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THE Pd/Cu–Cr_2O_3–Al_2O_3 CATALYSTS IN METHANOL SYNTHESIS REACTION

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The increase in both temperature and reaction pressure has been found to improve Cu:Cr:Al catalysts activity in methanol synthesis. The catalyst 2 %Pd/2CuO-1Cr_2O_3-2Al_2O_3 has the highest activity among other catalysts providing similar methanol yield.

Methanol synthesis (MS) is usually carried out under the pressure of 5 MPa and temperature around 250 °C over copper-zinc-aluminum (CZA) catalysts. Extensive research were carried out to increase activity of copper based catalysts [1]. Modification over copper-based catalysts lead not only to increase, for instance, methanol yield but also to decrease pressure and temperature of above mentioned process. CZA systems were largely modified by introducing metal oxides like thoseof Cr, Co, Ce instead of zinc or aluminum. L. Ma and M. Wainwright investigated modification of CZA catalysts by introducing chromium oxide by replacing zinc and/or aluminum oxides. Their results indicated increase in activity and selectivity in methanol yield [2].

Besides, improving the MetOH yield by introducing and/or replacing some oxides from commonly used CZA is also promoting catalytic systems by for example palladium. Such a promising effect of Pd dopping was described, for instance, by W.J. Shen et al. which obtained a high activity of methanol yield over ceria-palladium catalysts at the temperature lower than 200 °C [3].

The aim of this work was to determine the influence of the reaction pressure and temperature on the activity of copper-chromium-aluminum catalysts impregnated by palladium.

EXPERIMENTAL

Catalyst preparation. Nitrates of copper, chromium, and aluminum were used as a support mat erial precursor. Bi-oxides were prepared by coprecipitation method of appropriate hydroxides using ammonium hydroxide. The mixtures were dried (T = 100 °C for 24 h) and calcined in air atmosphere at various temperatures (400, 700, and 900 °C) for 3.5 h. Pd catalysts were prepared by wet impregnation method of oxides supports using aqueous solutions of palladium chloride and nitrate. The amount of Pd was given as weight metal fraction in number of 5 wt. %.

The specific surface area (BET). The specific surface area and porosity for catalysts and their supports were determined with an automatic sorptometer Sorptomatic 1900. Samples were prepared at 250 °C during 12 h evacuation and after that low temperature nitrogen adsorption-desorption measurements were carried out.

Temperature programmed reduction (TPRr-H_2). The TPR-H_2 measurements were carried out in an automatic TPR system AMI-1 in the temperature range 25–900 °C with the linear heating rate 10°/min. Samples (weight around 0.1 g) were reduced in hydrogen stream (5 %H_2 – 95 % Ar) with the gas volume velocity 40 cm^3/min. Hydrogen consumption was monitored by a thermal conductivity detector.

Phase composition - XRD measurements. Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano reflecting geometry. Copper CuK_α radiation from a sealed tube was utilized. Data were collected in the range 5–90° 2θ with step 0.0167° and exposition per one step of 27 s. Due to the fact that raw diffraction data contain some noise, the background during the analysis was subtracted using Sonneveld and Visser algorithm and next the data were smoothed using cubic polynomial. All calculations were done with X'Pert HighScore Plus computer program.

Catalytic activity tests. Activity tests in methanol synthesis reaction were carried out using the high pressure fixed bed reactor using a gas

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mixture of H_2 and CO with molar ratio 2:1, respectively, and a catalyst sample in number of 2.0 g. The process was carried out under elevated pressure (3 and 5 MPa) at 260 and 290 °C and reagents were analyzed by GC (gas chromatograph). Before activity tests all catalysts were pre-reduced for 2 h in a flow of 5 % H_2 – 95 % Ar mixture at 300 °C under atmospheric pressure. The steady-state activity measurements were taken after at least 12 h on the stream.

RESULTS AND DISCUSSION

The specific surface area. The results of specific surface area measurements of $CuO:Cr_2O_3:Al_2O_3$ catalysts described by molar ratios x:y:z = 0.5:1:2, 1:1:2, 2:1:2 as well as catalysts promoted by Pd obtained by impregnation using palladium nitrate are shown in Table. Received data for unpromoted copper catalysts calcined at 400 °C had specific surface area in the range of 181–236 m^2/g. Increasing in the calcination temperature from 400 to 900 °C causes a decrease in the surface area up to 10–17 m^2/g. The decrease in specific surface area can be explained by sintering process occurring at higher temperature and by formation of crystal structures during calcinations process. The calcination process carried out at 700 and 900 °C leads to spinel structures $CuCr_2O_4$, $CuAl_2O_4$ and α-Cr_2O_3, γ-Al_2O_3 formation which are all characterized by low values of specific surface area [4]. The presence of listed above spinel compounds were confirmed by XRD measurements (see XRD results).

