Impact of Incorporation of Active Nanoporous Components or Their Precursors in a CuAlO/CuAl Ceramometal Skeleton on the Properties in the Low-Temperature Water-Gas Shift Reaction

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ABSTRACT: Enhanced activity in low-temperature water-gas shift (LT-WGS) reaction of some ceramometal catalysts compared to conventional Cu−Zn−Al oxide catalyst was demonstrated. Porous ceramometals were synthesized from powdered CuAl alloys prepared by mechanical alloying with the addition of either CuAlexp powders produced by current spark explosion of Cu+Al wires or CuZnAl oxide obtained by coprecipitation. Their structural, microstructural, and textural characteristics were examined by means of X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray spectrometry, NMR, and adsorption methods, and catalytic properties were studied in the LT-WGS reaction. CuAlO/CuAl ceramometals were found to have mostly the egg-shell microstructure with the metallic cores (Al$_x$Cu$_{1-x}$, Al$_2$Cu, and Al$_4$Cu$_9$) and the oxide shell containing copper oxides and/or mixed oxides of copper and aluminum and, at same time, CuAlO/CuAl ceramometal with incorporated additives was found to create a more complicated microstructure. A large amount of X-ray amorphous oxides of copper and aluminum is typical for all composites. CuAl ceramometal was shown to be more active than the CuZnAl oxide catalyst in spite of a much lower specific surface area. The CuAl+CuZnAl catalyst consisting of prismatic granules showed a higher activity in comparison with CuZnAl oxide consisting of cylindrical granules. The activity of the composite granulated catalyst referred to its unit weight was more than 6-fold higher as compared to the oxide catalyst, while the activity per the surface area was found to be more than an order of magnitude higher due to much higher specific activity of small fraction and additively much lower diffusion limitation of granules.

INTRODUCTION

Low-temperature water-gas shift (LT-WGS) reaction (CO + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$) is a very important step of industrial hydrogen production. Many works devoted to activity and properties of catalysts for this process were published$^{1-5}$ and summarized in a series of reviews.$^{6-9}$ These catalysts are usually composed of Cu, Zn, and Al oxide composites prepared by coprecipitation or impregnation. One of the main problems of the LT-WGS reaction is a low activity of the conventional granulated CuZnAl oxide catalyst per the unit volume of the catalyst bed.$^3,10$ Traditionally, the activity can be enhanced by increasing copper dispersion$^4,11,12$ and its total surface area per the catalyst weight unit$^1,9$ or by chemical modification of the properties of highly dispersed copper. Another way to improve the catalyst performance is the increase in the density of the catalyst.$^14$ For example, in some cases, the catalysts containing a large amount of metal in the bulk can have improved volume activity in spite of the lower activity per the surface area. The other problem of the LT-WGS reaction is the poor access of reagents into the bulk of the catalyst granules due to the internal diffusion effect.$^{12}$ In the industry, large granules of catalysts are commonly employed. This is especially important for compact converters that can be employed for fuel cells.$^9$ However, most of the studies on WGS catalysts were carried out using small particle sizes, for which the diffusion inside the catalyst particles is not rate-limiting.

A possible way to increase the activity is the use of ceramometal catalysts with the enhanced real and loading density possessing also a developed system of transport
macropores and mesopores. Ceramometal catalyst includes metallic cores and oxide shell. Such catalysts could also prevent the emergence of temperature gradients within the catalytic layer due to a high thermal conductivity provided by the presence of metal particles in their bulk. For example, ceramometal catalysts synthesized from Al–Cu–Fe alloys through mechanical treatment followed by a high-temperature self-propagating synthesis were applied earlier for the steam reforming of methanol. These catalysts possess a complex microstructure consisting of the metal cores surrounded by the oxide shell with segregated nanoparticles of metallic Cu. The specific activity of copper was found to be changed non-monotonously with its dispersion. LT-WGS was performed also using copper–aluminum ceramometals produced from Cu–Al alloys. The activity of fine fraction per the unit volume in the case of the ceramometal catalyst was found to be lower by ∼15% as compared to the Cu–Zn–Al oxide catalyst, which was used as a reference sample. However, for coarse fraction, the activity of the ceramometal catalyst appeared to be higher by ∼15% as compared to the oxide catalyst. An essentially lower specific surface area of ceramometals was compensated by a greater bulk density, a developed macroporous structure, and a higher activity of metallic copper particles.

In the present study, specific surface area was developed using ceramometals with a high aluminum content. In addition, the incorporation of active powered components into the active ceramometal matrix was employed. The active powered components were represented by the Cu–Zn–Al oxide catalyst and the Cu–Al alloy powder obtained by the electrical explosion of wires. The activities of fine fraction and granules were compared with the structural and textural characteristics of synthesized catalysts. The activity of fine fraction of ceramometal catalysts was found to be higher than that for the CuZnAl oxide catalyst. The activity of granules of both catalysts was somewhat lower, but granules of ceramometal catalyst remained much more active.

