Methanol Synthesis in a Three-Phase Slurry Reactor with Ultrafine Catalysts

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Abstract—It is shown that the effective synthesis of methanol may be performed in the presence of ultrafine catalyst systems formed by drop thermolysis in situ in a slurry reactor. Using the X-ray powder diffraction and FTIR spectroscopy data on the evolution of Cu–Zn–Al-containing catalyst dispersion during activation and catalysis, possible reasons for ultrafine catalyst deactivation are considered.

Keywords: methanol synthesis, nanosized catalysis, three-phase slurry reactor, ultrafine and nanosized catalysts **DOI:** 10.1134/S0965544117070027

Methanol is one of the large-tonnage products derived from syngas in volumes above 60 million tonnes annually [1]. The existing technologies of methanol synthesis encounter the problem of evolved heat removal, which is solved either by feeding cold raw gas or with the use of reactor-built-in heat exchangers; the content of methanol in the products does not exceed 3–5 vol %. The low yield of methanol requires that the processes be performed with unreacted gas recycling; this circumstance decreases the total efficiency of the process [2].

The use of reactors that make it possible to efficiently remove evolved heat at higher methanol yields will improve the economic indicators of this process. A number of technological solutions are being developed for the effective removal of heat, for example, systems with the use of cold methanol injection. This trick provides an increase in the conversion of CO per pass to 50%; however, these schemes suffer from regulation complexity [3].

Another solution of this problem may involve the use of a slurry reactor, in which a solid catalyst is distributed in an inert liquid dispersion medium ensuring a more efficient heat exchange owing to much higher heat capacity and thermal conductivity than those of gases. Technologies in which fine (ultrafine or nanosized) solid catalyst particles suspended in a liquid phase are employed are regarded as the most promising [4]. Note that similar nanosized catalyst systems demonstrated high activity and selectivity in syngas conversion to liquid products by the Fischer—Tropsch method in a three-phase slurry reactor [5].

This paper concerns the preparation of nanosized copper-containing dispersions and the study of their

catalytic behavior in methanol synthesis in a slurry reactor.

EXPERIMENTAL

Catalyst systems were prepared by the method of drop thermolysis. Drop thermolysis was performed as follows: precursors copper, zinc, and aluminum nitrates taken at the desired ratio were dissolved in distilled water, and the resulting solution at a rate of 22 mL/h was added in an inert gas stream in molten paraffin under continuous stirring. The temperature during thermolysis was maintained in the range of 220–240°C in order to decompose nitrates to oxides. After addition of the whole volume of salt solutions, the resulting suspension was held in an argon stream for 2 h to remove the residual water. The content of oxides in the samples was 10 wt %.

The obtained samples contained the calculated amount of the metal oxide phase with composition of 100% CuO for Cu sample, 70% CuO-30% ZnO for Cu-Zn sample, and 60% CuO-30% ZnO-10% Al₂O₃ for Cu-Zn-Al sample.

The size of catalyst particles was measured by dynamic light scattering on a Malvern Zetasizer Nano ZS instrument. The medium weighed portion of the catalyst dispersion was used for analysis.

Catalytic tests were conducted in an autoclave-type facility with mechanical stirring in the flow regime with respect to gas at pressure of 5 MPa. The temperature of synthesis was raised from 200 to 300°C in increments of 20°C, and the WHSV of syngas with a molar ratio of CO : $H_2 = 1 : 2$ was varied in the range of 0.6–3.3 nL/(g_{cat} h⁻¹). The time of experiment at



Fig. 1. Size distribution of suspension particles. (a) Cu, (b) Cu–Zn, and (c) Cu–Zn–Al.

fixed temperature and syngas loading was 20 h. At the end of each period, the gas and liquid products were sampled for analysis. Before catalytic testing, in situ reductive activation was conducted at a pressure of 20 atm, temperature of 200°C, and time of 14 h.

The feed syngas and the gaseous products of synthesis were analyzed by gas chromatography on a Kristallyuks-4000 chromatograph equipped with a thermal conductivity detector using helium as a carrier gas. CO and N₂ were separated on a chromatographic column packed with molecular sieves CaA (3 m × 3 mm). CO₂ and hydrocarbons C₁–C₄ were separated on a HayeSep R packed column (3 m × 3 mm) with temperature programming: 80–200°C, 8°C/min.

The liquid products of synthesis were analyzed on a Kristallyuks-4000M chromatograph (flame ionization detector; nitrogen as a carrier gas) equipped with a Carbowax-20M/Chromaton-NAW (5 m × 4 mm) packed column with temperature programming: 50– 10° C, 3° C/min; $110-150^{\circ}$ C, 7.5° C/min, 10 min. Concentrations were quantified via the method of internal standard using isobutyl alcohol as a standard. The relative error of this method does not exceed 5%.

