Activity of Co-Cu/SiO₂ catalysts in the reaction of cyclopropane with hydrogen

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A series of Co—Cu/SiO₂ catalysts was studied by testing their activity in the reaction of cyclopropane with hydrogen in a microcatalytic pulse reactor. The experimental results have shown that an admixture of copper to cobalt enhances the hydrogenating and hydrogenolytic activity of this metal.

Была изучена серия катализаторов Co—Cu/SiO₂ на основании определения их эффективности при реакции циклопропана с водородом в импульсном микрокаталитическом реакторе. Экспериментальные результаты показали, что добавка меди к кобальту повышает его активность по отношению к гидрогенизации и гидрогенолизу.

The reaction of cyclopropane with hydrogen is a convenient testing criterion of the hydrogenating and hydrogenolytic activity of arbitrary catalyst because the reaction products may be methane, ethane or propane [1]

 $c - C_3 H_6 + H_2 \rightarrow C_3 H_8$ (A)

$$c - C_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6$$
 (B)

$$c - C_3 H_6 + 3 H_2 \rightarrow 3 C H_4$$
 (C)

Sinfelt et al. [2] revealed that all above products arose on Co/SiO_2 in contrast to Cu/SiO_2 on which only propane was formed. Recently, this reaction was used for testing the activity and selectivity of various bimetallic combined catalysts in powdered form, e.g. Ni—Cu [3], Pd—Au [4], and supported catalysts (Fe, Co,

Chem. zvesti 32 (4) 444-449 (1978)

ACTIVITY OF CATALYSTS

Ni)—Cu [5]. As found by *Sinfelt* and *Barnett* [6], the bimetallic catalysts consisting of metals of the IB and VIII group of the periodic system exhibit, in comparison with catalysts consisting only of a metal of the VIII group, a lower hydrogenolytic activity while the hydrogenating activity is preserved or even increased.

In this study we investigated new catalysts of the Co—Cu/SiO₂ type with varying ratio of copper to cobalt. Our aim was to elucidate the effect of increasing amount of copper on hydrogenating and hydrogenolytic activity of cobalt catalyst.

Experimental

Catalysts. For the preparation of catalysts we used these chemicals: $Co(NO_3)_2 \cdot 6H_2O$ (anal. grade), $Cu(NO_3)_2 \cdot 3H_2O$ (anal. grade), and Aerosil 380 (declared surface $380 \pm \pm 25 \text{ m}^2 \text{g}^{-1}$, chemical composition $SiO_2 > 99.8\%$, $Al_2O_3 < 0.05\%$, $Fe_2O_3 < 0.003\%$, $TiO_2 < < 0.03\%$, HCl < 0.025%, Degussa, GFR). The series of bimetallic catalysts with varying ratio of copper to cobalt was prepared by the simple coimpregnation procedure described in [5]. After drying in air at 110°C, the 1.00—1.25 mm fraction was sorted out and used for activation. The activation was carried out with pure hydrogen (flow rate 50 ml min⁻¹) in a reactor immediately before measuring in two stages: 14 h at 360°C and afterwards 1 h at 390°C. The characteristics of catalysts are given in Table 1.

Reactants. Cyclopropane (ICI, Macclesfield, Cheshire, Great Britain) was used without any purification. Hydrogen which served as a reaction component and simultaneously as carrier gas in chromatographic analysis of the products of catalytic reaction was continuously purified by passing through a heated system of columns packed with palladium catalyst and molecular sieve 5A.

Apparatus. The apparatus used and the method of measuring the temperature dependence have been described in preceding paper [5].

Analysis of reaction mixture. The chromatographic analysis was performed under these conditions: column (packing — Porapak Q, 50—80 mesh, length 2400 mm, inside diameter 6 mm, temperature 120°C), carrier gas — hydrogen (flow rate 50 ml min⁻¹), heat conductivity detector (temperature 80°C, heating current 175 mA).

Total surface. The total surface of catalysts was measured by the method of thermal desorption [7] under these conditions: adsorbate + carrier gas (13% Ar + 87% He), standard — Al₂O₃ (specific surface 55.5 m² g⁻¹), preparation of samples 60 min before surface measurement at 200°C in the stream of pure nitrogen (flow rate 50 ml min⁻¹). The calculated values of total surface are summarized in Table 1.

Processing of results

The chromatograms were evaluated by the method described in [5]. From eqns (A)—(C), the following expressions were derived for the conversion of cyclopropane to methane x_m , ethane x_e , and propane x_p

			Characterist	
r.	Metal content, %	Atom ratio	Co—Cu	
Catalyst	Co Cu	- Cu/Co	Amount	

Characteristics of catalysts										
alyst	Metal content, %		Atom ratio	Co—Cu/SiO ₂		Apparent activation energy, kJ mol ⁻¹				
	Со	Cu	- Cu/Co -	Amount g	Surface $m^2 g^{-1}$	°C	Hydrogenation	Hydrogenolysi		
1	5.00	1.08	0.2	0.2748	213	214-272	107	211		
2	5.00	2.16	0.4	0.2662	188	213-270	101	114		
3	5.00	3.24	0.6	0.2673	200	205-268	90	105		
4	5.00	4.31	0.8	0.2761	201	206-236	• 61	85		
5	5.00	5.39	1.0	0.2660	235	180—232	85	96		

