Effect of Temperature of Reduction on the Activity and Selectivity of a Coprecipitated Ni–Al_2O_3 Catalyst for the Fischer–Tropsch and Methanation Reactions

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Summary The reaction of CO with H_2 at 473 K and at low pressures over a coprecipitated Ni–Al_2O_3 catalyst has been examined; it has been found that both methane and higher hydrocarbons are formed and that the activity and selectivity of the catalyst depends on the temperature (and hence, the degree) of reduction, low temperatures favouring the production of higher hydrocarbons.

IT is generally considered that nickel is a selective methanation catalyst.[1] However, several recent papers[2,3] have reported investigations of the methanation of CO over Ni at temperatures in excess of *ca.* 520 K which have shown that relatively high proportions of higher hydrocarbons are also formed. Little attention has been paid to the latter (Fischer–Tropsch) activity of nickel, the main interest being in comparisons between various metals, for example Ru, Ni, and Re[2] and other elements of Group 8.[3] Van Barneveld and Ponec[4] have recently examined the influence of alloying Ni with Cu on the selectivity for the Fischer–Tropsch reaction at *ca.* 600 K and have found that while Cu decreases the activity of nickel, it also increases the selectivity towards higher hydrocarbon formation; the maximum proportion of higher hydrocarbons which they report is *ca.* 5%. We present in this communication results which show that both the activity and selectivity of a coprecipitated Ni–Al_2O_3 catalyst vary markedly as a function of the temperature of reduction of the catalyst and that the selectivity towards higher hydrocarbons of this catalyst can be >50%.

The catalyst containing 40% Ni by weight in its unreduced form, was prepared by coprecipitation from a solution of $Ni(NO_3)_2$ and $Al(NO_3)_3$ by the addition of Na_2CO_3 solution, both solutions being maintained at 368 K; the precipitate was aged at the same temperature for 90 min followed by filtration, washing, and overnight drying at 378 K. Before use, it was calcined at 723 K for 17 h and was then reduced in the reaction system (described below) in H_2 at an initial pressure of *ca.* 10 kN m^{-2} for 3 h after outgassing at < 1 mN m^{-2} for 1 h at the same temperature.

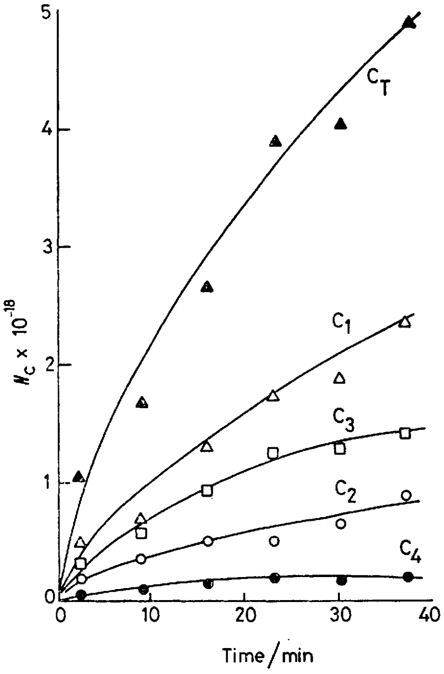

FIGURE 1. The reaction of CO with H_2 at 473 K over a 40% Ni–Al_2O_3 catalyst reduced in H_2 at 673 K for 3 h; the total number of carbon atoms in the products (▲), in methane (△), ethane (○), propene + propylene (□) and in butane + the butenes (●) are shown plotted against time of reaction.

The temperature of reduction, T, varied from 573 to 973 K and one sample was tested for activity without reduction. The reaction of CO with H_2 over the various samples was investigated in a constant volume recirculation reactor with g.l.c. analysis of the products; standard reaction mixtures of 0·67 kN m^{-2} of CO and 2·00 kN m^{-2} of H_2 were used in all the experiments reported here and the reaction temperature was 473 K throughout. Fresh samples of *ca.* 0·1 g of the catalyst were used for each experiment. Separate hydrogen chemisorption experiments, not reported here, showed that the nickel area of the catalyst increases with increasing reduction temperature.[5] *X*-Ray diffraction showed the presence of metallic Ni and NiO in the partially reduced samples; $NiAl_2O_4$ could not be distinguished.

