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**The Effect of Small Copper Contents on the Activity of Ni/ γ -Al₂O₃ Catalysts
in Methanation of CO₂**

Wpływ małych domieszek miedzi na aktywność katalizatorów Ni/ γ -Al₂O₃
w reakcji metanizacji CO₂

Влияние небольших примесей меди на активность катализаторов Ni/ γ -Al₂O₃ в реакции
метенирования углекислоты

Among a great number of publications concerning hydrogenation of carbon oxides, only two papers have dealt with this reaction on Ni-Cu alloys [1,2]. Studying the effect of various amounts of Cu addition on the reduction of Ni catalysts [3], the authors found it proper to examine also its effect on the activity of catalysts in hydrogenation of CO₂.

EXPERIMENTAL

Samples - Catalysts of the type Ni/ γ -Al₂O₃, obtained by coprecipitation with ammonium hydroxide from solution of nickel and aluminium nitrates, were studied [4]. Additions of copper into calcined samples were introduced by nitrate im-

pregnation. The systems without an addition of Cu were impregnated with distilled water under the same conditions.

Methods - The values of total surface area of the samples (S_t), were determined by the methods of Ar adsorption at -178°C ; active surface area (S_H) - by the methods of chemisorption of H_2 at 20°C . The average size of Ni crystallites (d_x) was determined from X-ray line broadening by using DRON - 2 diffractometer (USSR), $\text{Cu-K}\alpha$ radiation and a nickel monochromator, with an accuracy of the order of $\pm 30\%$ [5]. The activity of the systems in methanation of CO_2 was studied in a gradientless reactor on the catalyst grains of the order 1.2-1.02 mm at the ratio $\text{H}_2:\text{CO}_2=5:1$. The reaction rates discussed in this paper correspond to the constant degree of CO_2 conversion ($x_{\text{CO}_2} = 50\%$) and were calculated from isothermal functions $r_{\text{CH}_4} = f(x_{\text{CO}_2})$.

RESULTS AND DISCUSSION

Measurements for two series of catalysts after the reduction at 400 and 500°C were carried out. From the data of Table 1, it appears that only under precisely definite reduction conditions (400°C) and at very low amounts of Cu introduced, the increase in the active surface area of the system can be obtained. In other cases a very strong decrease in the surface area measured can be observed when the content of Cu increased. The reasons of this phenomenon are closely associated with segregation processes of alloys components and the enrichment of alloy surface by copper [3,6-8].

Figure 1 shows an example of the influence of increasing amount of Cu in catalysts containing 25.1 % Ni on the reaction rate (at 400°C) and area of hydrogen surface (S_H) after the reduction at 400° and 500°C . The changes in the reaction rate are quite analogous to those of the active surface area of Ni present on the surface of the metallic phase of the systems; this is obvious because their texture is practically the same (see Table 1), which means that the effectivity coefficient of the inner surface should be approximately constant.

Table 2 shows a relative activity of the catalysts (A) after the reduction at 400° and 500°C.

Table 1

No	Amount of Ni (wt)	Ni:Cu wt ratio	After reduction at 400°C			After reduction at 500°C		
			$S_t \frac{m^2}{g_{cat}}$	$S_H \frac{m^2}{g_{cat}}$	$d_X \%$	$S_t \frac{m^2}{g_{cat}}$	$S_H \frac{m^2}{g_{cat}}$	$d_X \%$
1.	12.9	-	259	1.6	30	222	5.8	26
2.	12.9	5000:1	280	1.6		239	5.0	
3.	12.9	1000:1	278	1.5		230	4.1	
4.	12.9	100:1	288	1.3		224	3.6	
5.	25.1	-	235	7.3	31	236	15.4	35
6.	25.1	5000:1	240	9.1		211	12.9	
7.	25.1	1000:1	248	8.9		235	14.9	
8.	25.1	100:1	250	4.5		228	8.3	
9.	25.1	10:1	256	0.9		213	1.2	

Table 2

Reduction temp. °C	Temperature of activity measurement °C	"A" at different Ni:Cu ratios							
		5000: 1		1000: 1		100: 1		10:1	
		12.9	25.1	12.9	25.1	12.9	25.1	25.1	
500	500	1.08	0.79	1.00	0.78	0.49	0.44	0.021	
	450	1.07	0.84	1.02	0.81	0.46	0.46	0.016	
	400	1.08	0.84	0.99	0.81	0.45	0.46	0.013	
	350	1.06	0.86	1.01	0.79	0.45	0.44	0.009	
	300	1.02	0.84	1.00	0.82	0.47	0.42	0.015	
400	400	1.01	1.18	1.04	1.21	0.44	0.62	0.014	
	350	1.08	1.16	1.03	1.20	0.34	0.49	0.006	
	300	1.03	1.20	0.98	1.20	0.21	0.32	0.003	

