

Bimetallic Au–Cu, Ag–Cu/CrAl₃O₆ Catalysts for Methanol Synthesis

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Abstract The influence of silver and gold addition on the activity and physicochemical properties of supported Cu/CrAl₃O₆ catalysts was the aim of this work. The reduction of CrAl₃O₆ support shows only one reduction stage attributed to Cr(VI) species reduction originating from previously oxidized binary oxide. Supported copper catalysts reduce in one or two stages depending on copper concentration representing the reduction of copper oxide—CuO, copper oxide chemically combined with Cr(III) oxide as copper chromite—CuCr₂O₄ and Cr(VI) species originating from surface chromate ions CrO₄²⁻. Additionally, the introduction of silver into supported copper catalysts Cu/CrAl₃O₆ can lead to the appearance of silver chromate phase. XRD investigations of support CrAl₃O₆ alone, supported copper and gold and silver promoted copper supported catalysts calcined at 400, 700 and 900 °C indicated the presence of highly amorphous alumina γ -Al₂O₃ like structure network in which some of cationic locations of aluminum were occupied by chromium atoms and small quantities of α -Cr₂O₃ phase. Additionally, for copper, silver–copper, and gold–copper supported catalysts the following oxide phases were distinguished: monometallic oxides CuO, Ag₂O, binary oxides CuAl₂O₄, Ag₂CrO₄, CuCr₂O₄ and even ternary oxide CuAlCrO₄. In the case of gold promoted copper supported catalysts metallic gold phase was detected. Activity tests carried out for these catalysts show that the most active was 20 wt.%

Cu/CrAl₃O₆ catalyst. Promotion of copper catalysts by silver improves the activity in methanol synthesis, what can be assigned to silver chromate formation. The analogical gold chromate like formation was not confirmed.

Keywords Methanol synthesis · CuAl₂O₄ · Cu/CrAl₃O₆ · CrAl₃O₆ · Ag₂CrO₄ · CuCrO₄

1 Introduction

Methanol is an important source for the production of many various chemicals and can be used as a fuel, source of hydrogen for fuel cells and as a safe carrier of energy. Commercially methanol is produced from synthesis gas (CO, H₂) mainly over Cu/ZnO catalysts [1, 2]. Additionally, copper–zinc oxide catalysts are used in many reactions, such as: synthesis of higher alcohols, the methanol steam reforming and water gas shift reaction. Many workers [3, 4] confirmed that activity of catalysts in methanol synthesis increases with the enhancement of metallic copper surface area until reaching a maximum at molar ratio Cu/ZnO equal 8. Additionally Fujitani et al. [5] established that not only Cu⁺ ions are essential for methanol synthesis but also metallic copper phase is active in this reaction and Cu⁺/Cu⁰ ratio determined the specific activity of this system.

In the present work the influence of noble metal (Ag, Au) addition on physicochemical and catalytic activity of copper dispersed on binary oxide CrAl₃O₆ support were investigated. The obtained samples were characterized by BET, TPR_{H2} and XRD techniques and their activity for methanol synthesis from H₂, CO and CO₂ mixture under atmospheric pressure using gradientless reactor were investigated.

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2 Experimental

2.1 Preparation of Catalysts

Catalysts were prepared by wet aqueous impregnation method. To prepare support precursor CrAl_3O_6 chromium and aluminium nitrates were used. The ammonia co-precipitated mixture of chromium and aluminium hydroxides with molar ratio $\text{Cr}:\text{Al} = 1:3$ were dried and calcined 3 h in air at 400 °C. The obtained material represented well mixed binary oxide with chemical formula CrAl_3O_6 . Metals phases (Cu, Au, Ag) were introduced on support surface by wet impregnation method with appropriate aqueous solution of their nitrates and HAuCl_4 and then the supported catalysts were dried and finally calcined in air at 400, 700 and 900 °C. Also the samples of supports Al_2O_3 and CrAl_3O_6 were calcined in the same conditions. The composition of supported catalysts can be represented by formula 1% Me to (5,10, 20)% $\text{Cu}/\text{CrAl}_3\text{O}_6$ where Me = Au or Ag. The binary oxides corresponding to following chemical formula: CuCrO_4 , Ag_2CrO_4 , and CuAl_2O_4 were prepared from appropriate nitrates of silver, copper, aluminium and chromium with suitable molar ratio.