## RESULTS AND DISCUSSION

### X-ray Diffraction (XRD)

According to XRD (Figure 1), dominant in the CuZnAl oxide precursor is the tenorite CuO phase (PDF #05-0661, space group C2/m, \( a = 4.684 \text{ Å}, b = 3.425 \text{ Å}, c = 5.129 \text{ Å}, \beta = 99.47^\circ \)) (Figure 1 and Table 1). Strongly broadened peaks, which can be assigned to the wurtzite-like ZnO phase (PDF #36-1451, P6_3mc, \( a = 3.249 \text{ Å}, c = 5.206 \text{ Å} \)) are also observed. According to the preparation procedure (Table 2), the aluminum content in the catalyst should be quite high. However, we did not detect any spinel-like phases, which could contain aluminum; this occurred because the heat treatment temperature was not high enough for crystallization of the spinel phase. The dominant phase of the CuAl(C) precursor is the intermetallic Al_Cu (PDF #24-0003, \( \overline{P}4_3m \), \( a = 8.702 \text{ Å} \)). Also, tenorite (CuO) and a solid solution Cu_{1−x}Al (Cu, PDF #04-0836, Fm_3m, \( a = 3.615 \text{ Å} \); Al, PDF #04-0787, Fm_3m, \( a = 4.049 \text{ Å} \)) were detected (Figure 1 and Table 1). The ceramometal CuAl catalyst contains a solid solution of aluminum in copper and an intermetallic, with the tenorite being the dominant phase (Figure 1 and Table 1).

After incorporation of precursors, the phase composition in complex composites is qualitatively retained. The same set of phases is observed: a solid solution (copper), copper oxide, and intermetallic. However, quantitative estimates revealed an essential non-additive effect. The content of copper oxide in complex composites with additives is almost 1.5 times higher than it could be expected from the composition of the precursors (Table 2) and their initial blend, whereas the content of alloys based on copper and aluminum is generally lower (Table 1). Powders in the mixture are likely to affect each other during hydrothermal treatment (HTT), thus changing the regularities of hydrothermal oxidation. In particular, aluminum can be partially leached, which increases the fraction of intermetallics. The remaining copper will be oxidized upon calcination in air, thus increasing the fraction of copper oxide. According to XRD analysis, alumina-containing compounds are absent, which may be related to their X-ray amorphous state.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectrometry (EDX). In the initial CuAlO/CuAl nanocomposite, at least four types of fragments, which occur also in more complex composites, can be distinguished (Figures 2–4). Dense homogeneous spherical particles with the composition close to Al_Cu intermetallic are observed (point 1, Figures 2–4 and Table 3). Some amount of oxygen in these points is caused by oxidation of the surface layer upon polishing in air. One can see also dense layered structures with the layers of distinctly different color (point 2a, Figures 2–4 and Table 3) and foam-like structures (point 2b, Figures 2–4 and Table 3). Fragments denoted as 2a,b,c have a high content of oxygen, aluminum, and copper (Table 3). Small fragments with a high copper content and a low content of oxygen, iron, and aluminum (point 3, Figures 2–4 and Table 3) were also detected; their composition is close to the solid solution of aluminum in copper.

CuAl composites with incorporated copper-aluminum powder have a more complicated microstructure (Figure 3). Along with fragments 1, 2a, and 3, they contain dense spheres with the core composition close to Al_Cu (point 4, Figure 3b and Table 3). Large amounts of loose spherical inclusions resembling translucent cotton balls with the size up to some tens of micrometers are observed. They are clearly seen at a greater magnification (Figure 3c). Such inclusions contain a large amount of copper, aluminum, and oxygen (point 2c, Table 3). It is known that the particles obtained by explosion have a noticeably smaller mean size, which does not exceed 100 nm. Presumably, in the mixing step, these particles...
are aggregated into big agglomerates, which are oxidized to form rounded fragments with a high content of aluminum, oxygen, and copper (point 2c, Figure 3). Looseness of such agglomerates prevents the formation of strong contacts between fragments during HTT and makes it impossible to synthesize mechanically strong ceramomets from explosion powders.

For the sample with incorporated CuZnAl oxide, particles of irregular shape marked with arrows in Figure 4 are observed instead of loose spheres in the ceramometal matrix of CuAl cermet. The composition of these particles is close to the oxide catalyst (point 5 in the inset of Figure 4a and Table 3). At a greater magnification, bright spots with a lower zinc content (point 6 in the inset of Figure 4a and Table 3) can be seen on the surface of these particles. Zinc oxide may partially dissolve in these regions during HTT, which decreases its concentration in these fragments.

