Carbon Dioxide and Carbon Monoxide Methanation by Supported Ruthenium Catalysts

Helen E. Ferkul, Deborah J. Stanton, James D. McCowan, and Michael C. Baird*
Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6

Ruthenium carbonyl clusters, adsorbed on oxide supports and thermally decomposed under hydrogen, are very active catalysts for the methanation of both carbon monoxide and carbon dioxide.

Dispersed ruthenium metal, prepared by the reduction of ruthenium salts impregnated on inert supports, has long been known to catalyse the hydrogenation of carbon monoxide to methane (low pressure) and polymethylenes (high pressures).[1-3] Very recently, several attempts to utilize ruthenium carbonyl clusters as catalyst precursors for CO hydrogenation have been reported; [4-8] in all cases, the catalysts exhibited low activities, short lifetimes, or low selectivities. However, this approach presents a very facile alternative to the more traditional methods of catalyst preparation. We now relate the results of a series of experiments using $Ru_3(CO)_{12}$,[9] $H_2Ru_4(CO)_{13}$,[10] $H_2FeRu_3(CO)_{13}$,[10] and $[(Ph_3P)_2N][CoRu_3(CO)_{13}]$[11] as catalyst precursors, including comparisons of catalyst activities as functions of both precursor and support. In some cases, our results differ considerably from earlier published data but, more interestingly, we find $Ru_3(CO)_{12}$ on γ-alumina, at least, is a very efficient catalyst for the hydrogenation of carbon dioxide. Hydrogenation of CO_2 appears to be a little studied subject, although there is interest in its catalysis by nickel.[12]

The cluster compounds were placed on dried (500 °C) λ-alumina, silica gel, or Na-Y zeolite by mixing the solid support with a solution of the cluster in n-pentane or di-ethyl ether for several hours under nitrogen. The solvents were then removed under reduced pressure, and the supported compounds were placed in a glass-lined tubular reactor in a stream of nitrogen. The catalyst systems, which contained *ca.* 1% by weight of metal, were then activated by heating to 200 °C in a stream of hydrogen (1 atm) for 12 h.

Catalytic activities were determined by passing synthesis gas ($H_2:CO$ ratios varied from 1.85:1 to 4:1) through the catalysts in the temperature range 200—400 °C (total pressure 1 atm, space velocities 1000—3750 h^{-1}). The products were collected as gases or liquids, and their distributions were monitored using a Hewlett Packard 5880 gas chromatograph.

The results of the study can be summarized as follows. (i) The major hydrocarbon product in all cases was methane although traces of C_2—C_4 hydrocarbons were also obtained. The yields of C_2—C_6 hydrocarbons obtained by others[8] under apparently very similar conditions were not observed. Indeed, as reported by Simpson and Whyman,[13] we find that $Ru_3(CO)_{12}$ on alumina is a very effective catalyst for the hydrogenolysis of alkanes to methane. (ii) Carbon monoxide conversions into methane generally increased with both increasing temperature and increasing $H_2:CO$ ratios, but varied considerably with different supports and catalyst precursors. In general, catalyst activities were highest using alumina as the support, and lowest on silica. The relative ordering of the clusters varied somewhat for each support, with the mixed cobalt–ruthenium carbonylate anion being inactive on both silica and the zeolite.

The best yields were obtained with $Ru_3(CO)_{12}$ on alumina (100% methane yields from an 81% conversion of carbon monoxide at 360 °C, $H_2:CO$ 4:1). Comparison with the well known $RuCl_3.3H_2O–Al_2O_3$ system[2] showed that, while the latter has somewhat higher activity, it also deactivates faster and is less readily regenerated under hydrogen at 200 °C.

(iii) Oxygen-containing by-products were water and carbon dioxide, the proportion of the latter decreasing drastically as the $H_2:CO$ ratio increased. This behaviour, which appears to be without precedent, suggested that the catalysts were also active for carbon dioxide methanation. While the use of ruthenium metal as such a catalyst at high pressures has been reported,[1] little work seems to have been done on low pressure methanation, and certainly the use of ruthenium carbonyl clusters for this type of chemistry has not been reported.

We find that $Ru_3(CO)_{12}$ on alumina is a very effective catalyst for the methanation of carbon dioxide at 275 °C, yields of 60—70% having been obtained on a single pass ($H_2:CO_2$ ratio 4:1). Again direct comparison with $RuCl_3.3H_2O–Al_2O_3$ showed that the latter is less active, requiring an operating temperature of *ca.* 365 °C to exhibit similar CO_2 conversions. While no studies of the catalyst system have as yet been made at higher pressures, it is anticipated that near quantitative conversions of carbon dioxide into methane will be possible. Such a result would be of great potential significance in view of current interest[14] in the use of carbon dioxide for the production of substitute natural gas. Furthermore, as the $Ru_3(CO)_{12}–Al_2O_3$ system smoothly hydrogenates CO_2 in the presence of CO, it may well be one of the most effective catalysts known for the methanation of mixtures of the two carbon oxides.

We thank Queen's University and the Natural Sciences and Engineering Research Council of Canada for financial support, and Johnson Matthey, Ltd., for the loan of ruthenium trichloride.

Received, 29th March 1982; Com. 360

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