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ON MECHANISMS OF CATALYTIC REACTIONS

Copper-Supported Catalysts in Methanol Synthesis and Water Gas Shift Reaction[1]

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Abstract—The comparative studies of physicochemical properties of Cu-support catalysts (support = ZnO, Al_2O_3, Cr_2O_3, $ZnAl_2O_4$, $FeAlO_3$, or $CrAl_3O_6$) and their catalytic activity in methanol synthesis and water gas shift reaction were the main goal of this work. The promotion effect of copper addition in both reaction was proved. The formation of spinel type structure $CuCr_2O_4$, $ZnAl_2O_4$ and binary oxide $CrAl_3O_6$, $FeAlO_3$ during calcination process was confirmed by XRD technique. Results showed that 20% $Cu/FeAlO_3$ had the best performance in water gas shift reaction. The best selective and active catalyst in methanol synthesis was 20% $Cu/ZnAl_2O_4$.

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Copper-containing catalysts have been used in many processes like ammonia synthesis (in which the water gas shift reaction is used to remove carbon monoxide from entering reaction gas), methanol synthesis (in which a copper catalyst facilitates the reaction), synthesis of high alcohols, water gas shift reaction (WGS), methyl tetrabutyl ether synthesis and many others [1–10].

Water gas shift reaction is industrially carried out with two different processes (high temperature WGS and low temperature WGS) with interbed cooling [11–13]. In the low temperature WGS CuO–ZnO–Al_2O_3 mixed oxide catalyst is used [14], but it has some significant drawbacks, such as the pyrophoric nature, susceptibility to poisoning and long pretreatment. Therefore, the low temperature WGS catalysts are not appropriate for automobiles and other portable applications. Furthermore, Fe_2O_3–Cr_2O_3 catalyst [11–13, 15] is used in the high temperature WGS reaction, and this system shows low performance under high CO_2 partial pressures [16].

Methanol is industrially produced from mixtures of carbon monoxide and hydrogen containing small amount of carbon dioxide [17]. The growing attention to the green-house effects caused by carbon dioxide has brought about studies of methanol synthesis from the mixture of hydrogen and carbon dioxide [18–20]. Typical catalysts for this synthesis are $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ and they are more active than supported precious metal catalysts [21, 22].

In recent years Cu-containing catalysts promoted by aluminum, chromium, vanadium, manganium oxides [1, 2], zirconia [23, 24], silica [25–28], cobalt and rare earth oxides [29–31] were used for production of methanol, higher alcohols and hydrocarbons through hydrogenation of carbon oxides. However, copper is still the main active component for methanol synthesis.

In the present work, we have prepared monometallic 20% Cu catalysts supported on $CrAl_3O_6$, $FeAlO_3$ and $ZnAl_2O_4$ and examined their physicochemical properties by the methods of BET nitrogen adsorption, temperature programmed reduction (TPR-H_2) and X-ray diffraction (XRD). The catalytic behavior of copper supported catalysts was studied in the hydrogenation of carbon dioxide to methanol and in the water gas shift reaction.

EXPERIMENTAL

Catalysts Preparation

Catalysts were prepared by wet aqueous impregnation method. In order to prepare $ZnAl_2O_4$, $FeAlO_3$, and $CrAl_3O_6$ (Zn : Al = 1 : 2, Fe : Al = 1 : 1, Cr : Al = 1 : 3) supports zinc acetate, iron nitrate, chromium nitrate and aluminum nitrate were used. The ammonia co-precipitated mixture of zinc and aluminum, iron and aluminum and chromium and aluminum hydroxides with appreciate molar ratio were dried and calcined during 4 h in air at various temperatures. Metal phase (Cu) was introduced on support surface by wet impregnation method with an aqueous solution of copper nitrate. Then the supported catalysts were dried at 120°C and finally they were calcined for 4 h in air at different temperatures. Copper loading was 20 wt %.

[1] The article is published in the original.

Table 1. BET surface areas of ZnO, Al_2O_3, Fe_2O_3, $ZnAl_2O_4$, $CrAl_3O_6$, $FeAlO_3$, and Al_2O_3 calcinated for 4 h in air at various temperatures

Support	Calcination temperature, °C	Specific surface area, m^2/g
Fe_2O_3	600	21
ZnO	400	37
Cr_2O_3	600	2
Al_2O_3	400	237
	700	140
	900	137
$FeAlO_3$	500	157
	700	71
	900	5
$ZnAl_2O_4$	600	63
$CrAl_3O_6$	400	157
	700	107
	900	93

Methods of Catalysts Characterization

The specific surface area and porosity. The specific surface area and porosity of catalysts and their supports were determined with 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 using BET method.

