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The Catalytic Reactions of CO and H_2O over Ruthenium in a Y-Type Zeolite

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When the $Ru(NH_3)_6^{3+}$ complex in a Y-type zeolite was reduced in H_2 to 380°C, the resulting sample was an active catalyst for the Kölbel–Engelhardt and water gas shift reactions. Following reduction, the ruthenium was located within the zeolite framework in the form of small particles less than 30 Å in diameter. The Kölbel–Engelhardt reaction proceeds via a sequential reaction pathway involving the water gas shift reaction followed by the methanation reaction. The only hydrocarbon observed at 300°C was CH_4. Under conditions favorable for CH_4 formation, the water gas shift reaction jumped to equilibrium conversions. This was attributed to a localized heating of the catalyst particles due to the exothermic nature of the methanation reaction. The kinetic parameters for the water gas shift reaction were determined in a continuous flow reactor operating at high flow rates. Comparison of the RuY to Ru/Al_2O_3 or Ru/SiO_2 demonstrates that the support does not play a major role in this reaction. Mechanistic studies indicate that the slow step may involve the interaction of an adsorbed OH species with an associatively adsorbed CO.

INTRODUCTION

The catalytic behavior of ruthenium-exchanged zeolites has been reported for a variety of reactions including the methanation (*1*), Fischer–Trospch (*2*), and water gas shift (*3*) reactions. Under methanation conditions Elliott and Lunsford (*1*) found good agreement between the turnover frequency for RuY zeolite catalysts and Ru/Al_2O_3 catalysts, although other supports have been shown to significantly alter the methanation activity (*4*). The activity of the RuY catalysts decreased with time under methanation conditions, presumably due to a buildup of surface carbon on the metal.

It has been demonstrated recently that, for some homogeneous systems, H_2O may be substituted for H_2 in reactions such as hydroformylation (*5, 6*) and deuterium exchange (*7*). While the catalytic activity of ruthenium zeolites for the conversion of synthesis gas has been extensively investigated, very little is known about the reactions of CO and H_2O over these catalysts.

The conversion of CO and H_2O to CO_2 and H_2, shown in Eq. (1),

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (1)$$

is known as the water gas shift (WGS) reaction. Industrially, this reaction is catalyzed by iron or copper based materials and is used for CO removal, as well as adjusting the H_2 content in synthesis gas. There have been several reports of homogeneous metal carbonyl complexes which are active for the water gas shift reaction (*8, 9*). The majority of homogeneous low-temperature WGS catalysts require a basic solution, and a mechanism which involves a formate type intermediate has been presented by Ungermann *et al.* (*8*). Ruthenium or iron carbonyls, operating in basic solution, are the most widely studied homogeneous catalysts.

Certain supported metals are also active catalysts for the WGS reaction. In one of the few comprehensive reports to date, Joy *et al.* (*10*) have concluded that the platinum group metals are preferred over the first row group VIII transition metals. The ranking of metals for the WGS activity was reported to be Rh > Pt, Ru > Pd > Ir, Ni, Co, Fe at 500°C.

Verdonck *et al.* (*3*) have recently re-

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ported that ionic ruthenium complexes supported in a variety of zeolites are active catalysts for the WGS reaction. On the basis of turnover frequency, the ruthenium zeolite catalyst was more active than the best homogeneous catalyst reported to date (*3, 11*). The active species was thought to be an ionic ruthenium complex which cycles between Ru^+ and Ru^{2+}.

In spite of the importance of the WGS reaction and the apparent activity of the supported platinum group metals for this reaction, relatively few investigations have been reported on this subject. In the few reports on supported ruthenium metal, the catalysts have not been completely characterized and the active form of ruthenium is not known (*10, 12*). This is surprising in view of the catalytic activity exhibited by homogeneous and ionic heterogeneous ruthenium catalysts.

The reaction of CO and H_2O to form CH_4, as shown in Eq. (2),

$$4CO + 2H_2O \rightleftarrows CH_4 + 3CO_2 \qquad (2)$$

or higher hydrocarbons is known as the Kölbel–Engelhardt reaction (*13*). The Kölbel–Engelhardt reaction has not received a great deal of attention in the Western literature to date although recent reports indicate that Co and Ni supported on alumina catalysts (*14*), as well as a RhY zeolite catalyst (*15*), are active for this reaction. In these studies the only products observed were CH_4, CO_2 and H_2.

The mechanism of the Kölbel–Engelhardt reaction has not been firmly established and there are two possible pathways by which the reaction may proceed. The first pathway involves the coupling of the water gas shift and methanation reactions as shown in Eq. (1) and Eq. (3).

$$3H_2 + CO \rightleftarrows CH_4 + H_2O \qquad (3)$$

The second possibility involves the direct reaction of H_2O and CO or surface carbon to form CH_4. While the first pathway has generally been accepted, a recent report by Rabo *et al.* (*16*) indicates that the direct reaction of H_2O and surface carbon to form CH_4 over Ni and Co catalysts may occur.

