

Mechanochemical Synthesis of Calcium and Copper Ferrite Catalysts for Medium-Temperature Carbon Monoxide Conversion

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Abstract—The mechanochemical synthesis of calcium and copper ferrites has been investigated by X-ray powder diffraction, X-ray crystallography, thermogravimetric analysis, IR spectroscopy, sedimentation analysis, and chromatography. The effects of mechanical activation and heat treatment on the formation of calcium ferrite with a perovskite structure and copper ferrite with a mixed spinel structure are demonstrated. Calcium and copper ferrites calcined at low temperatures (450–500°C) are catalytically very active in the water-gas shift reaction. CO conversion on calcium and copper ferrites yields a number of by-products. The concentrations of these by-products in the condensate have been determined.

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In recent years, the growing interest in hydrogen energy has caused particularly large demand for catalysts and sorbents used in the production of hydrogen and hydrogen-containing gases by the conversion of natural hydrocarbons [1–3].

The medium-temperature CO conversion stage in ammonia plants requires iron–chromium catalysts. The iron oxide and chromium contents of an unreduced iron–chromium catalyst are 85–93 and 6.5–10%, respectively [4]. Iron oxide for these catalysts is obtained by decomposing iron hydroxide or carbonate precipitated from an iron sulfate solution with ammonia or ammonium carbonate [4, 5]. Mixing iron oxide with chromic acid under vigorous mechanical treatment makes the resulting catalyst mechanically stronger and increases the CO conversion by 9–15% [6]. However, this method has the following drawbacks: considerable amounts of sulfur are present in the mixture; one of the components is chromium trioxide, a toxic substance; and the resulting catalyst possesses insufficient thermal stability and activity. The active phase in the iron–chromium catalysts is Fe_3O_4 resulting from the reduction of the stock mixture. Chromium oxide in the iron–chromium catalysts serves as a structure modifier. It is catalytically inactive, but it stabilizes the porous structure of the working catalyst. Without this modifier, the porous structure may be broken down because of sintering [5, 7].

Numerous data demonstrating the unique physical and chemical properties of perovskite and spinel ferrites have been reported to date [8–13]. This class of compounds includes $\text{Ca}_2\text{Fe}_2\text{O}_5$, which is used as a catalyst in the oxidation of carbon monoxide, hydrocar-

bons, and ammonia. This ferrite is an oxygen-deficient perovskite in which polyhedra are ordered so that layers of FeO_6^- octahedra and FeO_4^- tetrahedral alternate [11–13]. Calcium ions occupy holes between an octahedron and a tetrahedron. It is expected that this structure, which is stabilized by large calcium cations, will be very active and thermally stable in the water-gas shift (WGS) conversion of carbon monoxide. Mechanochemical activation affords fine-particle calcium ferrite and allows the subsequent heat treatment to be performed at a much lower temperature [10–12]. Here, we report the potential of the mechanochemical synthesis of calcium and copper ferrites in medium-energy-intensive apparatuses and the principles of the preparation of new-generation catalysts for the medium-temperature WGS reaction. Another purpose of our study was to elucidate the effect of mechanical activation on the subsequent thermal synthesis and on the catalytic properties of the resulting ferrites.

EXPERIMENTAL

Iron oxide was prepared as follows. An iron nitrate solution was treated with aqueous ammonia. The resulting goethite (FeOOH) precipitate was washed until the residual nitrate ion content was 0.2%. Subsequent heat treatment at 450°C yielded hematite ($\alpha\text{-Fe}_2\text{O}_3$). Calcium and copper ferrites were synthesized using analytical-grade copper oxide and reagent-grade calcium oxide. Mechanical activation was carried out in a VM-4 vibrating annular roller mill operated at a vibration frequency of 930 min^{-1} and, accordingly, an