2.2 Methods of Catalysts Characterization

2.2.1 The Specific Surface Area and Porosity

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

2.2.2 Temperature Programmed Reduction

The Temperature programmed reduction (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 to 95% Ar) with the gas volume velocity 40 cm^3/min . Hydrogen consumption was monitored by a thermal conductivity detector.

2.2.3 In situ Temperature Programmed and Conventional XRD Phase Analysis

Approximately 150 mg of sample which had been ground in an agate mortar, was packed in the glass ceramics (Macor) sample holder. The gas mixture 5% H_2 to 95% Ar was used as a reducing reagent for binary oxide support CrAl_3O_6 . The sample was heated at a nominal rate of 2 °C/min. The

high-temperature wide-angle X-ray diffraction data were collected using a PANalytical X'Pert Pro diffractometer equipped with an Anton Paar XRK900 reactor chamber every 50 °C starting from 50 °C and ending at 850 °C. The sample was scanned from 15° to 80° 2θ . A PANalytical X'Celerator detector based on Real Time Multiple Strip technology capable of simultaneously measuring the intensities in the 2θ range of 10–90° was used.

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 [6] and next the data were smoothed using cubic polynomial [7]. All calculations were done with X'Pert High Score Plus computer program [8].

2.2.4 Catalytic Activity Test

CO/CO_2 hydrogenation tests were carried out using gradientless reactor. Process was carried out under atmospheric pressure in the temperature range 200–520 °C, and reagents were analysed by GC (chromatograph). Catalysts (weight about 0.5 g) were reduced for 2 h in a flow of pure H_2 at 300 °C and atmospheric pressure, before activity tests. The catalysts were cooled to the reaction temperature (260 °C) and then the inlet flow was switched to reaction mixture of H_2 , CO and CO_2 with molar ratio 4:2:1, respectively. The steady-state activity measurements were taken after at least 12 h on stream. The analysis of the reaction products were carried out by on line a gas chromatograph equipped with FID detector and 10% Carbowax 1500 on Graphpac column. The concentrations of CO and CO_2 were monitored by GC chromatograph equipped with TCD detector (120 °C, 130 mA), and Carbopshere 60/80 (90 °C) column.

3 Results and Discussion

3.1 Specific Surface Area Measurements

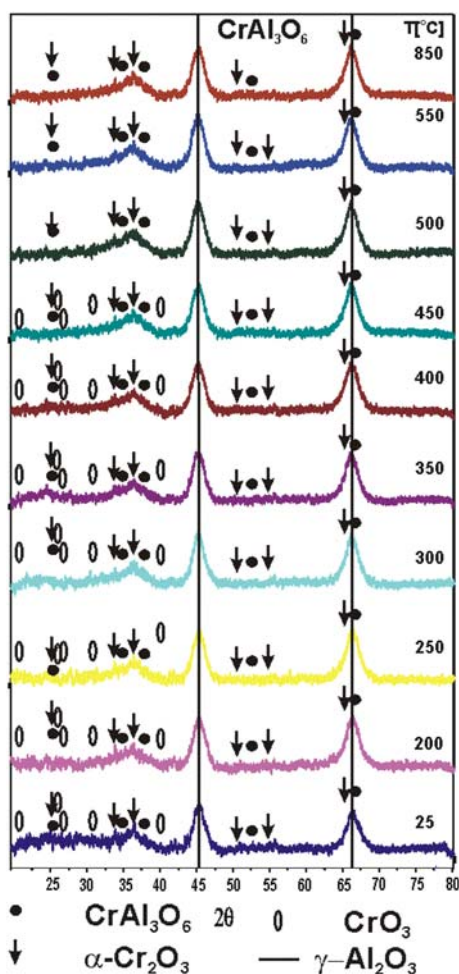
BET results for the calcined supports (Al_2O_3 , Cr_2O_3 , CrAl_3O_6) are provided in Table 1. The highest specific surface area has alumina oxide (237 m^2/g) calcined at 400 °C. The bioxide CrAl_3O_6 is characterized by substantially lower specific surface area (157 m^2/g) in comparison to Al_2O_3 . The increase of calcination temperature to 700 and 900 °C causes further decrease of surface area for Al_2O_3 and CrAl_3O_6 due to their sintering and recrystallization.