The copper catalysts systems doped by Pd calcined at 400, 700, and 900 °C showed only slight decrease in the value of specific surface area compared to undoped catalysts (Table).

Table. Specific surface area of Cu:Cr:Al and Pd/Cu:Cr:Al catalysts

Type of catalyst	**S_{BET}, m^2/g**		
	Calcination temperature, °C		
	400	**700**	**900**
$2CuO:1Cr_2O_3:2Al_2O_3$	181	37	15
2 % $Pd/2CuO:1Cr_2O_3:2Al_2O_3$	179	39	10
$1CuO:1Cr_2O_3:2Al_2O_3$	236	19	14
2 % $Pd/1CuO:1Cr_2O_3:2Al_2O_3$	224	69	15
$0.5CuO:1Cr_2O_3:2Al_2O_3$	193	36	10
2 % $Pd/0.5CuO:1Cr_2O_3:2Al_2O_3$	190	70	9

Phase compositions studies. The X-ray patterns of undoped and promoted by 2 % Pd (from $Pd(NO_3)_3$ solution) ternary catalytic systems like $xCuO:yCr_2O_3:zAl_2O_3$ after calcination in air at 400, 700, and 900 °C are shown in Fig. 1. The XRD patterns recorded for samples calcined at 400 °C confirmed presence of amorphous phases: γ-Al_2O_3 (35°, 65°) and CuO (40°, 45°, 62°).

The increase of the calcination temperature to 700 and 900 °C causes the growth of degree of crystallization for all samples. For all catalysts $CuO:Cr_2O_3:Al_2O_3$ the spinel and more complex phases were detected on the XRD profiles. The presence of following reflexes originating from appreciate crystallographic phases : γ-Al_2O_3, CuO, α-Cr_2O_3, $CuCr_2O_4$, $CuAl_2O_4$, $Al_2Cu_2Cr_2O_8$ were confirmed. The reflexes coming from spinel phase of $CuAl_2O_4$ was visible for $2\theta = 30°$, 39 °C while spinel $CuCr_2O_4$ was related to the reflexes situated for the angles of $2\theta = 35°$, 37.1° [4]. Formation of spinel compounds was caused by solid-solid interactions of CuO with Al_2O_3, and CuO with Cr_2O_3 at temperatures above 700 °C during calcinations process [4–6]. In our previous works for catalytic systems like 1 %Ag – 20 % $CuO/CrAl_3O_4$ the presence of copper chromite was detected already at 400 °C and also at 700 °C. The ternary oxide $Al_2Cu_2Cr_2O_8$ phase was also detected for catalyst like Cu:Cr:Al [7].

The significant effect of CuO and Cr_2O_3 loading on phase composition has been also found. The catalyst calcined at 700 and 900 °C with oxide ratio $CuO:Cr_2O_3:Al_2O_3$ = 2:1:2 showed presence of $Al_2Cu_2Cr_2O_8$ and $CuAl_2O_4$ phases, while decrease of CuO loading in case of other ternary oxides an additional spinel like structure $CuCr_2O_4$ was observed. This result can be explained by the fact that excess of Cr_2O_3 does not create $Al_2Cu_2Cr_2O_8$ and $CuAl_2O_4$ phases. In the case of catalyst described by molar ratio of $CuO:Cr_2O_3:Al_2O_3$ = 0.5:1:2, 1:1:2 $CuCr_2O_4$ spinel phase is formed The phase composition studies prepared by Luo and coworkers for CuO/ Al_2O_3 catalysts show phases like CuO and $CuAl_2O_4$. Their investigations concerned catalysts with increasing CuO loading (1.23–33.3 %) on aluminium oxide support. The results showed that for samples calcinated at 400–600 °C they detected only copper (II) oxide. While along the increase of calcination temperature, they detected also $CuAl_2O_4$ phase, which is also present in our XRD patterns.

