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Silica supported copper and cobalt binary oxides as catalysts for methanol decomposition: Effect of preparation procedure

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

The present investigation is focused on the effect of preparation procedure on the formation of catalytic active sites on silica supported copper and cobalt binary oxides. Samples with different Cu/Co ratio were obtained by unconventional "chemisorption-hydrolysis" technique consisted of deposition of Cu and Co ammonia complexes, followed by their hydrolysis and thermal decomposition. A conventional wetness impregnation with aqueous solution of the corresponding nitrate precursors was also used for the preparation of similar reference materials. The obtained samples were characterized by a complex of different physicochemical techniques, such as XRD, UV-Vis, FTIR spectroscopy and temperature-programmed reduction with hydrogen. Methanol decomposition to hydrogen and CO was used as a catalytic test in a view of its application as alternative fuel. The preparation techniques strongly affected the dispersion and oxidative state of copper and cobalt species which is easy approach to control their catalytic behaviour.

Key words: copper-cobalt mixed oxide; chemisorption-hydrolyses” technique; methanol decomposition

INTRODUCTION

Transition metal oxides, in particular copper oxides, are known to catalyse many reactions such as Fischer–Tropsch synthesis (FTS), CO_2 hydrogenation, steam reforming of methanol, methane, synthesis of methanol, CO preferential oxidation, and etc. [1 and ref. therein]. It was reported that the activity of such catalysts can be increased by mixing with another oxides [2]. In case of copper-cobalt spinel oxides the increased catalytic activity is usually assigned to the appearance of synergistic and/or cooperative effects between Cu and Co ions. Recently, Subramanian et al. [3] reported that the catalytic performance of mixed Cu and Co nanoparticles is higher that the Co–Cu core–shell nanoparticles. It was also reported that the decomposition of $CuCo_2O_4$ spinel provides formation of extremely active species for higher alcohols synthesis (HAS) due to the enhanced reduction of Co_3O_4 in the presence of Cu [4]. Obviously, the knowledge for the interaction between different components in binary Cu-Co oxides is a key factor for the optimization of catalytic formula of these materials and could be affected by the preparation method and Cu/Co ratio used. Besides, the catalytic support could be also an important parameter for the design of efficient catalysts by regulation of loaded particles dispersion, location and possibility for the appearance of strong metal-support interaction. Various supports, such as SiO_2, Al_2O_3, MgO, TiO_2, CeO_2 and ZrO_2, have been used to prepare cobalt and copper based catalysts [4-11]. It was established that the weaker interaction with SiO_2 support favors the reducibility of metal oxide particles, but promotes metal species agglomeration, especially with the increase of metal loading.

The aim of present study is to study the effect of preparation procedure on the formation of catalytic active sites on supported on SiO_2 bi-component copper and cobalt oxides with different Cu/Co ratio. “Chemisorption-hydrolysis" and conventional incipient wetness impregnation techniques were used for the samples preparation. The obtained materials were characterized by different physicochemical techniques, such as XRD, UV-Vis, FTIR and temperature-programmed reduction with hydrogen and tested as catalysts in methanol decomposition to hydrogen and CO as alternative clean and efficient fuel [12 and refs. therein].

EXPERIMENTAL

Materials

Conventional mesoporous SiO_2 (ID 2556, specific surface area of 400 m^2/g) was modified with cobalt and/or copper by novel “chemisorption-hydrolyses” technique (CH) as described in [13].

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The samples were obtained as follows: (i) impregnation (20 min. at room temperature) of 0.6 g SiO_2 with aqueous solutions (4 ml) containing the corresponding amounts of $[Cu(NH_3)_4](OH)_2$ (pH=9) and/or $[Co(NH_3)_4](OH)_2$ (pH=9) for the obtaining of 8 wt. % of metal; (ii) hydrolysis of the obtained product with distilled water (1 L) at 273 K for 30 min; (iii) filtration and drying at 373 K overnight. Similar modifications were prepared by conventional wetness impregnation technique (WI) from aqueous solution of the corresponding nitrate precursors. The obtained CH and WI samples were calcined in air at 623 K and 673 K for 4 h, respectively. All catalysts were denoted as xCoyCu/SiO_2, where x and y represent the weight content of each element.