Table 1 BET surface area for supports: CrAl₃O₆, Al₂O₃, Cr₂O₃ calcined 3 h in air at different temperature

Support	Calcinations temperature (°C)	Specific surface area (m ² /g)
CrAl ₃ O ₆	400	157
	700	107
	900	93
Al ₂ O ₃	400	237
	700	150
	900	137
Cr ₂ O ₃	600	2

3.2 Phase Composition

X-ray diffraction patterns for CrAl₃O₆ support reduced in atmosphere of hydrogen in function of temperature are presented in Fig. 1. The broad XRD reflexions confirming highly disordered amorphous character of obtained bioxide CrAl₃O₆ and small quantities of α -Cr₂O₃ phases are evident during reduction run [9]. The anticipated reduction effect

**Fig. 1** XRD powder spectra “in situ” reduction of CrAl₃O₆

up to 450 °C connected with the reduction of Cr⁶⁺ to Cr³⁺ is weakly visible on XRD patterns, what confirm that crystalline CrO₃ is reduced during this step. On the other hand the presence of amorphous superficial chromate like species can not be ruled out. Moreover, the lack of significant changes of phase composition during the reduction, confirm that decomposition of the CrAl₃O₆ and its segregation on α -Al₂O₃ and α -Cr₂O₃ not occur. These facts confirm high stability of this system.

The Cr(VI) polychromate—type oxospecies having different bonding with the support surface have been observed in the case of low Cr loading alumina-supported chromium catalysts [10]. The presence of α -Cr₂O₃ crystalline phase was observed for higher chromium content [11, 12]. During calcinations in air the analogical α -Cr₂O₃ and Cr(VI) oxospecies are postulated for nominal CrAl₃O₆ support in our work.

XRD patterns for the monometallic (5%Me/CrAl₃O₆, where Me = Cu, Ag, Au) supported catalysts are illustrated in Fig. 2. XRD reflections recorded for silver supported catalysts calcined 4 h in air at 400, 700 and 900 °C show besides of the amorphous Al₂O₃ phase silver chromate and copper chromite (Ag₂CrO₄ [13], CuCr₂O₄ [14]), and α -Cr₂O₃ phases [9]. Amin et al. [15] confirmed the existence of spinel phase CuCr₂O₄ recorded for Cu/Cr/CeO₂ catalyst after its calcinations [16, 17]. XRD analysis confirmed the formation of Ag₂CrO₄ and α -Cr₂O₃ phases in supported Ag/Cr₂O₃ catalysts obtained by calcining a mixture of chromic oxide gel and silver nitrate [13], were conducted and XRD analysis confirmed the formation of Ag₂CrO₄ and α -Cr₂O₃ phases. On the XRD data recorded for gold supported (5%Au/CrAl₃O₆) catalysts calcined at 400, 700 °C only CrAl₃O₆, metallic gold [15] and α -Cr₂O₃ [9] phases were observed.

For all copper supported catalysts the presence of copper chromite spinel-like structure (CuCr₂O₄) [15, 18], and small quantities of α -Cr₂O₃ were observed [9]. The same spinel phase CuCr₂O₄ and the formation of CuO phase were confirmed in copper-chromate (III) catalysts studied in work [15] where authors confirmed that the catalysts with the highest chromium content show the presence of crystalline CuCr₂O₄ phase but some α -Cr₂O₃ phase is still visible. In our work we obtained the similar results, catalysts with high copper content show considerable quantity of CuO, α -Cr₂O₃ and CuCr₂O₄ phases.

The XRD data recorded for 1%(Ag, Au) to 20% Cu/CrAl₃O₆ supported catalysts calcined in air at various temperature are presented in Fig. 3. The CrAl₃O₆ bi-oxide structure copper chromite CuCr₂O₄ [18], phases were confirmed for catalysts calcined at 400 and 700 °C. Additionally for silver doped copper catalysts the presence of silver chromate (VI) (Ag₂CrO₄) [13] and AlCrCuO₄, Cu₂Al₄O₇, γ -Al₂O₃ phases were detected. The presence of