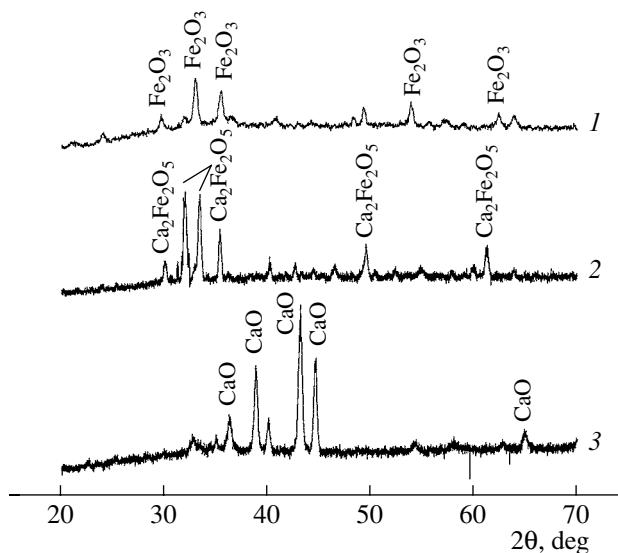


Fig. 1. X-ray diffraction patterns from calcium ferrite specimens synthesized at (1) $\text{CaO} : \text{Fe}_2\text{O}_3 = 1 : 1$ and $T_{\text{calcin}} = 450^\circ\text{C}$, (2) $\text{CaO} : \text{Fe}_2\text{O}_3 = 2 : 1$ and $T_{\text{calcin}} = 900^\circ\text{C}$, and (3) $\text{CaO} : \text{Fe}_2\text{O}_3 = 1.5 : 1$ and $T_{\text{calcin}} = 450^\circ\text{C}$.

acceleration of 3g or in a planetary mill operated at an acceleration of 11g.

X-ray diffraction phase analysis and structure determination were carried out on a DRON-3M diffractometer using $\text{CuK}\alpha$ radiation. Substructure parameters were calculated by the harmonic analysis of diffraction line profiles. The degree of inversion of the spinel structure was calculated by comparing the observed and simulated intensities of reflections. The structure amplitude F^2 relates the form factor f to the lattice basis: $F = \sum f(\cos \delta + i \sin \delta)$, where $\delta = 2\pi(hx + ky + lz)$ is the phase shift. Here, x , y , and z are atomic coordinates (basis) and h , k , and l are Miller indices. The intertransfer of cations results in their random redistribution. For this reason, in the calculation of the structure amplitude, the basis is taken to be the same as in the case of a normal spinel and the form factors of the tetrahedral and octahedral sites are changed as follows: $f_{\text{tetr}} = f_A(1 - \gamma) + f_B\gamma$ and $f_{\text{oct}} = f_A\gamma + f_B(2 - \gamma)$. Hence, the degree of inversion (γ) of the spinel $\text{A}[\text{B}_2]\text{O}_4 \rightarrow \text{A}_{1-\gamma}\text{B}_\gamma[\text{A}_\gamma\text{B}_{2-\gamma}]\text{O}_4$ can be determined [14, 15].

The size of the secondary particles of oxide powders was determined using an Analysette-22 particle sizer. Specific surface area was determined by the BET method using thermal argon desorption data. Thermo-gravimetric analysis was carried out on a Q-1500D thermoanalytical system at a heating rate of 5 K/min. IR spectra were recorded in the 400–4000 cm^{-1} range on a Specord M-80 spectrophotometer and on an AVATAR 360 ESP Fourier-transform spectrophotometer.

Catalytic activity in the WGS reaction was measured in a flow reactor. The gas stock had the following composition (vol %): CO, 12; CO_2 , 5; H_2 , 55; Ar, the balance. The steam-to-gas ratio was equal to unity. The gas VHSV was 5000 h^{-1} . The catalyst with a particle size of 0.5 mm was placed into the reactor and was reduced with a 50% H_2 + 50% He mixture. In order to determine the thermal stability of a catalyst, we first measured the CO conversion in the temperature range 250–400°C. After the first series of tests was complete, the catalyst was held at 600°C for 1 h (overheated) and was then cooled to 400°C. Next, the catalyst was retested throughout the temperature range examined. The thermal stability coefficient was calculated using the formula $K = \frac{\alpha_1}{\alpha_2} \times 100\%$, where α_1 and α_2 are the CO conversions after and before the overheating of the catalyst, respectively. The condensate was analyzed for impurities on a Kristall-Lyuks chromatograph.