Where "A" is the reaction rate on the Ni+Cu catalysts to reaction rate on Ni without Cu catalyst at the same temperature

As can be noticed the relative rates of the reaction for samples with various Cu content, reduced at 500°C, are independent of reaction temperature. With regard to samples reduced at 400°C, only for Ni:Cu ratio $\geq 1000:1$, such distinct reaction rates are independent of the temperature of activity measurements, but they depend only on the amount of Cu introduced. The systems 100:1 and 10:1 behave differently, showing a strong dependence on the temperature of activity measurements as well.

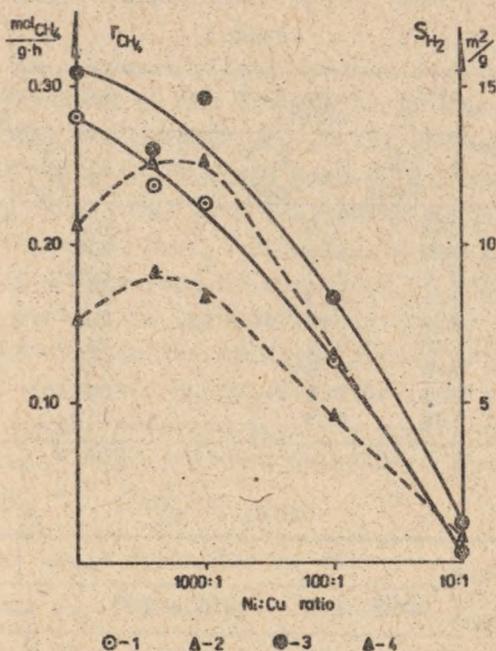


Fig. 1. Influence of the amount of Cu in catalyst containing 25,1% Ni on the reaction rate after reduction at 1 - 500°C and 2 - 400°C and active surface area after reduction at 3 - 500°C and 4 - 400°C

The differences in catalytic properties of the same systems, associated with changes in reduction temperature, as well as the amounts of Cu introduced (for temp. 400°C), induce us to analyse the influence of these factors on surface properties of the systems. Our opinion is that the segregation effect [3] may be responsible for such a considerable decrease in the activity, with the increased amount of Cu in the samples. However, this does not explain why after the reduction at 500°C all systems show a constant value "A" with the decreasing of reaction temperature, while after the reduction at 400°C reaction rate on the systems with Ni:Cu < 1000:1 decreases faster than on the system without Cu, and why this rate difference increases with increased copper amounts.

We consider, that the reduction of the systems at 500°C allows to form a Ni:Cu alloy system containing the whole amount of Cu introduced. The properties of this system do not change in the course of measurements at the temperature decrease and depend only on the amount of Cu in the system Ni:Cu ratio. During the same time the reduction at 400°C does not probably make it possible to form an alloy with the total amount of Cu at Ni:Cu ratio $\leq 1000:1$. It may be assumed that on the surface of the carrier, reduced copper, as a separate phase is also present which, as catalyst of CO conversion to CO₂, causes a change of the catalytic properties of such a multicomponent system. The rates and participation of surface reactions change which is expressed by "Excessive" rate decrease of CO₂ hydrogenation with respect to the system without Cu. This effect becomes greater with the increasing amount of Cu in catalysts.

In conclusion it may be pointed out that many factors must be taken into consideration in order to make a proper evaluation of the influence of copper introduced into nickel contacts.

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STRESZCZENIE

Przedstawiono wpływ dodatku miedzi na wielkość powierzchni aktywnej niklu i szybkość reakcji uwodorniania CO_2 po redukcji katalizatorów w 400°C i 500°C . Stwierdzono, że zmiany temperatury redukcji próbek są przyczyną różnic we własnościach katalizatorów $\text{Ni-Cu}/\gamma\text{-Al}_2\text{O}_3$.

Резюме

В данной работе представлено влияние прибавки меди на активную поверхность и скорость реакции метанирования CO_2 после редукции катализаторов в 400° и 500°C . Определено, что температурные изменения редукции обуславливают различия свойств катализаторов $\text{Ni-Cu}/\gamma\text{-Al}_2\text{O}_3$.