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Reactions of Cyclopropane on Nickel and Nickel–Copper Alloys

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The reaction of cyclopropane with hydrogen has been studied on nickel and nickel–copper alloy powders in a pulse reactor in the temperature range 40–350°C. The reaction proceeds via two parallel routes, namely an addition and a hydrocracking reaction. Alloying with copper influences both reactions in a different way, most probably because the intermediates of cyclopropane addition reactions are different from those which play a role in hydrocracking reactions.

INTRODUCTION

It has been shown in our previous papers (*1–4*) that adding Cu to Ni changes not only the activity of Ni catalysts but also the selectivity patterns of more complicated reactions. Alloying with Cu influences different reactions in different ways: for instance, the reactions on C–H bonds (addition of H_2 to the aromatic ring, exchange reactions of alkanes) are influenced to a lesser extent than reactions on C–C bonds (isomerization, dehydrocylization, hydrogenolytic fission). The cyclopropane (CP) molecule offers a possibility to study the changes in selectivity with alloying with respect to the two parallel reactions 1 and 2 (*5–8*):

$$\text{cyclo-}C_3H_6 + H_2 \rightarrow C_3H_8, \qquad (1)$$

$$\text{cyclo-}C_3H_6 + 2H_2 \rightarrow C_2H_6 + CH_4. \qquad (2)$$

At higher temperatures CP decomposes to methane by the overall reaction

$$\text{cyclo-}C_3H_6 + 3H_2 \rightarrow 3CH_4. \qquad (3)$$

Methane can arise in reaction 3 either by direct fission of CP into three fragments or by consecutive splitting of ethane and propane molecules.

Cyclopropane has an unsaturated character and reaction 1 is therefore analogous to the formation of two C–H bonds by addition of hydrogen to the C=C double bond. In reactions 2 and 3 also the C–C σ-bonds have to be broken and in view of our previous results (*1–4*) one can expect that these reactions will be influenced differently by using Ni-Cu alloys instead of pure Ni catalysts. While with hexane and also other alkanes the reaction of hydrogenolysis can be observed only at temperatures slightly above the temperatures closing the miscibility gap in Ni–Cu alloys, reaction 2 occurs at substantially lower temperatures (*5–8*), where separated phases (if present) are thermodynamically stable. Also this point makes cyclopropane an attractive object for studies. To obtain the important pieces of information in the easiest way we decided to study these problems on alloy powders reduced by H_2 at high temperatures and in the pulse microreactor (*6, 9, 10*).

EXPERIMENTAL METHODS

Alloys were prepared by thermal decomposition (at 400°C) in air of coprecipitated Ni–Cu carbonates, followed by reduction with hydrogen (at 350–400°C) (*11–14*). It is essential to complete the decomposition of the carbonates before starting the reduction in order to prevent side reactions of carbon dioxide with hydrogen. X-ray analysis showed the usual picture of these powders (*12, 13*); no signs of bulk phase

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separation and only small deviations from Végard's law were found.

Cadenhead and Wagner (*14*) have measured the adsorption of hydrogen per unit of the total surface area of catalysts prepared in a similar way as our alloys. They found that with regard to the hydrogen adsorption the surface of these powders behaved similarly to the evaporated alloy films. However, these films studied previously (*15*, *16*) by different methods revealed phase separation.

The pulse reactor used was of the usual type (*17*). The chromatographic column was 4 m × 0.6 cm diam, filled with Poropak Q. A flame ionization detector was used for detection (Becker, Delft). Gases were injected through a rubber septum injection port placed close to the reactor. The pressure of gases used was kept slightly above atmospheric pressure, and the flow of hydrogen (gas chromatographic carrier gas and one reaction component at the same time) was about 50 ml/min.

Gas chromatographic peak heights were converted by means of empirically found sensitivity factors to the respective numbers of moles of: (a) methane, (b) ethane, (c) propane and (d) cyclopropane. By means of these primary data the following parameters, all expressed as percentage, were evaluated: total conversion α from reactions (1) and (2), selectivity $S(\%)$, to hydrocracking by reaction (2) rather than (1) and the total (selective and nonselective) hydrocracking conversion N from reactions (2) and (3):

$$\alpha = \frac{b + c}{b + c + d} 100,$$

$$S = \frac{b}{b + c} 100,$$

$$N = \frac{1/3(a - b) + b}{1/3(a - b) + b + c} 100.$$

As previously reported (*6*, *7*, *18*) at low conversions a was slightly lower than b, although they should be equal according to the stoichiometric reaction. Therefore, in calculations of the lowest α and S an average $\frac{1}{2}(a + b)$ was used instead of b. In the whole range $\alpha < 100\%$ only reaction 2 was operating, so a simpler expression for α was used here than in previous work (6); in other words only after $\alpha = 100\%$ is reached $N > S$.

