Catalysis by Supported Metal Crystallites from Carbonyl Clusters. II. Catalytic Ethanol Synthesis from CO and H_2 under Atmospheric Pressure over Supported Rhodium Crystallites Prepared from Rh Carbonyl Clusters Deposited on TiO_2, ZrO_2, and La_2O_3

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Ethanol was catalytically produced in the CO–H_2 reaction under atmospheric pressure and at 150—250 °C over rhodium crystallite catalysts prepared from Rh carbonyl cluster compounds highly dispersed on La_2O_3, TiO_2, and ZrO_2. The activity and selectivity of ethanol formation depend on the kind of metal carbonyl cluster and metal oxide used as inorganic carriers. The catalysts prepared by the pyrolysis of smaller Rh carbonyl clusters such as $Rh_2(C_5H_5)_2(CO)_3$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$ on La_2O_3, TiO_2, and ZrO_2 show higher selectivity of the oxygenated products containing ethanol (main), acetaldehyde, and methanol. The ethanol contents in the oxygenated products increased considerably above 200 °C over the catalysts. CeO_2 and ThO_2 were also employed in the preparation of the pyrolysed catalysts to disperse the Rh carbonyl clusters, which catalyses the ethanol formation in the CO–H_2 reaction at atmospheric pressure.

The catalytic synthesis of hydrocarbons and oxygen-containing compounds from CO and H_2 (Fischer-Tropsch synthesis and synthesis of alcohols) is of interest from both a practical and theoretical point of view.[1)] The conventional metal catalysts containing Fe and Co are not selective, exhibiting considerably broad spectra of the product distribution. The formation of hydrocarbons and alcohols from CO–H_2 mixture is thermodynamically favorable, although higher pressures (in excess of 1 atm) are necessary to facilitate the formation of higher molecular weight products. It is important to study the surface reactions in catalytic hydrogenation of CO over supported metal catalysts to control rates and selectivity for the possible products in connection with the surface composition of the catalysts. The purpose of this study is to correlate the reactivities of highly dispersed noble metal catalysts in the CO–H_2 reaction with their chemical compositions, being associated with the dispersion of metal and composition on the surface, which depend on the systems and conditions of ctalyst preparations. The author has developed a method for the preparation of the dispersed metal crystallites on various metal oxides by using molecular metallic cluster compounds as specific precursors.[2)] Recently, Muetterties and others[3)] demonstrated that the metal carbonyl clusters such as $Ru_3(CO)_{12}$ and $Ir_4(CO)_{12}$ slowly produce methane and higher hydrocarbons in homogeneous hydrogenation of CO at 140—200 °C and 1—2 atm. The supported Rh, Pt, and Ir crystallites on ZnO and MgO prepared from the carbonyl clusters catalyse a selective methanol synthesis in catalytic hydrogenation of CO under atmospheric pressure.[4)] In this paper, a report is given on the direct catalytic ethanol formation from CO–H_2 mixture at atmospheric pressure over the Rh crystallites prepared from the carbonyl clusters deposited on specific metal oxides such as TiO_2, ZrO_2, and La_2O_3. The rates and product distribution in the CO–H_2 reaction over the supported Rh crystallite catalysts were observed by changing the reaction conditions and catalyst preparation using various Rh carbonyl cluster compounds and metal oxides as inorganic carriers.

Experimental

The catalyst preparation and CO–H_2 reaction were carried out in a closed circulating glass-reactor. Experiments were performed under atmospheric pressure in a pyrex glass tubular reactor operating in continuous flow in order to measure the one-path yields and selectivity of the reaction through the fixed-bed catalysts. Analysis of the oxygenated products and hydrocarbons was carried out by gas chromatography using Porapak Q, PEG 1500, alumina–DMF and active carbon columns, as reported.[4)] The oxygenated products in the CO–H_2 reaction were separately obtained in the condensed part with a Dry-Ice cooling trap in the circulating reactor. In the continuous flow reaction system, the gaseous product was collected at intervals in a glass flask containing water and analyzed by FID (Hitachi-FD6) gas chromatography with a 4 m PQ column. The rhodium carbonyl cluster compounds such as $Rh_2(C_5H_5)_2(CO)_3$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$ and Rh_{13}-$(CO_{23}H_{2-3}2NBu_4$ were obtained.[4)] $Rh_7(CO)_{16}3NEt_4$ was synthesized in the reaction with $Rh_4(CO)_{12}$ under CO atmosphere by the method of Martinengo and Chini[5)] and isolated as tetra ethylammonium salt, which was stored in a glass ampoule under He atmosphere. The Rh carbonyl clusters were deposited in high dispersion from their solutions onto the metal oxides such as La_2O_3, CeO_2, TiO_2, ZrO_2, and ThO_2. The removal of CO and residual organics (amines and cyclopentadiene) was accomplished in a vacuum or H_2 atmosphere by heat treatment of the supported samples. The procedure of catalyst preparation was carried out *in vacuo* or under an inert atmosphere of He and N_2 because of air-sensitivity of the carbonyl cluster compounds.