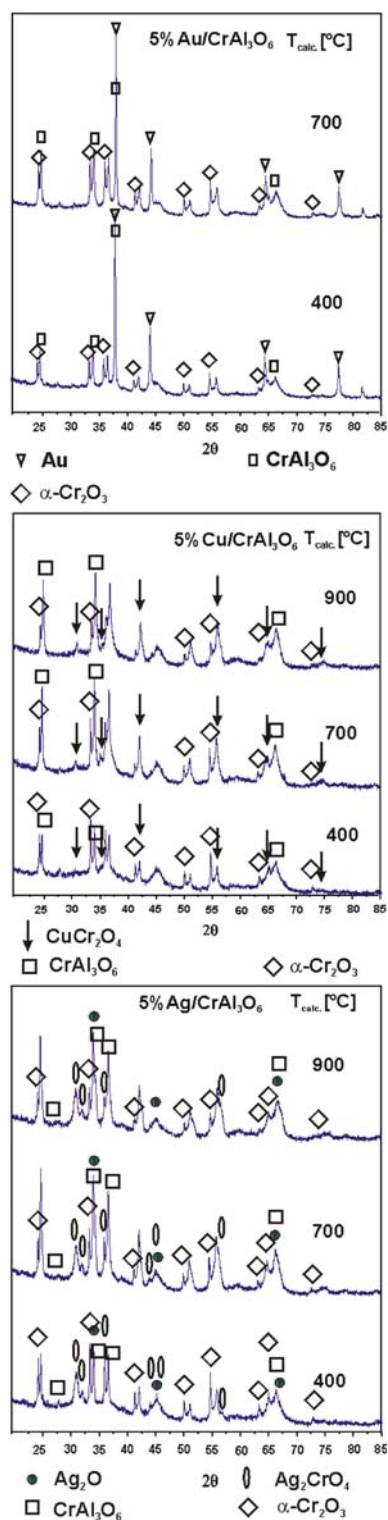


Fig. 2 XRD patterns for monometallic copper, silver and gold catalysts supported on CrAl_3O_6 calcined at 400, 700, 900 °C

copper oxide CuO was not established for catalysts with small content of copper (1%Ag to 5%Cu/ CrAl_3O_6), probably due to their high degree of dispersion and small sizes

of crystallites. The XRD data recorded for catalysts with high content of copper (20% Cu) showed presence of copper oxide CuO . This fact suggests that CuO phase can exist for of 1%Ag to 5%Cu supported catalysts but it is not experimentally observed due to low sensitivity of XRD method. The 1%Ag to (5, 10, 20)%Cu supported catalysts also did not show the presence of metallic silver crystallites [19].

The XRD results for 1%Au to 20%Cu supported catalysts calcined at 400 and 700 °C show reflections corresponding to metallic gold [20], and spinel structures AlCrCuO_4 , CuAl_2O_4 and CrAl_3O_6 phases. The quantity of spinel structure Cu(II)Cr(III)O_4 as well as Cu(II)O phase copper oxide phases grow for catalysts with higher content of copper. The increase of calcination temperature from 400 to 700 °C causes sintering for all samples and appearing the new CuAlCrO_4 phase.

3.3 Temperature Programmed Reduction Studies

The result of TPR measurements for CrAl_3O_6 , 10% CrO_3 to 90% $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Cr}_2\text{O}_3$ and appropriate bioxides–chromates (IV) of silver and copper are shown in the Fig. 4. CrAl_3O_6 shows one wide reduction effect located in temperature range 300–420 °C independently on calcination temperature. This effect is assigned to the reduction of previously oxidized Cr(VI) superficial chromate like groups CrO_4^{2-} . However this TPR effect observed for binary oxide is connected with atomically dispersed Cr^{x+} ($3 > x < 6$) atoms on support surface or presence highly amorphous CrO_3 phase not visible by XRD method. The increase of calcination temperature causes decrease of hydrogen consumption due to temperature induced dissociative decomposition of previously formed CrO_3 chemically bonded to $\gamma\text{-alumina}$ or $\alpha\text{-Cr}_2\text{O}_3$ surface. The reduction process for samples calcined at 400 °C: $\alpha\text{-Cr}_2\text{O}_3$, mechanical mixture of CrO_3 with $\alpha\text{-Al}_2\text{O}_3$ (corundum), and copper and silver chromates (III) are shown on the remaining TPR curves in Fig. 4. The comparison of TPR profiles allows to conclude that the same species Cr^{6+} are reduced in all above cases. Relatively small TPR effect observed for $\alpha\text{-Cr}_2\text{O}_3$ can be explained by low contribution of superficial Cr^{6+} species. The remaining three TPR curves representing copper (II) and silver chromate and copper (II) aluminate samples show the reduction effects taking place in the temperature range 200–400 °C which can be assigned to redox transformations leading to metallic phases: $\text{Cu}^{2+} \rightarrow \text{Cu}^0$ and $\text{Ag}^+ \rightarrow \text{Ag}^0$, respectively.