Methods of characterization

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 of 5.3 to 80° 2θ on a Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector. The average crystallite size was evaluated according to Scherrer equation. The UV–Vis spectra were recorded on the powder samples using a Jasco V-650 apparatus. The IR spectra (KBr pellets) were recorded on a Bruker Vector 22 FTIR spectrometer at a resolution of $1cm^{-1}$, accumulating 64 scans. The TPR/TG analyses were performed in a Setaram TG92 instrument in a flow of 50 vol% H_2 in Ar (100 cm^3 min^{-1}) and heating rate of 5 K min^{-1}.

Catalytic tests

Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas (50 cm^3 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.

RESULTS AND DISCUSSION

XRD patterns of the samples prepared by different procedures are shown in Fig. 1. The absence of any diffraction peaks in the patterns of all CH samples indicates the formation of 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 (Fig. 1) at 31.2°, 36.8°, 44.8°, 59.4° and 65.3° 2θ in the XRD pattern of Co/SiO_2 could be assigned to centered cubic (fcc) spinel structure (space group Fd3m) of Co_3O_4 [14]. The reflections at 35.5°, 38.7° and 48.6° 2θ in the pattern of Cu/SiO_2 are typical of pure monoclinic CuO (Tenorite, space group C2/c) [15]. The reflections in XRD patterns of bi-component materials are wider and less intensive which indicate formation of more finely dispersed metal oxide phase. The slightly changes in the lattice parameters of Co_3O_4 reveal insertion of metal ions into the spinel structure with the formation of $CuCo_2O_4$ (Table 1) [16]. Reflections typical of CuO could be detected with the increase of Cu loading in the samples. More information for the state of loaded metal oxide phases was obtained by UV-Vis (Fig. 2a) and FTIR spectroscopy (Fig. 2b).

Table 1. Phase composition, unit cell parameters and average crystallite size for WI samples.

Sample	Space Group	Unit cell, Å	Particles size, nm
Cu/SiO_2_WI	CuO - C2/c	4.682(2) 3.424(1) 5.128(1) 99.49(1)	42
Co/SiO_2_WI	Co_3O_4	8.086(5)	11
1Cu2Co/SiO_2_WI	Co_3O_4	8.124(7)	10
1Cu1Co/SiO_2_WI	CuO - C2/c	4.64(1) 3.430(5) 5.167(8) 99.74(8)	38
	Co_3O_4	8.118(8)	9
2Cu1Co/SiO_2_WI	CuO - C2/c	4.686(6) 3.428(5) 5.134(4) 99.57(4)	36
	Co_3O_4	8.116(9)	10

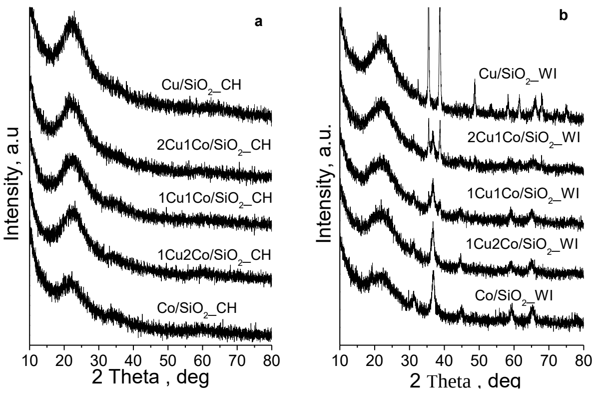

Fig. 1. XRD patterns of CH (a) and WI (b) modifications.

UV-Vis spectra of 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 Cu^{2+} ions in CuO crystallites [11]. The absorption in the 300–400 nm region indicates presence of small Cu-O-Cu oligomeric species. The broad absorption band at 400–550 nm and 650–800 nm in UV-Vis spectra of Co/SiO_2_WI are typical of 4T1(F)→4T1(P) transitions of octahedrally coordinated Co^{3+} and electronic ligand-field 4A2 (F)→4T1 (p) transition in tetrahedrally coordinated Co^{2+}, respectively which is in accordance with the XRD data (Fig. 1) for the presence of well crystallized Co_3O_4 phase [13]. The slight absorption at 453, 525, 585 and 650 nm in the spectrum of Co/SiO_2_CH could be assigned to the formation of amorphous Co_3O_4 phase, where tetrahedrally coordinated Co^{2+} ions in CoO_4 units are mainly surrounded by oxygen ligands from the silica matrix [17].