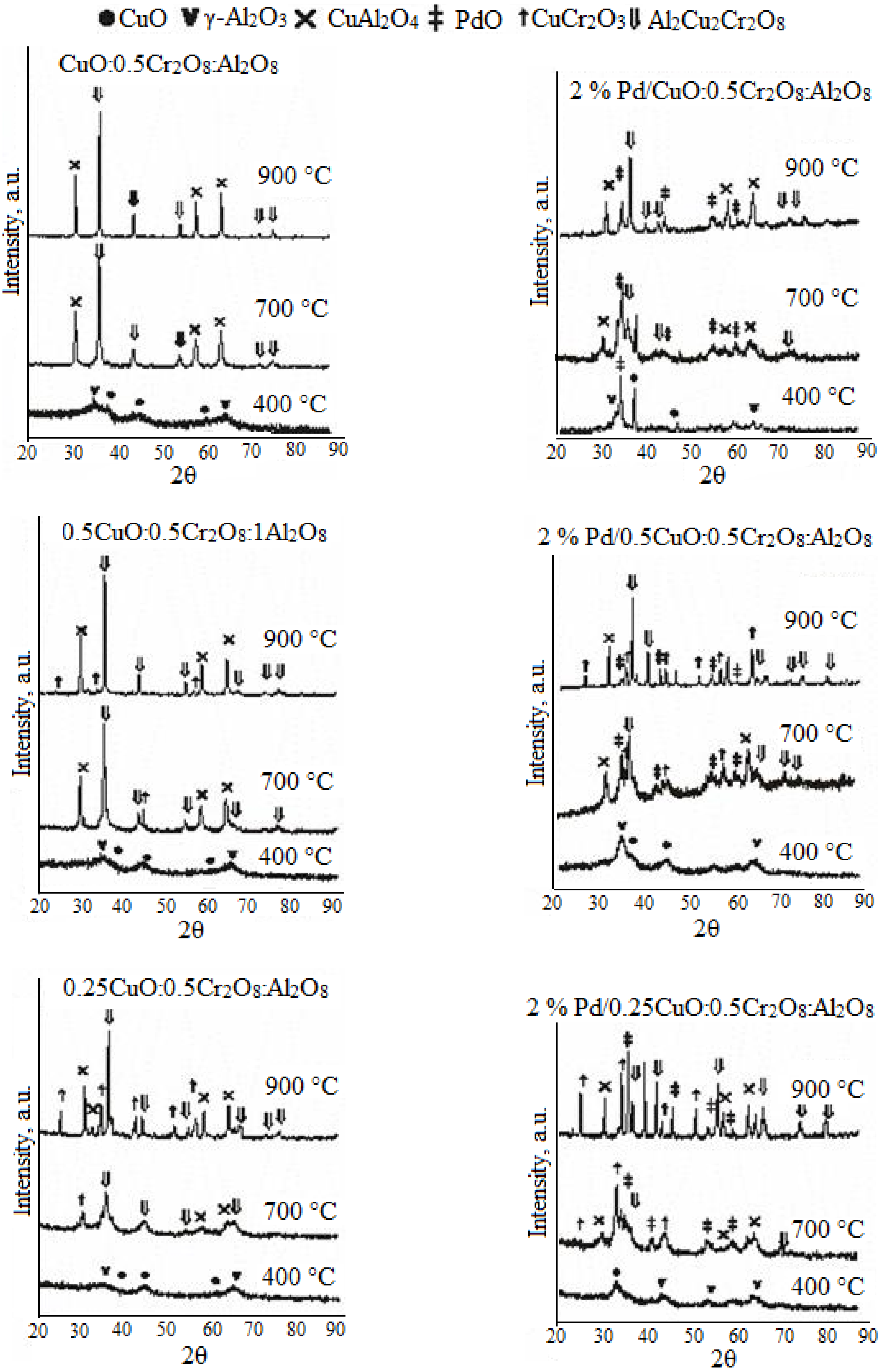
