

X-Ray Absorption Spectroscopy Study of ZnO-CuO-HPS Catalyst

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The current paper reports the X-Ray Absorption Spectroscopy (XAS) study of novel ZnO-CuO based on hypercrosslinked polystyrene (HPS) catalyst for liquid phase methanol synthesis. It was shown that for the initial catalyst both Cu and Zn exist in the 2+ electronic states. The reduction treatment leads to the change of the Cu electronic state to +1. It should be noted that after the reaction the electronic state of Cu does not change. The synthesized catalyst allows reaching methanol (MeOH) formation up to 2,300 mg-MeOH·kg-cat⁻¹·h⁻¹ under the chosen reaction conditions while methane (Me) formation decreases down to 60 mg-Me·kg-cat⁻¹·h⁻¹.

1. Introduction

Methanol is a widely used chemical that can be applied to various reactions, i.e. formalin synthesis, transesterification, alkylation etc. It can also be used as an alternative fossil fuel (Hong et al., 2016). The methanol synthesis is one of the key processes of chemical industry. There is two most studied ways to synthesize methanol: (i) methane oxidation (He et al., 2016) and (ii) carbon oxides reductive hydrogenation (Karelavic and Ruiz, 2015). Currently, methanol synthesis from synthesis gas can be realized by either two- (gas phase) (Wilkinson et al., 2016) or three-phase (liquid phase) (Ling et al., 2017) processes. Although liquid-phase methanol synthesis is developed mainly in the lab-scaling process, it has many advantages in comparison with gas-phase synthesis, such as simple reactor design, effective heat transfer allowing conducting process in the quasi-isothermal mode, the decrease of catalyst losses due to the attrition, lower process temperature and higher synthesis gas conversion.

The current industrially established synthesis of methanol relies on Zn-Cu based catalysts providing high activity. The high activity enables reaction temperatures around 523 K which favor thermodynamically the methanol formation and allow, in turns, lower operating pressure (Wen et al., 2016). However, the main drawback of that class of catalysts is their sensitivity to poisons, e.g. sulphur, halogens, and nitrogen containing compounds, which are preferably present in bioresource feedstock. The search for optimal reaction conditions as well as the development of new alternative catalytic systems and modifiers is of paramount importance. According to literature, the catalyst synthesis methodology (van den Berg et al., 2016), catalyst composition (Tisseraud et al., 2016) and structure (Großmann et al., 2017) play a key role in providing a high rate of methanol formation from syngas.

Nanoparticles of transition metals and their oxide clusters formed in different polymers represent an attractive possibility for the modification of catalytic properties and synthesis of efficient and stable catalysts. Hypercrosslinked polystyrene (HPS) is a rigid polymer with high mechanical and chemical stability that can be a good matrix for catalyst synthesis (Nemygina et al., 2016). HPS has high surface area and pore volume containing both small and large mesopores. Small mesopores are suitable for the formation of the active phase and larger mesopores can provide substrate transport to the active sites (Stepacheva et al., 2016).

In heterogeneous catalysts, the properties of the surface atoms play a vital role in the formation of active surface sites allowing facilitating substrate conversion. These properties strongly depend on such factors as the type and number of the surrounding atoms on the surface as well as the interaction between active phase and the support (Yang et al., 2016). A detailed description of active site structure is of the great importance in order to develop novel catalytic systems. There are many analytical methods for catalyst structure investigation, among them X-ray techniques are widely used. X-ray absorption spectroscopy (XAS) describes the electronic state of the active metals (X-Ray Absorption Near Edge Structure, XANES) as well as the size, shape and atomic arrangements of metal clusters (Extended X-Ray Absorption Fine Structure, EXAFS) (Zhao et al., 2015). In this work, a novel Zn-Cu catalyst based on the polymeric matrix of HPS for methanol synthesis was proposed. Due to the properties of HPS described in our previous works, the proposed catalyst also shows high stability and resistance to poisoning. To investigate the structure of the active sites of novel polymer-based ZnO-CuO catalyst XAS analysis was used.