The activity of catalyst systems was estimated from the CO conversion. Specific activity (A_{sp}) was calculated as the ratio of the amount of reacted CO to the amount of copper introduced in the catalyst suspension per unit time. Selectivity for reaction products was calculated as the ratio of the amount of carbon consumed for formation of the reaction product to the total amount of carbon in reacted CO (S_{MeOH} is selectivity for methanol, and S_{DME} is selectivity for dimethyl ether).

X-ray powder diffraction (XRD) analysis was conducted on a DIFREY 410 diffractometer (AO Nauchnye Pribory, St. Petersburg) using CrK_{α} radiation with a wavelength of 2.291Å. Focusing was performed by the Bragg–Brentano method. The registration track was composed of a curved position-sensitive detector.

Reflection IR spectra were registered on a HYPE-RION-2000 IR microscope coupled with a Bruker IFS-66 v/s FTIR spectrometer in the range of 4000– 600 cm^{-1} . Prior to catalyst sampling for XRD and IR analyses, the suspension was held in the immobile state for 24 h at 100°C to concentrate particles in the lower layer.

RESULTS AND DISCUSSION

At the initial step, the dimensional characteristics of the systems were studied in detail. As was shown in [6], the method of drop thermolysis makes it possible to form high-activity nanosized catalyst dispersions of Fischer-Tropsch synthesis. A similar approach to formation of catalysts was used in this study. The ratio of metals in a three-component copper-zinc-aluminum catalyst was chosen so that, in terms of chemical composition, it corresponded to the commercial catalyst of methanol synthesis MegaMax 507 (Clariant). In order to assess the effect of each component, we successively synthesized the following compounds: monometallic CuO catalyst containing only the active component; bimetallic CuO-ZnO catalyst additionally containing zinc oxide, whose role in conventional catalysts is assumed to involve only the stabilization of finely dispersed copper particles [7]; and three-component CuO-ZnO-Al₂O₃ catalyst with composition close to that of the commercial catalyst.

The introduction of precursor salts via the drop thermolysis yields stable nanosized suspensions; the nature of metal and the composition of the metal phase in the system insignificantly affect the size of primary structural suspension units: for all the studied samples, this parameter was on average 70–100 nm (Fig. 1). However, when the composition of the oxide phase was complicated by introducing two or three metals, an insignificant enlargement of particles of the dispersed phase took place. In this case, the tendency of the system toward formation of coarser agglomerates became more pronounced; their average size increased from 330 to 1000 nm (Table 1).

The activities of the synthesized catalysts are compared in Fig. 2.

It should be emphasized that the recrystallization of copper at temperatures above the Tammann point (190°C) is reckoned to be responsible for the deactivation of copper-containing catalysts. The catalyst activity at 200°C is practically independent of the compo-



Fig. 2. Dependence of CO conversion on synthesis temperature for catalyst samples containing Cu, Zn, and Al. (1) Cu; (2) Cu–Zn; and (3) Cu–Zn–Al.

sition of the metal-containing phase, and the conversion of CO is ~12%; however, for the monometallic system, it decreases abruptly (Fig. 2). After introduction of zinc and aluminum into the catalyst composition, its thermal stability is improved, and in the copper–zinc system, recrystallization begins at 220– 240° C. Copper–zinc–aluminum systems preserve

Table 1. Dimensional characteristics of suspension particles

| Sample | Size of suspension particles d, | Size of particles agglomerates d_{agl} , | | |
|----------|---------------------------------|--|--|--|
| | nm | nm | | |
| Cu | 70 | 330 | | |
| Cu–Zn | 100 | 700 | | |
| Cu–Zn–Al | 100 | 1000 | | |

activity up to 260°C; after that, their activity declines sharply, in consistency with the published data. The data on change in selectivity for methanol are summarized in Table 2.

The copper-zinc-aluminum catalyst preserves selectivity for methanol at a high level throughout the studied temperature range; at 300°C, selectivity is 75–80%. For this catalyst, the reduction in selectivity for the target product is primarily associated with the formation of dimethyl ether (Table 2). For monometallic and copper-zinc catalysts, the decline in selectivity for methanol is explained by formation of the gaseous products of synthesis with the concomitant decrease in the conversion of CO.

Thus, in the presence of the three-component Cu– Zn–Al catalyst, the maximum conversion of the feedstock is attained throughout the studied temperature range, while the selectivity slightly decreases from 97 to 92% as the temperature of synthesis increases from 220 to 260°C.