Preliminary results show that the catalyst is active at temperatures above *ca.* 410 K and a standard temperature of 473 K was chosen as it gave convenient rates, the reaction nearing completion in typical cases after 1—2 h depending on the activity of the sample. A typical experiment is shown in Figure 1 which shows the number of carbon atoms incorporated in each product molecule plotted as a function of time; in this case, about 15% of the CO had reacted after 30 min. The selectivity towards methane is throughout somewhat <50%, there being a slight increase in the later stages of the reaction; this increase was more marked after reduction at higher temperatures and indicates that higher hydrocarbons formed in the early stages of the reaction subsequently react to give methane by a secondary hydrogenolysis reaction. The C_3 and C_4 products consist of both saturated and unsaturated hydrocarbons and the proportion of the latter decreases in the later stages of the reaction, indicating preferential hydrogenolysis of the unsaturated molecules.

Figure 2 shows the initial activities and selectivities taken from plots such as in Figure 1 for the reaction at 473 K over the same catalyst as a function of the reduction temperature. Also shown for each reduction temperature is the % reduction achieved after 3 h calculated from the consumption of hydrogen during that time. On the left-hand axis are shown the activity and selectivity of a catalyst which had not been pre-reduced. It can be seen from Figure 2 that the degree of reduction increases with reduction temperature and that there is a concurrent rise in the activity of the catalyst. The selectivity towards methane formation initially falls slightly and then increases once more at a reduction temperature of *ca.* 723 K, remaining constant thereafter at *ca.* 65%. The rise in the selectivity occurs at the same reduction temperature as a distinct increase both in the rate of the reaction and in the degree of reduction of the catalyst. Similar changes in selectivity and activity have been noted with other catalysts prepared by similar methods.[5]

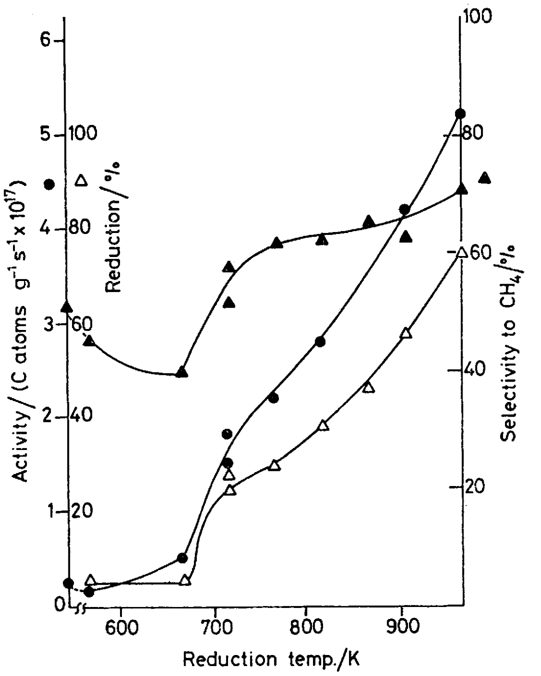

FIGURE 2. The activity (●), % reduction (△) and % selectivity towards methane (▲) as a function of temperature of reduction; the left-hand axis corresponds to an unreduced sample.

Clearly, the change in selectivity of the catalyst is associated with changes occurring on the surface during the reduction process. One possibility is that the formation of higher hydrocarbons occurs on unreduced sites and that methanation occurs on metallic nickel; however, the activity for formation of higher hydrocarbons increases up to a reduction temperature of *ca.* 673 K. It is therefore more probable that the sites first formed by reduction differ somewhat either in geometry or environment from those formed at higher temperatures, and favour the formation of higher hydrocarbons; the increase in activity and in the selectivity towards the formation of methane at higher reduction temperatures must be associated with the formation of massive Ni crystallites.

The present results clearly demonstrate the importance of the method of pre-treatment of a Ni–Al_2O_3 catalyst in determining its activity and selectivity.

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