In general, SEM and EDX data are qualitatively consistent with XRD data on copper oxide, metallic copper (the solid solution of aluminum in copper), and Al₄Cu₉ intermetallic (Tables 1 and 3). The absence of Al₂Cu intermetallic revealed by XRD may be related to its low concentration in the sample. In distinction to XRD, the point analysis detected many fragments with a high content of oxygen, aluminum, and copper (point 2, Figures 2–4). Most likely, all these fragments are X-ray amorphous and cannot be detected by XRD. Three types of the most typical composition can be distinguished for these fragments, which differ also in their morphology. Points 2a, 2b, and 2c are characterized by a decrease in oxygen concentration with increasing copper concentration (Table 3). They may correspond to copper oxides and/or mixed oxides of copper and aluminum in the X-ray amorphous state. Point 2a with the maximum copper content and minimum oxygen concentration is presented in Table 3. Black spots are the macropores.
content has a dense layered microstructure, which may be caused by the presence of both the oxide and metallic (in the form of oxidation-resistant alloys) layers. Point 2c is observed exclusively for ceramometals with incorporated CuAl particles, which are obtained by explosion. They are represented most likely by copper oxides, aluminum oxides, and/or mixed oxides in the X-ray amorphous state obtained by the oxidation of CuAl\text{exp} metallic particles. Point 2b represented by cellular foam fragments (Figure 2) is typical of this ceramometal, which was obtained from CuAl powders with a higher aluminum content.\textsuperscript{16} Such fragments were not observed earlier in ceramometal with a lower aluminum content.\textsuperscript{16} Probably, the increased aluminum content increases its oxidation and hydration degree during HTT and promotes the formation of such foam structures. The presence of copper in these structures suggests that copper is also involved in their formation upon HTT.

\textsuperscript{27}Al NMR. The static spin-echo \textsuperscript{27}Al NMR spectrum of the CuZnAl oxide catalyst (Figure 5, top) displays a broad line in the oxide region of the spectrum extended to the downfield side. Such a shape is characteristic feature of disordered materials exhibiting the quadrupole coupling constant distribution. Since the conductivity of this sample is quite poor, we were able to conduct a magic-angle spinning (MAS) NMR experiment with the rotation frequency sufficient for resolving the lines corresponding to tetrahedral and octahedral environments of aluminum. The 12 kHz MAS \textsuperscript{27}Al NMR spectrum of CuZnAl (Figure 6) is dominated by the line corresponding to aluminum in the octahedral environment (~0 ppm) Al\text{oh} with only a little shoulder at ~50 ppm that corresponds to tetrahedrally coordinated aluminum Al\text{th}. From decomposition of this spectrum into two lines shaped according to the Czjzek model,\textsuperscript{20} the Al\text{oh}:Al\text{th} ratio can be estimated as 9:1. Such a ratio is not characteristic of any aluminum oxide phase apart from \alpha-Al\textsubscript{2}O\textsubscript{3}; however, according

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Table 3. Data of Point Analysis of Ceramometal Catalysts According to EDX\textsuperscript{47}

| point no. | O (at %) | Al (at %) | Cu (at %) | Zn (at %) | microstructure | probable phases |
|-----------|---------|-----------|-----------|-----------|----------------|-----------------|
| 1         | 4−5     | 28−34     | 61−68     |           | dense, homogeneous, bright | Al\textsubscript{4}Cu\textsubscript{9} |
| 2a        | 14−16   | 32−36     | 49−54     |           | layered | CuO, CuAl\textsubscript{x}, CuAlO\textsubscript{x} |
| 2b        | 32−37   | 27−34     | 44−46     |           | cellular, foam | CuAl\textsubscript{2}O\textsubscript{4}Al\textsubscript{2}O\textsubscript{3} |
| 2c        | 24−26   | 28−31     | 32−40     |           | cotton-like, homogeneous | CuO, CuAlO\textsubscript{x} |
| 3         | 4       | 1−2       | 94−96     |           | dense, homogeneous, bright | CuAl |
| 4         | 2       | 60        | 38        |           | inhomogeneous sphere | Al\text{Cu} |
| 5         | 51−52   | 24−25     | 16        | ~8−9     | particles of irregular shape | Cu(Zn)Al\textsubscript{2}O\textsubscript{4} |
| 6         | 45−47   | 5−8       | 41−44     | 4−6      | bright spots on the surface of particles with irregular shape | CuO, ZnO |

\textsuperscript{47}Points are marked in Figures 2−4.