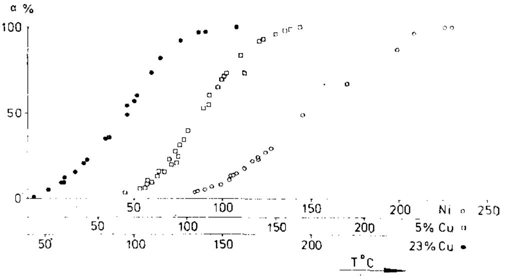


FIG. 1. Overall conversion as a function of the temperature (°C) for the three catalysts used: 0, 5 and 23% Cu (at %).

In an analogous way α was defined also for cracking of propane. Surface areas of catalysts were determined using a Sorptometer (Perkin–Elmer/Shell, Model 2120) and nitrogen–helium mixtures.

RESULTS

Results are presented in Figs. 1–5 and in Table 1. Figures 1 and 2 show the overall conversion α and the selectivity S as a function of the temperature for various typical catalysts. The data for other alloys follow the same pattern.

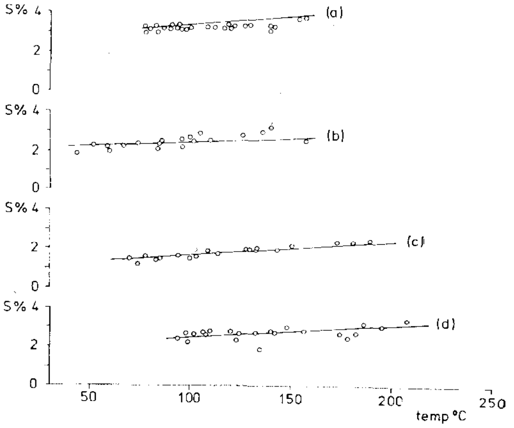


FIG. 2. Selectivity parameter S as a function of temperature (°C) for conversion $\alpha < 100\%$. Results are presented for the four catalysts used: (a) 5, (b) 23, (c) 45.5, and (d) 54.5 at % Cu.

The conversion parameter α characterizes the activity of the catalysts. Recent papers on the theory of pulse reactors showed (*19*) that the measured data are rather insensitive to the reaction kinetics. A pulse reactor is therefore unsuited for obtaining information on kinetics; its real value is in providing the possibility to gain easily data on selectivity in complicated reaction systems and possibly also on the temperature dependence of the reaction rates.

As a zeroth approximation the pulse can be idealized as having a rectangular form and the reactions in pulses can be considered as reactions in a discontinuous flow (F) of the feed. When the steady state is reached sufficiently quickly, the reaction rate in the pulse reactor is given by the same expressions as for the open-flow-reactors and we can write for the reaction rate per unit weight (r_w) or per unit surface area (r_s):

$$r_w = d\alpha/d\left(\frac{w}{F}\right) \div \alpha F/w \qquad (\alpha < 20\%)$$

$$r_s = d\alpha/d(sw/F) \div \alpha F/sw \qquad (\alpha < 20\%)$$

where s is the specific surface area of the catalysts. For low conversions (often up to $\alpha \sim 20 - 30\%$) the derivative is simply the ratio given by the last terms and the reaction rate is directly proportional to the conversion α. Therefore, activity parameters may be introduced: $A_w = \log(\alpha/w)$ or $A_s = \log(\alpha/sw)$ to characterize different catalysts at the same temperature and flow. The activation energy may be evaluated from $\log \alpha$ vs $1/T$ plots (for $\alpha < 20\%$). The comparison of different catalysts in terms of the activity parameters (A_w, A_s), the selectivity parameters (N, S) and the activation energy (E) is presented in Figs. 3–5 and in Table 1.

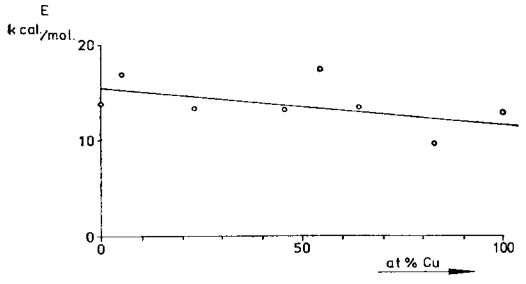


FIG. 3. Apparent activation energy for the overall reaction as a function of the composition of alloys (at % Cu).

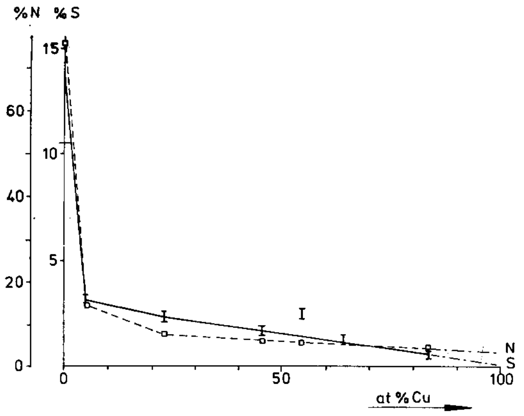


FIG. 4. Selective and total cracking of CP as a function of the composition of alloys (at % Cu). $S\%$ is determined at 90°C; N at 320°C (see text for definitions of S and N).

