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Deuterium Isotope Effects on Hydrogenation of Carbon Monoxide over Rhodium

Isotopic substitution of deuterium for hydrogen can modify the rate of carbon monoxide hydrogenation (*1–10*). Reports indicate that the rate of methane formation over ruthenium decreased (*1*), increased (*2*), or remained the same (*4, 5*), over Ni increased (*6–8*) or remained the same (*4, 5*), and over a Co/ThO_2 Kielselguhr catalyst increased upon substitution of deuterium. In this note we report an "equilibrium" deuterium isotope effect during methanation over rhodium polycrystalline foils; that is the rate of methane formation increased when D_2 was used as a reactant instead of H_2. The rate of CD_4 formation was found to be 1.5 times faster than the rate of CH_4 formation under the conditions used in this study ($CO:H_2$, 1:2, 6 atm total pressure, 250–450°C). This result is similar to that found on supported Ru catalysts by Kellner and Bell (*2*). The pressure dependence of the reaction is -1.0 ± 0.1 order in CO and $+1.0 \pm 0.1$ order in H_2, which implies competitive adsorption (*16*) of these two molecules on the surface. This data along with an activation energy of 25 kcal/mol for methane formation indicate that one of the final hydrogenation steps is rate limiting, as proposed by Kellner and Bell (*2*) over supported Ru catalysts.

EXPERIMENTAL

All the experiments were carried out in an ultrahigh vacuum (UHV)/high-pressure apparatus designed for combined UHV surface analysis and high-pressure reaction studies using small-surface-area catalyst samples, as described in detail previously (*11–12*). This system is equipped with four grid electron optics for LEED and AES, an ion gun for crystal cleaning, a quadrupole mass spectrometer, and a rectractable internal isolation cell that constitutes part of a microbatch reactor operating in the pressure range 10^{-2}–20 atm. The reaction cell and the external recirculation loop were connected to an isolatable pressure gauge, a magnetically driven micropump for reaction gas circulation, and a gas chromatograph sampling valve. Hydrocarbon product formation was monitored with HP5793 gas chromatograph equipped with a 12 ft. × $\frac{1}{8}$ in. Poropak N column and a flame ionization detector.

The rhodium foils, obtained from Engelhard (99.8%), were spot-welded to a rotatable manipulator using a series of Ta and Cu supports, that enabled these to be resistively heated to 1300 K without significant heating of any other part of the chamber. Both foil faces (front and back) were cleaned by repeated oxygen treatment and argon ion sputtering followed by annealing until no impurities (B, C, O, Si, or S) were detected by AES. Research purity H_2 (Matheson grade ≥99.99% atomic purity) was passed through a molecular sieve trap in a dry-ice/acetone bath prior to use. Deuterium was obtained from Liquid Carbonic (99.9%) and passed through a liquid-nitrogen trap prior to use.

Product formation was followed by gas chromatography. Initial reaction rates were determined graphically from the initial slopes of product accumulation curves as a function of time. They were reproducible to within 5%. Blank experiments ($CO:H_2$, 1:2, 6 atm, up to 400°C) on Rh covered with graphitic carbon formed by heating the crystal in a hydrocarbon atmosphere at 600°C, show a low level of catalytic activity, never higher than 10% of the activity

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measured for clean Rh at any given reaction temperature.

RESULTS AND DISCUSSION

The catalytic hydrogenation of carbon monoxide has been investigated on rhodium polycrystalline foils. Typical turnover frequencies (defined as product molecules/Rh atom-second) for methane production were 0.26 at 300°C, $CO/H_2 = 0.33$, and 6 atm total pressure; and 1.0 at 350°C, $CO/H_2 = 0.33$, and 6 atm total pressure. These turnover frequencies were calculated using the surface atomic density of Rh(111) (1.6×10^{15} Rh atoms/cm^2) and initial reaction rates. A typical product distribution for the reaction is shown in Table 1.

Under all the conditions of this study, the main product from the reaction is methane with small amounts of ethane and propane also being produced. The only by-product of the reaction was found to be water.

Figure 1 displays an Arrhenius plot for CH_4 formation, from which an activation energy for methanation on Rh polycrystalline foils of 25 ± 0.5 kcal/mol is calculated. Also shown in Fig. 1 is the corresponding plot when deuterium was substituted for hydrogen in the reaction mixture. An isotope effect is clearly observed, the rate of methane formation increased by a factor of 1.5 when deuterium was used as a reactant.

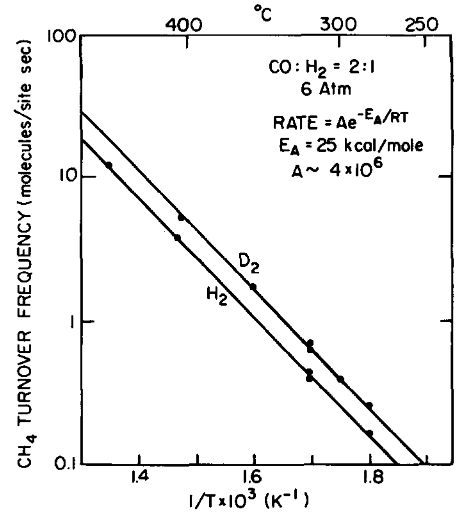

FIG. 1. Arrhenius plot for the initial rate of formation of CH_4 and CD_4 versus inverse temperatures over Rh polycrystalline foils. As is shown, the rate of CD_4 formation is 1.5 times the rate of CH_4 formation over the entire temperature range of this study.

