

Silica supported copper and cobalt oxide catalysts for methanol decomposition: Effect of preparation procedure

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Novel “chemisorption-hydrolysis” method was developed for preparation of supported on SiO₂ mixed copper and cobalt oxides. For comparison, similar materials were prepared by conventional impregnation technique. The state of loaded metal oxide species was studied by XRD, FTIR-KBr, FTIR-pyridine, UV-Vis, XPS and TPR techniques. The catalytic properties of the samples were tested in methanol decomposition. The variation in the preparation procedure provides the deposition of different metal oxide species and it is considered as simple approach to control the surface and catalytic properties in copper and cobalt oxide bi-component system.

Key words: copper and cobalt mixed oxides, “chemisorption–hydrolysis” method, methanol decomposition.

INTRODUCTION

Complex oxides with spinel structure, such as cobaltites, are of intensive investigation because of their remarkable optical, electrical, magnetic and catalytic properties [1 and refs. therein]. Their normal and inverse structure can be represented by a general formulas A[B]₂O₄ (normal spinel) and B[AB]O₄ (inverse spinel) respectively, where elements A and B denote divalent and trivalent metallic cations, which are octahedrally (inside the parenthesis) and tetrahedrally (outside the parenthesis) coordinated with oxygen ions [2]. In case of normal Co₃O₄ spinel structure, the Co³⁺ ions occupy the octahedral sites, while Co²⁺ is situated on the tetrahedral sites. For copper spinel materials, Cu_xCo_{3-x}O₄, transition to inverse spinel structure was established when x>0.2 [3]. In the inverse CuCo₂O₄ spinel, Co³⁺ ions occupy the tetrahedral and half of octahedral sites, while Cu²⁺ ions situate at the octahedral sites. It was reported that different synthetic procedures, such as

nitrate decomposition, urea combustion, co-precipitation, sol-gel, hydrothermal or mechanotechnical methods provide the formation of Cu_xCo_{3-x}O₄ spinel particles with different dispersion, shape, stoichiometry and cations distribution [1 and refs. therein]. Due to the more significant contribution of metal ions in octahedral position to surface activity rather than tetrahedral ions [4, 5], the preparation procedure seems to be easy and powerful way to control the cobaltite properties. Recently, the synthesis of metals or metal oxides in nanoscale form with well defined size, shape and crystallinity has gain significant attention because of their unique physico-chemical properties with a potential in many technological applications. However, the control and stabilization of nanoparticle size is still a matter of challenge and nowadays, the development of novel preparation procedures is in a focus of interest. In our previous studies we applied a new “chemisorption-hydrolysis” strategy to modify mesoporous silicas with copper [6] or cobalt [7] metal and metal oxide particles. The key step during this procedure was the formation of metal ammonia complexes, which interacted selectively with the surface silanol groups. As a result, formation of copper oxide nanoparticles with predominantly oligomeric and highly disordered crystal structure as well as hardly reduc-

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ible cobalt species strongly interacting with the support were produced.

The aim of the current study is to apply the novel “chemisorption-hydrolysis” (CH) strategy for preparation of silica-supported copper and cobalt oxide bi-component materials. The samples were characterized by XRD, UV-Vis, XPS, TPR, FTIR, FTIR of adsorbed pyridine, and compared with the similar materials obtained by conventional incipient wetness impregnation (WI) technique. All materials were tested as catalysts in methanol decomposition.

Recently, methanol, and in particular bio-methanol, has been overlooked as efficient energy source [8 and refs. therein]. It can be directly used in internal combustion engine, as well as successfully converted onboard into hydrogen for fuel cells electric cars. Methanol is a feasible alternative for cheap and safe hydrogen storage and supply, especially in case of small scale devices. Decomposed methanol could be also used as a source of synthesis gas for number of catalytic processes.

