

On the Apparent Controversy Regarding the Effect of Alloying on the Selectivity of the Fischer-Tropsch Synthesis

Intensive research on the mechanism of the Fischer-Tropsch synthesis performed in the last decade not only supplied essential new information but also showed a remarkable degree of agreement among the results of various laboratories. For example, results of various authors invariably show that (1) dissociation of CO precedes the hydrogenation in the prevailing mechanism leading to hydrocarbons in Ni (1-4), Co (5), Ru (3, 5, 6), Fe (7), Rh (8), and perhaps others; (2) dissociation of CO is a reaction requiring a large ensemble of sites, so that methanation or Fischer-Tropsch synthesis are very dramatically suppressed when an active Group VIII metal is alloyed with an inactive (e.g., Group Ib) one (2, 9-13).

Therefore, the more surprising was the apparent controversy concerning the effect of alloying on selectivity in the synthesis of higher hydrocarbons. As reported earlier (9) we observed an *enhancement* of the selectivity for hydrocarbons C_2 and higher (S_{2+}) by alloying Ni with Cu. This finding was in an agreement with early data on Fe-Cu catalysts, as reported by Shah and Perrotta (14). However, Luyten *et al.* (10), Dalmon and Martin (11), and Bond and Turnham (12) reported that alloying of Ni (10, 11) or Ru (12) with Cu *decreased* the S_{2+} -selectivity. The most obvious difference in the catalysts and techniques used by those who found an enhancement and those who found a suppression of S_{2+} by alloying was that the first group used unsupported alloys and the other supported alloys. Another potential source of the difference could have been the temperature range in which the authors studied the reaction. Since the problem of the influence of

alloying on the selectivity is important for both theoretical and practical reasons, we decided to perform a short study to elucidate the controversy.

We prepared unsupported Ni and alloys with 3, 10, and 40 at% Cu (in bulk), via carbonates, following the prescriptions of others (15, 16). These catalysts were thus prepared in the same way as those used in our earlier work (9). Catalysts on SiO_2 supports were prepared by essentially the same procedure: Merck silica gel was added to a solution of the nitrates in calculated amounts to prepare catalysts of loading 10 wt%, the carbonate(s) were (co)-precipitated, decomposed, and the resulting oxides reduced. Temperature of reduction of pure Ni was 615, 725, and 980 K; temperature of reduction of 10% alloy of Ni was 740 and 985 K. The Co-Cu alloy has been prepared without a carrier in the same way as Ni-Cu alloys (9, 15, 16).

A conventional flow apparatus, working at about 1 atm pressure has been used throughout (9). Product analysis has been performed by GLC (9). Selectivities in methane (S_1) and higher hydrocarbon production (S_{2+}) were defined as $S_1 = C_1/(C_1 + 2C_2 + 3C_3 + \dots)$; $S_{2+} = (2C_2 + 3C_3 + \dots)/(C_1 + 2C_2 + 3C_3 + \dots)$, where C_i is a molar concentration obtained from GLC peak heights after necessary recalculations.

The most relevant data of this short study can be summarized in three figures. Figure 1 shows the S_1 and S_{2+} selectivities for unsupported Ni and two alloys with 3 and 10% Cu. Figure 2 shows the most essential part of the data comparison on an enlarged scale. The 40% Cu behaved in an analogous way, confirming the trend of the curves in Figs. 1 and 2. At low temperatures the S_{2+}

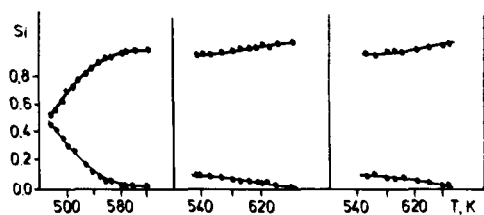


FIG. 1. Selectivity S_1 (upper curves) and S_{2+} (lower curves) as a function of temperature for three unsupported catalysts (from left to right): pure Ni, 3% Cu, and 10% Cu nickel-copper alloys.

selectivity is higher with Ni than with alloys; at higher temperatures the order is reversed. The same features of the S_{2+} temperature dependence and the same difference in behavior at low and high temperatures has also been found with the Co-Cu alloy (5% Cu) (see Fig. 3).

The same behavior as described above and as represented by Figs. 1-3 has also been found with Ni- and Ni-Cu-supported catalyst, reduced at various temperatures, as indicated above. When catalysts prepared under identical or similar conditions are compared, results with supported catalysts fully confirm the picture obtained with unsupported catalysts.

It can be expected that behavior shown in Figs. 1-3 is a quite general one but, for example, the temperature at which the curves for alloys and pure metals cross each other may depend on the particle size and details of experimental conditions.

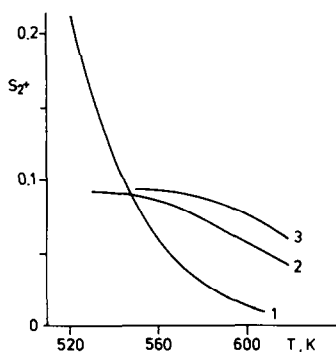


FIG. 2. A comparison of S_{2+} selectivities of three unsupported catalysts: pure Ni (1), a 3% Cu alloy (2), and a 10% Cu alloy (3).

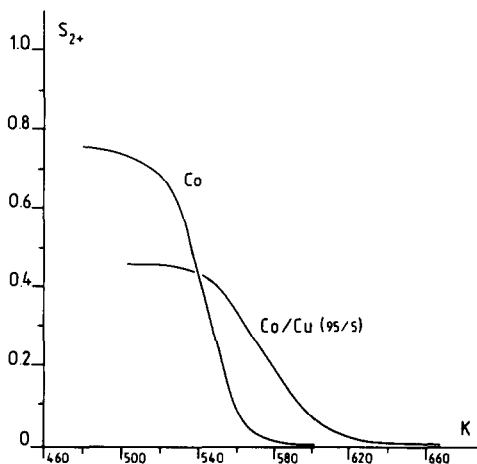


FIG. 3. Selectivity S_{2+} as a function of temperature: pure Co and a 5% Cu cobalt-copper alloy.

The message from the data obtained is quite clear. As far as the experimental data are concerned, both groups of authors were right. Alloying causes either an increase (9, 14) or a decrease (10-12) in S_{2+} , according to the temperature. However, it is also evident that the support from these data for a CO-insertion chain growth mechanism, on which we speculated in our earlier papers, is insufficient. In the meantime various authors (3, 17, 18) have shown that, indeed, CO insertion is not the main mechanism by which the hydrocarbon chains grow on the surface. The main mechanism appears to be an insertion of CH_x -units (3, 17, 18). The reason why at higher temperatures alloying increases S_{2+} is not exactly known. Biloen (19) could be right when he suggests that Cu suppresses the secondary reactions of chain splitting. The lower S_{2+} at low temperatures might, on the other hand, be related to the lower CH_x -surface concentration on alloy surfaces, or one could speculate on the different effects of carbon deposits at low and high temperatures, and so on. This problem requires another study.

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