

H₂-D₂ Kinetic Isotope Effect in CO Hydrogenation over Ru/SiO₂

By YOSHIHIRO KOBORI, SHUICHI NAITO, TAKAHARU ONISHI, and KENZI TAMARU

(Department of Chemistry, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan)

Summary The H₂-D₂ kinetic isotope effect was measured on a Ru/SiO₂ catalyst not only for the hydrogenation of CO but also for the hydrogenation of deposited carbon formed by disproportionation of CO; similar inverse kinetic isotope effects were observed in both cases, which led to the conclusion that the rate-determining step was the hydrogenation of carbon formed by dissociative adsorption of CO.

THERE is growing evidence to show that the hydrogenation of CO to form hydrocarbons proceeds on various transition metals¹ via the carbon formed by dissociative adsorption of CO, but the rate-determining step of the overall reaction still remains a controversial problem. Studies of the H₂-D₂ kinetic isotope effect for CO hydrogenation have yielded contradictory results. Sakharoff and Dokukina reported $\alpha = 0.77$ on a cobalt catalyst,² where α is the

ratio of the rate of the H₂-CO reaction to that of D₂-CO reaction, whereas McKee reported $\alpha = 2.2$,³ and Dalla Betta and Shelef reported the absence of any kinetic isotope effect, concluding the rate-limiting step to be CO dissociation.⁴ We have also measured not only the α value for CO hydrogenation but also that for the hydrogenation of deposited carbon formed by dissociative adsorption of CO over Ru/SiO₂, and obtained evidence that the rate-determining step was the hydrogenation of the carbon from dissociative adsorption of CO.

A 4.5 wt.% Ru/SiO₂ catalyst was prepared by impregnating silica (Aerosil) with an aqueous solution of RuCl₃ (Wako) followed by H₂ reduction for 20 h and evacuation for 2 h at 723 K. The reaction was carried out in a conventional closed-circulation system. Methane production was analysed by gas chromatography, whereas other hydrocarbon products were trapped by a liquid nitrogen trap during the reaction and were oxidized over Pd black (Nippon Engelhard) at 573 K with O₂ gas to form CO₂. The amount of CO₂ thus produced, which corresponds to the total carbon content of the hydrocarbon products with 2 or more carbon atoms (C₂⁺), was measured volumetrically or gas chromatographically.

The rate of CO hydrogenation was measured using 0.1 g of the catalyst and, prior to each run, the catalyst was reduced by H₂ or D₂ at the reaction temperature for 1 h. Figure 1 shows an inverse kinetic isotope effect ($\alpha = 0.57 \pm 0.12$ for methane and $\alpha = 0.43 \pm 0.11$ for C₂⁺ formation) for CO hydrogenation in the temperature range 413–473 K.

