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Preliminary communication

THE ACTIVITY OF SOLUTIONS OF $Ru_3(CO)_{12}$ AS CATALYSTS FOR THE FISCHER—TROPSCH REACTION

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Summary

Solutions of dodecacarbonyl-*triangulo*-triruthenium [$Ru_3(CO)_{12}$] have been shown to be catalyst precursors for the Fischer—Tropsch reaction; the catalyst formed under the reaction conditions is heterogeneous; no indication of homogeneous activity was found.

There has been considerable interest recently in the catalytic activity of soluble transition-metal cluster complexes. This originates principally from a suggestion [1] that such complexes, because they consist of a framework containing metal—metal bonds, may have some characteristics of heterogeneous catalysts. Should this be so, soluble clusters may, in solution, be able to effect catalytic conversions which have not, hitherto, been demonstrated with homogeneous systems. One such reaction is the conversion of synthesis gas (H_2 + CO) to a Schulz—Flory distribution of linear hydrocarbons from methane to polymethylene, as found in the Fischer—Tropsch reaction [2]*.

A recent patent application [4] describes the use of the triangular cluster complex $Ru_3(CO)_{12}$ in solution as a catalyst for the Fischer—Tropsch reaction; typical conditions were circa 100 bar synthesis gas (CO/H_2 1/1) at 300°C in heptane. In view of reports of soluble catalyst systems which convert synthesis gas to inter alia ethylene glycol [5], methanol [5,6], methane [7,8] and ethane [8] we undertook a more detailed study of the above Fischer—Tropsch reaction in an attempt to ascertain the possibility of any homogeneous activity [9].

Using an autoclave equipped with a sampling device, solution infrared spectra were taken of samples removed in the course of the reaction. An initial observation was that, during hydrocarbon formation at 250°C and 100 bar synthesis gas,

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*The formation of alkylbenzenes from a benzene solution of $W(CO)_6$ and $AlCl_3$ under synthesis gas has recently been described and may be considered to be a homogeneous Fischer-Tropsch-type reaction [3].

the samples contain at least three ruthenium complexes, which are probably in equilibrium under the reaction conditions as shown in eq. 1 [10].

$$H_4Ru_4(CO)_{12} \underset{-CO,\ +H_2}{\overset{+CO,\ -H_2}{\rightleftharpoons}} Ru_3(CO)_{12} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} Ru(CO)_5 \qquad (1)$$

Thus, cluster build-up as well as cluster rupture occurs under these conditions. Furthermore, it was clearly seen that during the reaction these soluble ruthenium species were lost from solution as evidenced by a gradual decrease in the intensity of the carbonyl stretching frequencies. A series of such infrared spectra taken over 25 h is shown in Fig. 1*. Significantly, the reaction continues after all ruthenium carbonyl complexes have been lost from the solution. The colourless solution remaining was tested for catalytic activity under the same conditions in a separate autoclave experiment and was found to be inactive; subsequent analysis of this solution revealed only trace quantities of soluble ruthenium species to be present. The residue remaining in the autoclave, however, was active for the Fischer—Tropsch reaction. Thus, a heterogeneous reaction can occur under these conditions with $Ru_3(CO)_{12}$ as the catalyst precursor**.

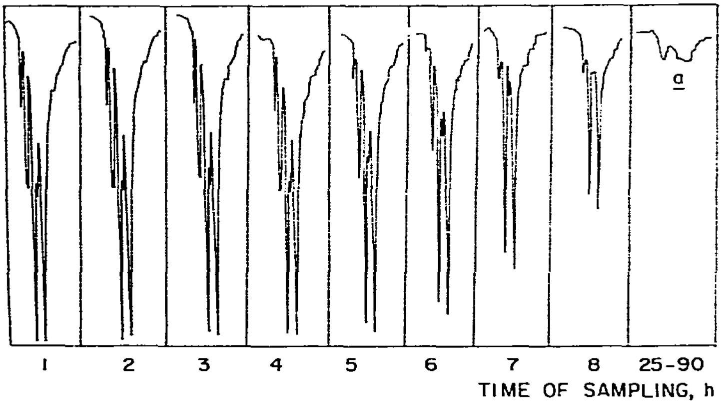

Fig. 1. IR spectra of the carbonyl stretching region (1950—2150 cm^{-1}) of solution samples taken from an autoclave. Initial charge: $Ru_3(CO)_{12}$ dissolved in heptane; H_2/CO 1/1 (pressure ≈ 115 bar; $T \approx 250°C$)*. a. Absorption entirely due to impurities on the plates of the IR cell; an identical spectrum is obtained with pure heptane.