Chem. zvesti 32 (4) 444-449 (1978)

ACTIVITY OF CATALYSTS

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

$$x_{e} = \frac{2E}{M + 2E + 3P + 3C} \cdot 100$$
 (2)

$$x_{p} = \frac{3P}{M + 2E + 3P + 3C} \cdot 100$$
(3)

where M, E, P, and C is the mole % of methane, ethane, propane, and cyclopropane (nonconsumed) in reaction mixture, respectively. The experimental data were evaluated according to the *Bassett—Habgood* equation [8]. This equation is applicable only to monomolecular reactions. Therefore, we had to carry out preliminary measurements and find out experimental conditions under which this equation was valid. The apparent activation energies of hydrogenation E_p and hydrogenolysis E_{m+e} were subsequently calculated from the following relations

$$\log\left[\frac{T}{273.15}\frac{x_{\rm p}}{x}\ln\frac{1}{1-x}\right] vs. T^{-1} \text{ (hydrogenation)}$$

and

$$\log\left[\frac{T}{273.15} \frac{x_{\rm m} + x_{\rm e}}{x} \ln \frac{1}{1 - x}\right] \text{ vs. } T^{-1} \text{ (hydrogenolysis) [9]}$$

where $x = x_m + x_e + x_p$.

Results and discussion

The temperature dependence of the conversion of cyclopropane is represented for hydrogenation (x_p) and hydrogenolysis $(x_m + x_e)$ in Figs. 1 and 2.

The shape of the plots indicates that the catalysts with higher content of copper exhibit a higher hydrogenating as well as hydrogenolytic activity. In Fig. 1 we can observe a gradual decrease in the values of x_p obtained with catalyst 4 (Cu/Co = = 0.8) and still more with catalyst 5 (Cu/Co = 1.0) at higher temperatures. We have found that, simultaneously with the formation of propane, the decomposition of this substance sets in which results in the above-mentioned observation. This phenomenon starts to appear at temperatures above 290°C. However, its effect was of little importance because the kinetic measurements were carried out at temperatures under 310°C. With catalysts 1, 2, and 3 (Table 1), the hydrogenolysis of propane was not observed. The plot in Fig. 3 expressing the ratio of the conversions to methane and ethane as a function of temperature shows a linear

Chem. zvesti 32 (4) 444-449 (1978)



Fig. 1. Conversion of cyclopropane to propane (x_p) as a function of temperature (atom ratio Cu/Co for individual catalysts: 1. 0.2; 2. 0.4; 3.0.6; 4. 0.8; 5. 1.0).



Fig. 2. Conversion of cyclopropane to methane and ethane $(x_m + x_e)$ as a function of temperature (atom ratio Cu/Co for individual catalysts: 1, 0.2; 2, 0.4; 3, 0.6; 4, 0.8; 5, 1.0).



Fig. 3. Temperature dependence of the conversion ratio of cyclopropane to methane and ethane x_m/x_e (atom ratio Cu/Co for individual catalysts: 1. 0.2; 2. 0.4; 3. 0.6; 4. 0.8; 5. 1.0; the highest temperature at which the reaction (C) does not proceed, yet: 1. 272°C; 2. 270°C; 3. 268°C; 4. 236°C; 5. 232°C).

course up to a certain temperature characteristic of each catalyst (in Fig. 3 marked with arrow). For this temperature, the molar ratio of methane to ethane is constant, *i.e.* reaction (C) does not proceed, yet. These observations give evidence that the temperature necessary for the start of reaction (C) decreases with increasing ratio of copper to cobalt.

The calculated apparent activation energies of hydrogenation and hydrogenolysis are summarized in Table 1. The values decrease with increasing proportion of copper in the catalyst. Furthermore, it ensues from the data for all catalysts that hydrogenolysis necessitates higher values of activation energy than hydrogenation.

We have ascertained by analyzing literary data that cobalt is practically immiscible with copper at the temperatures used for the preparation of catalysts [10-13]. We suppose that the role of copper consists in the reduction of the concentration of cobalt crystallites on the surface of catalyst. Owing to this dilution, the character of the bond of cyclopropane with the surface of catalyst changes

ACTIVITY OF CATALYSTS

which results in the change in the activity of catalyst. The effect of dilution is of more general operation. It has been also observed with alloys — for instance, in the hydrogenation of butadiene [14] on Pd—Au (wire) where gold functions as a diluent — as well as with simple supported catalysts — for instance, in the isomerization of hexanes on Ni/alumina with varying content of nickel [15]. *Sinfelt* [16] points out that an admixture of small amount of copper to nickel reduces the chemisorption of hydrogen on the surface several times. Since it is assumed that copper alone does not chemisorb hydrogen too much [17—19], its effect on the activity of cobalt catalyst may be explained on the basis of this fact.

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