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Figures:
- Figure 4. SEM micrograph of the polished surface of CuAl+CuZnAl ceramometal at (a) lower and (b) higher magnification. In the inset, an example of irregular-shaped particle is presented. Appropriate compositions of the numbered points are presented in Table 3. Black spots are the macropores.
- Figure 5. Static spin-echo \textsuperscript{27}Al NMR spectra of ceramometal catalysts (CuAl, CuAl+CuAl\text{exp}, and CuAl+CuZnAl) and their precursors (CuZnAl and CuAl\text{exp}). Dashed lines and arrow show the approximate positions of lines corresponding to the CuAl solid solution (CuAl\textsubscript{x}), CuAl intermetallic compounds (Al\textsubscript{2}Cu and Al\textsubscript{2}Cu\textsubscript{9}), and aluminum in the oxide environment (Al\textsubscript{2}O\textsubscript{3}). Ceramometal catalysts were designated as CuAl, CuAl+CuAl\text{exp}, and CuAl+CuZnAl for brevity. CuAl\text{exp}: a powdered alloy.

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to sample preparation conditions and XRD data, the presence of corundum is very doubtful. Therefore, it is safe to assume that aluminum in this sample is present mostly in the form of a disordered spinel phase, most likely of the CuAl$_2$O$_4$ composition according to the EDX data (analogous to point S in Table 3). The appearance of tetrahedral sites can be explained by a small admixture of some metastable alumina phase or inverse spinel of the same composition, which is often present together with Cu–Al or Zn–Al spinels. Spinel containing copper, zinc, and aluminum cations with a low concentration of aluminum cations are well known. The XRD data, where only the CuO phase is visible with the trace amounts of ZnO, also support the disordered character of such a spinel phase.

Spectra of other samples exhibit a set of lines similar to that reported earlier: the line at 0 ppm corresponds to the oxide environment of Al atoms (without distinguishing between Al oxides or other compounds such as Al spinels) and several lines are shifted downward due to the Knight shift, which is caused by the conduction electrons. However, the assignment of lines adopted earlier must undergo some corrections due to the accumulated data on the mechanically activated and cermet samples. Since the intensity of the line located at ~1000 ppm does not correlate with the amount of Al$_4$Cu$_9$ phase or is actually an overlap of two lines with different intensities. The results are consistent with the theoretical 1:3 ratio between the Al sites. According to the same work, the line located at ~1400 ppm, which appears in the spectrum of CuAl$_{exp}$ sample, corresponds to an intermetallic phase with Al$_4$Cu composition. A more detailed description of the $^{27}$Al NMR spectra of CuAl-based ceramometals will be published elsewhere.

The results obtained by deconvolution of the $^{27}$Al NMR spectra are summarized in Table 4. While compositions of CuZnAl and CuAl$_{exp}$ samples are completely different from one another, the products of their hydrothermal treatment seem very similar. The biggest difference between the CuAl sample and the mixed systems is the increased amount of CuAl$_{sol}$ solid solution in the former. Although the CuAl$_{exp}$ precursor contained the least amount of oxidized aluminum, the cermet obtained from it demonstrates the biggest AlO$_x$ content. This implies that alloy particles obtained by the explosion technique are unstable and readily react during the HTT or calcination steps. In any case, the addition of either CuZnAl or CuAl$_{exp}$ results in the alteration of the reaction pathway that takes place during HTT and calcination.

The most unusual NMR result is the detection of a large amount of aluminum represented by individual or mixed copper and aluminum oxides with the spinel structure, which are not observed by XRD. However, according to EDX, a lot of fragments containing Cu, Al, and oxygen together were detected (Table 3). These fragments may be Cu–Al oxides with a spinel structure. The same effect was earlier discovered for the Cu–Al oxides that were obtained by the “intergrowth” method. It can be concluded that the systems examined in our study contain large amounts of disordered X-ray amorphous mixed oxides of aluminum and copper.

Thus, it is difficult to compare directly the quantitative data obtained by XRD, EDX, and NMR. However, a comparative analysis makes it possible to “arrange” the complicated microstructure of the obtained composite systems and to reveal their similarity and distinctions. It is clear that the initial CuZnAl oxide catalyst comprises not only copper and zinc oxides but also a large amount of X-ray amorphous oxides containing both aluminum oxides and the mixed copper and aluminum oxides with the short-range order structure similar to that of a highly defective spinel. The CuAl$_{exp}$ explosion sample, in addition to various alloys (solid solution, Al$_4$Cu, and Al$_4$Cu$_9$), contains a large amount of aluminum oxide phases, which are also X-ray amorphous. A simple CuAl ceramometal

Figure 6. 12 kHz MAS $^{27}$Al NMR spectrum of CuZnAl. Spinning sidebands are denoted with asterisks.