EXPERIMENTAL

Materials

A commercial mesoporous silica (SiO_2 , Grace, BET – $300 \text{ m}^2\text{g}^{-1}$; pore volume – $1.43 \text{ cm}^3\text{g}^{-1}$) was used as a support for the preparation of mono- and bi-component copper and cobalt oxide materials. The modified “chemisorption-hydrolysis” procedure was applied for SiO_2 modification as was described in [6, 7]. $\text{Cu/SiO}_2\text{-CH}$ sample was prepared by addition of silica support to aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and NH_4OH (pH 9). After 20 min under stirring the slurry held in ice bath at 273 K, it was slowly diluted. The solid was separated by filtration, washed with water, dried and calcined at 773 K for 4 h. The sample, denoted as $\text{Co/SiO}_2\text{-CH}$ was obtained from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which was dissolved into a water solution containing NH_4NO_3 (mol NH_4NO_3 /mol Co =10/1) under stirring. The

solution was cooled at 273 K and slowly a 30% solution of H_2O_2 and NH_4OH were added. Finally, the temperature was increased to 333 K and after 2.5 hours the solution was cooled down to room temperature and the pH was adjusted to 9 with 28% solution of NH_4OH , before adding the support (SiO_2). The silica suspension was kept under stirring for 0.5 or 24 h and then it was diluted with water at 273 K and filtered. The solid was washed with water, dried and calcined in air at 773 K for 4 h. The bi-component $\text{CuCo/SiO}_2\text{-CH}$ material was prepared following the same procedure, using a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in NH_4OH (pH=9). Similar $\text{Cu/SiO}_2\text{-WI}$, $\text{Co/SiO}_2\text{-WI}$ and $\text{CuCo/SiO}_2\text{-WI}$ materials were prepared by impregnation technique from nitrate precursors and their decomposition in air at 773 K for 4 h. The samples composition is presented in Table 1.

Methods of investigation

Cobalt content in the samples was determined by Atomic Absorption Spectroscopy on Atomic Absorption Spectrometer 3100 – Perkin Elmer; flame: acetylene/air. Powder X-ray diffraction patterns were collected within the range from 5.3 to $80^\circ 2\theta$ with a constant step $0.02^\circ 2\theta$ on Bruker D8 Advance diffractometer with Cu K_α radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database. The IR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of $1\text{--}2 \text{ cm}^{-1}$, accumulating 64–128 scans. The UV–Vis spectra were recorded on the powder samples using a Jasco V-650 UV-Vis spectrophotometer equipped with a diffuse reflectance unit. The FTIR studies of pyridine adsorption were carried out with a BioRad FTS40 spectrophotometer equipped with mid-IR DTGS detector. The measurements were performed after activation of the samples at 773 K in air for 20 minutes followed by evacuation for 40 minutes and eventual reduction in hydrogen at the same temperature for 40 minutes.

Table 1. Samples composition and reduction degree, determined by TPR-TG analyses

Sample	Preparation procedure	Cu content (wt%)	Co content (wt%)	Reduction degree (wt%)
$\text{Cu/SiO}_2\text{-WI}$	WI	7.6	0.0	100
$\text{Co/SiO}_2\text{-WI}$	WI	0.0	7.6	96
$\text{CuCo/SiO}_2\text{-WI}$	WI	3.8	3.8	100
$\text{Cu/SiO}_2\text{-CH}$	CH	7.6	0.0	88
$\text{Co/SiO}_2\text{-CH}$	CH	0.0	6.3	50
$\text{CuCo/SiO}_2\text{-CH}$	CH	2.7	2.6	67

The absorption of pyridine was performed at room temperature and all spectra were recorded at room temperature after pyridine desorption at selected temperatures. The XPS analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized micro focused Al X-ray source (powered at 20 mA and 10 kV). The TPR/TG (temperature-programmed reduction/ thermogravimetric) analyses were performed in a Setaram TG92 instrument in a flow of 50 vol% H₂ in Ar (100 cm³.min⁻¹) and heating rate – 5 K.min⁻¹.

Catalytic experiments

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst, three times diluted with grounded glass), argon being used as a carrier gas (50 ml min⁻¹). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350–770 K with heating rate of 1 K.min⁻¹. On-line gas chromatographic analyses were performed on HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon based material balance. Before the catalytic experiments the samples were activated *in situ* in air at 773 K for two hours. The products selectivity was calculated as $X_i/X \cdot 100$, where X_i is the current yield of the product i and X is methanol conversion