Temperature programmed reduction. The TPR-H_2 measurements were carried out in automatic TPR system AMI-1 in the temperature range 25–900°C with the linear heating rate 10°C/min. Samples (weight about 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 (TCD).

XRD measurement. Room temperature powder X-ray diffraction patterns were collected using "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 2θ from 5° to 90° 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 in Methanol Synthesis and Water Gas Shift Reaction

Carbon dioxide hydrogenation tests were carried out in a fixed bed reactor using a gas mixture of H_2 and CO_2 with molar ratio 3 : 1. Process was carried out under elevated pressure (4 MPa) at 180 and 260°C. The reagents were analyzed by means of gas chromatograph (GC). Catalysts were pre-reduced for 2 h in a flow of 5% H_2 + 95% Ar mixture at 300°C under atmospheric pressure. The catalysts were cooled to the reaction temperature 260°C and then the inlet flow was switched to reaction mixture. The steady state activity measurements were taken after at least 12 h on the stream. The analysis of the reaction products were carried out by on-line gas chromatograph equipped with FID detector and 10% Carbowax 1500 on Graphpac column. The CO and CO_2 concentrations were monitored by GC equipped with TCD detector (120°C, 130 mA) and Carbopshere 60/80 column (90°C).

The catalytic activity in the water gas shift reaction was measured in a flow reactor. About 20 mg of catalyst was loaded into a quartz microreactor for the catalytic measurements. The reaction conditions were as follows: reaction temperature 350°C, ratio of $H_2O : CO = 2.5 : 1$, flow rate 40 cm^3/min, atmospheric pressure. The catalytic activities are averages of three measurements and were determined after 2 h on reaction stream.

RESULTS AND DISCUSSION

Specific Surface Area Measurements

The BET surface areas of the calcinated at various temperature supports (Al_2O_3, ZnO, Fe_2O_3, $ZnAl_2O_4$, $CrAl_3O_6$, and $FeAlO_3$) are shown in Table 1. The individual Al_2O_3 calcinated at 400°C had the largest specific surface area 237 m^2/g in comparison to Cr_2O_3 calcinated at 600°C that had the lowest surface area 2 m^2/g. The binary oxides had intermediate specific surface areas between alumina and second oxide. Moreover, $ZnAl_2O_4$ owned the smallest surface area in comparison to remaining binary oxides. On the contrary, XRD measurements for remaining bioxides confirmed (besides of binary oxide structures $CrAl_3O_6$, $FeAlO_3$ and spinel $CuCr_2O_4$ structures) additional monoxides phases of α-Fe_2O_3, α-Al_2O_3, γ-Al_2O_3, and α-Cr_2O_3 dependently on catalyst composition (see Figs. 1 and 2). This result can be connected with fact that in the case of zinc-aluminum binary oxide only spinel structure $ZnAl_2O_4$ phase was observed on the diffractogram after calcination process. This means that $ZnAl_2O_4$ spinel structure was fully crystallized and stable after calcination at 600°C.

Phase Composition

Figures 1 and 2 show the XRD results of supports and copper-supported catalysts after their calcinations at different temperature in air for 4 h. The fully crystallization of $ZnAl_2O_4$ spinel structure was proved in the case of zinc-aluminium binary oxide. The presence of zinc oxide in the case of copper catalysts sup-

ported on $ZnAl_2O_4$ can be explained by substitution of zinc ions by copper ions in $ZnAl_2O_4$ structure and formation of $CuAl_2O_4$ phase during calcination process (see our previous work). The phase composition study for remaining oxides (chromium-aluminium and iron-aluminium binary oxides) showed that these two materials are a mixture of binary oxide ($FeAlO_3$ and $CrAl_3O_6$) and monoxides α-Cr_2O_3, α-Fe_2O_3, α-Al_2O_3, and γ-Al_2O_3 according to examined sample.

Yang and co-workers [32] investigated the influence of calcination temperature on phase composition of Cu–Zn–Al (Cu : Zn : Al = 54.5 : 27.3 : 18.2) catalysts. XRD measurements showed that in the calcination temperature range 300–550°C ZnO, CuO, and Al_2O_3 phases are clearly observed in this system. During increasing of calcination temperature above 650°C the $ZnAl_2O_4$ spinel structure was formed by the reaction of ZnO and Al_2O_3.