RESULTS AND DISCUSSION

According to sedimentation analysis data, the starting iron oxide, which was obtained by the thermal decomposition of goethite, was largely made up of large particles with a size of $>10 \mu\text{m}$ (57.6%). The strong aggregates consisted of hematite particles, which had a block structure with a microblock size of 26 nm.

According to X-ray diffraction data, as a $\text{CaO} + \alpha\text{-Fe}_2\text{O}_3$ (1.5 : 1 mol/mol) mixture was mechanically activated in a vibrating mill, the calcium oxide disappeared in 5 min and an amorphous product formed (Fig. 1). Further milling did not cause any significant changes in the intensity of reflections from hematite. Apparently, in the presence of iron oxide, which is the harder component and has a larger specific surface area (13–18 mg/m^2), the grinding and amorphization of CaO , the softer component (3–5 mg/m^2), took place. The $\alpha\text{-Fe}_2\text{O}_3$ particles were coated by calcium oxide as fine crystals and as a 2D-ordered phase. Furthermore, it is possible that the products of mechanical activation mixed to combine into an amorphous hydrated compound [8, 9, 11, 12].

The mechanical activation of a $\text{CaO} + \alpha\text{-Fe}_2\text{O}_3$ (1 : 1 mol/mol) mixture yields an amorphous product containing well-crystallized calcium oxide. An analysis of X-ray diffraction data has demonstrated that the amorphization of $\alpha\text{-Fe}_2\text{O}_3$ is complete within 30–45 min. The reflections from $\alpha\text{-Fe}_2\text{O}_3$ disappear upon activation for 10–15 min, and only reflections from CaO remain in the diffraction pattern. The thermal treatment of the system at 700°C yields well-crystallized braunmillerite, $\text{Ca}_2\text{Fe}_2\text{O}_5$ (Fig. 1).

The catalytic activity of calcium ferrite in the WGS conversion of CO into hydrogen was studied at 280–400°C. The CO conversion was studied as a function of the $\text{CaO} : \alpha\text{-Fe}_2\text{O}_3$ ratio in the synthesis, calcination

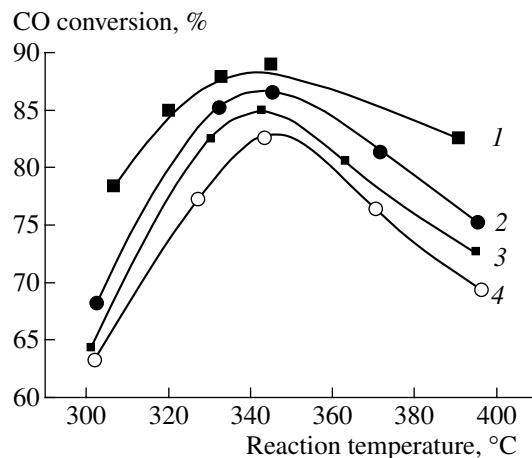


Fig. 2. CO conversion versus temperature for the WGS reaction over $\text{CaO} : \text{Fe}_2\text{O}_3 = 1.5 : 1$ specimens activated in a vibrating mill for 45 min and calcined at (1) 450, (2) 700, (3) 800, and (4) 900°C.

temperature, and activation time. In the synthesis of the ferrite in a vibrating mill, it is appropriate to add iron oxide in some excess in order to convert all of the calcium oxide, lest unreacted CaO reduce the catalytic activity of the system. For this reason, calcium ferrite to be subjected to activity tests was synthesized at $\text{CaO} : \alpha\text{-Fe}_2\text{O}_3 = 1.5 : 1$ mol/mol. The tests have demonstrated that the CO conversion depends strongly on the calcium ferrite calcination temperature (Fig. 2). All of the catalysts are most active at reaction temperatures of 330 to 360°C. The highest CO conversion (88.9%) is achieved with the catalyst heat-treated at the lowest temperature examined (450°C). Raising the heat treatment tempera-

ture diminishes the catalytic activity of the system. With the catalyst calcined at 900°C, the CO conversion is only 81.6%.

