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Influence of Alloying on the Selectivity in Fischer–Tropsch Synthesis by Nickel–Copper Alloys

There are some good reasons (*1*, *2*) why the interest in reactions of the Fischer–Tropsch type has recently increased. Besides being technically important, these reactions are also a very interesting object for selectivity studies. It is remarkable how metals which are very similar in hydrogenation (Co, Ni, Pd, Pt) differ in their activity and selectivity in reactions of hydrogen with carbon monoxide (*3*). It is equally surprising how little is known about the factors responsible for the selectivity of various metals in these reactions.

We have studied the reactions of carbon monoxide with hydrogen (reaction mixture 1:1) in an open flow apparatus (*4*) at atmospheric pressure and at a constant flow in all experiments (1 ml/sec). The total conversion was kept around 1% which eliminates possible complications due to mass and heat transfer. In all experiments we used 1 g of metal (alloy) catalyst of the indicated composition. The catalysts were nonporous Ni–Cu powders without carrier and were prepared from carbonates as already described (*4*, *5*). Analysis of the products was performed by glc. The activity of the catalyst was estimated from the sum of hydrocarbon concentrations and the selectivity was characterized by two parameters: $S_2 = C_2/(C_1 + C_2)$ and $S_3 = C_3/(C_2 + C_3)$, where C_i indicates how much CO was converted into hydrocarbons with i carbon atoms. Because only C_1, C_2, and C_3 hydrocarbons were formed in measurable amounts, with higher hydrocarbons in trace amounts only, the analysis of the selective behavior of catalysts was confined to these two parameters.

Figure 1 shows how the activity of the catalysts decreases by alloying. For comparison, the data from the paper on methanation by Ni–Cu films (*6*) at low pressures are also shown. Figure 2 shows the selectivity changes due to alloying at constant temperatures. The selectivities, S_i (at $T > 450$ K), are decreasing functions of temperature, and by alloying this curve is shifted to higher temperatures, so that at 593 and 613 K, the curves in Fig. 2 result.

When the CO feed is stopped after the steady state has been achieved, methane production continues over a considerable time interval, but ethane and propane disappear from the effluent gas almost instantaneously. When after some time the CO feed is reestablished, methane formation reaches the steady state more quickly than the higher hydrocarbons. However, the C_2/C_3 ratio is almost constant during this process nearing the steady state. It should be remembered here that according to previous work (*6*), CO admitted to a fresh (or hydrogen-covered) Ni surface preferentially (to other reactions) dissociated and disproportionated, and only after the surface had been modified to a certain extent by carbon being deposited on it did other reactions also achieve a steady state. On the other hand, the surface carbon is easily converted into methane in the absence of CO (*6*, *7*).

Three main points of the experimental results deserve further discussion:

(1) The activity toward the higher hy-

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drocarbon synthesis *decreases* with increasing Cu contents of the alloys in a way similar to methanation at low pressures (*6*). With methane we know this is because of the decrease in the number of ensembles (of Ni atoms) which can dissociate CO (*6*).

(2) At a given temperature, in the range where all catalysts revealed an activity, the selectivity toward higher hydrocarbons *increases* with Cu content.

(3) The synthesis of higher hydrocarbons requires the presence of carbon monoxide; the surface carbon is converted by hydrogen into methane only.

Considering all points simultaneously we arrive at the two following conclusions:

(i) As Fig. 1 strongly suggests, methanation and higher hydrocarbon synthesis might have some step(s) in common. If this is really so, the step must be the one which, along with methanation, is most strongly influenced by alloying, and this is the CO dissociation (*6*).

(ii) Synthesis of higher hydrocarbons is not a simple repetition of methane formation steps, such as, e.g., a polymerization of $-CH_2-$ groups (*8*, *9*) on the neighboring Ni sites (ensemble of sites is required). There are reasons to assume that CO is more directly involved in the propagation step (see 2 and 3).