The dependence of the methanation rate on the pressures of the reactant gases is shown in Fig. 2. This plot was determined by varying the partial pressure of each reactant gas while maintaining a constant temperature and total pressure, using argon as a buffer gas. Consequently the observed rate law for methanation is given by $R_{CH_4} = KP_{CO}^{-1}P_{H_2}^{+1}$. The reaction begins to be poi-

TABLE 1

Typical Product Distribution of the Catalytic Hydrogenation of CO

	$CO:H_2$, 1 : 2, 300°C, 6 atm	
Product	Turnover frequencies (molecules/Rh atom-sec)	mole %
CH_4	0.26	95
C_2H_6	0.01	4
C_3H_8	0.003	1
C_4^+	0.00	0

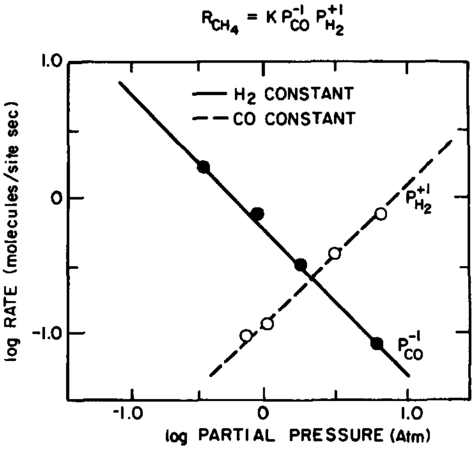

FIG. 2. Rate of methane formation versus the partial pressure of each reactant at a constant total pressure of 10 atm and constant temperature of 300°C (constant H_2 pressure of 3 atm for determination of CO dependence and constant CO pressure of 3 atm for determination of H_2 dependence). The resulting rate expression has the form $R_{CH_4} = KP_{CO}^{-1.0}P_{H_2}^{+1.0}$.

soned after about 1–3 h, depending on reaction conditions (higher temperatures and high CO/H_2 ratios lead to a faster rate of poisoning of the reaction). After poisoning of the reaction AES revealed a carbon-covered surface.

The products of the hydrogenation of CO on rhodium foils are alkanes (*14*) indicating that rhodium is a very good hydrogenation catalyst. The highest molecular weight hydrocarbon observed was propane, implying that the rate of carbon–carbon bond formation is slow relative to the rate of hydrogenation and desorption.

Deuterium isotope effects arise from two sources (*5, 10, 15*): first, the kinetic and second, the thermodynamic or equilibrium isotope effects. The kinetic isotope effect is the result of the difference in zero-point energy associated with the dissociating bonds containing the hydrogen isotope and can be approximated by the difference in zero-point energies for the reactants, $E_{0(\mathrm{D})} - E_{0(\mathrm{H})}$. The magnitude of $E_{0(\mathrm{D})} - E_{0(\mathrm{H})}$ can be evaluated from vibrational frequencies and for the C–H and C–D bonds the difference is about 1.1 kcal/mol, from which the ratio of the rate constants, $k_\mathrm{H}/k_\mathrm{D}$, is calculated to be as high as 3 at 300°C. However, a large kinetic isotope effect is rarely observed suggesting that some zero-point energy is associated with the activated complex, $E^*_{0(\mathrm{D})} - E^*_{0(\mathrm{H})}$.

The thermodynamic isotope effect arises from a change in the surface concentration of a reaction intermediate. The equilibrium constant ratio, $K_\mathrm{H}/K_\mathrm{D}$, is determined largely by the energy difference between the hydrogen-containing products (methane and water) and the reactant (hydrogen)

$$E_{0(\mathrm{CH_4})} - E_{0(\mathrm{CD_4})} + E_{0(\mathrm{H_2O})} - E_{0(\mathrm{D_2O})}) \\ -3E_{0(\mathrm{H_2})} - E_{0(\mathrm{D_2})}) = 5.4 \text{ kcal/mol.}$$

At lower temperatures the value of $K_\mathrm{D}/K_\mathrm{H}$ increases due to an exponential term in the partition function. Observed isotope effects result from a combination of the kinetic and thermodynamic effects (*15*). Since we have observed an equilibrium deuterium isotope effect, the rate-determining step of the reaction involves hydrogen.

Pressure dependence studies for the reaction gave a negative 1.0 ± 0.1 order in CO and a positive 1.0 ± 0.1 order in H_2. These values are typical for methanation catalysts (*16*) and generally explained by CO adsorbing very strongly on the surface and acting as a "self poison" of the reaction. Other studies (*17*) on rhodium methanation catalysts have been carried out at total pressures of 75 atm. These studies found the pressure dependence of the reaction to be proportional to Rate $= P_{\mathrm{H_2}}^{+1/2} P_{\mathrm{CO}}^{-1/2}$ suggesting that in our lower-pressure studies the RDS may shift from $\mathrm{C^* + H^* \rightarrow CH^*}$ step to $\mathrm{CH^* + H^* \rightarrow CH_2^*}$. This difference is in the direction expected from a decrease in the total pressure and an interesting set of future experiments would be to investigate the pressure dependence of the reaction at even lower total pressures.

CONCLUSIONS

In this note we have shown that a large equilibrium deuterium isotope effect is observed in the hydrogenation of CO over rhodium polycrystalline foils. We find the activation energy for the reaction to be similar to other methanation catalysts. Also we observe that the pressure dependence of the reaction obeys the rate law: $\mathrm{Rate}_{\mathrm{CH_4}} = KP_{\mathrm{H_2}}^{+1} P_{\mathrm{CO}}^{-1}$. These observations lead us to conclude that one of the final hydrogenation steps is indeed rate limiting.

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