JOURNAL OF CATALYSIS 49, 383–385 (1977)

Heterogeneous Methanation: Absence of H_2–D_2 Kinetic Isotope Effect on Ni, Ru, and Pt

Although the catalytic hydrogenation of CO is a relatively simple reaction, its mechanism on Group VIII metals has been difficult to establish unambiguously. The mechanistic pathways proposed first (*1*) were based on the formation of a carbide which is then hydrogenated to methane. More recently, partially hydrogenated oxygen-containing intermediates have been postulated (*1*). These surface species can be further hydrogenated to methane and water or can polymerize to higher hydrocarbons, alcohols, etc. Experimental evidence in support of the partially hydrogenated surface species was deduced mainly from two sources (*2*): (i) from coadsorption of H_2 and CO where the mutually enhanced adsorption implies surface compound formation, and (ii) from infrared data showing the presence of C–H and O–H surface structures.

More recent work on single crystal surfaces and polycrystalline films gives little evidence for the presence of an oxygen-containing surface complex. Wedler *et al.* (*2*) studied the interaction of H_2 and CO on Ni films up to temperatures of 353 K and found only small changes in the heat of adsorption and surface coverage. On Ni(III), Ertl and co-workers (*3*) observed similar results and, in addition, established by ultraviolet photoelectron spectroscopy that adsorbed CO maintains its molecular structure. Ruthenium behaves in a similar manner (*4*).

Independently of whether the rate determining step is the partial hydrogenation of CO to the proposed oxygenated intermediate or the further hydrogenation to products, the involvement of hydrogen should lead to a significant kinetic isotope effect when hydrogen is replaced by deuterium. In one instance on Ru powder, the hydrogen–deuterium kinetic isotope effect was found to be large; the ratio of CH_4/CD_4 formation rate was 2.2 over the temperature range of 300 to 420 K (*5*). We report here the measurements of hydrogen–deuterium kinetic isotope effects in the hydrogenation of CO on supported Ni, Ru, and Pt catalysts.

Initial reaction rates were measured in a Pyrex batch-recycle reactor described previously (*6*). The reactor was operated differentially with a very small conversion per pass and the total conversion generally below 1%. The gas chromatographic analysis employed a flame-ionization detector calibrated with pure CH_4 and pure CD_4. Deuterium (Matheson Co.) was >99.5% pure. The supported catalysts were prepared by incipient wetness impregnation of Dispal M alumina (Continential Oil Co.) or zirconia (NL Industries) and have been described in previous publications (*7, 8*). The reported metal surface areas, M_S, measured by hydrogen chemisorption, were: 5% Ni/ZrO_2, 159 μmol g^{-1}; 1.5% Ru/Al_2O_3, 54.8 μmol g^{-1}; and 10% Pt/Al_2O_3, 40.0 μmol g^{-1}.

The measured initial rates for Ni, Ru, and Pt are presented in Figs. 1, 2, and 3. The rates are expressed as turnover number, N, molecules of methane or total hydrocarbons produced per surface metal atom per second. Within the experimental

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ISSN 0021-9517

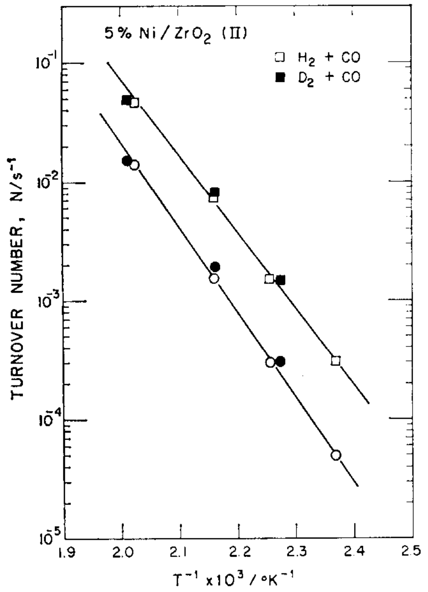

FIG. 1. Rate of hydrogenation of CO in H_2 (open points) or D_2 (closed points) to total hydrocarbons (□) and CH_4(O) on 5% Ni/ZrO_2 (II) catalyst. P_{H_2} = 0.5625 atm, P_{CO} = 0.1875 atm.