The phase composition and reduction behavior of 33.3% CuO/Al_2O_3 catalyst was studied in work [33]. The XRD measurements carried out for this sample after calcination at 700°C showed spinel structure $CuAl_2O_4$ formation. The influence of copper loading on phase composition of CuO/Al_2O_3 catalysts was also studied. Authors [33] observed that at low CuO loading (<5.88%) CuO phase was no visible on the diffraction lines due to its high dispersion. As the CuO loading achieves 5.88%, the diffraction peaks of $CuAl_2O_4$ spinel phase was observed. Intensity of $CuAl_2O_4$ diffraction peaks increases with increasing of CuO content from 5.88 to 20.0%. Further increasing of CuO loading causes that the intensity of $CuAl_2O_4$ diffraction peak is closed to that of 20.0%. This indicates that a part of CuO changes into $CuAl_2O_4$ via solid–solid interaction with Al_2O_3 [34]. After a large amount of $CuAl_2O_4$ has formed, the $CuAl_2O_4$ layer inhibits CuO diffusing into Al_2O_3 support.

We observed the same behavior for Cu/Al_2O_3 catalysts. In the case of low copper loading (5% Cu) we didn't detected CuO phase due to its high dispersion and low size of crystallites of CuO phase. Increasing of copper content caused the crystallization of copper oxide phase and additionally the formation of spinel structure as in above mentioned catalyst CuO/Al_2O_3. The same effect was observed in the case of spinel $CuAl_2O_4$ structure formation. The growth of copper loading from 5 to 20% caused the increasing of intensity of $CuAl_2O_4$ diffraction peaks.

In the works [35, 36] it was studied the phase composition of CuO–ZnO–Cr_2O_3 catalysts for higher alcohol synthesis. It was claimed that remaining system is a mixture of CuO, ZnO, and $CuCr_2O_4$ phases after calcination process. That confirmed our results.

Reduction Studies

Temperature programmed reduction technique was used to study the reduction behavior of all samples. The TPR profile for all catalytic systems are presented in Fig. 3. Hydrogen consumption curve recorded for binary oxide $FeAlO_3$ shows three reduction stage attributed to binary oxide $FeAlO_3$ and iron oxide reduction Fe_2O_3 (precision description of this process is presented in our previous works [37, 38]). Promotion of $FeAlO_3$ system by copper shifts the reduction effects into lower temperature and results in additional reduction stages. Those stages present copper oxide reduction ($Cu^{2+} \longrightarrow Cu^{+} \longrightarrow Cu^{0}$).

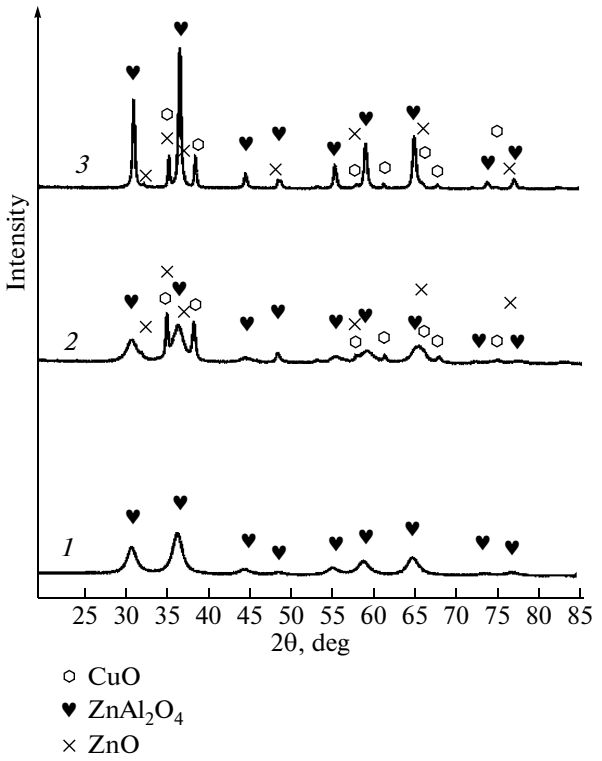


Fig. 1. Influence of calcination temperature and copper introduction on phase composition of zinc-alumina oxide: *1*—$ZnAl_2O_4$ calcinated at 600°C, *2*—20% $Cu/ZnAl_2O_4$ calcinated at 400°C, *3*—20% $Cu/ZnAl_2O_4$ calcinated at 700°C.