The last statement on the role of CO needs some additional comment. The presence of CO is necessary for the chain growth for the following reason as well. In the absence of CO, hydrogen is adsorbed to too great an extent, and this leads to a fast removal of surface species by hydrogenation. Nevertheless, if CO were not essential for the chain growth, one would expect that the methane formed and desorbed could also contain higher hydrocarbons formed before the flow of CO had been

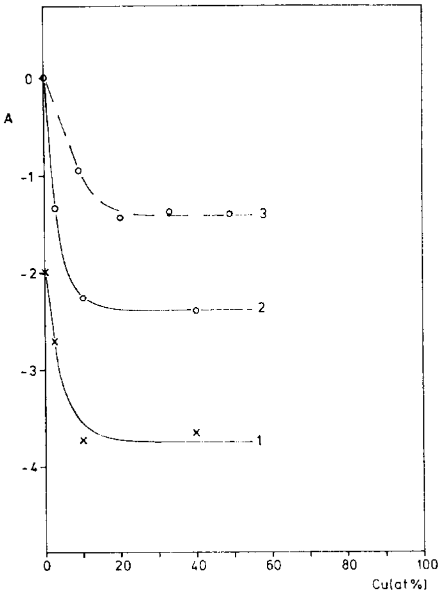

FIG. 1. Activity (logarithm of the rate in arbitrary units) as a function of alloy composition; T = 593 K, standard conditions. 1, formation of C_2 and C_3 hydrocarbons; 2, formation of methane. For comparison, data of an earlier paper on methane formation on alloy films (T = 573 K; total pressure, 0.6 Torr) are also shown (3, broken line).

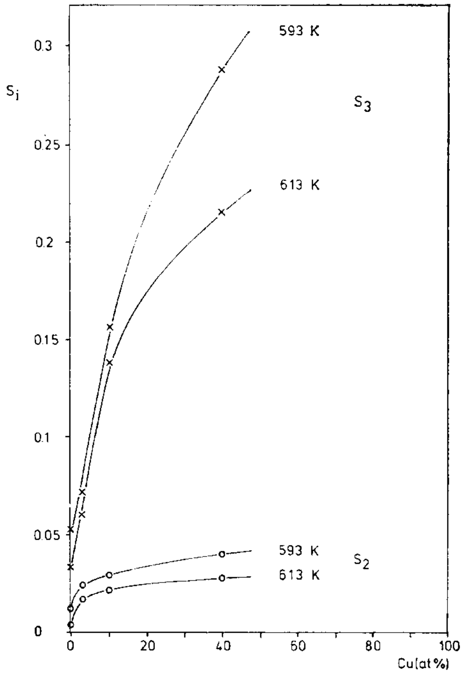

FIG. 2. Selectivity parameters, S, as functions of alloy composition. Temperatures at which various catalysts are compared are indicated. (For definition of S_2 and S_3, see text.)

stopped. In contrast to this expectation, higher hydrocarbons disappear almost instantaneously when the CO feed is stopped. Therefore, an explanation is preferred in which CO plays not only a "protective" role but also takes part in the chain growth process.

The selectivities defined as above are determined by the ratio of the two rates: rates of propagation and termination. In principle, both the increase of the first and the decrease of the second rate lead to higher values of S_i. It might be argued that on Ni–Cu alloys, as compared with Ni, the rate of termination is lower because of the lower surface concentration of hydrogen and lower rate of hydrogenation on alloys. However, many hydrogenation/dehydrogenation reactions were studied (*3, 5, 17*), and it has been found that on alloys the rate of hydrogenation per surface Ni atom is higher rather than lower in comparison with pure Ni. Therefore, it is assumed below that the increase of S_i is mainly due to a higher relative rate of propagation at the given temperature.

Let us examine which scheme can account for the phenomena observed. There are several mechanisms suggested in the literature, but we did not succeed in explaining the available data by any of them alone. However, as we shall see, a combination of various steps from different mechanisms can be very helpful.

