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NOTES

The Influence of the Support on the Catalytic Behavior of Ruthenium in CO/H_2 Synthesis Reactions

Recent studies have shown that titania can have a significant influence on adsorptive properties of a metal component dispersed on its surface (*1*). In addition, titania-supported nickel has been found to exhibit a large increase in activity and a significant shift in selectivity in the CO hydrogenation reaction (*2*). This behavior has been attributed to a strong metal–support interaction (SMSI) and, as a consequence, we have looked at other supported metal systems to determine whether metal–support effects also appear to exist. Ruthenium, with one of the highest specific activities in the CO hydrogenation reaction, was another metal in which we were greatly interested. In this note we describe the results of our study to observe the influence of the support material, including carbon, silica, alumina, and particularly titania, on the activity and selectivity of ruthenium catalysts in the CO hydrogenation reaction.

The Ru/TiO_2 catalyst was prepared from titania (Cab-O-Ti) obtained from Cabot Corporation and the Ru/carbon catalyst was made using Carbolac-1 also obtained from Cabot Corporation. Carbolac-1 is an activated carbon with a surface area of 950 m^2 g^{-1}. The catalysts were prepared using an aqueous solution of $RuCl_3 \cdot 3H_2O$ (Englehard Industries, Inc.), which was added to the supports using an incipient wetness technique (*3*). The unsupported ruthenium was prepared from the same $RuCl_3 \cdot 3H_2O$ salt by precipitation with concentrated NH_4OH which was added dropwise to the vigorously stirred metal salt solution over a 0.5-hr period. The precipitate was filtered, washed with 2 liters distilled water, and dried in air at 393 K for 16 hr. The other catalysts, gases, and details of the preparative processes have been described previously (*1*, *3–5*).

The chemisorption system and the low- and high-pressure reactor systems have been described previously (*1*, *2*, *4*). The procedures used for the chemisorption and reactor studies, with the exception of those used for the 4% Ru/carbon catalyst and for unsupported Ru, have been described elsewhere (*1*, *2*, *4–7*). The same procedure was followed for 4% Ru/carbon except that the final temperature utilized for both reduction and evacuation was 673 K in order to reduce metal sintering. The unsupported ruthenium sample was heated stepwise in flowing dihydrogen to only 673 K and reduced 1 hr at this temperature. After the kinetic measurements had been made, the used sample, which was never exposed to air, was heated again in flowing dihydrogen for 1 hr at 603 K, then evacuated 1 hr at 593 K prior to chemisorption measurements. For consistency, the dual isotherm technique for CO was also used for unsupported ruthenium (*8*).

The chemisorption results in Table 1 represent uptakes for both fresh reduced catalysts and samples which had been used in kinetic studies. Extremely low CO/Ru and H/Ru ratios are readily apparent for 2% Ru/TiO_2; however, these low ratios could not be explained by the presence of large Ru crystallites as discussed previously (*1*). For example, X-ray diffraction measurements did not detect the presence of large crystallites in the titania-supported catalyst. For other ruthenium catalysts, X-ray diffraction patterns indicated the presence of large Ru crystallites commensurate with

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TABLE 1

Chemisorption on Ruthenium Catalysts

Catalyst	CO uptake (μmol g^{-1}) Fresh	CO uptake (μmol g^{-1}) Used	CO/Ru[a]	H_2 uptake (μmol g^{-1}) Fresh	H_2 uptake (μmol g^{-1}) Used	H/Ru[a]
2% Ru/TiO_2	—	7.2	0.036	3.0	1.3	0.013
5% Ru/Al_2O_3	35	28.5	0.058	17.4	14.3	0.058
5% Ru/SiO_2	102	55	0.11	110	174	0.70
4% Ru/Carbolac	160[b]	70	0.18	38[b]	36	0.18
Unsupported Ru	—	142	0.014	—	168	0.034

[a] For used samples following atmospheric pressure kinetic studies.

[b] Reduced at 400°C.

those expected from the CO/Ru and H/Ru ratios obtained for the fresh samples. The H_2 uptake for the used 5% Ru/SiO_2 catalyst appears to be anomalously high and may be due to hydrogen spillover onto carbonaceous residue produced during the synthesis reaction (*9*).

Results from the kinetic studies conducted in the glass reactor at 101 kPa are listed in Table 2. Between each analysis, the catalyst was cleaned in pure hydrogen for 20 min as described earlier (*4*). Total CO conversions were typically kept well below 10% during the runs to determine kinetic behavior. In a few instances, higher conversions were obtained to facilitate product distribution determinations. The turnover frequencies were obtained by extrapolation of Arrhenius plots to 548 K.