Lindström et al. investigated reduction behavior of copper promoted catalysts with copper loading from 3 to 12 wt % ($Cu/Zn/Al_2O_3$, $Cu/Zr/Al_2O_3$, $Cu/Cr/Al_2O_3$) [39]. They suggested that $Cu/Zn/Al_2O_3$ catalysts with higher copper loading (12 wt %) show two peaks. These peaks are attributed to the stepwises reduction of copper(II) oxide ($Cu^{2+} \longrightarrow Cu^{+} \longrightarrow Cu^{0}$), which could indicate strong interaction between part of the copper and zinc oxide. Other catalysts (with low copper loading) were reduced in one stage.

TPR profile of $CrAl_3O_6$ system shows one wide reduction stage connected with Cr(VI) species reduction (precision description of this process was featured in our previous work [40]). Promotion of $CrAl_3O_6$ binary oxide by copper causes the appearance additional partially resolved three reduction stages which are attributed to copper oxides and spinel $CuCr_2O_4$

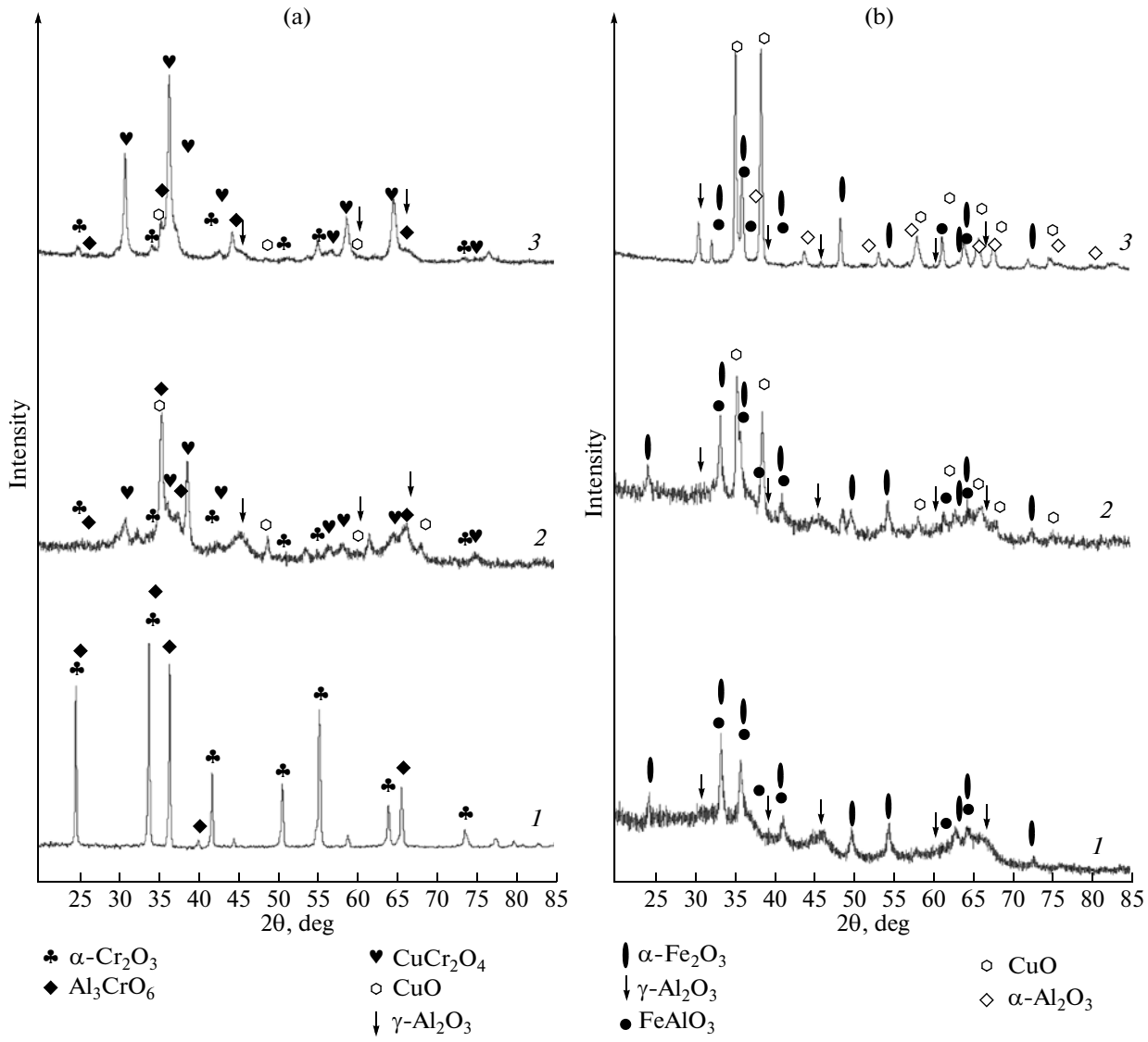


Fig. 2. Influence of calcination temperature and copper introduction on phase composition of binary oxides: (a) chromium-alumina oxide (*1*—$CrAl_3O_6$ calcinated at 400°C, *2*—20% $Cu/CrAl_3O_6$ calcinated at 400°C, *3*—20% $Cu/CrAl_3O_6$ calcinated at 700°C), (b) iron-alumina oxide (*1*—$FeAlO_3$ calcinated at 500°C, *2*—20% $Cu/FeAlO_3$ calcinated at 400°C, *3*—20% $Cu/FeAlO_3$ calcinated at 700°C).

reduction. The creation of this phase during calcination process was confirmed by XRD technique [40].