2. Materials and Methods

2.1 Materials

Hypercrosslinked polystyrene (HPS) was purchased from Purolite Int. (U.K.) as Macronet MN100 (functional groups – tert-amino groups, weak base capacity $0.5 \text{ mol} \cdot \text{L}^{-1}$, moisture 55 – 62 %, swell factor max $\pm 5 \%$, specific gravity $1.04 \text{ g} \cdot \text{mL}^{-1}$, specific surface area $1,000 \text{ m}^2 \cdot \text{g}^{-1}$). The 5-7 μm polymer granules were washed with acetone and water twice and dried under vacuum for 24 h. Sodium hydrogen carbonate (NaHCO_3), reagent-grade dodecane, isopropyl alcohol (IPA), tetrahydrofuran (THF), $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{NO}_3)_2$ was purchased from Reachim Ltd (Moscow, Russia) and used without purification. Reagent grade hydrogen of 99.99 % purity was received from TverGasService (Tver, Russia). Distilled water was purified with ElsiAqua water purification system.

2.2 Synthesis of CuO/ZnO-containing catalysts based on MN-100

The catalyst with equal amounts of ZnO and CuO (10 % each according to loading) was prepared using consecutive impregnation of HPS with $\text{Zn}(\text{CH}_3\text{COO})_2$ and then with $\text{Cu}(\text{CH}_3\text{COO})_2$ solutions followed by co-precipitation in both cases.

Consecutive impregnation of MN-100 with $\text{Zn}(\text{CH}_3\text{COO})_2$ and $\text{Cu}(\text{CH}_3\text{COO})_2$ in a solution of THF, methanol and distilled water was carried out in two steps. First, 0.845 g of $\text{Zn}(\text{CH}_3\text{COO})_2$ were dissolved under nitrogen in 7 mL of the solvent mixture consisting of 5 mL of THF, 1 mL of water and 1 mL of methanol, to which 3 g of MN-100 were added. The suspension was continuously stirred for 10 min to allow absorption of the solution by the polymer granules. Then the sample was treated with the Na_2CO_3 solution (1.69 g of Na_2CO_3 in 7 mL of H_2O), and after 10 min stirring, it was dried at 343 K for 1 h.

In the second step, the Zn-containing catalysts were treated for 10 min with the solution of 0.843 g of $\text{Cu}(\text{CH}_3\text{COO})_2$ in the solvent with the same composition. Then the resulted sample was treated with the Na_2CO_3 solution once more. The catalyst was washed with water at $\text{pH} = 6.4 - 7.0$ and dried at 343 K. It was dried at 343 K for 1 h. The ZnO and CuO contents were 10.0 wt. % each according to loading. This sample was designated as MN100-Zn-Cu (10 %/10 %).

2.3 Testing of Cu-Zn containing catalyst

The catalyst testing was performed in the flow mode reactor reported by Bykov et al. (2014). A typical experiment was carried out as following: 0.5 g of the catalyst in 15.0 mL of a complex solvent consisting of IPA and dodecane were loaded in the reactor equipped with a propeller mixer (stirring rate 250 rpm). Then the hydrogen pressure was set at 3.0 MPa with the flow 45 mL/min and the mixture was heated up to 443 K. After the catalyst saturation for 1 h, hydrogen was substituted for synthesis gas composed of 79.38 % H_2 , 0.12 % N_2 , 20.49 % CO, 0.01 % CO_2 and the stirring rate was increased up to 750 rpm. The synthesis gas pressure was set at 2.0 MPa with the gas feeding rate $270 \text{ mL} \cdot \text{min}^{-1}$. The outgoing steam-gas flow was directed into the chromatographic system of on-line analysis (Kristallux 4000, Chromatech, Russia) along the heated line through the return pressure valve and removed from the system through a flow meter.

