Hydrogenation of cyclopropane on supported metal catalysts

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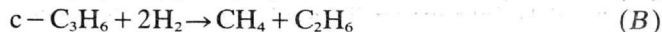*P. J. Šafárik University, 041 67 Košice*

In this study Fe/SiO_2, $Fe—Cu/SiO_2$, Co/SiO_2, $Co—Cu/SiO_2$, Ni/SiO_2, $Ni—Cu/SiO_2$, and Cu/SiO_2 catalysts of the hydrogenation of cyclopropane were investigated in a microcatalytic pulse reactor. On the basis of the temperature dependence of the logarithm of apparent rate constants the apparent activation energies of the reaction and the order of the activity of catalysts were determined. It was found that the addition of copper influenced the activity and selectivity of catalyst in a characteristic manner.

В работе были изучены катализаторы гидрогенизации циклопропана на базе Fe/SiO_2, $Fe—Cu/SiO_2$, Co/SiO_2, $Co—Cu/SiO_2$, Ni/SiO_2, $Ni—Cu/SiO_2$ и Cu/SiO_2 в импульсном микрокаталитическом реакторе. Из измеренных температурных зависимостей логарифма кажущихся констант скоростей были рассчитаны кажущиеся энергии активации и определен ряд катализаторов по их активности. Было обнаружено, что добавка меди оказывает характеристическое влияние на активность катализаторов и избирательность реакции.

Willstätter and *Bruce* [1] were the first researchers who hydrogenated cyclopropane. They used nickel supported on pumice for this reaction. Later, *Bond et al.* [2—7] investigated the kinetics of this reaction, too. In 1963 *Knor et al.* [8] published a paper on chemisorption and hydrogenation of cyclopropane on nickel. *Sinfelt et al.* [9] investigated this reaction in a flow reactor by using nickel, cobalt, platinum, and copper supported on silicon dioxide. On these metals the reaction proceeded in different ways: Methane and ethane arose on nickel and cobalt besides propane and only propane was registered on platinum and copper. *Merta* and *Ponec* summarized the information from preceding years [8—12] and described the course of these reactions as follows

$$c - C_3H_6 + \ \ H_2 \rightarrow C_3H_8 \qquad (A)$$
$$c - C_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \qquad (B)$$
$$c - C_3H_6 + 3H_2 \rightarrow 3CH_4 \qquad (C)$$

Recently, attention was especially paid to the problems of the reaction mechanism [13, 14] and to the study of catalytically active alloys [14, 15].

This paper is concerned with some other catalysts supported on silicon dioxide and, in particular, with the effect of copper added to metals of the iron group on their overall activity and the selectivity of cyclopropane hydrogenolysis.

Experimental

Materials

Hydrogen. The gas used for hydrogenation served simultaneously as carrier medium in chromatographic system for the determination of the products of catalytic reaction. Hydrogen was continuously purified by flowing through a system of columns packed with industrial palladium catalyst (Cherox 40-00) and molecular sieve 5A. After the passage through purifier the content of oxygen did not exceed 4 p.p.m.

Cyclopropane. The product of the house ICI (Macclesfield, Cheshire, Great Britain) was used without further purification. The air content (2×10^{-1} %) was estimated by chromatographic analysis.

The following chemicals were used for the preparation of the active component of supported metal catalysts: $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3) \cdot 3H_2O$. All chemicals were of anal. grade. Aerosil 200 served as support [data of the producer (Degussa, GFR): chemical composition $SiO_2 > 99.8\%$, $Al_2O_3 < 0.05\%$, $Fe_2O_3 < 0.003\%$, $TiO_2 < 0.03\%$, $HCl < 0.025\%$; surface (BET), 200 ± 25 m^2 g^{-1}].

All catalysts were prepared as follows: The weighed amounts of nitrates and Aerosil 200 were wetted with redistilled water and transformed into suspension. These amounts were so chosen that the content of metals (Me = Fe, Co, Ni) in reduced catalyst was either 10% Me or 9% Me + 1% Cu (Table 1). After thorough stirring the mixture thus prepared was dried in air for 8 h at 110°C. The dried substance was crushed and the 1.00—1.25 mm fraction was separated. The catalysts were reduced *in situ*. The weight amounts of all catalysts (metals + support) were equal (0.21 g). The activation was carried out in two consecutive stages:

1. in a ($N_2 + H_2$) mixture (4:1) with the overall flow rate of 100 ml min^{-1} for 15 h at 300°C;

2. in pure hydrogen with the overall flow rate of 50 ml min^{-1} for 2 h at 400°C (for catalysts consisting of Fe and Fe—Cu at 500°C).

Apparatus

The diagram of the apparatus is shown in Fig. 1. The system consists of three parts, *i.e.* purifier, reactor with accessories, and analytical equipment. The individual parts of the system and the optimum conditions of chromatographic analysis have been described [16].