RESULTS AND DISCUSSION

X-ray diffraction patterns (Fig. 1) of the samples prepared by different procedures are performed to identify the presence of crystalline phase. The absence of any diffraction peaks in the patterns of all CH samples indicates that this procedure provides the formation of very finely dispersed metal oxide phase despite the samples composition. Just the opposite, well defined reflections are visible in the patterns of all materials prepared by WI procedure. The reflections at 35.5, 38.7 and 48.7° 2θ in the pattern of Cu/SiO₂_WI could be indexed to pure monoclinic (Tenorite, space group C2/c) crystallites of CuO [9]. The diffraction peaks at 2θ = 31.2, 36.8, 44.8, 59.4 and 65.3° in the pattern of Co/SiO₂_WI can be indexed to a pure face centered cubic (fcc) structure (space group Fd3m) of Co₃O₄ normal spinel [10]. The XRD reflections for the bi-component CuCo/SiO₂_WI sample are wider and less intensive, indicating formation of mixture of more finely dispersed metal oxide phase as compared to the mono-component materials, which parameters are well

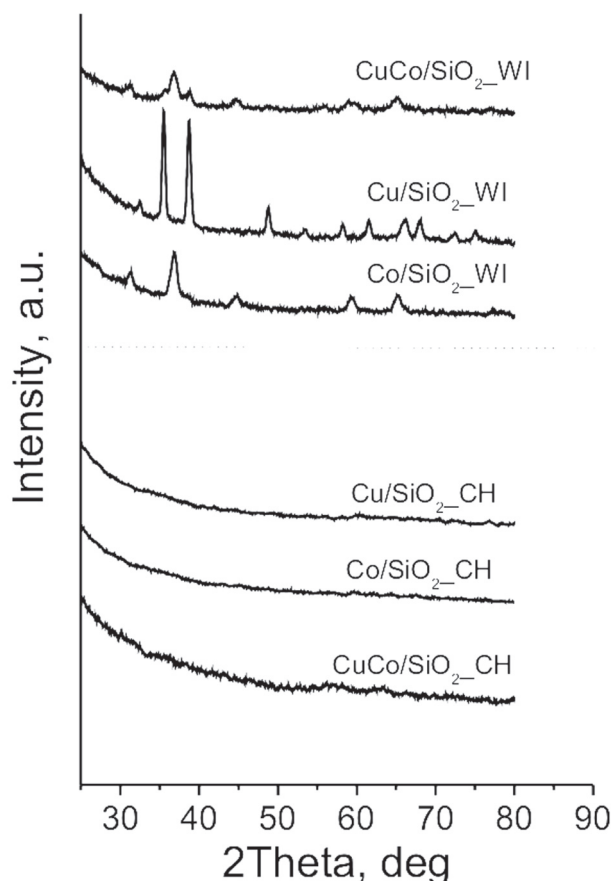


Fig. 1. XRD patterns of mono- and bi-component copper and cobalt oxide silica modifications prepared by CH and WI technique

fitted with the cubic (fcc) structure (space group Fd3m) of Cu_xCo_{3-x}O₄ spinel oxide and monoclinic CuO. The slight changes in the lattice parameters for the spinel phase in bi-component material are due to partial replacement of Co²⁺ ions in octahedral position (ionic radii 52.5 pm) by larger Cu²⁺ ions (ionic radii 73 pm) [11].

More information for the state of loaded metal oxide phases was obtained by combined UV-Vis, FTIR and XPS spectroscopic study. The UV-Vis spectra (Fig. 2) of both mono-component copper materials represent absorption band at about 240 nm and a broad band in a 600–800 nm region which could be assigned to the absorption of Cu²⁺ ions in CuO crystallites [12 and refs. therein]. The absorption in the 300–400 nm region indicates presence of small Cu-O-Cu oligomeric species, which fraction seems to be larger in the case of Cu/SiO₂_CH. (Fig. 1). The broad band at around 215 nm in the spectrum of Co/SiO₂_WI can be assigned to charge transfer from O²⁻ to Co³⁺. The two broad bands at 400–550 nm and 650–800 nm are typical of