Table 4. Phase Composition of Samples According to $^{27}$Al NMR Data

| sample* peak position | Al$_4$Cu$_9$ (1000 ppm, %) | CuAl$_{sol}$ (1000 ppm, %) | Al$_4$Cu$_9$ (600 ppm, %) | AlO$_x$ (0 ppm, %) |
|-----------------------|-----------------------------|-----------------------------|---------------------------|-------------------|
| CuZnAl               | 81 3 6 0 1 9               | 81 4 1 9 5 9               | 81 7 6 0 1 9             | 81 7 6 0 1 9       |
| CuAl$_{exp}$ (alloy) | 71 5 1 5 6 3               | 71 5 1 5 6 3               | 71 5 1 5 6 3             | 71 5 1 5 6 3       |
| CuAl                 | 5 8 1 4 1 9               | 5 8 1 4 1 9               | 5 8 1 4 1 9             | 5 8 1 4 1 9       |
| CuAl + CuZnAl        | 5 8 1 4 1 9               | 5 8 1 4 1 9               | 5 8 1 4 1 9             | 5 8 1 4 1 9       |
| CuAl + CuAl$_{exp}$  | 7 1 5 1 5 6 3             | 7 1 5 1 5 6 3             | 7 1 5 1 5 6 3           | 7 1 5 1 5 6 3     |

* Ceramometal catalysts were designated as CuAl, CuAl+CuAl$_{exp}$, and CuAl+CuZnAl for brevity.
includes the metallic cores, which contain aluminum and copper alloys, and the oxide moiety (CuO, CuAlO$_2$, and AlO$_2$). Samples with incorporated additives have close phase and chemical compositions with respect to copper and aluminum. It seems that hydrothermal and oxidative treatments essentially average these characteristics. The presence of a large amount of X-ray amorphous oxide components is a common feature of all the tested catalysts.

**Catalytic Properties in LT-WGS.** As seen in Figure 7, CO conversion on the ceramometal catalyst is approximately 2-fold higher than that on the oxide CuZnAl catalyst in the temperature region of 210–240 °C. As seen from the slope of the curves, nearly the same ratio will be retained at temperatures below 210 °C. This was not observed earlier for the cermet sample with a lower aluminum content. It should be noted that the contact time for the CuAl sample was shorter by more than a factor of 1.5 as compared to CuZnAl (Table 5). A higher aluminum content in the initial Cu-Al powder is the egg-shell microstructure (Figure 2) and is likely to increase the concentration of active sites per unit weight of the catalyst. This is why the ceramometal is more active than the oxide catalyst.

Another reason of a higher activity of our ceramometal catalyst could be the effect of alumina content on the phase composition of catalysts. For our ceramometal catalyst, the mass ratio of Al$_4$Cu$_9$ intermetallide to that of the Cu(Al) solid solution is equal to 0.55 by XRD data or 0.73 by NMR data. Since, due to the skin effect, NMR data mainly correspond to the near-surface layer while XRD data to the bulk of the catalyst, this implies that the relative content of this intermetallide in the near-surface layer is substantially higher for ceramometal with a higher content of aluminum (20% in our case and 13% in ref 16). Namely, this intermetallide (more precisely, the oxide layer on its surface) generates more active sites for the WGS reaction as discussed in detail earlier.

The CuAl ceramometal with incorporated Cu−Al alloy additives obtained by explosion as well as the CuZnAl catalyst are even more active (Figure 7). The temperature dependence of CO conversion for the CuAl+CuAlexp sample, which reversibly goes to a plateau in the temperature region of 210–240 °C, is not quite clear. Obviously, the higher activity is determined by the addition of CuAlexp which, as was noted above, has the cotton-like texture (Figure 3). Presumably, at a high temperature, this texture facilitates a transition of the reaction from the kinetic region to diffusion one. Unfortunately, the CuAlexp powder is not consolidated into a firm ceramometal upon HTT and calcination, so we could not estimate separately the activity of this ceramometal. This question needs further studies.

For ceramometal with incorporated CuZnAl catalyst, a high conversion is reversibly retained also at 240 °C (Figure 7). Contact time differs for different catalysts (Table 5). Thus, to enhance the objectiveness, we compared efficient first-order rate constants estimated according to the model of a plug-flow reactor instead of conversions at the same temperature (Table 5). The difference between rate constants of a small fraction of CuAl ceramometal and CuZnAl oxide catalyst is about 3-fold. The effect, first of all, is related to the difference in the density of the catalysts. The apparent density of CuAl is 3.8 g/cm$^3$ and 2.0 g/cm$^3$ for CuZnAl. So, the activity per unit volume is higher for the ceramometal catalyst. While related to per mass of the small fraction of catalysts, this difference is much lower (1.1 and 1.8 s$^{-1}$g$^{-1}$, Table 5). In this case, a higher activity of the ceramometal catalyst is related to a higher concentration and a higher activity of Cu active sites. This effect was discussed in detail earlier.