In the present study, the catalytic activity of the RuY zeolite for the reaction of CO and H_2O was monitored in an attempt to distinguish between these two pathways for CH_4 formation. The activity of this catalyst for the WGS reaction was measured and compared to the activity of Ru/Al_2O_3 and Ru/SiO_2 catalysts.

METHODS

The RuY zeolite samples were prepared by standard ion exchange using NaY (Linde lot #Y52-3365-94) as the starting material (*17*). The $[Ru(NH_3)_6]Cl_3$ salt (Strem) was used as the source of ruthenium for all of the catalysts. Following exchange, the RuY catalyst was air dried and then stored over a saturated solution of NH_4Cl to ensure complete hydration of the samples. The Ru/Al_2O_3 catalyst was prepared by impregnation of the $Ru(NH_3)_6^{3+}$ complex onto Catapal alumina (Al-223-L14) which had been calcined in air at 350°C for 16 hr. The wet catalyst was air dried at 25°C for several days. The Ru/SiO_2 catalyst was prepared in the same manner using Davison grade 57 silica gel. The hydrated RuY catalyst was found to contain 2 wt% ruthenium, whereas the Ru/Al_2O_3 and Ru/SiO_2 samples contained 1.1 and 1.0 wt%, respectively. The loading of the RuY catalyst corresponds to 3.5 Ru per unit cell or 19% of the cation exchange capacity.

All of the gases used in this study, with the exception of the ^{13}CO (Merck) and He (Airco) were purchased from Matheson. The ^{13}CO was enriched to 99% ^{13}C. The CO and H_2, as well as gas mixtures containing 3.9% CO/He, 17% CO/He, and 20% H_2/He, were Matheson ultra high purity grade. The D_2O (99%D) was purchased from Aldrich Chemical Company. All of the gases except ^{13}CO and H_2O were passed through a Cr^{II}/SiO_2 oxygen scavenger prior to use (*17*).

The kinetic studies were conducted using a continuous flow reactor which was constructed from Pyrex (*17*). The flow system was designed so that the H_2O saturator and the reactor could be bypassed when necessary. The entire system was heated to 100°C with heating tape to prevent H_2O condensation. The flow rate through the reactor was controlled by a mass flow controller (Alltech Associates) which compensated for changes in downstream temperatures or pressures.

Prior to loading the ruthenium catalysts in the flow system, the samples were pressed and then broken into small chips of 20–40 mesh. Pretreatment for the RuY and Ru/Al_2O_3 catalysts consisted of slowly raising the temperature (1°C/min) from 25 to 380°C in a 1 : 1 mixture of H_2 and He. The total flow rate used for the pretreatment was 140 cm^3/min. The total reduction time was 17 hr. The catalyst was then purged with He at 380°C to remove any chemisorbed H_2 from the ruthenium surface.

The Ru/SiO_2 catalysts were pretreated using a very high flow rate of H_2 (3.5 liters/min). The temperature was raised from 25 to 420°C at 5°C/min and then held at 420°C for 1 hr. The H_2 flow was then replaced with He at 335°C for 1 hr. The Ru/SiO_2 catalyst was inactive when preheated in the same manner as the RuY or Ru/Al_2O_3 samples.

The He/CO/H_2O mixture was passed over the catalyst and the products monitored by gas chromatography. Steady state was usually achieved within 30 min following initiation of the gas flow through the reactor or a change in reaction conditions. All kinetic measurements were made with the reaction at steady state.

The mechanistic studies and H_2 chemisorption measurements were conducted in a closed Pyrex recirculation system which was attached to a high vacuum system (*17*). The standard pretreatment for the ruthenium catalysts used in the recirculation system consisted of evacuation at 25°C to 10^{-3} Torr followed by H_2 reduction from 25 to 380°C. Following reduction the catalyst was evacuated at 380°C to a final pressure of 5×10^{-5} Torr.

The ruthenium particle size was determined by the chemisorption of H_2 at 25°C, as well as by transmission electron microscopy (TEM). The electron micrographs were obtained using a Hitachi HU-11E electron microscope. The accelerating voltage was 50 kV and the beam current was adjusted to 30 μA. The maximum resolution of the electron microscope was approximately 3.4 Å.

The X-ray photoelectron spectra for the RuY catalyst was measured with a Hewlett Packard 5950 A spectrometer using monochromatic Al$K\alpha$ X-rays (1486.6 eV). The binding energies were referenced to the Si 2s line at 154.0 eV and were reproducible within ±0.2 eV. The XPS were routinely recorded in the region of the Ru_{3d} (275–295 eV), Si_{2s} (145–165 eV), Si_{2p} (95–115 eV), Al_{2p} and Na_{2s} (58–78 eV), and O_{1s} (525–545 eV) levels.