The turnover frequencies in columns 2 and 4 of Table 2 are based on the assumption that an adsorbed H atom defines an active site. The H_2 uptake on the fresh reduced sample is used because this is the most commonly reported metal surface area measurement and it allows direct comparison with other reported values. On this basis, the high turnover frequencies reported previously for ruthenium supported on alumina and silica are observed again for 2% Ru/TiO_2 and for unsupported ruthenium. However, the specific activity for carbon-supported ruthenium is much lower. Because of the inhibition of CO and H_2 chemisorption on TiO_2-supported Ru, the turnover frequencies based on these values are best considered as maximum values. For comparison, a second turnover frequency is presented for Ru/TiO_2 in Table 2. These values are calculated assuming 100% Ru dispersion and represent minimum values of specific

TABLE 2

Kinetic Behavior of Ruthenium Catalysts

P = 101 kPa, H_2/CO = 3

$$N_{\mathrm{CH_4}} = Ae^{-E_{\mathrm{CH_2}/RT}}P_{\mathrm{H_2}}P_{\mathrm{CO}}{}^{Y}$$

Catalyst	$N_{\mathrm{CH_4}}$ at 548 K (sec^{-1} × 10^3)[a]	N_{CO} at 548 K (sec^{-1} × 10^3)[a]	X	Y	$E_{\mathrm{CH_4}}$ (kJ mol^{-1})	E_{CO} (kJ mol^{-1})
2% Ru/TiO_2	125	390	2.0	−0.5	91.7 ± 8.4	82.5 ± 5.4
2% Ru/TiO_2	3.7[b]	11.7[b]				
5% Ru/Al_2O_3	147	266	1.6	−0.6	101.3 ± 5.0	76.6 ± 4.2
5% Ru/Al_2O_3	8.2[c]	29[c]				
5% Ru/SiO_2	68	90	1.1	−0.8	113	91.7
4% Ru/Carbolac	17	18	—	—	102	—
Unsupported Ru	101	—	1.5	−1.3	94.6	—
Unsupported Ru	8.9[d]	18[d]				

[a] Based on H_2 uptake on fresh sample.

[b] Based on the assumption of 100% dispersion.

[c] Measured at 485 K.

[d] Measured at 490 K.

activity. Table 2 also includes nonextrapolated turnover frequencies which were measured directly at tempertures far below 548 K. The H_2 and CO partial pressure dependencies of 2% Ru/TiO_2 in the methanation reaction, 2.0 and $-1/2$, respectively, are similar to values reported earlier for 5% Ru/Al_2O_3 (*4*). A wider variation occurs, however, when these dependencies are compared to those determined for 5% Ru/SiO_2 and unsupported ruthenium, and may represent a modification of the CO bonding on titania-supported Ru. All catalysts had methanation activation energies near 100 kJ mol^{-1} (24 ± 3, kcal mol^{-1}).

The first reports of specific activities of ruthenium catalysts for CO hydrogenation have shown a rather wide range of values (*4*, *10–12*); however, King has recently reported that turnover frequencies declined as Ru dispersion increased (*12*). Although the reason for this correlation is not known, the low activity of 2% Ru/TiO_2, assuming it is highly dispersed, is consistent with this pattern. The higher values of turnover frequencies in Table 2 are in excellent agreement with those obtained from transient reactor techniques because Dautzenberg *et al.* (*13*) have recently reported high CO turnover frequencies for a 3% Ru/Al_2O_3 catalyst which are in excellent agreement with the value reported for 5% Ru/Al_2O_3 (*4*). At 483 K, a H_2/CO ratio of 1, and 10 kPa total pressure, Dautzenberg *et al.* calculated a turnover frequency for total CO conversion of 0.160 sec^{-1} whereas N_{CO} values of 0.11–0.12 sec^{-1} can be estimated for the 5% Ru/Al_2O_3 catalyst in Table 2 by assuming that the partial pressure dependencies for total CO conversion are similar either to those reported by Vannice (*4*) for methanation or to those reported by Dalla Betta *et al.* (*10*) for CO conversion. Dautzenberg *et al.* periodically cleaned their catalyst between each measurement by flowing pure hydrogen over it and increasing the temperature to 523 K. This periodic cleaning to maintain a clean Ru surface, which was also done by Vannice (*4*), may be responsible for the high specific activity.

Product distributions obtained at specific temperatures are listed in Table 3 along with the total CO conversion for each run. The choice of the gc temperature program sometimes precluded accurate determinations of the C_3 and C_4 olefin/paraffin ratio because of a tailing water peak. The distributions in Table 3 were obtained in the high-pressure, stainless-steel reactor system. Certain runs were repeated in this reactor to obtain effluent gas samples which were submitted to Exxon's Analytical and Information Division for additional analysis using capillary gas chromatography. These

TABLE 3

Selectivity of Ruthenium Catalysts

$H_2/CO = 3$, $P = 101$ kPa

Catalyst	T (K)	CO conversion (%)	Product distribution (mole%)									C_2+/C_1 wt ratio
			C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	C_5	C_6^+	
2% Ru/TiO_2	501	1.8	54	6	5	16		10		5	4	2.7
5% Ru/Al_2O_3	502	10.6	66	1	9	6		9		6	4	1.8
5% Ru/SiO_2	492	7.1	72	0	9	2	3	0.3	7	7	<1	1.3
4% Ru/Carbolac	507	1.6	98	0	2	0	0	0	0	0	0	0.04
Unsupported Ru	476	17.5	59	tr	9	10		<1	6	6	9	2.5

results agreed closely with our results and confirmed the olefin/paraffin ratios we obtained.