Results and Discussion

Catalytic Etanol Formation from CO and H_2 over the Rh Crystallites on La_2O_3 Prepared from $Rh_4(CO)_{12}$.　0.11 g of $Rh_4(CO)_{12}$ was deposited from a hexane solution onto 20 g of lanthanum oxide (La_2O_3, 99.9% purity, Nakarai Chem. Reagent Co.,) which was evacuated at 320 °C for 13 h prior to use. The solvent was then removed by evaporation at room temperature. The sample pellets

Table 1. Product distribution in CO–H_2 reaction over the pyrolysed catalyst on La_2O_3 prepared from $Rh_4(CO)_{12}$

CO (cmHg)	H_2 (cmHg)	T (°C)	CO conv. (% in 5 h)	Product distribution (mmol in 10 h)							
				CH_3OH	C_2H_5OH	CH_3CHO	CH_3COOCH_3	CH_4	C_2	C_3	C_4
20	45	170	7.2	0.165	0.036	–	–	0.10	+	+	–
20	45	195	11.3	0.38	0.19	+	–	0.068	0.002	0.008	+
20	45	205	15.2	0.62	0.36	+	–	0.17	0.005	0.013	+
20	45	225	36.4	0.74	1.12	+	–	0.56	0.026	0.082	0.026
15	48	195	14.6	0.32	0.21	+	–	0.11	+	0.008	+
30	35	195	5.9	0.20	0.19	+	–	0.038	+	+	+

The volume of the reactor was 320 ml. + denotes less than 0.001 mmol in 10 h.

(*ca.* 5—10 mesh) for the CO–H_2 reaction were prepared by pressing the supported material under pressure of 400 kg/cm^2, and charged in a Pyrex glass reactor. Desorption of CO from the supported $Rh_4(CO)_{12}$ sample proceeded under evacuation (10^{-3}—10^{-4} mmHg) by raising the temperature upto 180 °C for 2 h. After pyrolysis, a mixture of CO and H_2 (molar ratio 1 : 1—2 under total pressure of 45—65 cmHg) was circulated with *ca.* 50 ml/min flow rate through the catalyst pellets. The oxygenated products containing C_2H_5OH, CH_3CHO, and CH_3OH were catalytically obtained in a certain induction period (*ca.* 5 h) at 150—250 °C. Methane and a small amount of C_2—C_4 hydrocarbons were also formed in gas phase. The reproducible rates of the oxygenated products and hydrocarbons were measured by changing the reaction temperatures and ratios of CO to H_2 partial pressure in a wide range. Typical results are summarized in Table 1. The carbon efficiency of oxygenated products per CO consumed was between 60 and 90% over the pyrolysed catalyst in the temperature range 150—200 °C. At temperatures below 190 °C, methanol contents in the oxygenated products were relatively high, the yields of ethanol increasing considerably with temperature rise above 200 °C. The apparent activation energy of methanol, ethanol and methane formation was estimated at 11, 20, and 28 kcal/mol, respectively. At higher CO/H_2 ratios of the mixture gas, the formation of C_1—C_4 hydrocarbons was suppressed and ethanol selectivity increased comparatively, although total CO conversion decreased. It should be noted that lanthanum oxide as an inorganic support was completely inactive for the CO–H_2 reaction at 120—320 °C, even after prolonged heat treatment under hydrogen.