2.4 XAS measurements methodology

XAS measurements were carried out at BM23 station of ESRF (Grenoble, France). The Cu K-edge (8,959 eV) and Zn K-edge (9,659 eV) X-ray absorption spectra were recorded in the transmission mode using a Si(111) double crystal monochromator. Samples pressed in self-supporting wafers were measured at 30 K. The spectrum of proper metal foil was recorded simultaneously between the second and a third ionization chamber for energy calibration purposes. The special care was taken to avoid ambient atmosphere contamination. For sample preparation, the optimum weight to maximize the signal-to-noise ratio was pressed into a 13-mm diameter pellet in a glove bag (a dried He atmosphere) and completely wrapped in polyimide (Kapton) adhesive tape. Analysis of the XAFS spectra was performed with the software VIPER for Windows (Klementiev, 2012).

The required scattering amplitudes and phase shifts were calculated by the ab initio FEFF8.10 code for CuO, Cu₂O, ZnO and CuZn. At least duplicate spectra were recorded to ensure data reproducibility.

The fitting was done in the k- and r-spaces. The shell radius r, coordination number N, Debye-Waller factor σ^2 and adjustable “muffin-tin zero” ΔE were determined as fitting parameters. The errors of the fitting parameters were found by decomposition of the statistical χ^2 function near its minimum, taking into account maximal pair correlations.

3. Results and Discussions

3.1 Testing of Cu-Zn containing catalyst

The HPS-based catalysts were tested in the liquid-phase methanol synthesis in continuous mode varying the solvent composition. The mixture of IPA and dodecane was used (total volume of the liquid phase was 15 mL in each experiment) as a solvent. Figures 1 and 2 show the results of testing of bimetallic MN100-Zn-Cu (10%/10%) catalyst.

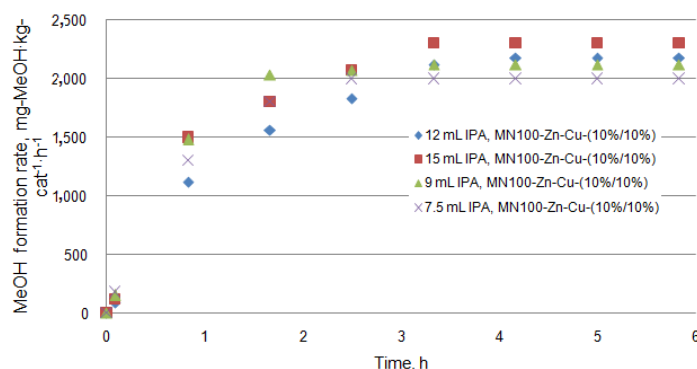


Figure 1: Formation of methanol over MN100-Zn-Cu (10%/10%) catalysts

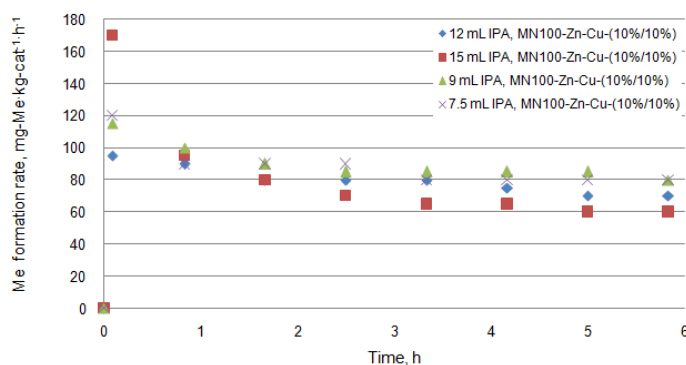


Figure 2: Formation of methane over MN100-Zn-Cu (10%/10%) catalysts

The synthesized Zn-Cu containing catalyst allows high methanol formation with low selectivity to methane production while compared with industrial catalysts. It was also demonstrated that for the synthesized catalytic systems the increase of the fraction of the polar solvent (IPA) leads to an increase of the methanol formation rate (Figure 1).

3.2 XAS study of ZnO-CuO-HPS catalysts

To estimate the structure of catalytically active sites three samples of ZnO-CuO-HPS catalyst prepared by the consecutive impregnation (initial (as received), treated with H₂+H₂O₂ and after the catalysis) were studied by XAS analysis.