In the industry, catalysts are commonly used in the granulated form. CO conversion for the most active granulated CuAl+CuZnAl sample strongly exceeds that for CuZnAl granules (Figure 8). Note that this occurs at a smaller weight and volume of the catalyst. If contact time and weight of the catalysts are taken into account, then even a greater difference in specific activity is obtained. The apparent rate constants per the unit volume are approximately 3.5 times higher for cermet granules in comparison with the oxide catalyst, whereas per the unit weight, there is more than a 6-fold excess (Table 5). This effect is not related to the different shape of granules: cylindrical for oxide catalyst and prismatic for the ceramometal one (see Experimental Section). The ratio of geometrical volume of the granules to their geometrical surface differs only slightly. For granules of CuZnAl, it is equal to ~0.08, whereas for granules of CuAl cermet, it is equal to ~0.06. In addition,
due to a smaller cross section, the average distance between reactor walls and granules is much greater for cermet, which increases the probability of breakthrough and can only decrease the apparent activity of cermet granules in comparison with the granules of the oxide catalyst. Hence, the granulated ceramometal catalyst with incorporated oxide catalyst shows an essentially higher activity than the neat oxide catalyst granules. Along with the zinc promotion, the most important factor increasing the activity of granules is a specific pore structure of ceramometals.

**Textural Properties of the Catalysts.** Table 6 lists the main textural characteristics of studied catalysts. The specific surface area of the CuAl ceramometal catalyst is lower almost by an order of magnitude as compared to the CuZnAl oxide catalyst, and its total pore volume and the mesopore volume are much smaller as well. The mesopore volume of the ceramometal with incorporated additives increases both for CuAl and CuAl+CuZnAl, but not more than 1.5-fold.

Thus, a greater activity of ceramometal catalysts in comparison with the oxide one is caused by a higher concentration of active sites on the surface or by their much greater activity. This is confirmed by analysis of the specific (per the surface unit) rate constants of catalysts (Table 6). For ceramometal catalysts, such specific catalytic activity exceeds that of the oxide catalyst by more than order of magnitude. The specific activity of the CuAl+CuZnAl catalyst can be even described by the additive model of contributions from CuAl (80%)+CuZnAl (20%) giving in sum 0.11 s⁻¹ m⁻³. So, the surface area is not the main factor of the effectiveness of ceramometal catalysts. The specificity of surface structure and chemical composition provide their much higher activity.

A comparison of the rate constants shows that the activity of the granules per unit weight of the CuZnAl catalyst decreases more than 2-fold as compared to the fine fraction (Table 5), from 1.1 to 0.4 s⁻¹ g⁻¹. This is related to the complete absence of macropores, which provides a poor permeability of granules (Table 5). For the CuAl+CuZnAl ceramometal, on the contrary, the activity increases from 1.8 to 2.6 s⁻¹ g⁻¹ as compared with the CuAl catalyst (Table 5). More than a 6-fold difference in the specific activity of oxide and ceramometal granules related to the weight unit is obtained (Table 5).

For the ceramometal catalyst with incorporated CuZnAl oxide, the specific activity per the surface area unit remains almost the same for its fraction and granules (0.10 and 0.12 s⁻¹ m⁻²). For the oxide catalyst, the activity for granules as compared with that for its fraction decreases by three times (Table 6). Only diffusion limitation inside granules can explain this effect. In comparison with the oxide catalyst, ceramometal catalysts, especially those with incorporated additives, have essential advantages since their macropore volume constitutes more than a half of the total pore volume (Table 6) in contrary to nanotubes. Macropores in ceramometals are clearly seen in SEM images as black spots (Figures 2–4). These pores are absent in the oxide catalyst (see inset in Figure 4a).

### CONCLUSIONS

Porous ceramometals were synthesized from powdered CuAl alloys with the addition of CuAlexp powders produced by current explosion or CuZnAl oxide obtained by coprecipitation. Their structural, microstructural, spectral, textural, and catalytic properties were examined by means of XRD, SEM with EDX, NMR, and adsorption methods. The initial CuAl ceramometal was shown to have a complicated microstructure, which includes the egg-shell fragments with metallic cores (AlCu₁₋₄, Al₅Cu, and Al₅Cu₃) and the oxide shell containing copper oxides and/or mixed copper and aluminum oxides. Highly porous oxide fragments with a similar composition were also detected. In the case of incorporation of CuAlexp alloy powder produced by current explosion, the cotton-like fragments were additionally found; they were formed from aggregated CuAl nanoparticles, which are oxidized to the oxide state after hydrothermal treatment and calcination. Upon incorporation of the CuZnAl oxide catalyst, particles of irregular shape are additionally observed in the complex composite. All the composites contain large amounts of X-ray amorphous copper and aluminum oxides.