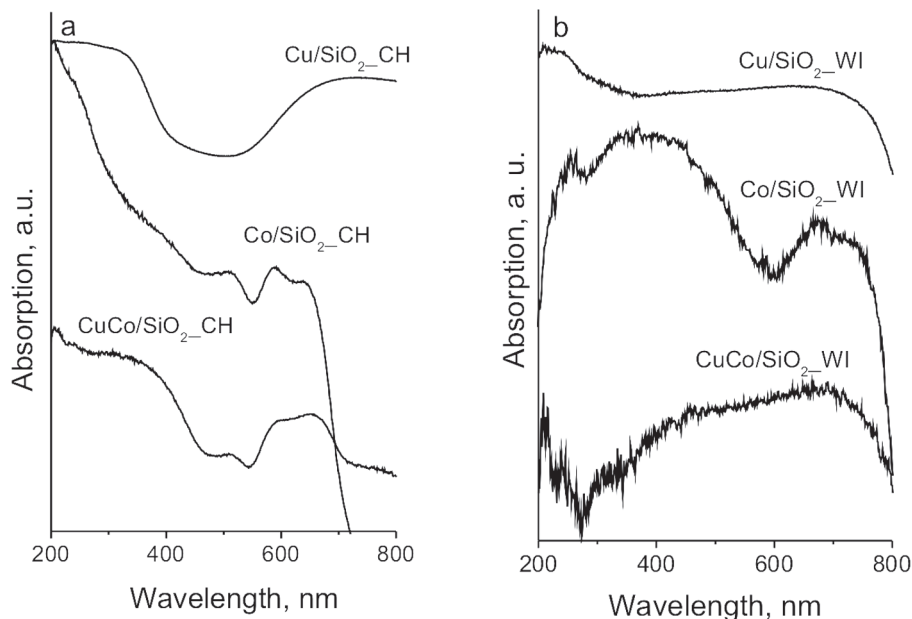


Fig. 2. UV-Vis spectra of copper and cobalt modifications obtained by CH (a) and WI (b) methods

4T1(F)→4T1(P) transitions of octahedrally coordinated Co^{3+} and electronic ligand-field $4A_2$ (F)→ $4T_1$ (p) transition in tetrahedrally coordinated Co^{2+} , respectively. In accordance with the XRD data, (Fig. 1) this evidences presence of well crystallized Co_3O_4 phase. These bands are less resolved in the spectrum of $\text{Co/SiO}_2\text{-CH}$ sample, but the appearance of well pronounced peaks triplet at 525 nm, 583 nm and 654 nm is detected. According to [13] it could be attributed to Co^{2+} species in tetrahedral coordination in CoO_4 units, which includes oxygen ligands from the silica matrix due to strong interaction with it. The changes in the position and relative part of the main absorption peaks for Co_3O_4 in the UV-Vis

spectrum of $\text{CuCo/SiO}_2\text{-WI}$ indicate changes in the distribution of cobalt ions probably due to their partial substitution with copper ones and formation of $\text{Co}_x\text{O}_{3-x}\text{O}_4$ spinel oxide. The UV-Vis spectrum of $\text{CuCo/SiO}_2\text{-CH}$ differs significantly from the spectrum of $\text{CuCo/SiO}_2\text{-WI}$. It could be interpreted as superposition of the spectra of both $\text{Cu/SiO}_2\text{-CH}$ and $\text{Co/SiO}_2\text{-CH}$ mono-component materials, but the small changes in the position and intensity of the main peaks do not excluded also slight interaction between individual oxides.

The formation of well crystallized Co_3O_4 phase in $\text{Co/SiO}_2\text{-WI}$ sample is also evidences by FTIR spectroscopy (Fig. 3a) with the appearance of well