The reduction behavior of copper chromites investigated in the works [22, 41] shows that treating of $CuCr_2O_4$ in flowing hydrogen at elevated temperature results in the decomposition of the copper chromite to metallic copper and chromia. The same results we observed for 20% $Cu/CrAl_3O_6$ catalytic systems [40].

Any reduction process was observed during TPR run in the case of $ZnAl_2O_4$ support material. Promotion of spinel structure system by copper caused the appearance of two partially resolved peaks connected with CuO reduction in the case of catalyst calcinated at 400°C. Increasing temperature of calcination process to 700°C causes the appearance of high temperature reduction effect. Evidence of this peak confirmed the formation of $CuAl_2O_4$ spinel phase and explained the substitution zinc ions by copper ions in $ZnAl_2O_4$ structure [42].

Activity Tests

Table 2 and Fig. 4 compare the activity of copper supported catalysts in methanol synthesis and water gas shift reaction. Table 2 shows the conversions of carbon monoxide on 20% Cu/support catalysts at 350°C during water gas shift reaction. It is seen that all supports materials were active in WGS process.

From obtained data we can easily observed that $CrAl_3O_6$ and $ZnAl_2O_4$ binary oxides exhibit better per-

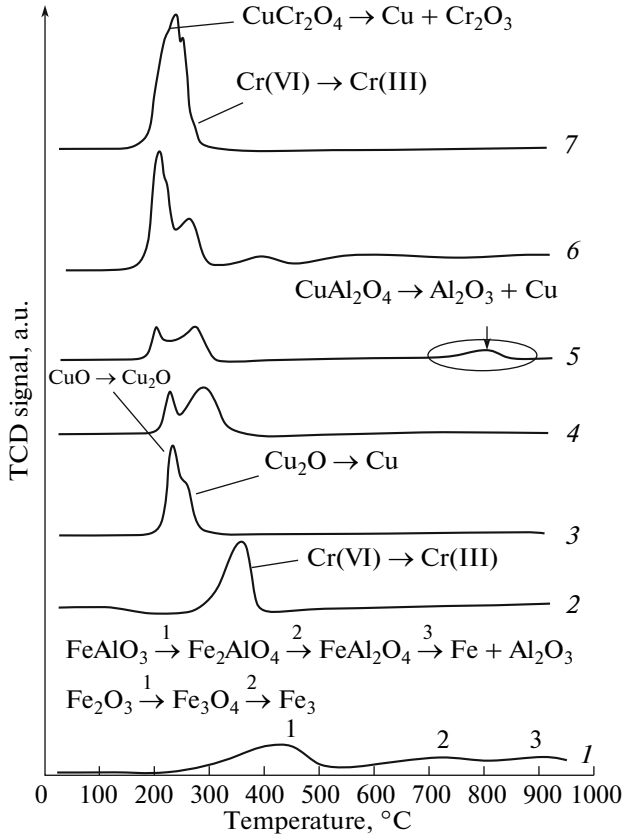
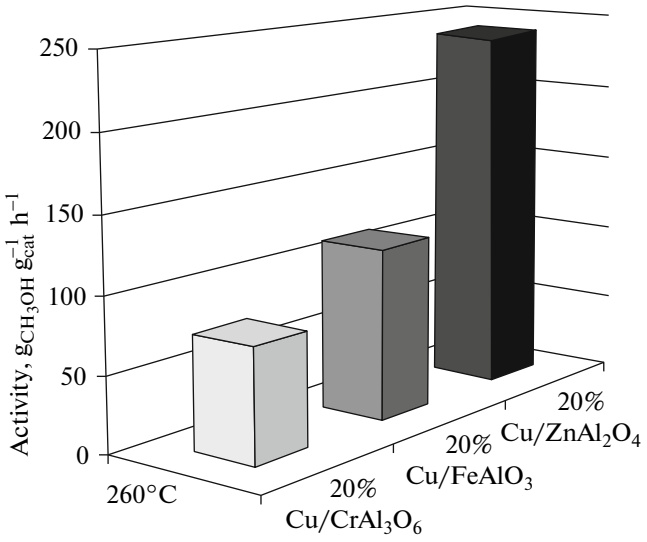