Comparable results by Kanervo and Krause [21] investigating the reduction of chromium catalysts $\text{CrO}_x/\text{Al}_2\text{O}_3$ showed one reduction effect in varying temperature range of reduction. Additionally they suggested that location and consumption of hydrogen depends on chromium loading and they conclude that alumina support can stabilize Cr^{6+}

Fig. 3 XRD patterns for bimetallic Cu–Ag, Cu–Au catalysts supported on CrAl₃O₆ calcined in air at 400, 700, 900 °C

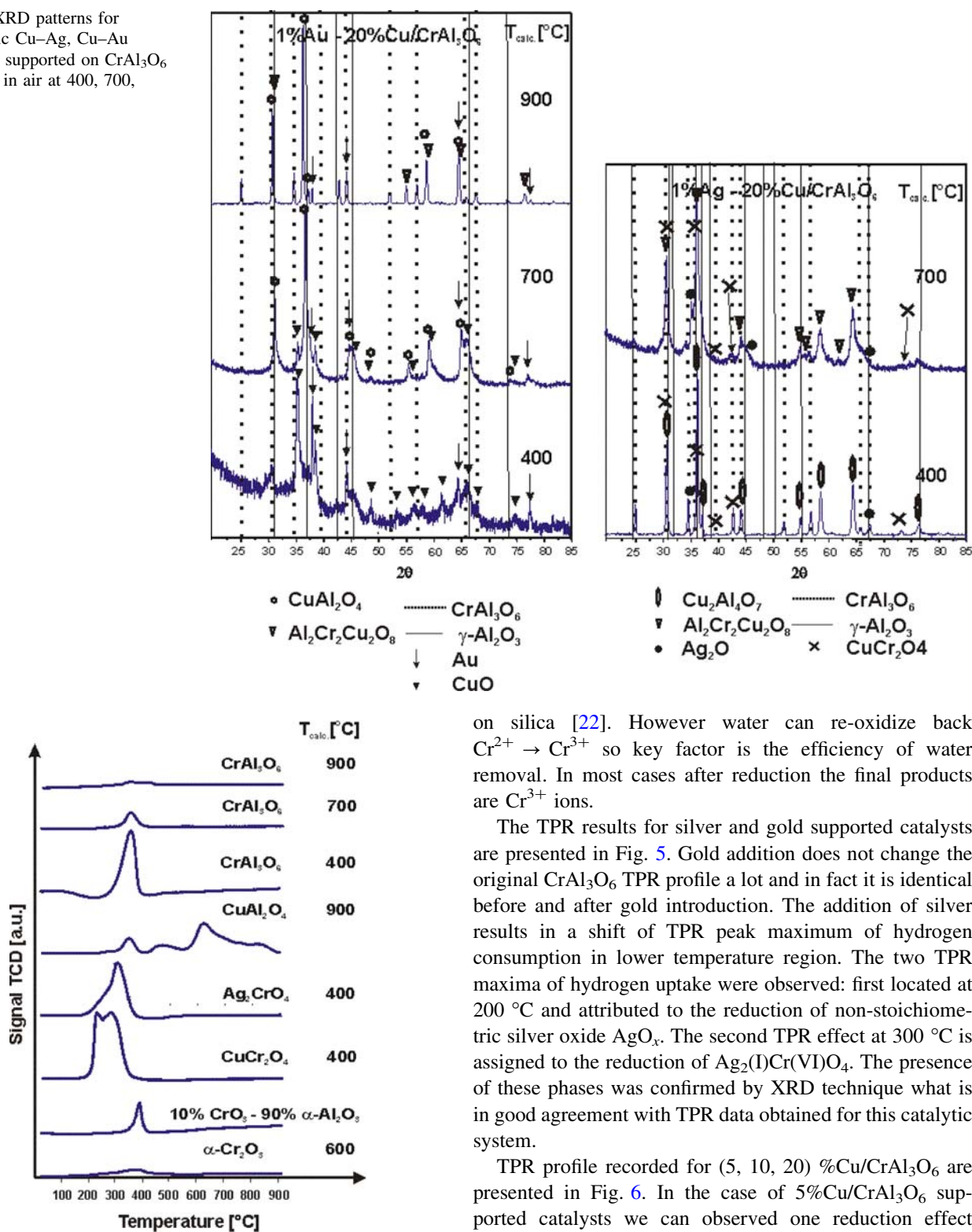


Fig. 4 TPR profiles for chromium oxides, CrAl₃O₆, CuAl₂O₄, CuCr₂O₄, Ag₂CrO₄ calcined in air at various temperature

species involved in reversible redox process Cr(VI) \rightleftharpoons Cr(III). Chromium ions Cr⁶⁺ can be reduced also to Cr²⁺ when they are present on the α -Cr₂O₃ surface or supported

on silica [22]. However water can re-oxidize back Cr²⁺ \rightarrow Cr³⁺ so key factor is the efficiency of water removal. In most cases after reduction the final products are Cr³⁺ ions.