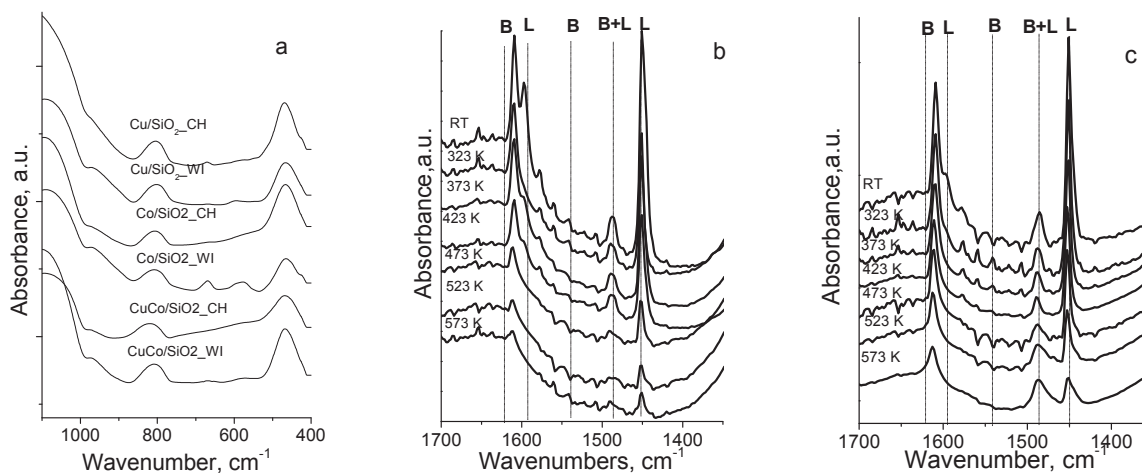


Fig. 3. FTIR spectra of copper and cobalt modifications obtained by different procedures (a) and FTIR of adsorbed pyridine for $\text{CuCo/SiO}_2\text{-CH}$ treated in oxidative (b) and reduction (c) atmosphere

Table 2. XPS data for selected modifications

	Element	BE, (eV)	Concentration (at %)	M/Si Ratio
Cu/SiO ₂ _CH	Cu 2p	933.0	5.34	0.21
	Si 2p	103.4	25.35	
Co/SiO ₂ _CH	Co 2p	781.7	3.78	0.15
	Si 2p	103.5	25.80	
CuCo/SiO ₂ _CH	Co 2p	781.2	1.41	0.05
	Cu 2p	933.0	0.85	0.03
	Si 2p	103.3	26.29	
CuCo/SiO ₂ _WI	Co 2p	778.8	0.68	0.03
	Cu 2p	932.6	1.10	0.05
	Si 2p	103.4	22.35	

resolved bands at 580 cm⁻¹ and 665 cm⁻¹. According to [1] they could be assigned to Co-O stretching vibration mode of Co³⁺ ions in octahedral hole or Co²⁺ ions in tetrahedral hole, respectively. These peaks are less pronounced in the spectrum of Co/SiO₂_CH sample, which is in a good correlation with the UV-Vis and XRD data, indicated very low extent of crystallization of spinel Co₃O₄ phase. The broad band at around 590 cm⁻¹ in the spectrum of Cu/SiO₂_WI is due to stretching vibrations in CuO particles. It is red shifted for Cu/SiO₂_CH probably due to strong interaction of CuO oligomers with the silica support. The observed simultaneous decrease in intensity of the bands at about 665 cm⁻¹ and 580 cm⁻¹ with a tendency of red shifting of the latter in the spectrum of CuCo/SiO₂_WI as compared to the spectra of the corresponding individual oxides could be assigned to the appearance of new type of Co-O stretching vibration mode of Co³⁺ and Cu²⁺ ions in tetrahedral and octahedral coordination, respectively [1]. This spectroscopic data indicate that the loaded metal oxide phase in this sample is not a simple mixture of individual CuO and Co₃O₄ oxides. This conclusion is not valid for CuCo/SiO₂_CH sample where a continuous adsorption in the whole 800–600 cm⁻¹ region is observed. Selected samples were studied by XPS method and data from the analyses are listed in Table 2. The Co 2p_{3/2} peaks in Co/SiO₂_CH and CuCo/SiO₂_CH are observed at ca. 781.7 eV and 781.2 eV, respectively, with the appearance of satellite peak at ca. 5.5 eV higher energy aside from the Co 2p_{3/2} peak. According to the literature data [14], these BEs do not correspond to the BEs typical of polycrystalline Co₃O₄ and CoO phase. So, in accordance with UV-Vis and FTIR measurements, the observed XPS data could be assigned to presence of species with unknown stoichiometry, which are in strong interaction with the silica support. In agreement with [15], the higher values of

BE for Co/SiO₂_CH could be assigned to presence of cobalt silicate Co₂SiO₄ phase as well. This interaction seems to decrease in CuCo/SiO₂_CH, probably due to the appearance of additional interaction with copper species. The higher values of BEs of Cu 2p in Cu/SiO₂_CH and CuCo/SiO₂_CH correspond to Cu²⁺ in highly dispersed oxide species. For comparison, in case of CuCo/SiO₂_WI, BE of Cu 2p is lower, while BE of Co 2p is below the reported for Co₃O₄. Thus, XPS spectra confirm slight interaction between copper and cobalt species when they are supported by CH method, contrary to the WI obtained materials. We should stress on higher surface concentration of Cu ions in case of CuCo/SiO₂_WI as compared to CuCo/SiO₂_CH, which in agreement with the XRD, UV-Vis and FTIR data, confirms their different location, probably in more exposed (octahedral) position in Cu_xCo_{3-x}O₄ spinel for the former material.