RESULTS AND DISCUSSION

Catalyst Characterization

The reduction of RuY zeolite samples in H_2 has been studied by several authors (*1*, *18–20*) and, in the absence of O_2, results in a well-dispersed system. For example, when a RuY sample was evacuated to 400°C prior to H_2 reduction, the average ruthenium particle size was 10 Å (*1*). However, when H_2 was present during the dehydration procedure, the average particle size was 20 Å (*20*).

The formation of small ruthenium particles in the present study was confirmed by TEM and H_2 chemisorption measurements (Table 1). For both the fresh and the used catalysts, the particle size distribution was narrow with most particles having measured diameters of less than 30 Å (Fig. 1). The small increase in particle size following reaction of CO and H_2O was similar to that observed under methanation conditions (*1*). Particle size measurements by TEM for the Ru/Al_2O_3 catalyst were not possible

TABLE 1

H_2 Chemisorption on the Ruthenium Catalysts

Catalyst	Amount H_2 adsorbed (μmole/g)	Dispersion	$\bar{d}^a$ (Å)	$\bar{d}^b$ (Å)
Fresh				
2 wt% RuY	44	0.46	20	23
2 wt% RuY (evac)[c]	84	0.89	10	—
1.1 wt% Ru/Al_2O_3	17	0.34	30	—
1 wt% Ru/SiO_2	—	—	—	—
Used				
2 wt% RuY	37	0.37	25	24
2 wt% RuY (evac)[c]	61	0.62	15	—
1.1 wt% Ru/Al_2O_3	14	0.27	37	—
1 wt% Ru/SiO_2	9	0.18	50	—

[a] Measured by H_2 chemisorption.

[b] Measured by TEM.

[c] RuY evacuated to 400°C, then reduced in H_2 at 400°C for 16 hr.

due to interference of the support. It appeared, however, that particles larger than 100 Å were not present, either before or after reaction.

An XPS study was conducted on the RuY catalyst to determine the location of the ruthenium particles. The $Ru_{3d_{5/2}}$ binding energies which were determined relative to the Si_{2s} peak, as well as the calculated Ru_{3d}/Si_{2p} and Si_{2p}/Al_{2p} ratios, are summarized in Table 2. It is evident that the ruthenium in both the fresh and used catalysts

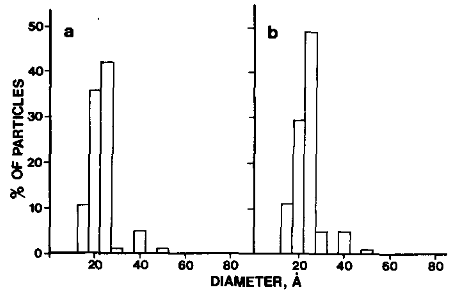

FIG. 1. Particle distribution determined from TEM for (a) RuY reduced in H_2 to 380°C; (b) used RuY catalyst.

was located within the zeolite framework. Significant migration of the ruthenium to the external surface would have been indicated by $Ru_{3d_{5/2}}/Si_{2p}$ ratios larger than those observed for the evacuated sample (*18*).

The apparent inconsistency of 20–40 Å particles residing within the zeolite can be resolved in two ways. The first explanation, proposed by Verdonck *et al.* (*20*), involves the localized destruction of the lattice to form cracks and holes on the order of 20–40 Å in diameter. Filling of these voids by ruthenium metal would result in the particle sizes measured in this study. The alternative explanation is that in the presence of H_2O, H_2, and residual NH_3, the mobility of ruthenium is increased resulting in the agglomeration of ruthenium in several adjacent supercages where the particles may

TABLE 2

Summary of ESCA Data for RuY Catalysts

Sample	Binding energy $Ru_{3d_{5/2}}$ (eV)	$Ru_{3d_{5/2}}/Si_{2p}$ ($\times 1000$)[a]	Si_{2p}/Al_{2p}
RuY, evacuated to 400°C	280.7	15.1	2.59
RuY, He and H_2 to 380°C	281.0	11.6	2.77
RuY, used catalyst, He and H_2 to 380°C, CO/H_2O (1 : 1) at 300°C	280.3	9.1	2.91
RuY, heated to 400°C in O_2, H_2 at 400°C	279.4	31.4	2.70
Theoretical	—	24	2.45

[a] $Ru_{3d_{5/2}}/Si_{2p} = \dfrac{A_{Ru_{3d_{5/2}}}}{A_{Si_{2p}}} \times \dfrac{\sigma^{Si_{2p}}}{\sigma^{Ru_{3d_{5/2}}}}$, where σ values are from Scofield (*21*).

actually be connected through the 12 membered windows. A similar model for the formation of Pd° particles in a Y-type zeolite has been proposed by Bergeret *et al.* (*22*). While the resolution of the TEM measurements was not sufficient to distinguish between individual supercages, many of the larger particles appeared to be a combination of two or more smaller particles (*17*).