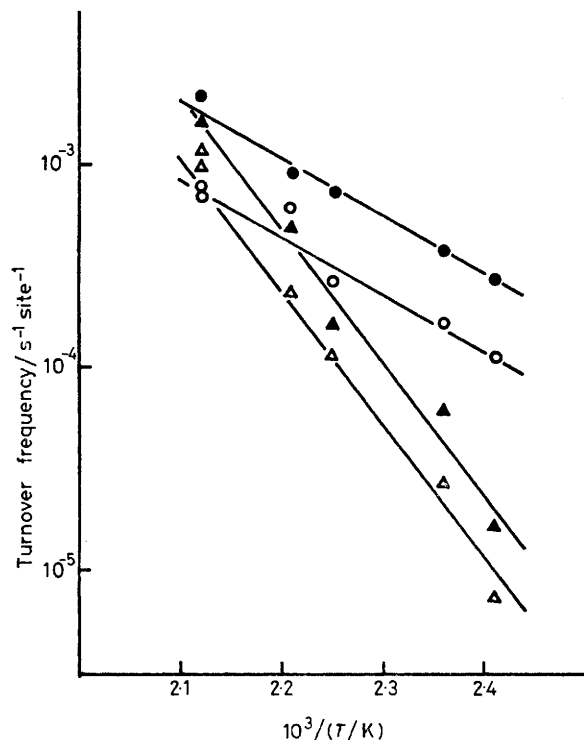


FIGURE 1. The rates of methane and C₂⁺ hydrocarbon formation in the reactions of CO-H₂ and CO-D₂ over Ru/SiO₂. $P(\text{H}_2) = 60$ Torr, $P(\text{CO}) = 30$ Torr. Turnover frequency (the number of carbon atoms in the hydrocarbons produced per second divided by the number of surface metal atoms) was calculated by taking the amount of adsorbed CO at room temperature (2.8 ml-S.T.P./g of catalyst)† as corresponding to the number of surface metal atoms: Δ , methane (CO-H₂), apparent activation energy 130 ± 5 kJ/mol; \blacktriangle , methane (CO-D₂), 122 ± 8 kJ/mol; \circ , C₂⁺ hydrocarbon (CO-H₂), 55 ± 6 kJ/mol; \bullet , C₂⁺ hydrocarbon (CO-D₂), 52 ± 3 kJ/mol.

† The unit 'ml-S.T.P./g of catalyst' means the amount of CO adsorbed (calculated as a volume at 273 K and 1 atm) per gram of catalyst.

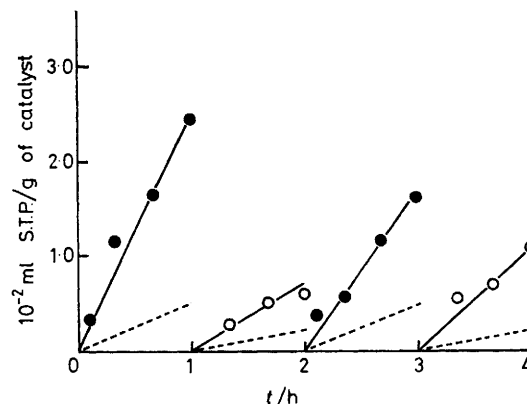


FIGURE 2. Formation of methane at room temperature by the hydrogenation or deuteration of deposited carbon formed by CO disproportionation at 423 K over Ru/SiO₂. $P(\text{H}_2) = 26$ Torr, initial amount of CO(ads) = 2.4 ml-S.T.P./g of catalyst; initial amount of deposited carbon corresponds to 0.19 ml-S.T.P./g, which was estimated from the amount of CO₂ produced in the disproportionation reaction. After each hydrogenation (deuteration) reaction for 1 h, the gas phase was replaced by D₂ (H₂): \circ , hydrogenation; \bullet , deuteration; broken lines, methane formation by hydrogenation or deuteration of CO(ads) measured in the absence of deposited carbon.

We then measured the kinetic isotope effect for hydrogenation of the carbon deposited by disproportionation of CO, using 3.1 g of the catalyst. Introducing CO to the clean catalyst at 423 K led to disproportionation of CO and a small amount of active carbon species accumulated on the catalyst. After evacuation for a short time at 423 K, H₂ or D₂ was introduced to the carbon deposited on the surface at 297 K, and the rate of CH₄ or CD₄ production was measured. The time courses of the reaction are shown in Figure 2, which indicates that the production of CD₄ is faster than that of CH₄; α was determined to be 0.54 ± 0.17 from the average of several runs.

The inverse kinetic isotope effect can be interpreted in terms of a larger surface concentration of CD_x than of CH_x because of the thermodynamic stability of CD_x, and the similar α value in the hydrogenation of both CO and deposited carbon strongly suggests that the rate-determining step for the hydrogenation of CO over ruthenium catalysts involves the hydrogenation of dissociated carbon.

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³ D. W. McKee, *J. Catal.*, 1967, **8**, 240.

⁴ R. A. Dalla Betta and M. Shelef, *J. Catal.*, 1977, **49**, 383.