Note, the changes in the position and relative part of the main absorption peaks for Co_3O_4 in the UV-Vis spectra of bi-component materials, prepared by WI technique. Taking into account XRD data, this observation could be assigned to the formation of $Co_xO_{3-x}O_4$ spinel phase. The UV-Vis spectra of bi-component CH materials seem to be superposition of the spectra of mono-component Cu/SiO_2_CH and Co/SiO_2_CH materials, but the observed small changes in the position and intensity of the main peaks do not excluded slight interaction between individual oxides.

Additional information for the state of loaded active phase was obtained by FTIR spectroscopy. The broad band at around 590 cm^{-1} in the FTIR spectrum of Cu/SiO_2_WI is due to Cu-O stretching vibrations in the CuO particles, which is in consistence with XRD and UV-Vis data. This band is broader and shifted to lower frequency for the Cu/SiO_2_CH sample, which according to [18] is due to the strong interaction of CuO oligomers species with the silica support. The bands at 570 and 650 cm^{-1} in the FTIR spectra of all cobalt containing WI materials (Fig. 2b) could be assigned to Co-O stretching vibrations of Co^{3+} and Co^{2+} ions in octahedral and tetrahedral coordination, respectively, which is typical of well crystallized spinel Co_3O_4 phase [19]. They are slightly shifted to higher frequency for Co/SiO_2_WI, indicating formation of cobalt oxide species with higher bond order [20] for this sample. A continuous increase of the absorption in the 600–500 cm^{-1} region for all CH modified materials (Fig. 2b) is observed. According to [19] and taking into account XRD and UV-Vis data, this could be assigned to the presence of different Co-containing phases (CoO, CoO(OH), etc.) and absence of well crystallized spinel Co_3O_4 phase.

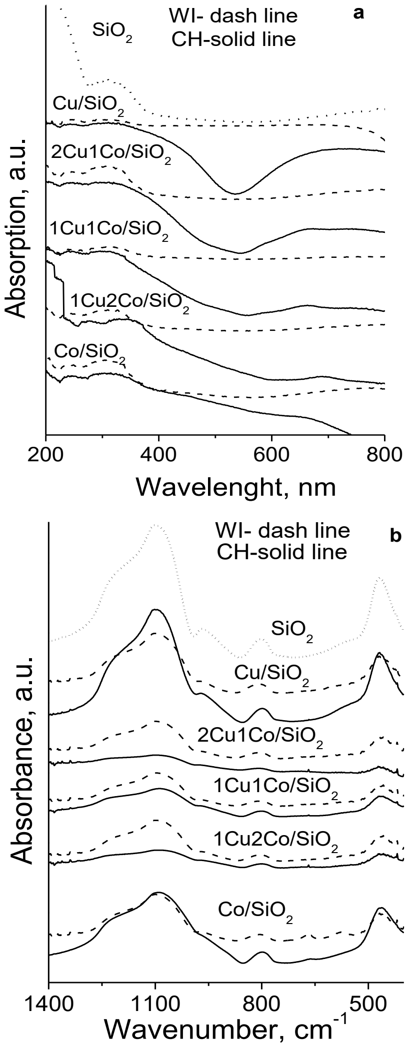

Fig. 2. UV-Vis (a) and FTIR (b) spectra of CH (solid line) and WI (dash line) modifications.

Further information for the metal ions environment in different materials is obtained by the TPR-TG and TPR-DTG profiles of the samples (Fig. 3). For both mono-component copper modifications, TPR-DTG effects in the 410- 530 K region are registered. For Cu/SiO$_2$_CH, this effect is shifted to about 40 K lower temperature, which could be due to the reduction of more finely dispersed phase in this sample. The observed weight loss (Table 2) corresponds to 80 % reduction of CuO to Cu^0 for the WI modification and to about 60 % for its CH analogue, respectively. This indicates that CH technique favours the formation of more easily reducible and highly dispersed copper phase than WI method, which is in accordance with our previous data [13, 21].