For example, a mechanism (*3, 8, 9*) via polymerization of separated CH_2 units or the propagation via dehydrocondensation of carbene alcohol (*3, 9, 11*) units needs several (at least two) neighboring Ni sites, and one would expect a decrease and not an increase of selectivity (at the given T) when an active Ni component is dispersed in an almost inactive matrix of Cu. Moreover, simple polymerization of CH_2 units does not require carbon monoxide for other than a protective function which seems to be in contrast with points 2 and 3. It should also be stressed that the experiments with ketene (*13*) revealed that the CH_2 group can start chain growth but not propagate it; the CO group can do both.

Another mechanism suggested in the literature (*10*) is essentially a repeated insertion of CO into the metal–hydrogen bond (initiation) or metal–alkyl bond (propagation). While propagation by CO insertion is compatible with the findings in this paper (see 2 and 3) and the literature data (*13*), we find it difficult to accept insertion of CO in the metal–hydrogen bond as initiation. First, this does not seem to be an easy reaction in the metal–organic chemistry, and second, such a step (a formation of a CO–H or $CO–H_2$ additive complex) should manifest itself also in methane formation. Contrary to this, methane formation on Ni proceeds via dissociation of CO (*6, 7*). Further, why should such a one-site mechanism (*10*) be affected so strongly (see Fig. 1) by dilution of Ni in Cu?

We have seen that we are running into difficulties with all mechanisms. However, a combination of elements of various mechanisms from the literature can result in a new mechanism which can explain our data as well as a number of results from the literature. Such a mechanism is as follows:

(a)	$CO \rightarrow C + O$	initiation
(b)	$C + xH \rightarrow CH_x$	initiation
(c)	$CH_x + CO_{ads} \rightarrow (CH_xCO)$	propagation by insertion
(c′)	$CH_xCO + mH \rightarrow H_2O + CH_xCH_{m-2}$	
(c″)	$CH_xCH_{(m-2)} + CO \rightarrow (C_2H_{(x+m-2)}CO)$	propagation by insertion
(d)	$CH_xCH_{m-2} + yH \rightarrow$ desorbable products	termination by hydrogenation

Alloying of Ni with Cu decreases the number of Ni ensembles (*6*) which are necessary for the initiation step (a) but at the same time it increases the chance to find a nondissociated carbon monoxide on the surface. These facts, which are among others confirmed by infrared data (*12*) can explain the decrease in activity accompanied by an increase in S_2 and S_3 selectivities if Ni is alloyed with Cu.

It is known that various fragments of hydrocarbon or other compounds (*9, 10, 13*) can start the Fischer–Tropsch synthesis and that an insertion of CO into a metal–hydrocarbon bond is an easy reaction. Also these facts fit into the picture above.

The scheme suggested (a–d above) comprises also a hydrogenolytic splitting of a carbon–oxygen bond. Recently, it has been found (*17*) that similar requirements hold with regard to the size of Ni ensembles for both CO dissociation (*6*) and carbon–oxygen bond splitting upon inter- and intramolecular dehydration of alcohols. Therefore, an ensemble of Ni sites which can start the hydrocarbon chain by CO dissociation can also split the C–O bond after CO insertion.

Poisoning of catalysts by sulfur strongly decreases the activity in methanation and in the Fischer–Tropsch synthesis of higher hydrocarbons (*14*). It is known that sulfur decreases the extent of dissociation of adsorbed CO molecules (*15*). On the other hand, sulfur increases the selectivity toward higher hydrocarbons (*14*). Also these findings are easily understandable on the basis of the mechanism suggested above.

Another interesting point is the role of promoters. It has been reported that an optimum concentration of a promoter (or a poison like sulfur) leads to a maximum yield of higher hydrocarbons. If the promoter regulates the rate and extent of the dissociative CO adsorption, its function and the existence of its optimum concentration would also be understandable with the mechanism suggested.

Thus, to conclude, new facts on the selectivity changes due to alloying are presented and a speculative mechanism is suggested which is in good agreement with the data presented here and some data available in the literature.

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