Table 3 shows that a wide variation occurs in product selectivity over the various ruthenium catalysts. If the unsupported ruthenium is used for a base-case comparison, the formation of higher-molecular-weight hydrocarbons expected from Ru at these low temperatures is clearly evident. However, the C_2+/C_1 weight ratio for this unsupported catalyst should be somewhat enhanced, compared to the supported catalysts, because of the low temperature of 476 K. Silica has little effect on product distribution, and olefin formation over both unsupported and silica-supported ruthenium is very minimal. Although reaction conditions are significantly different than those used by King (*12*), the C_2+/C_1 weight ratios listed in Table 3 are comparable to those he reported at 405 kPa and 523 K. The major difference is in the behavior of the unsupported ruthenium; however, the 50 K higher temperature used by King would be expected to lower this C_2+/C_1 ratio markedly. The selectivity of carbon-supported ruthenium is dramatically shifted to methane, with small quantities of ethane being the only other detectable product. The carbon support therefore appears to affect both the activity and selectivity of ruthenium. A trend toward increased olefin production and decreased methane formation appears to begin with alumina-supported ruthenium and is further enhanced when titania is used.

Methane formation and olefin formation over Ru/Al_2O_3 and Ru/TiO_2 catalysts can be altered by changes in reaction conditions, as shown in Table 4. Here 2% Ru/TiO_2 is compared with 5% Ru/Al_2O_3, since the latter catalyst was the only other Ru catalyst in this study to produce significant amounts of olefins. At low pressure and low H_2/CO ratios, the Ru/TiO_2 catalyst produces twice as many olefins and half the methane as Ru/Al_2O_3. Increasing the pressure to 10 atm further reduced methane make to 14 wt% over the 2% Ru/TiO_2 catalyst, but also reduced the C_2–C_4 olefin fraction although the quantity of C_5+ olefins increased. However, the quantity of olefins obtained from Ru/Al_2O_3 is still substantially lower than that obtained from titania-supported ruthenium, and methane formation over Ru/TiO_2 at pressures above atmospheric is significantly lower than over other supported ruthenium catalysts reported recently in the literature (*12*, *14*).

At this time, the nature of the interaction between the support and the Ru crystallites is unclear. We attribute this alteration in adsorptive and catalytic properties for titania-supported ruthenium to a strong metal–support interaction (SMSI). There are several possible origins of these interactions which include the epitaxial stabilization of preferred crystal faces, transfer of elec-

TABLE 4

Effect of Pressure on the Selectivity of TiO_2- and Al_2O_3-Supported Ruthenium

$H_2/CO = 1$, $T = 535$–547 K

Catalyst	Pressure (kPa)	CO conversion (%)	Product distribution (wt%)								
			C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	C_5	C_6+
2% Ru/TiO_2	101	1	26	12	5	20	8	15	4	10	1
5% Ru/Al_2O_3	101	2	47	5	8	21		6	1	6	5
2% Ru/TiO_2	980	7	14	2	4	14	7	16	4	17	22
5% Ru/Al_2O_3	980	10	24	1	5	12	4	6	5	12	32

trons between the metal particles and the support, or a combination of both. Presently, these aspects of metal–support interactions are under intense investigation, but conclusive evidence regarding the relative importance of these factors is not yet available. However, from a simplified point of view, the changes in catalytic activity could be explained in the following manner. When reduced at higher temperatures, electron-acceptor defect sites are created in TiO_2 (*15*). In addition, the presence of a group VIII metal can catalyze the reduction of TiO_2 to Ti_4O_7 (*16*). Therefore, it is possible that the defect sites formed by these higher-temperature reduction steps can interact with the dispersed metal and reduce the *d*-band concentration of electrons in the metal crystallites. Whereas this effect might be expected to shift the catalytic behavior of nickel on titania toward that of cobalt in agreement with experimental results, the effect on ruthenium is less predictable. The catalytic behavior of Tc has not been reported although activities for Mo and Re are much lower than that for Ru in the CO hydrogenation reaction (*17*). It should be noted, though, that Rh also has a lower specific activity than Ru in this reaction (*4*). The enhancement of olefin formation is consistent, however, with the supposition that the % *d*-character of the Ru crystallites is reduced by an interaction with the titania. From the work of Beeck on ethylene hydrogenation, a reduction in the % *d*-character of a metal was found to correlate with a decrease in activity (*18*); therefore, a decrease in the rate of hydrogenation of olefinic intermediates in the Fischer–Tropsch synthesis reaction would increase the probability that such species could desorb as olefinic products.

Alumina and silica supports do not alter turnover frequencies and molecular weight distributions markedly although alumina does increase the olefin/paraffin ratio to some extent. However, carbon strongly shifts selectivity toward methane formation and also reduces specific activity. It is interesting that Ozaki and coworkers found that carbon-supported ruthenium was much less active than alumina- or silica-supported ruthenium in the ammonia synthesis reaction (*19*). Apparently the same trend may exist for the hydrogenation of these two isoelectronic molecules—CO and N_2, with carbon supports reducing the catalytic activity of ruthenium in these reactions. Further studies are clearly required to determine the reasons for this behavior.

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