There is a possibility, however, that the heterogeneous reaction masks any homogeneous activity. Prevention of the decomposition of the ruthenium complexes under Fischer—Tropsch conditions would, therefore, be necessary to observe any activity occurring in solution. To eliminate the possibility of decomposition induced by impurities introduced into the autoclave during filling, particular care was taken to remove air and moisture from the system. Taking these precautions it was possible, by using a constant pressure of ca. 100 bar of synthesis gas and raising the temperature slowly to 250°C, to maintain the equilibrium shown in eq. 1 without decomposition for 26 h. In this system no

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[*] $\nu(CO)$ for (a) $H_4Ru_4(CO)_{12}$; (b) $Ru_3(CO)_{12}$ and (c) $Ru(CO)_5$ in heptane are (a) 2081s, 2067vs, 2030m, 2024s, 2008w; (b) 2060vs, 2029s, 2010m; and (c) 2035vs, 1999vs cm^{-1}, respectively [11].

[**] Ruthenium metal is well known as an active catalyst for the Fischer—Tropsch reaction [12].

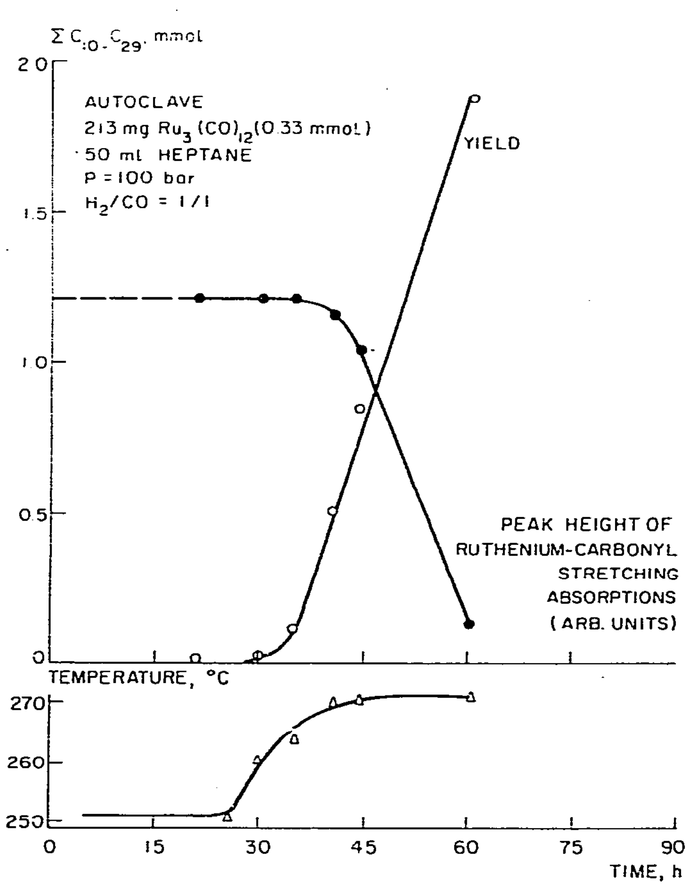

Fig. 2. Hydrocarbon formation from CO and H_2.

catalytic reduction of carbon monoxide took place. Raising the temperature slowly to 270°C resulted in the slow formation of linear alkanes; coincident with this activity, however, was the deposition of insoluble ruthenium species from the solution as observed by a decrease in the intensity of the carbonyl stretching frequency (see Fig. 2).

From the above observations, especially the lack of activity of soluble ruthenium complexes shown in eq. 1, it can be definitively stated that these complexes are not homogeneous catalysts for synthesis gas conversion under the above conditions. A heterogeneous reaction is taking place and, with the present data available, there is no reason to suggest that a homogeneous reaction is occurring.

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