

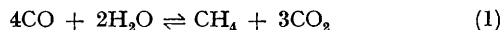
Methane Formation from Carbon Monoxide and Water over a Rhodium Y Zeolite Catalyst

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Summary Rhodium Y zeolite in the reduced form is an effective catalyst for the selective conversion of carbon monoxide and water into methane.

ALTHOUGH hydrocarbon synthesis *via* the reaction of CO and H₂ has been the subject of numerous studies, relatively little attention has been given to the direct formation of methane from reaction (1). This reaction, known as the



Kölbl-Engelhardt reaction occurs over, *e.g.*, iron-iron oxide catalysts, and is presumed to involve a water-gas shift reaction, followed by the Fischer-Tropsch synthesis. The iron-iron oxide catalyst is believed to undergo a series of steps which depends on a delicate balance between the reduced and oxidized state of the catalyst.¹ We now report on the catalytic activity of a RhY zeolite for reaction (1).

The catalyst was prepared by exchange of Rh³⁺ ions into a NaY zeolite (Linde), using 3.5 l of 1.85 × 10⁻⁴ M rhodium nitrate with 3.0 g of zeolite. The degree of exchange was 20%, which corresponded to 2.2% Rh by weight. The catalyst was degassed for 1 h at 25 °C, 1 h at 100 °C, and in 100 °C increments (1 h each) to 400 °C. At the latter temperature the catalyst was reduced in recirculating H₂ for 16 h with a cold trap in the system. The carbon monoxide and the reaction products were analysed by gas chromatography. A Porapak Q column was used at 70 °C for the separation of CO, CH₄, and CO₂. Hydrogen was separated over a molecular sieve 13X column at room temperature and was oxidized to H₂O over a CuO bed at 370 °C. The oxidation step greatly enhanced the sensitivity for H₂ in the He carrier gas.

The catalytic reaction over 0.2 g of RhY zeolite was carried out in a 248 cm³ closed-loop recirculating flow reactor in the temperature range 280–340 °C. Water (15 Torr) and carbon monoxide (22 Torr), after being thoroughly mixed, were admitted to the catalyst. After each experimental run, hydrogen was recirculated at the

reaction temperature for about 1 h in order to obtain a reproducible activity. The catalyst activity was stabilized after a few experimental runs. A typical result obtained at 329 °C is shown in the Figure. In the initial stage of the

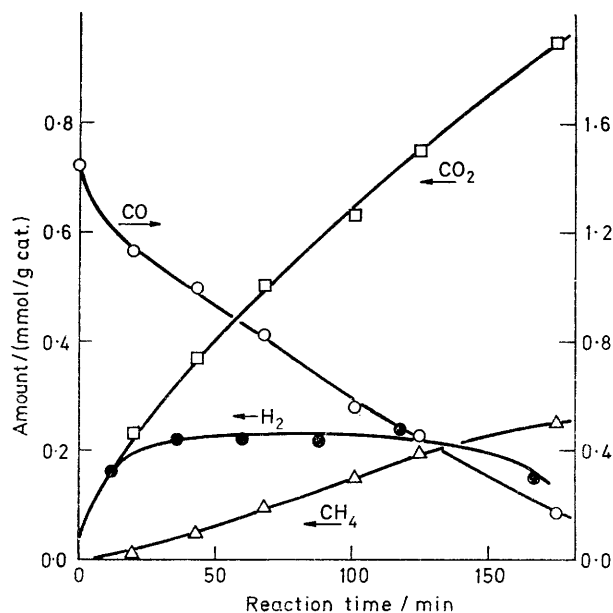


FIGURE. Amount of CO₂, H₂ and CH₄, and unchanged CO as a function of reaction time at 329 °C over a RhY zeolite. The reactant gas contained 15 Torr of H₂O and 22 Torr of CO.

reaction nearly equimolar amounts of CO₂ and H₂ were formed. After 10 min, methane was formed linearly with time, and the hydrogen concentration remained constant. In this region, methane and carbon dioxide were formed stoichiometrically according to equation (1). Furthermore, a carbon balance was achieved with respect to removal of CO and formation of gas-phase products.

* 1 cal = 4.184 J.

From the variation of the rate of disappearance of CO with temperature, after the initial stages of reaction, an activation energy of $21.4 \text{ kcal mol}^{-1}$ † was determined. A decrease in H_2 was observed at 329°C when the conversion of CO exceeded about 80%. The plateau in the H_2 concentration was not significantly affected by the reaction temperature, in contrast to the rates of formation of CO_2 and CH_4 .

The products contained no hydrocarbons other than CH_4 . The high selectivity for the formation of CH_4 is similar to the methanation of carbon dioxide on polycrystalline Rh,² and can be contrasted with the reaction of CO and H_2 on Al_2O_3 -supported Rh,³ for which higher hydrocarbons were observed. Similar selectivities for the CO_2 - H_2 and CO - H_2

reactions were also found in our preliminary work on the RhY catalyst.

These results are consistent with the occurrence of a water-gas shift reaction followed by the hydrogenation of CO_2 to form methane. The significant amounts of H_2 in the gas phase suggests that the rates of the two reactions are comparable. It is difficult, however, to rule out the direct catalytic reaction between CO and H_2O from the kinetic data in the Figure.

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³ M. A. Vannice, *J. Catalysis*, 1975, **37**, 449.