Hydrogenation of CO over the Rh Crystallites on La_2O_3 Prepared from Various Rh Carbonyl Clusters. A number of Rh carbonyl cluster compounds, such as $Rh_2(C_5H_5)_2(CO)_3$, $Rh_6(CO)_{16}$, $Rh_7(CO)_{16}3NEt_4$, and $Rh_{13}(CO)_{23}2NBu_4$ were employed instead of $Rh_4(CO)_{12}$, as precursors in the preparation of pyrolysed catalysts on lanthanum oxide. Each carbonyl cluser compound (0.10 g) was deposited onto the La_2O_3 powder (20 g) from the solution of tetrahydrofuran ($Rh_6(CO)_{16}$ and $Rh_{13}(CO)_{23}H_{2-3}2NBu_4$) and of acetone ($Rh_7(CO)_{16}3NEt_4$). The supported material was loaded in the reactor of the closed circulating reaction system (total volume 420 ml). After pyrolysis at 180 °C for 2 h and hydrogen treatment at 200 °C for 1 h, the CO–H_2 reaction took place by circulation of a mixture gas (CO/H_2=*ca.* 0.5, 65 cmHg) over the catalysts. $Rh_2(C_5H_5)_2(CO)_3$ was dispersed on La_2O_3 from the hexane solution.

Decomposition of the supported cluster was accomplished under H_2 atmosphere (60 cmHg) at 180 °C for 2 h and evacuated for a few minutes. The rates and product distribution in a catalytic hydrogenation of CO were measured over these pyrolysed catalysts in the temperature range 150—250 °C. The reproducible results are given in Table 2. It was suggested that the pyrolysed catalysts from smaller Rh clusters such as Rh_2—Rh_6 exhibit a relatively higher selectivity of oxygenated products containing mainly ethanol and methanol. On the contrary, C_2—C_4 hydrocarbons were produced at higher contents of the products over the catalysts prepared from larger carbonyl clusters such as Rh_7—Rh_{13}. The composition in the oxygenated products exhibited almost the same spectra over all the pyrolysed Rh cluster catalysts. With a rise in the reaction temperature above 200 °C, the content of acetaldehyde in the products increased a little and C_2—C_4 hydrocarbons were produced with higher yields over the catalysts from larger Rh carbonyl clusters. It is of interest that the catalyst based on $Rh_2(C_5H_5)_2(CO)_3$ and La_2O_3 produced catalytically methyl acetate in the CO–H_2 reaction above 200 °C. The catalysts kept almost the same rates and selectivity of ethanol formation in prolonged runs of about 20 days. Accordingly, with Rh carbonyl clusters as precursors, the relative yields of ethanol per unit Rh weight changed over the pyrolysed catalysts on La_2O_3 in the order:

$$Rh_2(C_5H_5)_2(CO)_3 < Rh_4(CO)_{12} > Rh_6(CO)_{16} > Rh_7(CO)_{12}3NEt_4 > Rh_{13}(CO)_{23}H_{2-3}2NBu_4.$$

For comparison, the Rh catalyst was prepared conventionally by hydrogen reduction (350 °C 15 h) of the impregnated $RhCl_3$ on La_2O_3 (2.5% Rh weight loading) from the aqueous solution. When a CO–H_2 mixture was admitted onto the catalyst at 200 °C, a small amount of the oxygenated products containing ethanol and methanol was obtained after a long induction period of several days. The reproducible results in the CO–H_2 reaction over the catalyst showed relatively smaller CO conversion and lower selectivity of the oxygenated products. Methane and higher hydrocarbons were preferentially produced above 200 °C (Table 2). The results suggest that the Rh carbonyl clusters play the role of specific precursor to prepare the supported catalyst on La_2O_3, which catalyses the selective formation of oxygenated products in a CO hydrogenation

TABLE 2. PRODUCT DISTRIBUTION IN $CO–H_2$ REACTION OVER THE PYROLYSED CATALYSTS ON La_2O_3 PREPARED FROM VARIOUS Rh CARBONYL CLUSTER COMPOUNDS