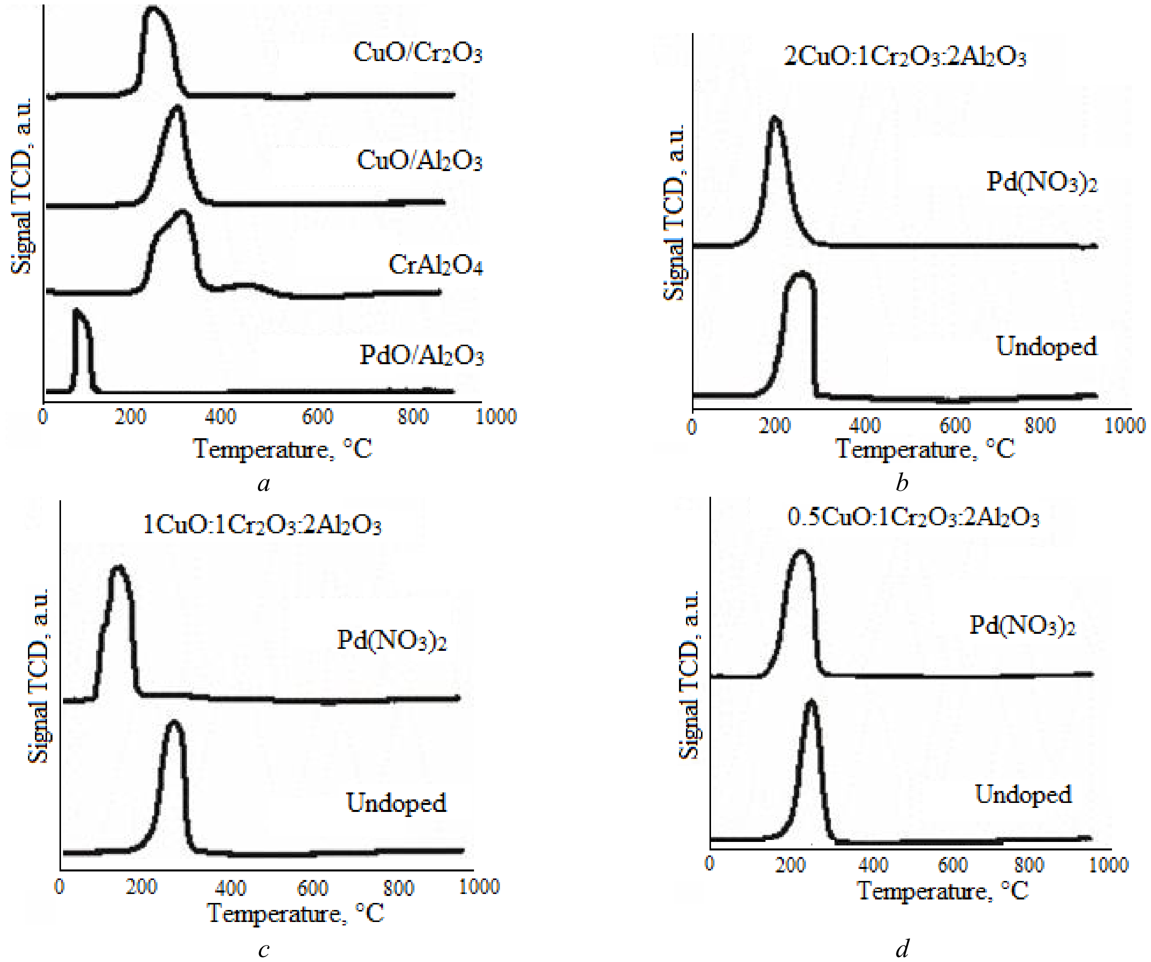