Figure 3(a) shows Cu K-edge XANES of three these samples with CuO reference compound. In contrast, the energy position of the Cu K-edge, the intensity of the white line and the shape of XANES observed for the initial catalyst is similar to that in the spectrum of CuO reference. It means that Cu in initial catalyst exists as the Cu²⁺ electronic state. The energy position of the Cu K-edge, the intensity of the white line and the shape of XANES observed for both treated and after catalysis samples differ from CuO reference. The presence of the pre-edge

peak in these two spectra shows that copper exists as the Cu^{1+} electronic state. The EXAFS oscillations shape observed for treated and after catalysis samples differ from CuO and resemble one to another. The Fourier transformation of EXAFS oscillations three ZnO-CuO-HPS samples and reference are presented in Figure 3(b).

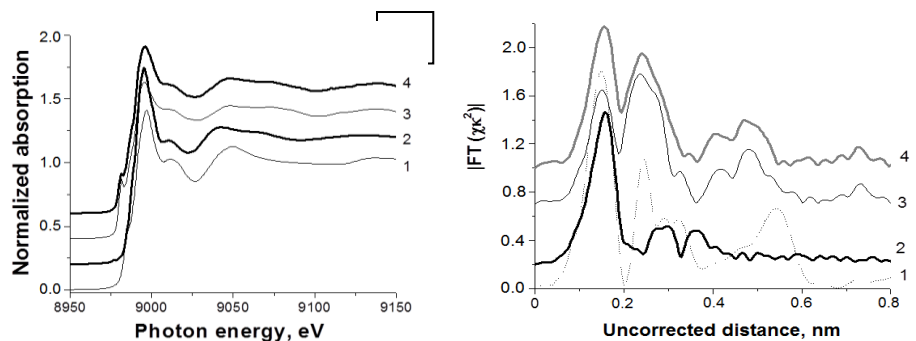


Figure 3: Cu K-edge XANES (a) and FT of Cu K-edge EXAFS spectra (b) of the Cu samples: 1 – CuO reference; 2 – ZnO-CuO-HPS - initial; 3 – ZnO-CuO-HPS – treated, 4 - ZnO-CuO-HPS – after catalysis

The Fourier Transformation (FT) of EXAFS spectra of all three ZnO-CuO-HPS samples differ from CuO reference. The shape of both treated and after catalysis sample is the similar one to another except the first peak intensity and more visible shoulder near 0.35 nm uncorrected distance in the spectrum of treated samples. More, these spectra differ from the observed for initial sample. The Cu FT EXAFS spectrum of initial catalyst was fitted in both r- and k-spaces with one shell model – oxygen shell around the central absorbing Cu atom whereas spectra of the treated and after catalysis samples – with three-shells model – O, Zn and Cu. There is one narrow peak in the spectrum of CuO reference that corresponds to the first and second coordination shells containing 4 oxygen atoms at 0.195 and 0.196 nm real distances from the central Cu atom. The next set of peaks before 0.4 nm uncorrected distance corresponds to the third, fourth and fifth coordination shells containing 4, 4 and 2 copper atoms at 0.290, 0.308 and 0.317 nm real distances from the central Cu atom.

Table 1 shows the model fit results for ZnO-CuO-HPS samples. The first shell contains in average 3 O atoms at the real distance 0.196 nm in the initial sample. The first shell in the treated catalyst contains in average 1.5 O atoms at the real distance 0.189 nm. The second shell contains in average 1 Zn atom at the real distance 0.252 nm. The third shell contains in average 2 Cu atoms at the real distance 0.299 nm.