Kinetic Studies

Following pretreatment in the flow system, all three ruthenium samples were active catalysts for the conversion of CO and H_2O. When a 1:1 CO/H_2O mixture (28 Torr each) was passed over the ruthenium catalysts at 300°C and a W/F (weight of catalyst/total flow rate at STP) of 1.0×10^{-2} g min cm^{-3}, stable catalyst activity was observed with respect to time. This was in contrast to the decrease in activity due to the buildup of surface carbon under methanation conditions (*1*). However, recent reports in the literature have indicated that the deposition of excess surface carbon on a commercial Ni catalyst was prevented by the presence of H_2O (*23*). Therefore, it was not surprising that the ruthenium catalysts were not deactivated through surface carbon buildup under the conditions employed in this study.

Varying the flow rate while the reaction temperature was held constant at 300°C resulted in essentially the same CO conversions for the Ru/Al_2O_3 and Ru/SiO_2 catalysts. The product distribution as a function of W/F for the Ru/Al_2O_3 catalyst is shown in Fig. 2. The curve for H_2O is not shown for clarity as mass balances for C and H were 100%. At W/F values below 1.0×10^{-2} g min cm^{-3}, the only products observed were CO_2 and H_2 produced via the water gas shift reaction. As the value of W/F was increased above 1.0×10^{-2} g min cm^{-3}, CH_4 was observed although CO_2 was still the predominant product. As the amount of CH_4 increased, the amount of H_2 observed decreased relative to CO_2. This decrease corresponded to three times the amount of CH_4 which was observed. The selectivity to CH_4 increased to 11% as the value of W/F approached 4.5×10^{-2} g min cm^{-3}. The product distribution and selectivities over the Ru/SiO_2 catalyst were identical to those observed for the Ru/Al_2O_3 catalyst.

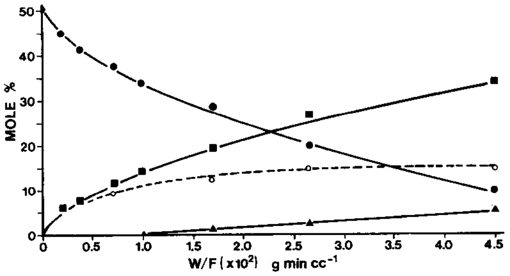

FIG. 2. Product distribution as a function of W/F at 300°C for the Ru/Al_2O_3 catalyst. (■) CO_2; (●) CO; (▲) CH_4; (--) H_2.

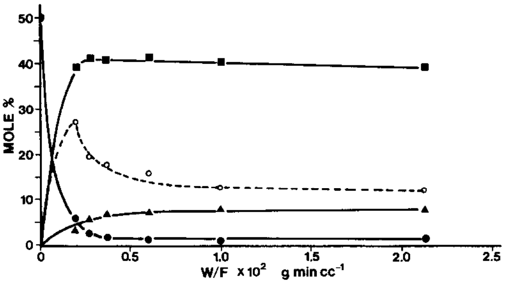

FIG. 3. Product distribution as a function of W/F at 300°C for the RuY catalyst. (■) CO_2; (●) CO; (▲) CH_4; (--) H_2.

The CO conversion over the RuY catalyst was greater than 96% over the entire range of flow rates which were measured; however, the selectivity to CH_4 was somewhat dependent on the flow rate. As the value of W/F increased from 2.0×10^{-3} to 2.1×10^{-2} g min cm^{-3}, the selectivity to CH_4 increased from 8 to 19% (Fig. 3). The amount of H_2 which was observed decreased as the amount of CH_4 increased.

In an attempt to observe CH_4 at lower CO conversions, a series of experiments was conducted in which the flow rate was held constant and the temperature was raised from 230 to 320°C. The partial pressures of CO and H_2O were each held at 28

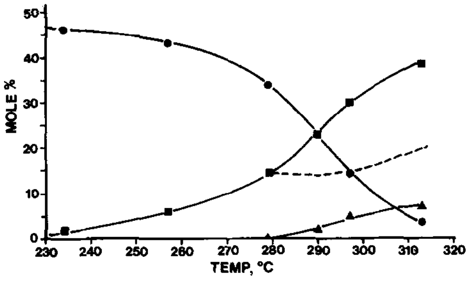

FIG. 4. Product distribution vs temperature for Ru/Al_2O_3 at W/F = 0.03 g min cm^{-3}. (■) CO_2; (●) CO; (▲) CH_4; (--) H_2.

Torr. The results which were obtained using the Ru/Al_2O_3 catalyst are shown in Fig. 4. For a W/F value of 3.0×10^{-2} g min cm^{-3}, the CO conversion increased from 5% at 235°C to 95% at 313°C. When the flow rate was adjusted so that the value of W/F was 1.0×10^{-2} g min cm^{-3}, a similar curve, shifted by approximately 20°C, was obtained. In both cases, the only products observed below CO conversions of 30% were equimolar amounts of CO_2 and H_2. The first appearance of CH_4 was noted at approximately 35% CO conversion for both values of W/F.