Generally, the optimization of surface acid-base and redox properties is of key importance to control the catalytic behavior of solid catalysts, in particular in conversion of methanol molecule, which can be very flexible in presence of different catalytic sites [16]. In our study more information for these characteristics was obtained by FTIR of adsorbed pyridine and TPR study. Selected FTIR data are presented in Fig. 2b, c. The observed intensive peak at 1450 cm⁻¹ and the small ones at 1488 cm⁻¹ and 1610 cm⁻¹ in the spectra of CuCo/SiO₂_CH (Fig. 2b) could be assigned to the adsorbed on Lewis acidic sites pyridine, while no bands corresponding to Brønsted acid sites (1550 cm⁻¹, 1620 cm⁻¹ and 1640 cm⁻¹) are registered [17]. The amount of adsorbed pyridine is 0.057 mmol.g⁻¹ and 0.187 mmol.g⁻¹ for Co/SiO₂_CH and CuCo/SiO₂_CH, respectively, indicating much higher acidity for the bi-component material. The preservation of the FTIR spectra (Fig. 2c) and the amount of adsorbed pyridine (0.189 mmol.g⁻¹)

for the CuCo/SiO₂-CH sample after the reduction treatment (similar reductive conditions are created during the catalytic test) confirms the stability of these acidic sites. For comparison, their changes are more pronounced for pure Co/SiO₂-CH sample, where after reduction the adsorbed amount of pyridine was reduced to 0.041 mmol.g⁻¹.

TPR-DTG profiles for all studied materials are shown in Fig. 4. For both pure copper modifications the main reduction effect is observed in 400–550 K region. The weight loss corresponds to one step Cu²⁺ → Cu⁰ reduction transition. The shifting of this effect to lower temperature for Cu/SiO₂-CH indicates easily reducible and highly dispersed copper phase compared to the IW material though the lower reduction degree (Table 1) suggest also the presence of a small fraction of unreducible copper species. Rather different are the TPR profiles for mono-component cobalt modifications. Taking into account the data from the physicochemical study (see above), step-wise reduction of Co₃O₄ to CoO and then to Co of particles with different dispersion occurs on Co/SiO₂-WI, while reduction of strongly interacted with the silica, mainly

Co²⁺ species is assumed for Co/SiO₂-CH (Fig. 4, Table 1). TPR profiles for bi-component materials reveal different state of metal oxide phase in them. Single effect, which is slightly shifted to lower temperature than the one registered for Cu/SiO₂-WI, is observed for CuCo/SiO₂-WI. In accordance with XRD and spectroscopic data it corresponds to reduction of Cu_xCo_{3-x}O₄ spinel phase. The reduction behaviour of CuCo/SiO₂-CH (Fig. 4, Table 1) confirms the assumption done above, that the strong interaction of different metal oxide species with silica matrix renders difficult their interaction.

Figs. 5a,c represent data for the catalytic activity of the samples in methanol decomposition after their pretreatment in oxidative or reductive atmosphere, respectively. The selectivity to CO, which formation is directly related to hydrogen production from methanol, is shown in Figs. 5b, d. Methane, carbon dioxide, dimethyl ether and C₂-C₃ hydrocarbons are also registered as by-products. Despite the method of samples preparation, well defined tendency for catalytic activity increase for bi-component materials as compared to their mono-component analogues, is registered. This effect is better pronounced for the sample obtained by WI method, where higher selectivity to CO is also found. Note, that bi-component materials preserve their higher activity also after the treatment in reductive atmosphere (Fig. 5c).