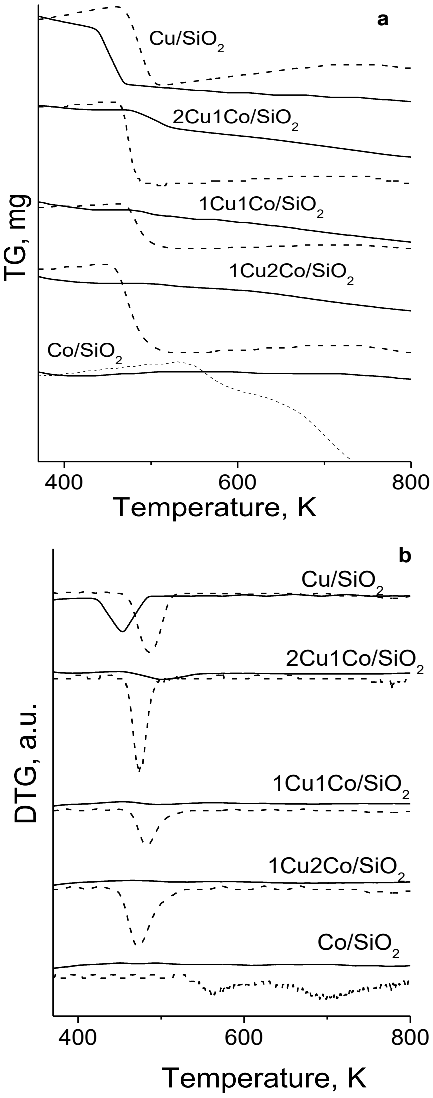

Fig. 3. TPR-TG (a) and TPR- DTG (b) profiles of CH (solid line) and WI (dash line) modifications.

At the same time the observed weight loss for mono-component cobalt materials corresponds to 67 % reduction of Co_3O_4 to metallic Co for the WI modification and below 30 % for its CH analogue. This could be assigned to the reduction of cobalt ions in lower oxidative state and/or strongly interacted with the silica support. Indeed, according to the UV-Vis and FTIR spectra, predominantly presence of Co^{2+} could be assumed for the later material (Fig. 4, Table 2). Taking into account our previous study [13], we could not also fully exclude the formation of finely dispersed cobalt silicate species [22, 23]. Single effect, which is slightly shifted to lower temperature as compared to Cu/SiO$_2$_WI, is observed for all bi-component WI materials.

Table 2. Samples composition and reduction degree, determined by TPR-TG analyses

Sample	Cu, wt %	Co, wt%	T$_{ini}$, K	T$_{max}$, K	Reduction degree, %
Cu/SiO$_2$_CH	8.2		416	454	80
2Cu1Co/SiO$_2$_CH	4.8	2.3	455	502	55
1Cu1Co/SiO$_2$_CH	3.5	3.6	455	500	33
1Cu2Co/SiO$_2$_CH	2.4	4.2	470	520	31
Co/SiO$_2$_CH		10.5	458	472, 612, 760	27
Cu/SiO$_2$_WI	8.2		455	486	60
2Cu1Co/SiO$_2$_WI	4.8	2.3	451	474	91
1Cu1Co/SiO$_2$_WI	3.5	3.6	456	483	42
1Cu2Co/SiO$_2$_WI	2.4	4.2	446	472	85
Co/SiO$_2$_WI		105	523	562, 698	67

In accordance with XRD and spectroscopic data this could be assigned to the reduction of $Cu_xCo_{3-x}O_4$ spinel phase. The variations in the reduction behaviour of all bi-component CH modifications (Fig. 4, Table 2) indicate that the strong interaction of different metal oxide species with the silica matrix renders difficult the interaction between them. In Figure 4 are presented data for the catalytic activity of the samples in methanol decomposition.

Higher catalytic activity is observed for all bi-component materials as compared to mono-component ones, when WI technique was used for their preparation. Here the selectivity to CO was about 90-100%. Relatively lower catalytic activity and selectivity to CO due to formation of CH_4, C_2-C_3 hydrocarbons, DME and CO_2 (up to 20 %) as by-products was observed for their CH analogues. The changes in the specific catalytic activity (SA), calculated per unit metal at selected temperature is presented in Fig. 4 c.