Table 1: The best model fit parameters of Cu K-edge EXAFS spectra of ZnO-CuO-HPS catalyst

Sample	Path	r, nm	N	σ , nm ²	ΔE , eV
initial	Cu-O	0.196 ± 0.001	2.84 ± 0.15	0.70 ± 0.1	12.2 ± 0.8
treated	Cu-O	0.189 ± 0.002	1.5 ± 0.18	0.7 ± 0.2	5.2 ± 2.0
	Cu-Zn	0.252 ± 0.002	1.0 ± 0.4	0.32 ± 0.26	3.1 ± 1.0
	Cu-Cu	0.299 ± 0.002	2.3 ± 0.3	1.10 ± 0.4	3.1 ± 1.0
after catalysis	Cu-O	0.192 ± 0.001	2.0 ± 0.17	0.79 ± 0.14	5.1 ± 1.0
	Cu-Zn	0.254 ± 0.002	1.0 ± 0.4	0.43 ± 0.23	5.2 ± 3.0
	Cu-Cu	0.301 ± 0.002	3.5 ± 0.5	1.90 ± 0.4	6.6 ± 2.1

The first shell in after catalysis sample contains in average 2 O atoms at the real distance 0.192 nm. The second shell contains in average 1 Zn atom at the real distance 0.254 nm. The third shell contains in average 3 Cu atoms at the real distance 0.301 nm. Cu K-edge XAS study of ZnO-CuO-HPS samples shows that Cu in these samples exists in the same 2+ electronic state as in the initial sample. The treatment of initial sample by $\text{H}_2\text{O}_2 + \text{H}_2$ results in the copper reduction to Cu^+ . The electronic state of Cu does not change during catalysis. The reduction treatment of the initial sample leads to the twice decrease in O atom content in the local surrounding of central Cu atom and the decrease in the distance between these two atoms. Zn atom appears in the local structure of Cu atom in the treated and after catalysis samples. The third shell containing Cu atoms finds in the local structure of Cu atom in the treated and after catalysis samples. In total, the presence of origin substrates and products results in the minor increase in O atoms content accompany with the minor extending of real distance and the major increase in Cu atoms content.

Figure 4(a) shows Zn K-edge XANES of ZnO-CuO-HPS samples with ZnO reference compound. Figure 4(b) shows the FT EXAFS oscillations of ZnO-CuO-HPS samples and reference.

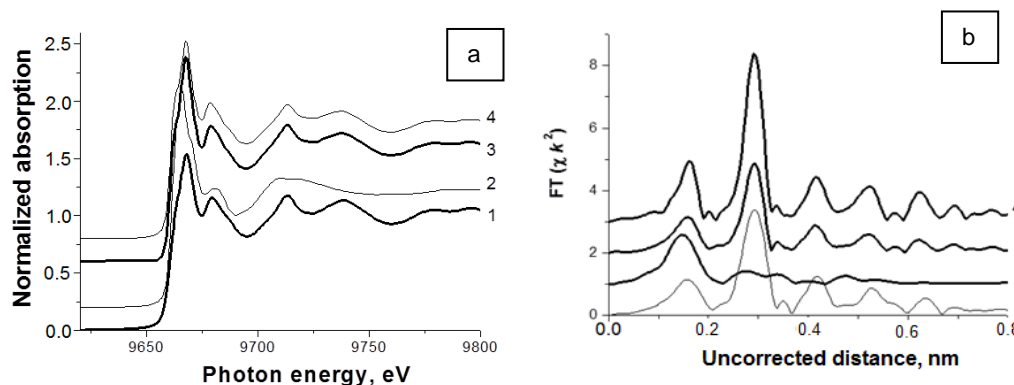


Figure 4: Zn K-edge XANES (a) and FT Zn K-edge EXAFS spectra (b) of the samples: 1 – ZnO reference; 2 – ZnO-CuO-HPS - initial; 3 – ZnO-CuO-HPS – treated, 4 - ZnO-CuO-HPS – after catalysis