So, the incipient wetness impregnation of silica with copper and cobalt nitrates and their further treatment in air promote the formation of finely dispersed, but well crystallized Cu_xCo_{3-x}O₄ spinel particles. Here, the Cu²⁺ ions incorporated into the octahedral sites share the oxygen with adjacent Co²⁺, leading to the formation of Cu-O-Co surface species. The TPR and FTIR of adsorbed pyridine clearly demonstrated that the Cu-Co interaction provides an increase in redox activity and Lewis acidity as compared to the individual oxides and facilitates methanol decomposition in synergistic manner [16]. The combined XRD, UV-Vis, FTIR, XPS and TPR study indicates that “chemisorption-hydrolysis” method leads to the formation of strongly interacted with the support copper and cobalt species, where metal ions exist also in lower oxidative state. This renders difficult the formation of mixed oxide species and, as was well illustrated by FTIR (pyridine) and TPR measurements, and changes the proportion between the acidic and redox functionality. Thus, the prevailing acidic functionality over the redox one for the bi-component materials obtained by CH procedure provides relatively lower catalytic activity and lower selectivity to CO formation. Note, that despite the method of preparation and contrary to individual oxides, bi-component samples exhibit high catalytic activity even after the reduction treatment. We assign this phenomenon to the

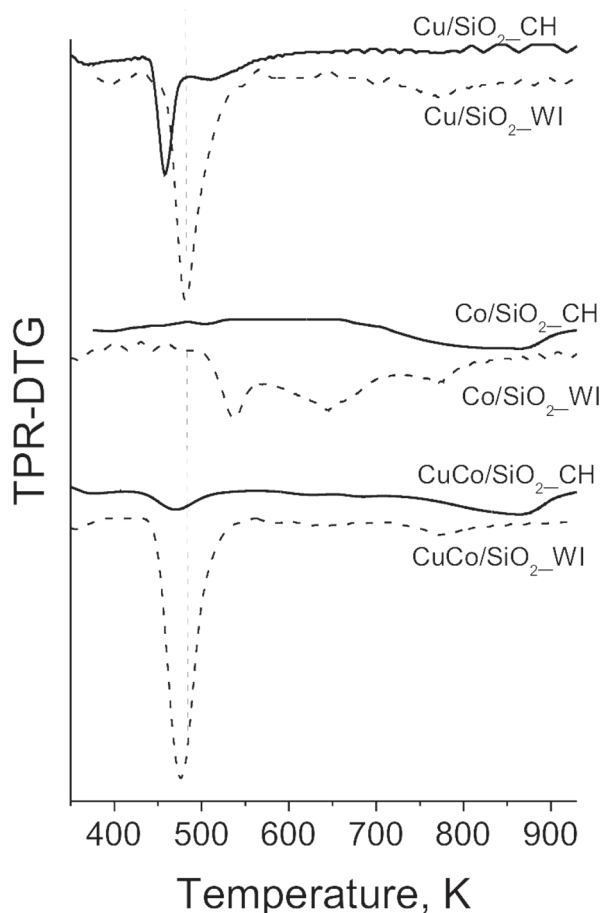


Fig. 4. TPR-DTG profiles of different modifications

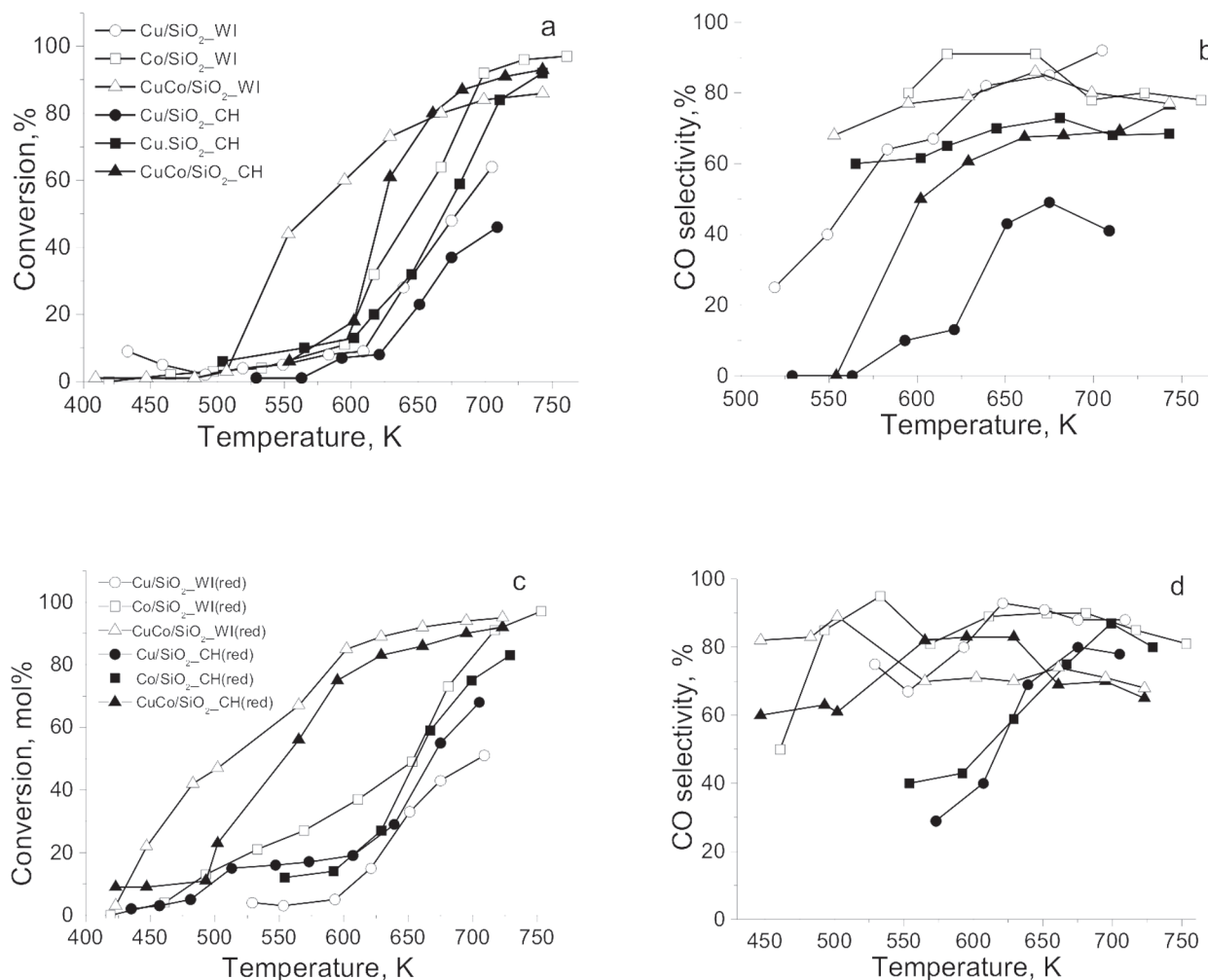


Fig. 5. Methanol conversion (a, c) and CO selectivity (b, d) for the materials treated in air (up) and hydrogen (down) materials