Fig. 1. XRD patterns for Cu:Cr:Al and Pd/Cu:Cr:Al catalyst after calcination at 400, 700, 900 °C

Reduction studies. The reduction studies were performed for ternary and promoted ternary catalysts due to explanation of individual component interaction. For better understanding the reduction behavior of investigated catalysts, at the first stage of our measurements we studied TPR of references materials Cr_2O_3, CuO/Cr_2O_3, PdO/Al_2O_3, CuO/Al_2O_3. The profiles of temperature programmed reduction for reference compounds are presented in Fig. 2, *a*. The TPR result recorded for PdO/Al_2O_3 system showed that palladium oxide is reduced in the low temperature range 60–110 °C (Fig. 2).

The reduction profile of CuO/Al_2O_3 supported catalysts indicates directly that reduction of copper (II) oxide to metallic copper takes place in the temperature range 210–350 °C. Reduction profile of CrO_3 system presents one TPR profile connected with reduction of Cr(VI) species to Cr(III) species. The maximum of this process is located at 380 °C.

In the next investigation we performed TPR measurements for 20 %Cu/Cr_2O_3. On the reduction curves we can easily distinguish one wide reduction profile. The maximum of hydrogen consumption peak is situated at about 250 °C suggested that this profile can be attributed to the CuO, $CuCr_2O_4$ and Cr(VI) species reduction [8].



a *b*

c *d*

Fig. 2. TPR profiles of reference compounds *(a)* for Cu:Cr:Al and Pd/Cu:Cr:Al catalyst with molar ratios 2:1:2 *(b)*, 1:1:2 *(c)*, 0.5:1:2 *(d)*

Reduction measurements of unpromoted catalysts $xCuO:yCr_2O_3:zAl_2O_3$ show presence of TPR profiles consisting usually one effect. The reduction of ternary systems with ratio of copper oxide to chromium oxide equal 2 or 1 run in the temperature range 200–280 °C (Fig. 2, *b*). The wide reduction stage represent reduction of CuO, $CuCr_2O_4$ and Cr(VI) species according to the reaction 1, 3 or 4 (see below). Decreasing in CuO/Cr_2O_3 molar ratio to 0.5 caused slight increase in the end of reduction temperature to 300 and 350 °C for $0.5CuO:1Cr_2O_3:2Al_2O_3$ and $1CuO:2Cr_2O_3:1Al_2O_3$ (Fig. 2, *c* and 2, *d*), respectively. Analogous effect of CuO reduction was detected by Zhifei Wang and coworkers: in their case of copper-chromium catalyst, the maximum hydrogen consumption peak correlated to CuO was observed around 290 °C. With the increase in chromium oxide loading hydrogen consumption peak shifts into higher temperatures, what was explained by authors by formation of copper chromate [9] According to our pervious investigations we postulate that shift could not be caused by copper chromite but by chromium (VI) which reduces to Cr(III).

Catalysts impregnated by Pd (from $Pd(NO_3)_2$ solution) show the begin of maximum hydrogen consumption peak in the temperature range of 200–220 °C for catalysts $CuO:Cr_2O_3:Al_2O_3$ representing molar ratios 2:1:2 and 1:1:2 (Fig. 2). These values are lower than that in the case of undoped catalysts (250 °C). The situation differs for the catalyst with molar ration 0.5:1:2, its maximum hydrogen consumption peak starts at higher temperature than that of undoped one.

Reaction 1. $CuO + H_2 \rightarrow Cu + H_2O$

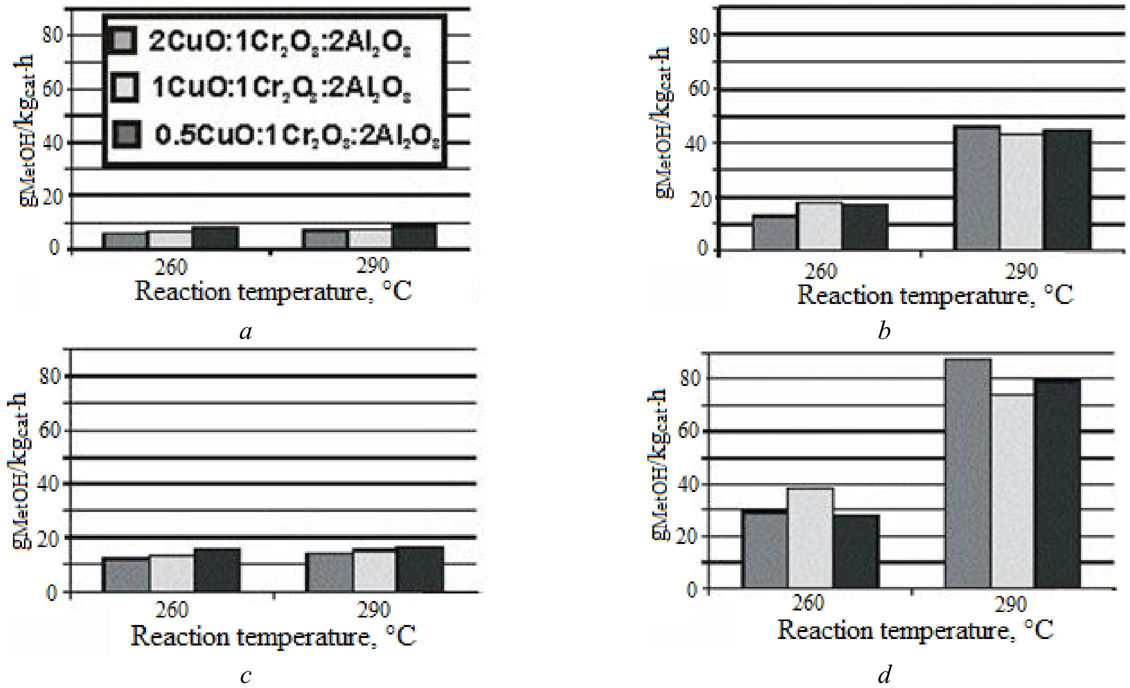
Reaction 2. $PdO + H_2 \rightarrow Pd + H_2O$