The results which were obtained when the same experiment was performed using the RuY catalyst are shown in Fig. 5. As the temperature was raised from 235 to 294°C, the CO conversion increased from 5 to 40%. As in the case of the Ru/Al_2O_3 catalyst, the only products observed at low conversions were CO_2 and H_2. Raising the temperature from 294 to 298°C increased the conversion of CO to 97%. This jump in conversion was accompanied by the appearance of CH_4 in the reaction products, as well as a decrease in gas phase H_2.

The flow rate had a pronounced effect on the temperature at which this jump occurred. As the value of W/F increased from 1.0×10^{-3} to 5×10^{-2} g min cm^{-3}, the "jump" temperature decreased from 295 to 250°C. This drastic increase in conversion was observed at every value of W/F which was measured and always occurred when CH_4 was first produced.

The drastic change in conversion was also dependent on the direction in which the temperature was varied. When the temperature was raised from 230°C at a W/F value of 2.1×10^{-2} g min cm^{-3}, the CO conversion jump was observed around 283°C over a fresh RuY catalyst. Conversely, the conversion was observed to drop from 96 to 15% between 267 and 258°C when the temperature was lowered from 300°C. It was possible to reproduce this effect several times over the used catalyst with no apparent loss in activity.

It is apparent that the formation of CH_4 from CO and H_2O occurred via a sequential reaction pathway involving the WGS and methanation reactions. In every case, the only products which were observed at low CO conversions, i.e., less than 30–40%, were equimolar amounts of CO_2 and H_2 formed via the WGS reaction. Under conditions suitable for CH_4 formation, the major product was CO_2 in all cases with a significant amount of H_2 also being observed.

A direct reaction pathway, such as the one proposed by Rabo *et al.* (*16*), would account for the high selectivity to CO_2;

$$4CO \xrightarrow{300°C} 2C_a + 2CO_2 \quad (5)$$

$$2H_2O + 2C_a \rightarrow CH_4 + CO_2 \quad (6)$$

however, the large amounts of H_2 observed in the products would be inconsistent with this mechanism. Furthermore, in contrast to the results for supported Ni and Co (*16*), the initial product observed following reaction of H_2O with surface carbon over a RuY catalyst was H_2 (*24*).

The unusual support effect which was observed for the RuY samples can be explained by the sequential reaction pathway:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (1)$$

$$3H_2 + CO \rightleftarrows CH_4 + H_2O \quad (3)$$

Over the range of temperatures used in this study, the equilibrium constant for reaction (1) varies from 50 up to 140. Assuming that the amount of CO_2 observed was indicative

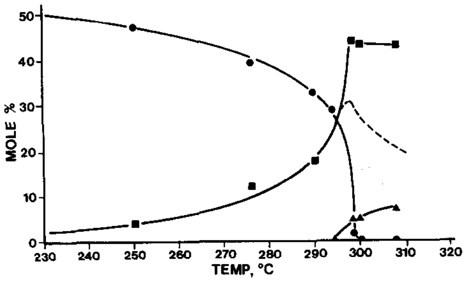

FIG. 5. Product distribution vs temperature over RuY at W/F = 0.01 g min cm^{-3}. (■) CO_2; (●) CO; (▲) CH_4; (--) H_2.

of the extent of reaction (1), equilibrium conversions were confirmed in the region where CH_4 was produced. However, it was not immediately obvious why the formation of CH_4 would result in a sudden jump to equilibrium conversions for the WGS reaction. There appear to be two explanations for this behavior.

It is possible that the formation of CH_4 would result in the liberation of surface sites through the hydrogenation of excess surface carbon or adsorbed CO. Such an explanation is tenuous as a similar jump in conversion was not observed for the Ru/Al_2O_3 or Ru/SiO_2 catalysts. Furthermore, the buildup of excess surface carbon under WGS conditions would have resulted in a deactivation of the catalysts and such an effect was not observed.

A more plausible explanation involves the localized heating of the catalyst particles and a subsequent increase in CO conversion. While the value of ΔH_f° for the WGS reaction is only -9 kcal $mole^{-1}$, the methanation reaction is highly exothermic with a ΔH_f° of -49.3 kcal $mole^{-1}$. As CH_4 begins to form, the heat generated by the methanation reaction must be dissipated or the catalyst temperature will increase.

In view of the fact that the macroscopic temperature of the catalyst bed did not increase perceptibly during CH_4 formation, this heating effect was thought to be restricted to the ruthenium particle (*17*). By extrapolation of the low conversion portion of the curve in Fig. 5 to higher temperatures, it was estimated that, in the absence of CH_4 formation, a localized temperature increase of only 15–20°C would result in equilibrium conversion of the WGS reaction.