Catalyst	T (°C)	CO conv. (% in 5h)	Product distribution in carbon efficiency[a)] (%)							
			CH_3OH	C_2H_5OH	CH_3 CHO	CH_3 $COOCH_3$	CH_4	C_2	C_3	C_4
$Rh_2Cp_2(CO)_3$–La_2O_3	220	1.9	25.6	54.8	3.0	0.8	13.3	1.0	2.2	+
(0.0 8g) (20 g)	250	8.5	2.9	50.3	2.4	4.4	29.4	9.6	6.6	1.5
$Rh_4(CO)_{12}$–La_2O_3	205	14.9	41.7	48.3	+	–	17.4	0.3	2.3	0.2
(0.10 g) (20 g)	224	36.4	20.2	61.1	+	+	11.9	0.8	4.4	1.3
$Rh_6(CO)_{16}$–La_2O_3	220	16.4	17.7	46.6	3.6	+	18.9	3.8	4.9	3.3
(0.10 g) (20 g)	242	25.5	10.3	45.8	1.5	+	25.9	6.5	7.9	2.0
$Rh_7(CO)_{16}3NEt_4$–La_2O_3	220	14.8	8.9	32.8	4.6	+	13.5	14.0	19.4	6.8
(0.10 g) (20 g)	240	20.1	4.6	13.8	3.0	+	26.0	18.6	26.0	8.2
$Rh_{13}(CO)_{23}H_{2-3}2NBu_4$–$La_2O_3$	225	15.5	6.4	28.9	2.4	+	22.5	19.8	19.8	6.6
(0.16 g) (20 g)	255	20.7	+	15.4	1.8	+	24.6	24.8	24.2	9.5
$RhCl_3$[b)]–La_2O_3	220	4.7	10.7	17.1	+	+	65.4	6.2	7.9	1.4
(0.13 g) (20 g)	240	6.5	8.1	8.5	+	+	45.7	12.8	19.0	5.7

$CO:H_2=20:45$ cmHg. a) Carbon efficiency$=(i\ Ci/\sum i\ Ci)\times 100$: i=carbon number of the product. b) The catalyst was reduced by hydrogen at 350 °C.

under mild reaction conditions.

Ethanol Formation in $CO–H_2$ Reaction over the Pyrolysed Catalysts of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ Deposited on TiO_2, ZrO_2, CeO_2, and ThO_2. Other metal oxides such as TiO_2, ZrO_2, CeO_2, and ThO_2 were found to act as promoters for ethanol formation in catalytic hydrogenation of CO over the supported Rh crystallite catalysts. $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ (0.10 g) were similarly deposited onto each metal oxide (TiO_2 99.9% Merck Co., ZrO_2 99.9% Nakarai Chem. Reagent Co., CeO_2 99.9% Wako Pure Reagent Co., and ThO_2 99.9% Kishida Chem. Reagent Co.,)[6)] 20 g from the solutions. The pressed pellets of the supported materials were charged in the closed circulating reactor (320 ml). After pyrolysis *in vacuo* at 180 °C for 2 h, a mixture of CO and H_2 was introduced and circulated at 150 and 250 °C. The oxygenated products containing mainly ethanol were produced in a wide temperature range over the pyrolysed catalysts. The reproducible rates and product distribution in the $CO–H_2$ reaction are given in Table 3. The product distribution illustrates a remarkable specificity for ethanol formation in the oxygenated products. The selectivity of the oxygenated products was relatively higher over the catalyst on ZrO_2 than that on TiO_2 and CeO_2, and gave comparatively smaller formation of C_1–C_4 hydrocarbons. The olefinic products of C_2—C_4 hydrocarbons increased considerably by employing the liquid nitrogen trap, instead of Dry-Ice cooling, to collect the hydrocarbon products at higher temperatures. The $CO—H_2$ reaction readily proceeded over the pyrolysed Rh carbonyl cluster catalysts on ThO_2 at 150—180 °C to produce the oxygenated products containing methanol and ethanol. By raising the temperature above 190 °C, the higher hydrocarbons such as C_5H_{12}, C_6H_{14}, and C_7H_{16}[7)] were considerably formed, and the yields of the oxygenated products decreased although CO conversion was very high. TiO_2 and ThO_2 may accelerate the condensation and dehydration of the oxygenated products at a catalyst surface. The product distribution and rates in the $CO–H_2$ reaction over the Rh crystallite catalysts markedly depend on the kind of metal oxide.[4)] The pyrolysed catalysts prepared from Rh carbonyl clusters on ZnO, MgO, BeO, and CaO (Ia and IIa metal

TABLE 3. PRODUCT DISTRIBUTION IN $CO–H_2$ REACTION OVER THE PYROLYSED CATALYSTS ON VARIOUS METAL OXIDES PREPARED FROM $Rh_4(CO)_{12}$