Activity of the CuAl ceramometal was shown to be higher as compared to the CuZnAl oxide catalyst in spite of its much lower specific surface area. It was supposed that highly active sites are present on the ceramometal surface but are absent in the oxide catalyst. The specificity of surface structure and chemical composition provide a much higher activity of ceramometals. This effect needs to be studied more carefully. Also, a higher density of ceramometal catalyst is of importance.

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**Table 6. Textural Properties of the Ceramometal Catalysts and Oxide Catalyst**

| sample | δ_w g/cm³ | ρ_g g/cm³ | SSA, m²/g | K°, s⁻¹·m⁻³(gran) | V_p, g/cm³ | V_m, cm³/g | V_macr, cm³/g | D_macr mm |
|--------|-----------|-----------|----------|-------------------|------------|------------|-------------|-----------|
| CuAl   | 3.8       | 5.1       | 13.0     | 0.14              | 0.07       | 0.03       | 0.04        | 7.2       |
| CuAl+CuAlexp | 2.8       | 4.9       | 15.4     | 0.14              | 0.15       | 0.04       | 0.11        | 10.0      |
| CuAl+CuZnAl | 2.9       | 5.0       | 21.4     | 0.10 (0.12)       | 0.14       | 0.06       | 0.08        | 10.4      |
| CuZnAl | 2.0       | 4.0       | 122      | 0.01 (~0.003)     | 0.25       | 0.25       | <0.001      | ~4        |

Ceramometal catalysts were designated as CuAl, CuAl+CuAlexp, and CuAl+CuZnAl for brevity. δ_w apparent density of granules; ρ_g real density of catalysts; V_p, total pore volume; SSA, specific surface area; V_m, micro- and mesopore volume; V_macr = V_p - V_m - macro pore volume; D_macr mesopore diameter.
The activity of the CuAl+CuZnAl granulated catalyst was found to be higher as compared to CuZnAl granules. This effect is related to the developed macropore structure. So, the increase in the catalyst density as well as the developed macropore structure can significantly improve the granulated catalysts performance in LT-WGS, thus depending not only on the properties and concentration of active sites on the surface of catalysts.

**EXPERIMENTAL SECTION**

**Preparation Procedure.** Aluminum powder (PAP-2, GOST 5494-95, Russia) with platelet-shaped particles (typical sizes: 10–40 microns) and electrolytic copper powder (PMS-1, GOST 4960-75, Russia) of dendritic shape were used as starting materials.

a) Mechanical activation (MA) of the mixture containing (wt %) 80Cu+20Al was used to synthesize the powdered CuAl alloy as a precursor (at %, Cu:Al = 63:37). MA was carried out in a high-power planetary ball mill APF (the diameter of milling steel balls = 5 mm; ball-to-powder mass ratio = 8:1; powder weight = 100 g; and ball acceleration = 20 g). The activation time was 9 min. The volume of the milling stainless steel vial was 1 L. To prevent sticking of the powder to balls and vial walls, ethanol was used as a process control agent. It was added into the vial 30 s before the start of milling.

b) The product of mechanical activation (CuAl alloy) was blended with the powdered CuAl, prepared by electrical explosion of wires (Cu:Al = 1:1) or the powdered CuZnAl oxide catalyst prepared by thermal decomposition of CuZnAl hydroxycarbonate that was obtained by precipitation from nitrate solutions using a sodium carbonate solution with subsequent washing and thermal treatment at 350 °C (atomic ratio Cu:ZnAl = 50:30:20). The blends were then loaded into a stainless steel die specially designed to ensure free access of water and hydrogen release.

c) The loaded die was placed into the vessel with boiling water and kept there for 5 h (hydrothermal treatment, HTT). This step provides the formation of strong monoliths due to conjugation of the aluminum oxidation reaction and the creation of contacts between the particles due to generation of aluminum hydroxides. Similar to the MA step, the oxidation of Al in the HTT step diminishes the extent of exothermic Cu−Al interaction in the calcination step.

d) The monolithic product of HTT was removed from the die, dried for 1 h at 120 °C, and calcined under air at 550 °C. This yields a mechanically strong material and develops the mesoporous structure of ceramometals. The ceramometal catalysts have the cuboid shape with a cross section of 3.2 × 3.2 mm and a height of 5 mm.

Al–Cu_{exp} bimetallic nanoparticles were prepared by the electrical explosion of wires (EEW) in an argon atmosphere, the pressure of the gas mixture being 3 × 10^3 Pa. The twisted aluminum and copper wires were used to prepare bimetallic nanoparticles. The mass ratio of copper in nanoparticles was 50 wt %. To obtain bimetallic nanoparticles, wires were twisted together before the EEW. A high-density current pulse (∼10^7 A/cm^2) was then applied to the twisted wires; the current pulse was produced by the discharge of a capacitor bank of a pre-defined capacity (Cu) charged to a pre-defined voltage (U). When the current pulse propagated through the wires, the explosive dispersion of metal and the fast expansion of explosion products (metal vapor aerosol) into the atmospheric gas (argon) took place. Here, the explosion products were cooled and nanoparticles emerged. As nascent nanoparticles are pyrophoric after the synthesis, they were passivated by slow air leak-in.