reduction of metal ions, which were stabilized in ordered spinel structure, providing the formation of highly dispersed metal phase. Further investigations are in progress.

CONCLUSION

The modification procedure is a powerful strategy to control the formation of copper cobaltite on SiO₂. The strong interaction of individual metal oxide species with silica support, which realizes during the “chemisorption-hydrolysis” method renders difficult the formation of well crystallized spinel phase, which leads to the formation of less active methanol decomposition catalysts as compared to the conventional incipient wet impregnation technique.

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МЕД И КОБАЛТ МОДИФИЦИРАНИ СИЛИЦИЕВООКСИДНИ КАТАЛИЗАТОРИ ЗА РАЗЛАГАНЕ НА МЕТАНОЛ: ВЛИЯНИЕ НА МЕТОДА НА ПОЛУЧАВАНЕ

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(Резюме)

Разработен е нов метод, наречен „хемосорбция-хидролиза“, за получаване на нанесени върху SiO₂ смесени мед-кобалт оксидни катализатори. За сравнение, аналогични материали са получени чрез използването на традиционен метод на импрегниране. Състоянието на нанесените металооксидни частици е характеризирано чрез Рентгенова дифракция, ИЧ-КВг, ИЧ на адсорбиран пиридин, УВ и Рентгенова фотоелектронна спектроскопия, Температурно програмирана редукция с водород. Каталитичните свойства на образците са изследвани в реакция на разлагане на метанол. Промените в процедурата на модифициране води до формирането на различни металооксидни частици, което предоставя лесен подход за контрол на повърхностните и каталитични свойства на мед-кобалт оксидната би-компонентна система.