The localized heating of the catalyst particles would also explain the hysteresis observed in the conversion curves as a function of temperature. Increasing the temperature from 250°C resulted in the formation of CO_2 and H_2 via the WGS reaction and at some point, in this study around 45% CO conversion, the partial pressure of H_2 became sufficiently high so that H_2 could compete with CO and H_2O for adsorption sites. When this occurred, CH_4 was produced along with a release of 49.3 kcal $mole^{-1}$ and a jump in the rate of the WGS reaction. Lowering the temperature from this point, however, did not result in an immediate drop in CH_4 production as the amount of H_2 in the gas phase was relatively large. The production of CH_4, and therefore equilibrium conversions for the WGS reaction, would continue as the temperature was lowered until, at some point, the thermal energy supplied to the catalyst was not sufficient to sustain this synergistic reaction and the production of CH_4 would cease.

The importance of the partial pressure of H_2 with regard to CH_4 formation was confirmed by passing an equimolar mixture of $CO/H_2O/H_2$ (24 Torr each) over a RuY catalyst at a W/F of 1.0×10^{-2} g min cm^{-3} while the temperature was varied. The conversion jump was still observed although the critical temperature was shifted down by approximately 15°C. In the region of high CO conversions, the selectivity to CH_4 increased to 30% under these conditions.

It should be emphasized that CH_4 was never observed over the RuY catalysts at less than 95% conversion when the ruthenium particles were still inside the zeolite. Furthermore, varying the CO/H_2O ratio from 1 to 0.22 did not alter this behavior. Methane was observed over a RuY catalyst at lower conversions only after the catalyst had been exposed to a small amount of O_2 at relatively low temperatures. Under this condition ruthenium is known to migrate to the external surface of the zeolite. Controlled sintering of the RuY catalyst in O_2, however, was unsuccessful and irreproducible results were obtained. In general, sintering in O_2 resulted in a severe loss in activity with small amounts of CO_2 and H_2 being the only products observed.

In view of the importance of the WGS reaction in the formation of CH_4, the kinetics of this reaction were studied using the flow reactor operating at conversions less than 5%. In order to achieve such low conversions, the partial pressures of CO and H_2O were raised to 110 Torr and the value of W/F was lowered to 4×10^{-3} g min cm^{-3} or less. Under these conditions, the only products observed were CO_2 and H_2. It should be pointed out, however, that the higher pressures of CO and H_2O did not alter the jump in CO conversions with CH_4 formation as described earlier.

The specific rates for CO_2 formation over the three catalysts are given in Table 3. The turnover frequencies, N (sec^{-1}), were calculated by dividing the specific rate by the amount of exposed ruthenium as determined by H_2 chemisorption. In contrast to the ionic ruthenium catalysts (*3*), a correlation between support acidity and catalyst activity based on turnover frequency was not observed in the case of reduced ruthenium. Furthermore, the infrared spectra of adsorbed CO on the RuY and Ru/Al_2O_3 catalysts were identical, both before and after reaction (*17*). Therefore, a strong support effect such as that reported by Vannice (*4*) for the methanation reaction can be ruled out in the case of these reduced ruthenium WGS catalysts.

The pressure dependencies, as well as the apparent activation energies (Ea), were determined using the following rate equation:

$$\text{rate} = Ae^{-Ea/RT}P_{CO}{}^{n}P_{H_2O}{}^{m}. \qquad (7)$$

The reaction orders were determined by varying the partial pressure of CO between 28 and 113 Torr while holding the partial pressure of H_2O constant at 118 Torr, and then varying the partial pressure of H_2O from 25 to 118 Torr while keeping the partial pressure of CO constant at 110 Torr. Apparent activation energies were determined by varying the reaction temperature between 220 and 310°C while holding the partial pressures of CO and H_2O at 110 Torr.

The kinetic parameters are summarized in Table 3. The reaction orders with respect to CO were nearly equivalent for all three catalysts with an average value of −0.87; whereas, the reaction orders with respect to H_2O ranged from 0.5 to 0.7. The apparent activation energies which ranged from 22 to 29 kcal mole^{-1}, were in good agreement with the value of 24.6 kcal mole^{-1} reported for a Pt metal catalyst (*25*). Joy *et al.* (*10*) have recently reported apparent activation energies of 19.9 and 21.4 kcal mole^{-1} for supported Pt and Rh, respec-

TABLE 3

Kinetic Parameters for the Water Gas Shift Reaction

Catalyst	Rate (μmol CO_2 g^{-1} sec^{-1})	$N(\times 10^3)^a$ (sec^{-1})	n	m	Ea^b (kcal/mole)
RuY	2.1	28	-0.87 ± 0.05	0.7 ± 0.1	29 ± 2
Ru/Al_2O_3	1.1	39	-0.86 ± 0.05	0.56 ± 0.05	22 ± 1
Ru/SiO_2	0.75	42	-0.88 ± 0.05	0.65 ± 0.05	24 ± 1

[a] At 280°C with $P_{CO} = P_{H_2O} = 110$ Torr, W/F = 5×10^{-3} g min cm^{-3}.