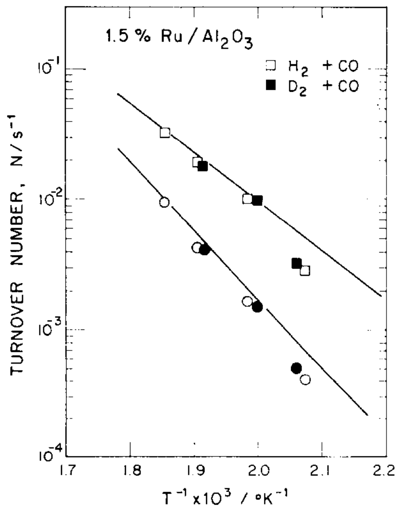

FIG. 2. Rate of hydrogenation of CO in H_2 (open points) or D_2 (closed points) to total hydrocarbons (□) and CH_4 (O) on 1.5% Ru/Al_2O_3. P_{H_2} = 0.5625 atm, P_{CO} = 0.1875 atm.

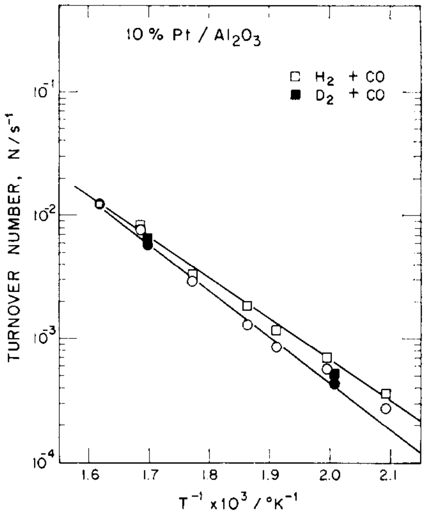

FIG. 3. Rate of hydrogenation of CO in H_2 (open points) or D_2 (closed points) to total hydrocarbons (□) and CH_4 (O) on 10% Pt/Al_2O_3. P_{H_2} = 0.5625 atm, P_{CO} = 0.1875 atm.

reproducibility, the rate of methane formation using H_2 or D_2 is identical on all three catalysts. This is also true for C_{2+} hydrocarbon production on Ni and Ru where these products represent a substantial fraction of the hydrocarbons produced. It should also be noted that some data were obtained on a well-dispersed 5% Pt/Al_2O_3 sample, with an H/Pt adsorption ratio greater than 1, and in this case as well, the CH_4 and CD_4 formation rates were identical to those presented in Fig. 3. These data are inconsistent with the results of McKee (*5*) obtained on Ru powder. In this latter work, different conditions were used and different kinetics were obtained. This may have resulted in a system with a different mechanism. A second possibility is a problem with the analytical system used. The molecular leak to a mass spectrometer could result in different sensitivities to CH_4 and CD_4. Actual calibration of the analytical system was not discussed.

The catalysts studied span the Group VIII metals from the most active, Ni and Ru, to one of the least active, Pt (*9*). The absence of the isotope effect over the investigated temperature range constitutes strong evidence for the noninvolvement of hydrogen in the rate-determining step. A mechanism more consistent with the present observations would include the scission of the C–O bond as the slow step, followed by rapid hydrogenation of the fragments. The presence of H_2 in the measured kinetics and the observed enhanced coadsorption of CO and H_2 may be due to interaction between the adsorbed CO and H on adjacent or the same surface metal atoms.

Such a mechanism is supported by the results of Wentrcek *et al.* (*10*) where CO rapidly decomposed at 553 K on supported Ni to give surface carbon with a carbide-like Auger electron spectrum. In the presence of hydrogen, this surface carbide is hydrogenated to methane at a faster rate than that expected for a bulk carbide. Dissociative adsorption of CO has been observed at temperatures as low as 400 K on polycrystalline Ni (*11*) and on a single crystal Ni (111) surface at temperatures above 450 K (*3*). Also Araki and Ponec (*12*) used ^{13}CO to form a surface layer of dissociated carbon which upon subsequent reaction with $^{12}CO + H_2$ resulted in the exclusive formation of $^{13}CH_4$ with no apparent induction period.

Adsorbed hydrogen (or deuterium) under reaction conditions does, however, affect the strength of the C–O bond of adsorbed carbon monoxide. This interaction is clearly shown by the shift of the C–O band on Ru to lower frequencies in the presence of adsorbed hydrogen (*13*), thus facilitating its scission.

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Received February 4, 1977; revised May 8, 1977

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