Fig. 3. TPR profiles for reducible binary oxides and copper-supported catalysts after calcinations at various temperatures: *1*—$FeAlO_3$ (500°C), *2*—$CrAl_3O_6$ (400°C), *3*—20% Cu/Al_2O_3 (400°C), *4*—20% $Cu/ZnAl_2O_4$ (400°C), *5*—20% $Cu/ZnAl_2O_4$ (700°C), *6*—20% $Cu/FeAlO_3$ (400°C), *7*—20% $Cu/CrAl_3O_6$ (400°C).



Catalyst	Selectivity, %
20% $Cu/ZnAl_2O_4$	93
20% $Cu/FeAlO_3$	21
20% $Cu/CrAl_3O_6$	61

Fig. 4. Catalytic activity and selectivity of copper-supported catalysts in methanol synthesis at 260°C (reaction pressure 4 MPa).

formance in comparison with $FeAlO_3$ system which demonstrated only 70% selectivity to main product CO_2 (other observed product in all cases was methane). The best selectivity revealed $CrAl_3O_6$. Promotion of support by copper caused the increase of CO conversion and selectivity. The growth of CO conversion about two times for all catalysts was observed. On the other hand, the selectivity to CO_2 was in the same range as before promotion of bioxides by copper. In the case of $FeAlO_3$ system only addition copper leads to significantly growth of selectivity to main product (CO_2) from 70 to 96%.

The influence of different support on activity of copper catalyst in methanol synthesis was studied in this work too. The catalytic activity expressed in $g_{CH_3OH}\ g_{cat}^{-1}\ h^{-1}$ and selectivity of copper supported catalysts in hydrogenation of CO_2 are presented in Fig. 4. The comparison of catalytic activity of copper catalysts supported on various carriers showed that the most suitable system in methanol synthesis is 20% $Cu/ZnAl_2O_4$ catalyst which showed high selectivity and activity. The worst is 20% $Cu/FeAlO_3$ system, which demonstrated the lowest selectivity to methanol.

Thus we can do the next conclusions.

1. The calcination temperature and composition of system strongly influence on phase composition and reduction behavior of copper supported catalysts.

2. XRD results confirm the formation of $ZnAl_2O_4$, $CrAl_3O_6$, $FeAlO_3$, $CuAl_2O_4$, and $CuCr_2O_4$ binary oxides phases depending on the catalysts composition.

3. The catalytic activity in methanol synthesis and water gas shift reaction depends on the type of support. The enough high activity in methanol synthesis was found for 20% $Cu/FeAlO_3$ catalyst, but it showed low

Table 2. The activity of supports and copper-supported catalysts in water gas shift reaction (350°C, $H_2O : CO = 2.5 : 1$)

Catalyst	CO conversion, %	Selectivity to CO_2, %
$CrAl_3O_6$	36	100
$FeAlO_3$	38	70
$ZnAl_2O_4$	43	92
20% $Cu/CrAl_3O_6$	66	97
20% $Cu/FeAlO_3$	84	96
20% $Cu/ZnAl_2O_4$	78	100

selectivity to methanol. The highest selectivity in methanol synthesis was observed for 20% $Cu/ZnAl_2O_4$.

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