The reference sample was the same CuZnAl bulk oxide catalyst shaped by pressing (similar to the commercial one) and synthesized by heat treatment of the mixed Cu–Zn–Al hydroxy carbonate, and the CuZnAl oxide catalyst initially possessed a cylindrical shape (diameter, ∼5 mm; height, ∼5 mm).

**Characterization.** X-ray diffraction (XRD) patterns of powders were recorded in the 2θ range 15–95° with a step of 0.05° and a counting time of 3 s per step by means of a D8 Advance powder diffractometer (Bruker AXS) equipped with a one-dimensional Lynx-Eye detector using Cu Kα radiation. The quantitative analysis was carried out using Rietveld refinement in TOPAS-4.2, 21999, 2009 software. The average size of the crystallites was determined taking into account the instrumental peak broadening. Scanning electron microscopy (SEM) studies of the catalysts were performed on a JSM 64605V microscope (JEOL Ltd.) equipped with an energy-dispersive spectroscopy unit EDX INCA (Oxford Inst.).

Solid-state $^{27}$Al NMR experiments were carried out using a Bruker Avance 400 spectrometer in a 9.4 T constant magnetic field. The spectra were recorded at $^{27}$Al resonance frequency of 104.31 MHz. Static spectra were acquired with solid-echo pulse sequence $\pi/8-\tau-\pi/8$, where the length of $\pi/8$ pulse was 0.5 μs and the interpulse delay $\tau$ was 15 μs. The magic-angle spinning (MAS) spectrum of the CuZnAl sample was recorded with a simple $\pi/8$ one-pulse excitation at a 12 kHz rotation frequency. Sequence repetition delay was 0.5 s in all cases, and from 1024 to 8192, transients were recorded depending on the signal intensity. All spectra were obtained at room temperature with a standard 4 mm Bruker probe. Al(H$_2$O)$_6$ solution was used as an external chemical shift reference at 0 ppm. Decomposition of the static spectra in Dmfit software was done with pseudo-Voigt functions to obtain the best fit.

The total pore volume of the monolith was calculated from the values of true and apparent densities. True density was measured using a helium pycnometer (Autopycnometer 1320, Micromeritics). The fraction of micropores and mesopores (called for brevity the “mesopores”) as well as the specific surface area (SSA) were determined from adsorption isotherms of nitrogen recorded at 77 K using an ASAP-2400 Micromeritics instrument. The total pore volume was estimated from reversal values of apparent and real densities (V$_{total} = 1/\rho_a - 1/\rho_a$). The macropore volume was estimated from the difference of the total and mesopore volumes. Apparent density of granules ($\rho_{app}$) was estimated through the mass and geometric sizes of granules.

The catalysts were activated in the mixture of 5% H$_2$ in He at 13,250–22,400 h$^{-1}$ and 270 °C for 2 h with a temperature ramp of 2°/min. The activity was measured at a pressure of 1 bar in the mixture of CO:H$_2$O:H$_2$ = 8:42:50; a catalyst (0.14–0.25 mm fraction) was mixed with quartz sand in a ratio of 1:8. To provide the isothermal mode of reactor operation, the reactor was placed in a blow-off oven. All catalytic data are given for the catalysts that reached a steady-state activity (after continuous operation for at least 25 h). As a measure of
activity, we used the conversion of CO (x) and rate constant. The rate constant (s^-1) for a plug flow reactor without taking into account the reverse reaction can be calculated from

\[ k = \frac{1}{t} \ln \frac{1}{1 - x} \]

where \( t \) is the contact time (s) and \( x \) is the conversion.

The activity of granules was studied in a special Temkin-type single-row reactor,\(^{30}\) in which 10 granules of the catalyst (“gran”\) were placed. To improve mass transfer and heat removal during the exothermic reaction, 10 copper kegs (small barrels) of 5 mm in diameter and 5 mm in height were placed between catalyst granules. So, half of the total reactor volume (2.25 cm\(^3\)) was loaded by kegs. The indicated reactor with an inner diameter of 5.3 mm was also mounted in a blow-off oven. The CuZnAl catalyst initially possessed a cylindrical shape (diameter, ~5 mm; height, ~5 mm), while the ceramometal catalyst possessed a prismatic shape (3.2 × 3.2 × 5 mm). The total mass of the catalysts was 1.36 g for CuAl+CuZnAl\(_{gran}\) and 2.24 g for CuZnAl\(_{gran}\). The total volume of the reactor with granules and kegs was 2.37 cm\(^3\) (GHSV = 22,000 h\(^{-1}\)).

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