The TPR results for silver and gold supported catalysts are presented in Fig. 5. Gold addition does not change the original CrAl₃O₆ TPR profile a lot and in fact it is identical before and after gold introduction. The addition of silver results in a shift of TPR peak maximum of hydrogen consumption in lower temperature region. The two TPR maxima of hydrogen uptake were observed: first located at 200 °C and attributed to the reduction of non-stoichiometric silver oxide AgO_x. The second TPR effect at 300 °C is assigned to the reduction of Ag₂(I)Cr(VI)O₄. The presence of these phases was confirmed by XRD technique what is in good agreement with TPR data obtained for this catalytic system.

TPR profile recorded for (5, 10, 20) %Cu/CrAl₃O₆ are presented in Fig. 6. In the case of 5%Cu/CrAl₃O₆ supported catalysts we can observe one reduction effect connected with the copper chromate (III) CuCr₂O₄ reduction.

The reduction temperature for CuO species is situated in the temperature range from 200 to 250 °C according to some literature data [23–25]. The obtained reduction profile for monometallic copper catalyst 5%Cu/CrAl₃O₆ is

Fig. 5 Influence of calcination temperature on TPR profiles of Au/CrAl₃O₆ and Ag/CrAl₃O₆

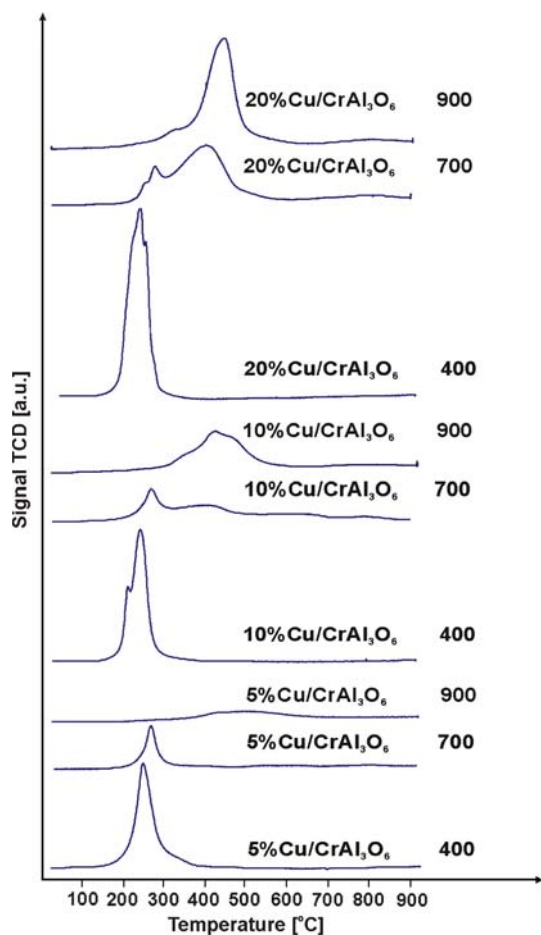
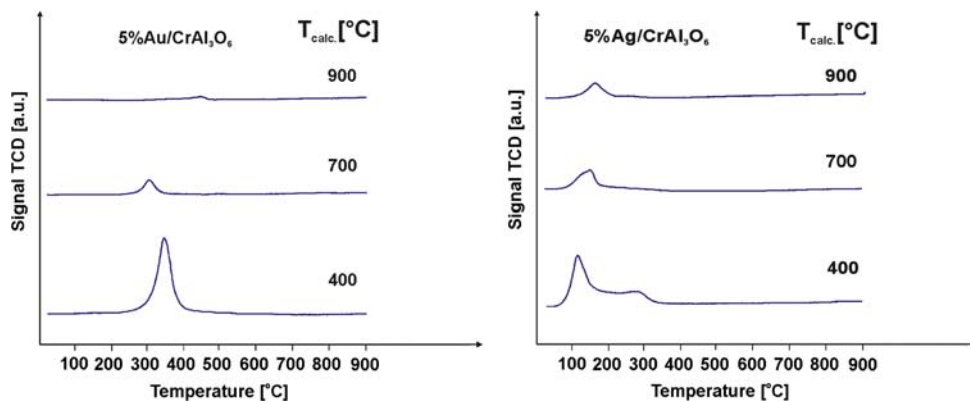