[b] Rate = $Ae^{-Ea/RT}P_{CO}{}^{n}P_{H_2O}{}^{m}$, where Ea is the apparent activation energy.

tively, although NO and SO_2 were also present in their reaction mixture.

Mechanistic Studies

When 28 Torr of CO and 28 Torr of H_2O were exposed to a RuY catalyst at 300°C in the recirculation system, the results in Fig. 6 were obtained. The initial products which were observed were CO_2 and H_2. The initial rate of CO_2 production was 4.6 μmole g^{-1} sec^{-1} which agrees with a value of 4.5 μmole g^{-1} sec^{-1} calculated using the rate law measured for the WGS reaction in the flow system.

Data obtained in the recirculation system also are consistent with the proposed heat effect in which it was assumed that the rate of the WGS reaction was larger than the rate of methanation under similar reaction conditions. When 20 Torr of CO and 40 Torr of H_2 were passed over the RuY catalyst in the absence of H_2O, the turnover frequency at 280°C for CH_4 formation was 11×10^{-3} sec^{-1} which is much lower than the turnover frequency of 124×10^{-3} sec^{-1} for the WGS reaction, corrected for a pressure of 20 Torr CO and 110 Torr H_2O.

Following the first 20 min of reaction in the recirculation system, CH_4 was observed in the gas phase (Fig. 6). The amount of CO_2 and CH_4 continued to increase up to a reaction time of 80 min while the amount of gas phase H_2 leveled off. The increase in selectivity to CH_4 at $t > 80$ min was attributed to the hydrogenation of CO_2;

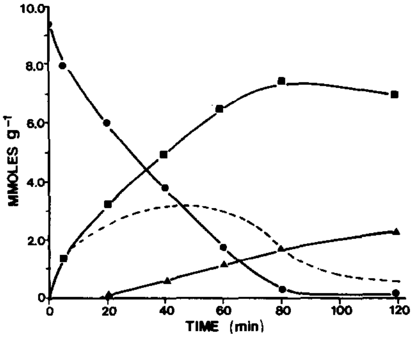

FIG. 6. Product distribution vs time for RuY at 300°C in the recirculation system for $P^{\circ}_{CO} = P^{\circ}_{H_2O} = 28$ Torr. (■) CO_2; (●) CO; (▲) CH_4; (--) H_2.

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \qquad (8)$$

which has been reported to occur over supported ruthenium (*26*). While the hydrogenation of CO_2 has also been observed over a RhY catalyst, the rate was thought to be negligible in the presence of CO (*27*). When the reaction was repeated using the same catalyst, identical results were obtained indicating that the induction period for CH_4 formation was not due to an irreversible change in the ruthenium surface.

When 30 Torr of CO_2 was added to the reaction mixture the catalyst activity, as well as selectivity to CH_4, was not significantly altered. Similarly, exposure of the catalyst to 25 Torr of H_2O at 300°C prior to reaction did not alter the catalyst activity. However, the addition of H_2 to the reaction mixture had a pronounced effect on the reaction profile as indicated in Table 4. As the partial pressure of H_2 was increased to 16 Torr, the induction period for CH_4 formation decreased to less than 1 min. Higher pressures of H_2 resulted in the formation of CH_4 as the primary product. It is apparent that, in both the flow and recirculation systems, the formation of CH_4 did not begin until the partial pressure of H_2 was approximately equivalent to the partial pressures of CO and H_2O. This indicates that, under reaction conditions, H_2O is preferentially adsorbed over H_2 on the ruthenium surface.

The mechanism of the WGS reaction over the group VIII metals has not been extensively investigated; however, the following mechanism has been suggested for Pt catalysts (*10, 25*):

$$CO + s \rightleftarrows CO_a \qquad (9)$$

$$H_2O + 2s \rightleftarrows OH_a + H_a \qquad (10)$$

$$CO_a + OH_a \rightleftarrows CO_2 + H_a + s \qquad (11)$$

$$2H_a \rightleftarrows H_2 + 2s \qquad (12)$$

where s denotes a surface site. Reaction (11)

TABLE 4

Effect of H_2 on CH_4 Formation over a RuY Catalyst in Recirculation System

$P^{\circ}_{H_2}$ (Torr)	$\frac{P^{\circ}_{H_2}}{P^{\circ}_{H_2O}}$	$\frac{P^{\circ}_{H_2}}{P^{\circ}_{CO}}$	Rate[a]	Time (min)[b]	CH_4/CO_2[c]
0	0	0	4.6	20	0
6	0.28	0.20	2.3	5	0
10	0.48	0.35	2.0	4	0.2
16	0.83	0.57	—	<1	0.5
20	0.83	0.71	—	0	0.6
30	1.25	1.07	—	0	1.4

[a] Rate expressed as μmole CO reacted g^{-1} sec^{-1}, reaction run at 300°C.