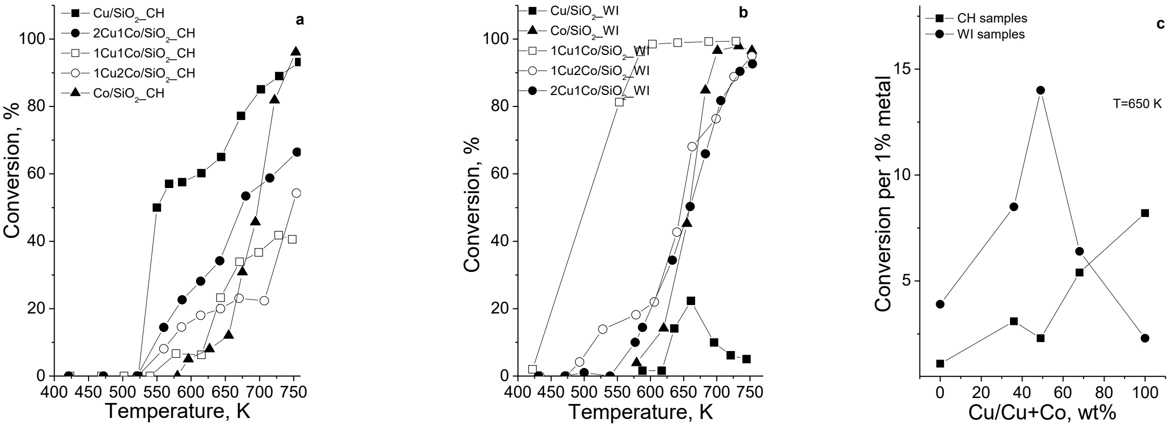

Fig. 4. Methanol conversion *vs* temperature of CH (a) and WI (b) samples and specific catalytic activity calculated per unit metal (wt. %) at 650 K (c).

With the exception of pure copper materials, the SA values are significantly lower for all cobalt-containing samples, obtained by CH technique. Taking into account the data from the physicochemical analyses (see above) this could be assigned to the facile formation of cobalt species in lower oxidation state and/ or strongly interacted with the silica support. The observed relatively low selectivity to CO on these materials could be due to the formation of additional surface acidic sites. Just the opposite, WI method promotes the formation of finely dispersed, but well crystallized $Cu_xCo_{3-x}O_4$ spinel particles. Obviously, the located on the octahedral sites Cu^{2+} ions share the oxygen with adjacent Co^{2+}, leading to the formation of highly active Cu-O-Co species, in higher for $1Cu1CoSiO_2$_WI [13]. This leads to an increase in redox activity and Lewis acidity and facilitates methanol decomposition to CO and hydrogen in synergistic way.

CONCLUSION

The applied preparation techniques allow stabilization of metal oxide particles in different oxidation state and dispersion, which reveals the possibility to fine control of the surface and catalytic properties of Cu and Co bi-component system. “Chemisorption–hydrolysis” technique ensures formation of finely dispersed and strongly bonded to the silica support Co^{2+} containing species. This renders difficult the formation of well crystallized spinel phase and leads to the formation of less active catalysts in comparison with the conventional incipient wetness impregnation technique.

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БИ-КОМПОНЕНТНИ КАТАЛИЗАТОРИ ЗА РАЗПАДАНЕ НА МЕТАНОЛ НА ОСНОВАТА НА МОДИФИЦИРАН С ОКСИДИ НА МЕДТА И КОБАЛТА СИЛИЦИЕВ ДИОКСИД: ВЛИЯНИЕ НА МЕТОДА НА НАНАСЯНЕ

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(Резюме)

Настоящото изследване е насочено към изясняване на влиянието на процедурата на модифициране на SiO_2 върху състоянието на нанесената би-компонентна мед- и кобалт- оксидна фаза. Получени са образци с различно съотношение Cu/Co чрез използване на метода на „хемосорбция-хидролиза”, състоящ се в отлагане на амонячни комплекси на медта и кобалта и следващото им хидролизиране и разлагане. Аналогични референтни образци са получени чрез прилагането на традиционния метод на омокряне с водни разтвори на съответните нитрати. Получените материали са изследвани посредством редица физикохимични методи, като XRD, UV-Vis, FTIR и температурно програмирана редукция с водород. Като каталитичен тест е използван разпадане на метанол до водород и CO с оглед възможността за използването му като алтернативно гориво. Използваните в настоящето изследване техники на модифициране водят до стабилизиране на металооксидни частици в различно окислително състояние и дисперсност, което разкрива възможност за фин контрол на каталитичните свойства на би-компонентните материали.