Catalyst	T (°C)	CO conv. (% in 5 h)	Product distribution in carbon efficiency (%)							
			CH_2OH	C_2H_5OH	CH_3CHO	O.P.[a)]	CH_4	C_2	C_3	C_4
$Rh_4(CO)_{12}$–TiO_2	195	42.2	8.2	47.1	+	+	19.9	6.1	11.7	6.9
(0.10 g) (20 g)	210	45.6	3.9	22.8	+	+	42.2	9.6	14.8	6.8
$Rh_6(CO)_{16}$–TiO_2	195	29.4	4.6	39.6	3.5	+	20.2	10.2	21.9	1.2
(0.10 g) (20 g)	210	38.4	4.8	33.3	0.8	+	29.9	4.5	16.2	9.8
$Rh_4(CO)_{12}$–ZrO_2	180	5.2	25.1	57.7	0.3	–	17.1	+	0.5	+
(0.10 g) (20 g)	215	23.3	14.8	47.0	0.6	–	34.3	0.8	1.2	0.7
$Rh_4(CO)_{12}$–ThO_2	160	15.2	9.6	50.9	+	+	12.5	4.6	17.7	4.6
(0.10 g) (20 g)	175	39.5	12.7	39.1	+	+	21.9	2.7	13.2	10.0
$Rh_4(CO)_{12}$–CeO_2	205	8.4	26.4	35.0	2.0	–	22.1	3.1	9.7	1.8
(0.10 g) (20 g)	238	19.5	10.4	38.8	2.2	–	27.1	6.8	10.2	4.4

$CO:H_2=20:45$ cmHg. The volume of the reactor was 320 ml. a) O.P.=other oxygenated products containing a small amount of C_3H_7OH and C_4H_9OH.

oxides) selectively produced methanol in the reaction. Ethanol and C_2-oxygenated products were obtained over the catalysts dispersed on La_2O_3 and CeO_2 (IIIa metal oxides) and TiO_2, ZrO_2, and ThO_2 (IVa metal oxides). In contrast, C_1—C_5 hydrocarbons (mainly methane) were preferentially produced with less than 5% selectivity of the oxygenated products (mainly ethanol) over the Rh crystallites on SiO_2 gel and γ-Al_2O_3 (IIIb and IVb metal oxides). Methane was selectively formed with lower CO conversion over the catalyst on SnO_2, V_2O_5, and P_2O_5 in the CO–H_2 reaction. It seems that the half-hydrogenated intermediates in catalytic hydrogenation of CO are influenced by the surface properties of the metal oxides dispersing Rh crystallites. Surface properties such as acidity or basicity of metal oxides might be correlated with product distribution in the CO–H_2 reaction over those supported Rh crystallite catalysts.

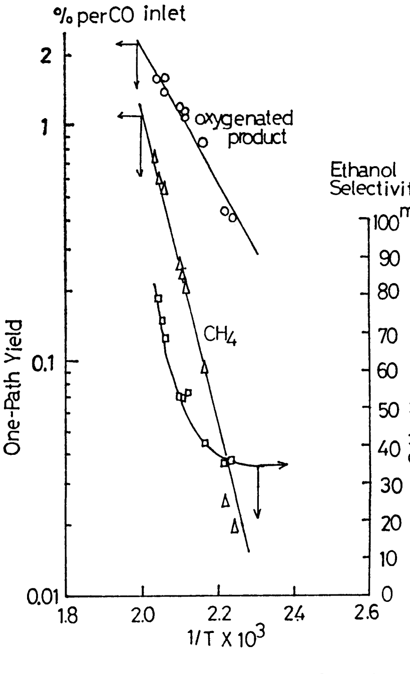

Fig. 1. Temperature dependency of methanol, ethanol, and methane formation over the pyrolysed catalyst on La_2O_3 prepared from $Rh_4(CO)_{12}$. $Rh_4(CO)_{12}$ 0.30 g (0.40 mmol) and La_2O_3 38 g, 0.43% Rh wt dispersion. Activated under hydrogen stream (1 atm, 40 ml/min) at 200 °C. CO(15 ml/min) and H_2 (40 ml/min). -○-: One-path yield (% per CO inlet) of the oxygenated products containing methanol and ethanol, -△-: one-path yield (% per CO inlet) of methane, -□-: mol % of ethanol in the oxygenated products produced. (ethanol)/(methanol)+(ethanol) × 100.