The stage of the reductive pretreatment of contacts is a complex procedure for forming reaction sites in catalyst systems of methanol synthesis, because the active phase of these catalysts is the interface of closely spaced pairs Cu⁺ and Cu⁰ rather than the metallic copper [8]. The problem is that the reduction of CuO is accompanied by a pronounced evolution of heat $(-\Delta H = 79 \text{ kJ/mol})$. Therefore, local overheating of the catalyst is feasible. As a result, the entire surfaceactive copper accessible to the reaction transforms into the state with an oxidation number of zero and subsequent recrystallization occurs. In the industry, the

| Catalyst | Synthesis temperature, °C | $S_{\rm MeOH}, \%$ | $S_{\rm DME},\%$ | $A_{ m sp} 	imes 10^6,$ $ m mol_{ m CO}/(m mol_{ m Cu} m s^{-1})$ |
|----------|------------------------------|--------------------|------------------|---|
| Cu | 200 | 98 | _ | 40 |
| | 220 | 43 | — | 26 |
| | 240 | _ | _ | 5 |
| Cu–Zn | 200 | 97 | — | 62 |
| | 220 | 98 | — | 91 |
| | 240 | 99 | _ | 85 |
| | 260 | 66 | _ | 56 |
| | 280 | 28 | — | 23 |
| | 300 | 15 | — | 17 |
| Cu–Zn–Al | 200 | 95 | — | 81 |
| | 220 | 97 | — | 113 |
| | 240 | 93 | _ | 133 |
| | 260 | 92 | 1.7 | 136 |
| | 280 | 86 | 5.6 | 34 |
| | 300 | 77 | 10.2 | 37 |

Table 2. Main parameters of three-phase methanol synthesis in the presence of copper-containing ultrafine catalysts



Fig. 3. Main parameters of three-phase synthesis of methanol in the presence of ultrafine Cu-Zn-Al catalyst: (1) productivity; (2) conversion of CO; and (3) content of MeOH at the output of the reactor.



Fig. 4. Diffraction patterns of (*a*) paraffin, (*b*) as-prepared Cu–Zn–Al sample, (*c*) Cu–Zn–Al sample after activation, and (*d*) deactivated Cu–Zn–Al after catalysis ((\blacklozenge) Cu; (\blacklozenge) ZnO; (\blacklozenge) CuO; (\bigstar) CuO; (\bigstar) CuO;

degree of reduction of copper is checked via its activation in a stream of nitrogen-diluted hydrogen mixtures; in particular, stationary catalysts of low-temperature methanol synthesis are activated at a hydrogen content of 3-10%.

In this study, the composition of the reductive medium for the Cu–Zn–Al catalyst was optimized under conditions of the slurry reactor (Table 3).

The maximum values of CO conversion (~35%) were attained at the hydrogen content in the reducing gas in the range of 10-15%. An increase in the concentration of hydrogen during activation led to decrease in the degree of conversion of the feedstock,

Table3. Effectofreductivemediumcompositionon the activity of ultrafine Cu-Zn-Al catalyst in the three-
phase synthesis of methanol

| Content of H ₂ | 2 | 10 | 15 | 30 | 100 |
|-----------------------------|------|------|------|------|-----|
| in the activation gas, $\%$ | | | | | |
| Conversion of CO, % | 26.1 | 34.5 | 35.8 | 30.0 | 7.6 |

and after catalyst treatment with 100% H_2 , this parameter was not above 8%. When a low-concentrated hydrogen-nitrogen mixture (2% H_2) was used for activation, the conversion of CO was not above 24–26%. The presence of a maximum makes it possible to assume that, at low hydrogen concentrations, the catalyst reduction is insufficient, while at high concentrations, the transition of the surface copper to the state with an oxidation number of zero is feasible.

Thus, it may be proposed that the effective heat exchange provided by the liquid dispersion medium in the slurry reactor ensures a more uniform distribution of temperature within the entire reactor volume and allows catalyst activation in a more severe regime compared with conventional technologies.

The distinctive feature of methanol synthesis under the studied conditions is that the conversion of CO decreases markedly as the syngas feed rate is decreased below 1.2 nL/(g_{cat} h). A similar result is observed for the effect of pressure [9]. Although the equilibrium degree of conversion usually increases with pressure, in [9], this value decreased. In accordance with [6], this fact may be attributed to the accumulation of liquid products of synthesis in the reaction zone. In addition, a decrease in the conversion of CO may be associated with the accumulation of water in the reaction zone, which in the presence of CO_2 in the reaction medium causes zinc oxide decomposition and catalyst deactivation [10]. As the syngas feed rate is increased from 1.2 to 1.9 $nL/(g_{cat} h)$, the conversion of CO slightly decreases from 35 to 30%; however, productivity grows to $170 \text{ g}_{\text{MeOH}}/(\text{kg}_{\text{cat}} \text{ h})$ owing to a large load.