Fig. 6 Influence of calcination temperature on TPR profiles of Cu/CrAl₃O₆

observed at about 250 °C, what it is in good accordance with literature data [26]. From XRD data recorded for this catalyst (see Fig. 2) one can postulate that the reduction peak should be assigned to copper oxide CuO or copper chromate CuCrO₄ reduction. Jones and McNicol [26] confirmed that combination of copper oxide with first-row

transition metal ion (Cr) produces the same TPR_{H2} profile as that obtained from reduction of CuO species.

The TPR profile recorded for 10%Cu and 20%Cu/CrAl₃O₆ supported catalysts show two unresolved peaks can be observed on the reduction profile. First effect can be attributed to the copper oxide CuO reduction; second one can be connected with copper (II) chromate (III) reduction. The significant decrease of reduction effects was observed with the growth of calcination temperature for all samples. This fact can be explained by thermally induced dissociative decomposition of copper and chromium (VI) oxides and significant sintering of samples.

The TPR results for copper catalysts promoted by silver and gold are shown in Fig. 7. Bimetallic silver–copper and gold–copper catalysts reveal intermediate reduction behavior between appropriate monometallic catalysts. Addition of gold or silver results in the decrease of maximum temperature of reduction. The increase of copper load results in growth of reduction Cu(II)Cr(III)O₄ reduction. The difference in TPR profiles is observed for gold doped series catalysts. The occurring high temperature effect can be connected to the reduction of copper aluminate CuAl₂O₄.

3.4 Activity Tests

The methanol synthesis tests were carried out on monometallic (5, 10, 20%) Cu/CrAl₃O₆ and bimetallic 1%(Au or Ag) to 5%Cu/CrAl₃O₆ catalysts under atmospheric pressure in gradientless reactor using H₂:CO:CO₂ mixture. The temperature characteristics of catalytic activity of mono and bimetallic catalysts expressed in mol CH₃OH g_{cat.}⁻¹ h⁻¹ are presented in Figs. 8 and 9. Results show that catalytic activity increases with growth of copper content. The most effective catalyst for methanol synthesis seems to be 20%Cu/CrAl₃O₆ and its high activity can be explained by the presence of high acceptability of copper ions Cu⁺ being the active sites on the catalyst surface. Lower activity for 5% and 10% Cu supported catalysts in

Fig. 7 Influence of calcination temperature on TPR profiles of 1%Ag to Cu/CrAl₃O₆ and 1%Au to Cu/CrAl₃O₆

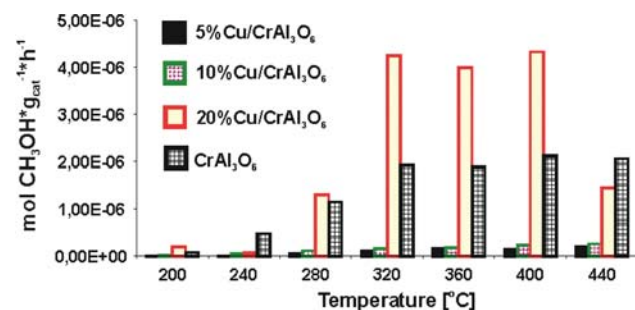
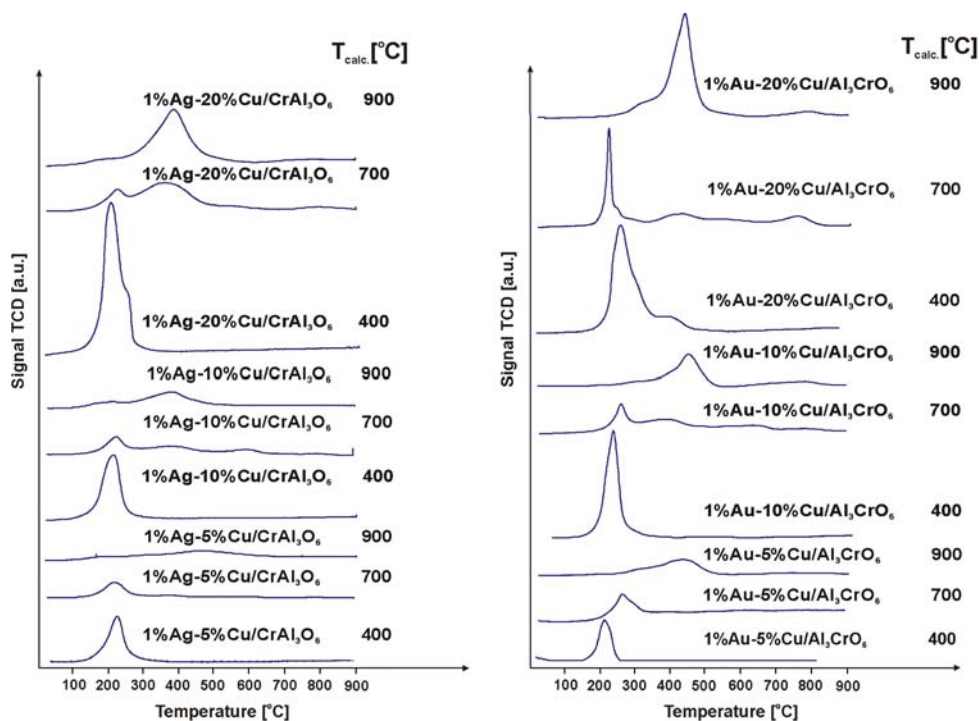