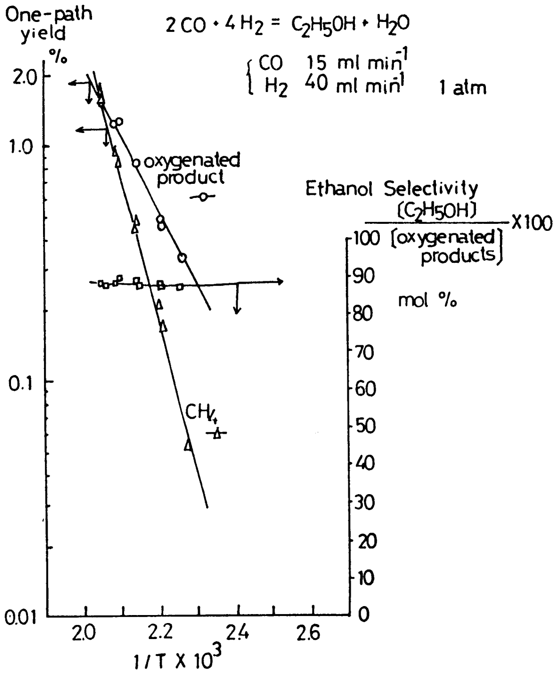

Fig. 2. Temperature dependency of the formation of oxygenated products and methane over the pyrolysed catalyst on TiO_2 prepared from $Rh_4(CO)_{12}$. $Rh_4(CO)_{12}$ 0.35 g (0.47 mmol) and TiO_2 38 g in 0.50 Rh wt % dispersion. Activated under hydrogen stream (1 atm, 40 ml/min). CO(15 ml/min) and H_2 (40 ml/min). -○-: One-path yield (% per CO inlet) of the oxygenated products containing ethanol, methanol and acetaldehyde, -△-: one-path yield (% per CO inlet) of methane, -□-: mol % of ethanol in the oxygenated products formed.

CO–H_2 Reactions in Continuous Flow System under Atmospheric Pressure over the Pyrolysed Catalysts Prepared from $Rh_4(CO)_{12}$ on La_2O_3 and TiO_2. The CO–H_2 reaction was carried out operating the continuous flow mode using a 50 cm Pyrex glass tubular reactor, 18 mm in diameter. A pellet catalyst (*ca.* 20 ml) of the supported $Rh_4(CO)_{12}$ on La_2O_3 or TiO_2 (in 0.5% Rh loading) was charged in the reactor, and 2 mm glass beads were packed above and below the catlayst bed. The reactor was placed vertically in an electric furnace. CO and hydrogen were supplied from the respective cylinders. After measuring the flow rates of CO and H_2 separately, the gases were mixed and brought to contact with the catalyst bed at the flow rates 30—100 ml/min. The gaseous product was transferred from the bottom of the reactor in a 100 ml flask containing water. The oxygenated products collected at intervals were analyzed by FID gas chromatography using PQ column, and C_1—C_4 hydrocarbons by alumina-DMF and active carbon columns. Removal of CO was accomplished by slow heating of the catalysts at 180—200 °C in a stream of pure hydrogen for 2 h. The 1 : 1—2 mixture of CO and H_2 was reacted at 180—250 °C. The stationary rates and product distribution of the reaction were attained in the continuous flow for 10 h at 200 °C. The one-path yields of methanol, ethanol, and methane were measured at various temperatures under constant space velocity. The results are shown in Figs. 1 and 2. The formation of other C_2-oxygenated products and C_2—C_4 hydrocarbons was negligibly small. The ethanol content in the oxygenated products was found to be almost constant over the pyrolysed catalyst on TiO_2 in a wide temperatures range. On the other hand, the ethanol content was markedly dependent on the reaction temperature over the catalyst on La_2O_3, increasing with rise in temperature. By increasing the ratios of CO/H_2 the selectivity of the oxygenated products increased and the C_1—C_4 hydrocarbon formation was suppressed considerably, as measured over the catalysts in the closed circulating reactor system.

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6) The metal oxides employed gave in a negligible amount the oxygenated products and hydrocarbons in the CO–H_2 reaction at elevated temperatures above 250 °C.

7) The oily products were analyzed by temperature-programmed gas chromatography using Polapak Q column.