Measurements of the temperature dependence were performed with freshly activated
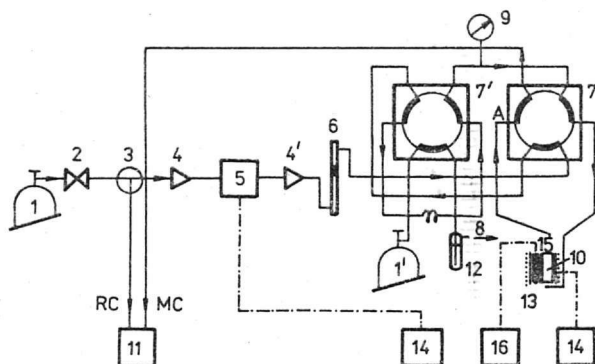
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Fig. 1. Diagram of the apparatus.
1. Pressure gas vessel with hydrogen; *2*. reducing valve; *3*. distributor; *4,4'*. needle valves; *5*. purifier; *6*. rotameter; *7,7'*. dosing valves; *8*. capillary; *9*. manometer; *10*. reactor; *11*. chromatograph; *12*. manostat; *13*. resistance furnace; *14*. autotransformer; *15*. thermocouple; *16*. automatic electron tube potentiometer; RC — reference cell of katharometer; MC — measuring cell of katharometer.

catalysts. The pulses of cyclopropane were dosed through a capillary of the volume of 0.252 ml into the stream of hydrogen which served as a reaction component and carrier gas as well (flow rate of hydrogen 50 ml min^{-1}). The technique of dosing was as follows: After activation the reactor was cooled to the first working temperature T_1 and a pulse of cyclopropane was dosed. As soon as the products of the catalyzed reaction had been recorded, the temperature was raised to 400°C for Co, Co—Cu, Ni, Ni—Cu, and Cu and to 550°C for Fe and Fe—Cu and the reactor was kept for 10 min at this temperature. Afterwards it was cooled again to the second working temperature T_2 ($T_2 > T_1$). At this temperature another pulse of cyclopropane was dosed. In this way the measurements were performed in the whole temperature interval. The activity of catalyst was checked by comparing it with the activity of the same catalyst determined at a certain arbitrary temperature [16]. There was no observable decrease in activity during the measurements of the temperature dependence.

Processing of results

The content of nonconverted cyclopropane and reaction products (methane, ethane, and propane) was determined chromatographically [17]. On the basis of eqns (*A—C*) the expressions were derived for overall conversion of cyclopropane x and selectivity s of the hydrogenolysis of cyclopropane into methane and ethane

$$x = \frac{M + 2E + 3P}{M + 2E + 3P + 3C} \cdot 100 \tag{1}$$

$$s = \frac{M + 2E}{M + 2E + 3P} \cdot 100 \tag{2}$$

The quantity

$$u = \frac{M}{E} \tag{3}$$

was also evaluated. The symbols M, E, P, and C denote the percentage (by volume) of methane, ethane, propane, and cyclopropane (nonconsumed) in the mixture after catalyzed reaction.

A programme was made for the calculation of quantities x, s, and u. As it had been proved by previous measurements that the reaction was of the first order with respect to cyclopropane [16], the *Bassett—Habgood* equation could be used [18] and the apparent activation energies of the overall reaction E_a were calculated from the plot [19] of

$$\log \left[\frac{T}{273.15} \ln \frac{1}{1-x} \right] \textit{vs. } T^{-1}$$

Results and discussion

The values of the calculated apparent activation energies E_a and the values of u are summarized in Table 1. The plot of

$$\log \left[\frac{T}{273.15} \ln \frac{1}{1-x} \right] \textit{vs. } T^{-1}$$

is presented in Fig. 2. Conversion x and selectivity s as functions of temperature are presented in Figs. 3—5. The relationships in Fig. 2 enable us to compare the activities of individual catalysts on the basis of different temperatures [20] necessary for achieving equal conversion. Thus the investigated catalysts may be

Table 1

Apparent activation energies E_a of the reaction between cyclopropane and hydrogen and the values of parameter u

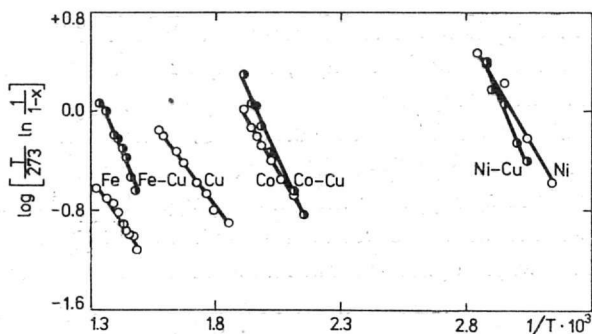| Catalyst	Temperature °C	E_a kJ mol^{-1}	u
Fe/SiO$_2$	400—480	62.0	3.9—5.2
Fe—Cu/SiO$_2$	400—480	89.2	2.0—3.8
Co/SiO$_2$	190—250	67.4	0.8
Co—Cu/SiO$_2$	190—250	88.3	0.8
Ni/SiO$_2$	45— 78	69.5	0.8
Ni—Cu/SiO$_2$	55— 75	90.8	0.8
Cu/SiO$_2$	265—363	52.3	—