The energy position of the Zn K-edge in spectra of ZnO-CuO-HPS catalyst is similar to that in the spectrum of ZnO reference. It means that Zn in these catalysts exists as the Zn^{2+} electronic state. The analysis of the intensity of the white line and shape of EXAFS oscillations show that the Zn species in all samples of catalysts differ from that in ZnO and each other. There are two narrow peaks in the spectrum of ZnO reference. The first peak corresponds to the first and second coordination shells containing 1 and 3 oxygen atoms at 0.179 and 0.204 nm real distances from the central Zn atom. The second peak corresponds to the third and fourth coordination shells containing 6 and 6 zinc atoms at 0.321 and 0.325 nm real distances from the central Zn atom. The FT EXAFS spectrum of ZnO-CuO-HPS initial sample differs from ZnO reference. The FT EXAFS spectra of all three samples show the first peak at a slightly shorter uncorrected distance as compare to ZnO reference. The intensity of the second peak differs in all spectra of ZnO-CuO-HPS samples. The first and second peaks of the Zn FT EXAFS spectra of the initial sample was fitted in both r- and k-spaces with a two-shells model – oxygen and zinc shells around the central absorbing Zn atom. The first and second peaks of the Zn FT EXAFS spectra of the treated and after catalysis samples were fitted in both r- and k-spaces with a three-shells model –O, Cu and Zn around the central absorbing Zn atom. The results of the model fit are presented in Table 2.

Table 2: The best model fit parameters of Zn K-edge EXAFS spectra of ZnO-CuO-HPS catalyst.

Sample	Path	r, nm	N	σ , nm ²	ΔE , eV
initial	Zn-O	0.200 ± 0.001	3.97 ± 0.4	0.98 ± 0.21	6.4 ± 1.0
	Zn-Zn	0.317 ± 0.001	1.80 ± 0.2	0.62 ± 0.04	8.5 ± 1.3
treated	Zn-O	0.197 ± 0.002	3.05 ± 0.36	0.51 ± 0.17	6.5 ± 2.3
	Zn-Zn	0.252 ± 0.004	1.1 ± 0.2	1.0 ± 0.1	27 ± 6
after catalysis	Zn-O	0.198 ± 0.002	3.14 ± 0.57	0.15 ± 0.02	11 ± 3
	Zn-Cu	0.255 ± 0.01	0.85 ± 0.1	1.2 ± 0.1	10 ± 3
	Zn-Zn	0.322 ± 0.001	13.8 ± 2.3	0.52 ± 0.1	4.0 ± 1.4

It is seen that the first shell in the local structure of central Zn atom contains average 3-4 O atoms at the real distance 0.197-0.200 nm in all three samples. The second shell contains about 2 Zn atoms at the real distance 0.317 nm in the initial sample. In common with finding Zn atom in the second shell of central Cu atom (from Cu K-edge EXAFS), the presence of 1 Cu atom at approximately the same real distance from central Zn atom is observed from Zn K-edge EXAFS. The third shell in the treated samples contains about 8 Zn atoms at the real distance 0.321 nm. The content of Zn atoms increases up to about 14 after catalysis. Zn K-edge XAS study of ZnO-CuO-HPS samples showed that Zn in these samples exists in the same 2+ electronic state. The reductive treatment of initial sample and catalysis result in the decrease in O atom content (4 vs 3) and distance (0.200 vs 0.197-0.198 nm) in the local surrounding of central Zn atom and the increase in Zn atom content (8.5-13.8 vs 2) and distance (0.321-0.322 vs 0.317). The reduction treatment and catalysis lead to occurrence of 1 Cu atom near from central Zn atom.

4. Conclusions

In the current work, a novel catalyst based on the polymeric matrix was proposed for methanol synthesis from synthesis gas. The synthesized ZnO-CuO embedded into the polymeric matrix of HPS was found to be the

active, selective and stable catalyst for liquid phase methanol synthesis allowing decreasing reaction temperature from the conventional 523 - 543 K down to 443 K. XAS study of ZnO-CuO-HPS samples showed that Cu in the initial catalyst sample exists in the Cu²⁺ electronic state. The treatment of the initial sample with H₂O₂+H₂ results in the copper reduction to Cu⁺. The electronic state of Cu does not change during catalysis. The reduction treatment of initial sample leads to the twice decrease in O atom content in the local surrounding of central Cu atom and the decrease in the distance between these two atoms. Zn atom appears in the local structure of Cu atom in the treated and after catalysis samples.

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