace of methanol and ethanol was detected in the condensed products at temperatures above 200 °C. The pyrolysed catalysts on other metal oxides such as SnO_2, WO_3, and V_2O_5 yielded a negligible amount of methanol or other oxygenated products. At elevated temperatures methane was obtained in a large amount over these catalysts. The metal oxides used in the experiments were completely inactive for CO hydrogenation. This suggests that the reactivities of the supported Rh crystallites from carbonyl clusters are markedly dependent on the kind of metal used as inorganic carrier. The basic metal oxides such as ZnO, MgO, CaO, and BeO were found to be the optimal carriers to prepare highly selective Rh crystallite catalysts for methanol synthesis under mild reaction conditions.

Catalytic Hydrogenation of CO over the Supported Platinum and Iridium Crystallites on ZnO and MgO Prepared by Pyrolysis of the Carbonyl Cluster Compounds. Pt carbonyl cluster anion salts such as $Pt_9(CO)_{18}2NEt_4$ and $Pt_{15}(CO)_{30}2NEt_4$ were dispersed from tetrahydrofuran solutions onto ZnO and MgO powders in 0.5—1.0 Pt wt% loading. After removal of the solvent at room temperature, the resulting substance charged in the closed circulating Pyrex-reactor (*ca.* 420 ml) was heated *in vacuo* up to 180 °C. The desorption of CO from each dispersed Pt carbonyl cluster salt proceeds almost completely in a vacuum or H_2 flow (1 atm).[3] This was confirmed by temperature-programmed technique using gas chromatography and mass spectrometry. The desorption temperatures of the Pt clusters on γ-Al_2O_3 and ZnO were 150 °C for $Pt_{15}(CO)_{30}2NEt_4$ and 165 °C for $Pt_9(CO)_{18}2NEt_4$, respectively. The hydrogenation of CO took place reproducibly at 180—250 °C by introducing a CO–H_2 (1 : 2 molar ratio) gas onto the pyrolysed catalysts. Methanol was also catalytically produced with a small amount of methane. Ethanol and higher hydrocarbons (C_2—C_4) were detected in a negligible amount in the reacton. The methanol yields per Pt weight over the catalyst on MgO were higher than that on ZnO under similar reaction conditions. For comparison, the conventional Pt metal catalyst was prepared from the impregnated H_2PtCl_6 on ZnO (Kadox 25) in 2.5 Pt wt% loading, followed by hydrogen reduction at 350 °C for 15 h. The resulting catalyst showed considerably lower CO conversion, producing mainly methane with less than 5% selectivity of methanol formation in CO–H_2 reaction under atmospheric pressure.

$Ir_4(CO)_{12}$ was dissolved in tetrahydrofuran, and

Table 4. Product distribution in CO–H_2 reaction over pyrolysed catalysts on ZnO and MgO prepared from Pt and Ir carbonyl cluster compounds

Catalyst	T (°C)	CO conv. (% in 10 h)	Product distribution (mmol 10 h)						Methanol select. (%)
			CH_3OH	C_2H_5OH	CH_4	C_2	C_3	C_4	
$Pt_9(CO)_{18}2NEt_4$–ZnO	220	5.7	0.19	—	0.01	—	—	—	95
(0.17 g) (20 g)	260	6.9	0.24	—	0.015	—	—	—	94
$Pt_{15}(CO)_{30}2NEt_4$–ZnO	240	3.2	0.12	—	+	—	—	—	99
(0.15 g) (20 g)	260	5.4	0.20	—	0.005	—	—	—	98
$Pt_{15}(CO)_{30}2NEt_4$–MgO	170	13.9	0.48	+	0.006	—	—	—	98
(0.28 g) (20 g)	200	26.3	0.89	0.003	0.012	—	—	—	98
$Ir_4(CO)_{12}$–ZnO	240	2.2	0.072	—	0.011	—	—	—	87
(0.10 g) (20 g)	270	8.6	0.18	—	0.051	—	—	—	78
$Ir_4(CO)_{12}$–ZnO	270	0.5	0.005	—	0.015	—	—	—	25
(0.10 g) (20 g)	305	1.2	0.006	—	0.037	—	—	—	14

CO: H_2 = 15: 45 cmHg. The volume of the reactor was 420 ml. (+) denotes less than 0.001 mmol.

deposited on 20 g of ZnO or MgO powder. On coming in contact with MgO powder, the pale-yellow solution of $Ir_4(CO)_{12}$ turned deep-red, probably due to the formation of Ir_6-carbonyl clusters such as $Ir_6(CO)_{15}^{2-}$ salt[8] completely adsorbed on MgO. Removal of CO, after evaporating the solvent, was accomplished *in vacuo* at 180 °C for 2 h. Methanol was catalytically produced at higher temperatures above 240 °C after a long induction period over the pyrolysed Ir crystallite catalyst on ZnO. No ethanol and higher hydrocarbons were obtained in CO–H_2 reaction over Ir crystallite catalyst. The catalyst prepared by pyrolysis of $Ir_4(CO)_{12}$ on MgO gave a trace of methanol for the oxygenated product, and mainly methane from CO–H_2 mixture reactant. Typical results of methanol synthesis over the Pt and Ir crystallite catalysts are summarized in Table 4. It is suggested that the pyrolysed catalysts of Pt and Ir carbonyl clusters on ZnO and MgO also catalyse methanol synthesis under atmospheric pressure, although the specific methanol conversions were relatively lower than those from Rh carbonyl clusters. The activity and selectivity of methanol formation in CO–H_2 reaction depend on the catalyst preparation by selecting metal carbonyl clusters as well as metal oxides as inorganic carriers.

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