[b] Time at which CH_4 first appeared. Measured by extrapolation of the first three points for CH_4.

[c] Ratio at $t = 5$ min.

was thought to be the slow step in the mechanism.

When the reaction was carried out using D_2O in place of H_2O in the absence of H_2, the initial rate of CO_2 formation was 2.9 ± 0.1 μmole g^{-1} sec^{-1} as compared to 4.6 ± 0.3 μmole g^{-1} sec^{-1} reported earlier. This leads to a calculated primary kinetic isotope effect (k_{H_2O}/k_{D_2O}) of 1.5 ± 0.1. It therefore appears that the breaking of the O–H bond is involved in the rate limiting step for the formation of CO_2 and H_2. The reaction orders and kinetic isotope effect which were observed in this study are in good agreement with the mechanism presented above. Assuming reaction (11) is the slow step, the rate of CO_2 formation can be expressed as:

$$\text{rate} = k\theta_{CO}\theta_{OH} \qquad (13)$$

where θ_{CO} and θ_{OH} are the surface coverages of CO and OH, respectively (*28*). In the case where CO is strongly adsorbed relative to H_2O the predicted rate expression reduces to (*17*):

$$\text{rate} = k' P_{CO}^{-1} P_{H_2O}^{0.5}. \qquad (14)$$

While the postulate of associative adsorption of CO on Pt may be valid, it may not be correct in the case of ruthenium (*29*). However, the associative adsorption of CO on ruthenium at higher temperatures is not without precedence as Kobayashi and Shirasaki (*30*) have reported the formation of $Ru(CO)_n$ species at 150°C.

Several experiments were carried out to determine if an active carbon intermediate could possibly play a role in the WGS reaction. Following reaction of the CO/H_2O mixture, the gas phase was evacuated and H_2 admitted to the catalyst. After several hours of H_2 exposure at 300°C, only a trace of CH_4 was observed in the gas phase (*31, 32*). It therefore appears that a significant amount of surface carbon was not formed during reaction of CO and H_2O at 300°C.

Carbon-13 isotope tracer experiments designed to explore the role of surface carbon in the WGS reaction were inconclusive as described in a separate communication (*24*). Following deposition of surface carbon the rate of the WGS reaction was several orders of magnitude less than that observed for a fresh RuY catalyst. Nevertheless, the incorporation of a surface carbon intermediate into the reaction mechanism cannot be completely ruled out. If the reaction proceeds via the dissociative adsorption of CO;

$$CO + 2s \rightleftarrows C_a + O_a \qquad (15)$$

$$H_2O + 2s \rightleftarrows OH_a + H_a \qquad (10)$$

$$C_a + OH_a \rightleftarrows CO_a + H_a \qquad (16)$$

$$CO_a + O_a \rightleftarrows CO_2 + 2s \qquad (17)$$

$$2H_a \rightarrow H_2 + 2s \qquad (12)$$

and reaction (16) was the rate limiting step, the predicted reaction orders would be −0.5 and 0.5 for CO and H_2O, respectively, for the case where CO was strongly adsorbed. The experimental order with respect to CO of −0.87 is closer to the value of −1 predicted from the nondissociative mechanism. Although this agreement does not confirm the former mechanism, the weight of evidence seems to favor a nondissociative mechanism for the WGS reaction. This mechanism is supported by the related homogeneous studies (*8*, *9*).

CONCLUSIONS

Following H_2 reduction, the RuY zeolite samples were active catalysts for both the Kölbel–Engelhardt and water gas shift reactions. The formation of CH_4 occurred through a sequential reaction mechanism involving the water gas shift and methanation reactions. In the region of low conversion, only the WGS reaction was observed; whereas, the formation of CH_4 was accompanied by a jump in CO conversion. This was attributed to a localized heating of the ruthenium particles due to the exothermic nature of the methanation reaction. This heating effect resulted in equilibrium conversions for the WGS reaction.

While the turnover frequency for the WGS reaction for the RuY catalyst was slightly lower than for either the Ru/Al_2O_3 or Ru/SiO_2 catalysts, a correlation between support acidity and catalyst activity was not evident. The apparent activation energies which were measured for all three ruthenium catalysts were in agreement with those reported for Pt and Rh catalysts.

There appear to be two possible mechanisms for the WGS reaction which are consistent with the kinetic parameters. The slow step in both reactions involves the interaction of a surface OH species with either an adsorbed CO or surface carbon to form a COOH or COH type intermediate. The mechanism involving associatively adsorbed CO appears to give a better fit to the kinetic parameters and therefore was adopted in this study. However, further evidence is necessary before either mechanism can be discounted.

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