DISCUSSION

The results presented here are in general agreement with those previously published (*6*). However, the extrapolation of S towards low temperatures with the data

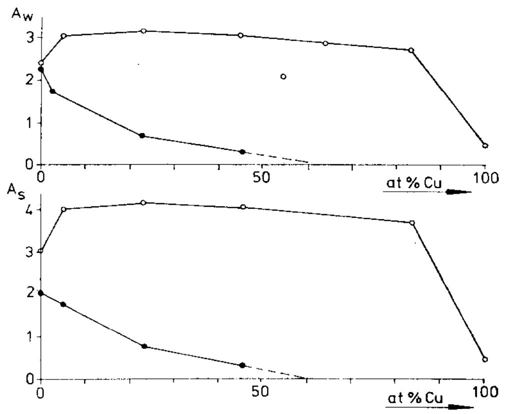


FIG. 5. Activity parameters A_w and A_s (see text for definitions) as a function of alloy composition (at % Cu). Upper curves A_w and A_s are for cyclopropane at 90°C, lower curves A_w and A_s are for propane at 320°C.

TABLE 1

Cu (at %)	Activity[a] A_w	Activity[a] A_s	Activity[b] A_w	Activity[b] A_s	$S(\%)$[c]	E_{act} (kcal/mol)
0	2.3	3.1	2.3	2.1	10.5–15.5	13.9
5	3.0	4.0	1.8	1.8	3.0–3.3	16.9
23	3.1	4.1	0.7	0.8	2.0–2.65	13.3
45.5	3.0	4.0	0.4	0.3	1.30–1.90	13.2
54.5	2.1	2.9			2.25–2.75	17.4
64	2.8	3.6			1.10–1.40	13.4
83.5	2.7	3.7			0.35–0.74	9.5
100	0.3	0.5			—	12.7

[a] $A_w = \log(\alpha/w) + 2$; $A_s = \log(\alpha/sw) + 4$; activity in the reaction of cyclopropane, at 90°C.

[b] $A_w = \log(\alpha/w) + 1$; $A_s = \log(\alpha/sw) + 2$; activity in the reaction of propane, at 320°C.

[c] Interval of values comprises the dispersion of experimental points and a slight increase of S with temperature.

on films in that study (*6*) was not justified. We found during this work that powders reduced at 200°C revealed higher S (as, e.g., films) than samples reduced and sintered at 350–400°C and, therefore, the value of S for films at low temperatures is higher then the extrapolated S-value for powders, as found in this work.

The present data and also recent quantum mechanical calculations (*20*) show that some older views on the mechanism of cyclopropane reactions should be modified. According to the calculations (*20*) cyclopropane cannot form π-complexed species and simulate ethylene, as was repeatedly suggested in the literature (*6*, *8*, *22*, *23*). Thus, π-complexed species cannot be intermediates in the reaction schemes. On the other hand, the lowest excited state of cyclopropane is nearer to the linear structure (open ring structure) which makes the existence of this type of species in the adsorbed state more likely.

The rate of hydrocracking according to reaction 2 reveals the same dependence on the Cu content in alloys (monotonic decreases, starting at the lowest Cu concentration) as hydrocracking of propane, or, e.g., ring opening of methylcyclopentane (*3*). However, the ring opening of cyclopropane by reaction 1, which is, as already mentioned, similar to hydrogenation reactions and different from a cracking-like opening of a saturated methylcyclopentane ring, is influenced by Cu in the same series of alloys, quite differently (see Fig. 5). This can best be understood if the reactions 1 and 2, i.e., reaction of simple addition and of hydrocracking, proceed via different routes or intermediates. Intermediates involved in CP-cracking must be very similar to the intermediates of alkane cracking. This view has some direct consequences.

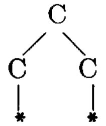
If the most popular α–γ intermediate  is used correctly in the reaction schemes of the addition reaction, another intermediate, or at least a modification of this one, must be used in the cracking reaction. For example, an α, β, γ adsorbed intermediate might be discussed. Another possibility is to assume α-γ intermediates are required for cracking reactions and another intermediate for hydrogen addition. To this end an insertion mechanism (*21*) or propylene-like (or allyl-like) intermediates suggested earlier (*22*) may be used.

Figure 5 shows that alloying with Cu has even a certain promotion effect. This can be explained assuming a direct influence of Cu on the reactivity of adsorbed intermediates (optimum chemisorption bond strength) of the hydrogen addition. However, the following indirect effects of Cu must also be considered. Alloying with Cu can favor addition by simply suppressing the competing reaction route, leading to the cracking products. Further, the self-poisoning by carbonaceous, firmly adsorbed residues is also lower when cracking is suppressed and, therefore, the proportion of the working surface is higher. In this way a promotion effect also results.

ACKNOWLEDGMENTS

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