Fig. 8 Catalytic activity of CrAl₃O₆ and monometallic supported catalysts

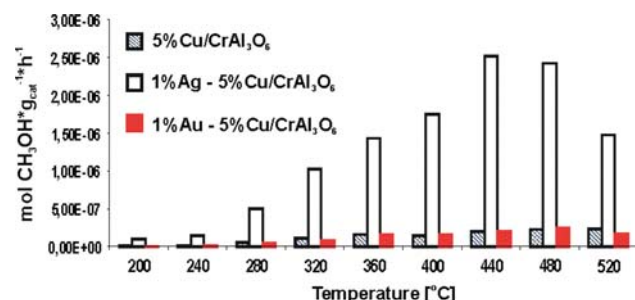
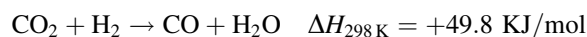


Fig. 9 Catalytic activity of copper, bimetallic 1%Ag to 5%Cu and 1%Au to 5%Cu supported catalysts

comparison to CrAl₃O₆ bixide support can be probably explained by the fact that almost entire copper is in the state of copper (II) chromite (CuCr₂O₄). Copper catalyst promoted by silver showed the significant improvement of

the catalytic activity for 5%Cu/CrAl₃O₆ catalyst probably due to formation of silver chromate (VI) Ag₂CrO₄ compound during preparation step which seems to be active in methanol synthesis. Copper catalysts promoted by gold does not influence on activity of Cu/CrAl₃O₆ catalysts. Additionally silver ions can create active sites on catalysts surface. The selectivity to methanol decreased with increasing temperature, which was related to the growth of the participation of the endothermic reaction of reverse water gas shift reaction playing crucial role in methanol synthesis reaction:



The maximum of methanol yield is located in temperature range 320–460 °C. Further increase of reaction temperature leads to the significant fall of catalyst activity in methanol synthesis.

4 Conclusions

1. TPR reduction effect observed for CrAl₃O₆ support itself is attributed to the reduction of previously oxidized surface species Cr(VI) → Cr(III).
2. Introduction of copper or silver on CrAl₃O₆ support surface leads to the formation of appropriate oxides CuO, Ag₂O and copper chromite (CuCr₂O₄) and silver chromate (Ag₂CrO₄) during catalyst calcination.
3. TPR profiles for highly loaded monometallic Cu/CrAl₃O₆ and bimetallic Ag–Cu/CrAl₃O₆ supported

catalysts represent the reduction of copper and/or silver oxides and depending on calcination temperature silver chromate and copper chromite.

4. XRD patterns after catalyst calcination in air confirmed the presence of following oxidic forms: monooxides—amorphous Al_2O_3 , $\alpha\text{-Cr}_2\text{O}_3$, CuO and Ag_xO , bioxides— $\text{Cr}_x\text{Al}_{1-x}\text{O}_6$, CuAl_2O_4 , CuCr_2O_4 , Ag_2CrO_4 and ternary oxide AlCrCuO_4 and metallic gold phase.
5. Support CrAl_3O_6 alone is active in methanol synthesis. The most active appeared 20% $\text{Cu}/\text{CrAl}_3\text{O}_6$ and 1% Ag to 5% $\text{Cu}/\text{CrAl}_3\text{O}_6$ catalysts.

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