If drop thermolysis is performed in the medium of paraffin (Fig. 4a), the resulting suspension is composed predominantly of the oxides of introduced metals (Fig. 4b). The shape and great width of reflections and their low intensity indicate a high dispersity of crystallites, in agreement with the results of dynamic light scattering studies. The most pronounced reflections are observed at angles of $2\theta = 49.5^{\circ}$, 54.4° , 59.9° , 75.4°, 93.5°, 99.5°, 109.0°, 113.5°, 131.8°, which correspond to copper(II) oxide. In addition, reflections in the angular range $2\theta = 54.4^{\circ}$, 99.5°, 109.0° may correspond to zinc oxide; thus, it is probable that the mixed copper and zinc oxide phase may form. The reflection at an angle of $2\theta = 40.1^{\circ}$ was assigned to Al₂O₃ The absence of other reflections due to aluminum oxides may be explained by its low content in the sample.

In the XRD spectra of the sample after reduction (Fig. 4c), reflections related to copper(II) oxide are absent. Intense reflections in the spectrum at angles $2\theta = 67.1^{\circ}$, 79.3°, 128.2° correspond to the state of copper in the zero oxidation number. The broadening of reflections in the range of $2\theta = 65.6^{\circ}$, 127.0° and a weak reflection at $2\theta = 137.5^{\circ}$ make it possible to assume that the copper(I) oxide phase is present. The characteristic reflections of zinc oxide are preserved



Fig. 5. IR spectra of (*a*) paraffin, (*b*) Cu–Zn–Al after activation, and (*c*) deactivated Cu–Zn–Al sample after catalysis.

after reduction; however, the peaks become narrower. On the basis of this observation, it may be inferred that the crystallites of zinc oxide enlarge partially.

The XRD spectra of the sample that lost activity (Fig. 4*d*) after catalysis exhibit narrower reflections compared with the activated sample (Fig. 4*c*). This fact indicates further enlargement of crystallites for all of the components.

In Fig. 5, the IR spectra of the initial paraffin are compared with the spectra of the samples after activation and catalysis in paraffin. In the IR spectra of the samples after catalysis, bands corresponding to paraffin with a considerably altered structure predominate. The band at 730 cm⁻¹, which characterizes the ordered linear paraffin chains, is practically absent. This observation indicates a strong change in the conformation of paraffin units and may be explained by their arrangement around a nanosized metal-containing particle to form spherical shells. The spectrum of the sample after activation exhibits weak bands at 1570 and 1730 cm⁻¹ corresponding to ionized and acidic carboxylate groups, respectively. Probably, during the decomposition of the introduced metals nitrates, the partial oxidation of paraffin occurs to afford $C(O)O^{-}$ and C(O)OH terminal groups that are preserved even after activation. As follows from the intensity of absorption bands, the amount of these groups does not exceed 0.1%. Of special note is that the formed fatty acids and their salts are used for stabilization of nanosized suspensions [11]. After catalysis, the absorption bands due to $C(O)O^{-}$ and C(O)OH groups are absent; this circumstance probably facilitates the enlargement of catalyst particles.

In the spectrum of the sample inactive after catalysis, new broad bands appear at 970, 990, and 1288 cm⁻¹. These bands cannot be assigned to paraffin but may be attributed to the overtones of long-wave bands of M-O bonds (200–500 cm⁻¹) in metal oxides. Note that after activation these bands were absent probably because during catalysis the surface of catalyst particles transformed into a more oxidized state. Because in accordance with the XRD data (Fig. 3), after catalysis, copper is preserved in the zero-valence state and zinc is present in the form of oxide, it may be assumed that zinc oxide concentrates on the catalyst surface.

Thus, this study has revealed that the effective threephase synthesis of methanol may be accomplished in the three-phase slurry reactor in the presence of ultrafine catalyst systems formed in situ in the hydrocarbon dispersion medium. It has been shown that drop thermolysis provides an opportunity to produce nanosized catalyst suspensions containing components whose structure and composition are analogous to those of commercial low-temperature heterogeneous catalysts of methanol synthesis. These ultrafine catalyst systems are activated in a more severe regime compared to conventional catalysts. It is found that partial oxidation of the dispersion medium occurs during the synthesis of the mentioned ultrafine catalysts from nitrates. This circumstance may contribute to additional stabilization of the nanosized suspension.

It has been shown that during catalysis the size of copper and zinc oxide crystallites grows apparently owing to the recrystallization of copper, despite the improved heat exchange in the slurry reactor. The recrystallization of Cu and the reduction of Cu_2O to Cu^0 apparently lead to the loss of catalyst activity.

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