Reaction 3. $CuCr_2O_4 + H_2 \rightarrow Cu + Cr_2O_3 + H_2O$

Reaction 4. $CuAl_2O_4 + H_2 \rightarrow Cu + Al_2O_3 + H_2O$

Reaction 5. $Cr(VI) \rightarrow Cr(III)$.

Catalytic activity tests. Activity tests were determined for selected catalysts ($CuO-Cr_2O_3-Al_2O_3$) at two reaction temperatures (260 and 290 °C). Before the activity tests all catalytic systems were activated due to reduction at 300 °C for 2 h in a reduction mixture 5 % –95 % Ar under atmospheric pressure. The reaction was carried out from CO/H_2 mixture with synthesis gas ratio1:2 under the pressure of 3 and 5 MPa. The results of the activity tests are presented in Fig. 3.



a *b*

c *d*

Fig. 3. Catalysts activity at 260 and 290 °C for Cu:Cr:Al *(a, c)* and Pd/Cu:Cr:Al *(b, d)* catalysts under the pressure of 3 and 5 MPa, respectively

Catalytic activities show one common correlation, the improvement of methanol yield was observed with the increase of reaction temperature for all the catalysts $CuO-Cr_2O_3-Al_2O_3$ undoped and impregnated by Pd.

Undoped catalysts present activities around 8 $g_{MetOH}/kg_{cat}\cdot h$ under the pressure 3 MPa while with the increase in pressure to 5 MPa their activity increase to 16 $g_{MetOH}/kg_{cat}\cdot h$ independently on the catalysts molar ratio. Analogous tendency was observed with catalysts promoted by palladium. For impregnated catalysts the activity was 5 times higher in comparison to undoped systems and also an increase of process pressure improves the methanol yield to 88 $g_{MetOH}/kg_{cat}\cdot h$. Samei et al. carried out methanol synthesis over Cu:Zn:Al catalysts from CO_2 rich feed (p = 4.5 MPa, T = 240 °C) obtaining activity at the level of 500 $g_{MetOH}/kg_{cat}\cdot h$ [10], but an increase in reaction pressure increases the methanol yield, what shows results of L. Ma and and M. Wainwright who obtained methanol yield on the level of 4800 $g_{MetOH}/kg_{cat}\cdot h$ under the pressure 5 MPa [2].

Describing the influence of reaction temperature it is important to note that for unpromoted catalysts the increase in temperature from 260 to 290 °C has no significant influence on their activity. On the other hand, palladium systems are characterized by higher methanol yield, 3 to 5 times higher at 290 °C than that at 260 °C.

CONCLUSIONS

The impregnation by palladium improves methanol yield over copper-chromium-aluminum catalysts around 3 times comparing to unpromoted systems. The increase in both temperature and reaction pressure improves Cu:Cr:Al catalysts activity, more significant in this case was increase in pressure what caused increase 2 times in methanol yield. The highest activity was for the catalyst 2 %Pd/2CuO-1Cr_2O_3-2Al_2O_3 in comparison to other catalysts which have similar methanol yield.

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Каталізатори Pd/Cu–Cr_2O_3–Al_2O_3 в реакції синтезу метанолу

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Виявлено, що збільшення температури та тиску поліпшує активність каталізаторів Cu:Cr:Al в реакції синтезу метанолу. Каталізатор 2 % Pd/2CuO-1Cr_2O_3-2Al_2O_3 має найвищу активність серед інших каталізаторів, які забезпечують аналогічний вихід метанолу.

Катализаторы Pd/Cu–Cr_2O_3–Al_2O_3 в реакции синтеза метанола

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Обнаружено, что рост температуры и давления улучшает активность катализаторов Cu:Cr:Al в реакции синтеза метанола. Катализатор 2 % Pd/2CuO-1Cr_2O_3-2Al_2O_3 имеет наивысшую активность среди других катализаторов, обеспечивающих аналогичный выход метанола.