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Fig. 2. $\log \left[\dfrac{T}{273.15} \ln \dfrac{1}{1-x} \right]$ as a function of T^{-1} for overall reaction.

arranged in the following order: Ni > Ni—Cu > Co—Cu > Co > Cu > Fe—Cu > Fe. The relationships for the couples Fe and Fe—Cu, Co and Co—Cu, Ni and Ni—Cu show similar character. It appears that the activity of bimetallic combinations decreases with decreasing temperature more rapidly than the activity of corresponding monometallic catalysts. The effect of the addition of copper on the conversion x and selectivity s for the reaction between cyclopropane and hydrogen is illustrated in Figs. 3—5. As for nickel catalysts (Fig. 3), the addition of copper results in a decreased conversion with respect to pure nickel in the investigated temperature interval. But the course of the relationships indicates that at temperatures above 80°C the conversion of Ni—Cu must be greater than it is on pure nickel. That is in good agreement with the results obtained by *Beelen et al.* [14] who studied the reaction on pure Ni—Cu alloys and found this fact at 90°C. At higher temperatures a similar phenomenon is to be observed with Fe and Co and their compositions with copper. For Fe catalysts the characteristic temperature of
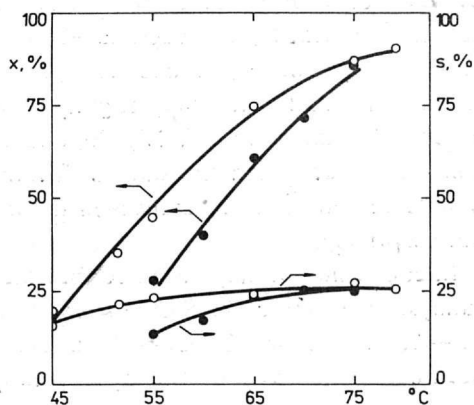

Fig. 3. Variation of conversion x and selectivity s with temperature for Ni/SiO$_2$ (O) and Ni—Cu/SiO$_2$ (●).

384°C above which this phenomenon appears may be found out by extrapolating the relationship of x vs. T. For Co catalysts it may be observed in the whole region of the temperatures used (Fig. 5).

The selectivity of reaction s is a measure for the occurrence of hydrogenolytic products. As obvious from Figs. 3—5, it decreases in the presence of the catalysts containing an admixture of copper in the whole temperature interval. The effect of copper is also evident from the values of the apparent activation energies listed in Table 1 which are always higher for bimetallic compositions than for the corre-
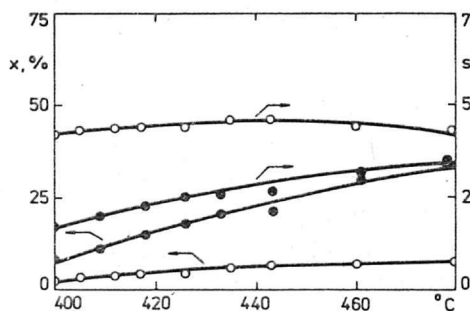

Fig. 4. Variation of conversion x and selectivity s with temperature for Fe/SiO$_2$ (O) and Fe—Cu/SiO$_2$ (●).
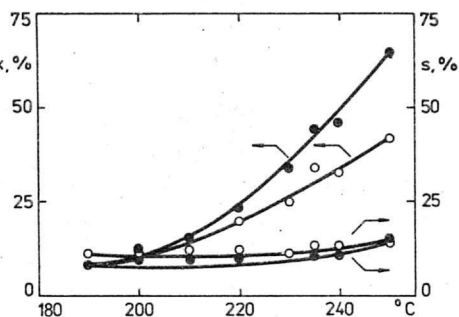
Fig. 5. Variation of conversion x and selectivity s with temperature for Co/SiO$_2$ (O) and Co—Cu/SiO$_2$ (●).

sponding monometallic catalysts. Special attention ought to be paid to the values of the quantity u given in this table. As a matter of fact, this value enables us to decide whether reaction (C) takes place. Eqns $(A$—$C)$ show that this quantity should be constant provided only reaction (A) and reaction (B) proceed (numbers of the moles of methane and ethane are equal). In literature it is stated that this quantity exceeds the unit value only slightly at low conversions [14]. This fact was also observed in this study for Ni, Co, and their compositons with Cu. On the other hand, it ensues from the data in Table 1 that all the three reactions manifest themselves on both Fe catalysts in the investigated temperature interval, which is not surprising.

In conclusion, it may be stated that the addition of copper to the Fe, Co, and Ni catalysts supported on SiO$_2$ manifests itself both by increased conversion (on Fe—Cu above 384°C, Co—Cu above 200°C, and Ni—Cu above 80°C) and decreased selectivity of the hydrogenolysis of cyclopropane into methane and etha..e in the whole temperature interval investigated.

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