The iron and calcium compounds may undergo carbonation and hydration during mechanical activation. The IR spectra of the samples calcined at 400–600°C show strong absorption bands at 1300–1500 cm^{-1} , which are characteristic of carbonates. These bands disappear almost completely as the calcination temperature is raised to 900–1000°C. Furthermore, according to thermogravimetric data, the samples calcined at lower temperatures show a marked weight loss at $T = 200$ –700°C [16, 17]. Therefore, crystalline braunmillerite does not form at the oxide activation stage, but the formation of a mixed amorphous hydroxocarbonate is possible. As a consequence, the low-temperature calcium ferrite samples are anion-modified and are catalytically more active than the high-temperature samples [11, 13].

Unactivated copper and iron oxides are known to combine into copper ferrite only upon heat treatment at 1000°C for 24 h [8, 9]. We found that, after a $\text{CuO}/\text{Fe}_2\text{O}_3$ (1 : 1) mixture is mechanically activated for 30 min in a vibrating mill, copper ferrite appears upon heat-treatment above 600°C. Heat treatment at 800°C results in well-crystallized copper ferrite characterized by strong reflections indicating interplanar spacings of 2.95, 2.52, 2.05, and 1.48 Å (Fig. 3). After the 15-min-long activation of the starting components in a planetary mill, copper ferrite forms at a temperature as low as 400°C. Normal, inverse, and mixed spinel are generally distinguished, which differ from one another in the way the M^{2+} and M^{3+} cations occupy the eight tetrahedral and sixteen octahedral sites. In a normal spinel, the eight M^{2+} cations occupy the eight tetrahedral sites and

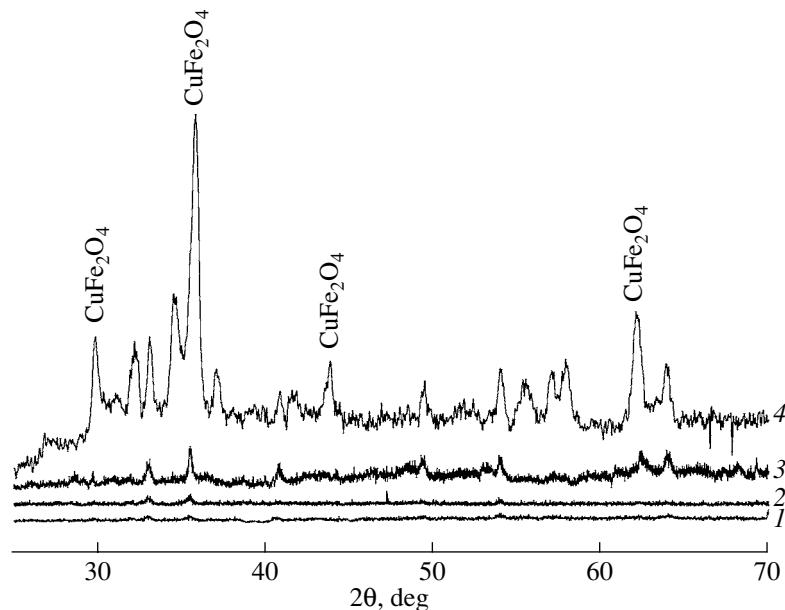


Fig. 3. X-ray diffraction patterns from copper ferrite calcined at (1) 450, (2) 500, (3) 600, and (4) 800°C. $\text{CuO} : \text{Fe}_2\text{O}_3 = 1 : 1$.

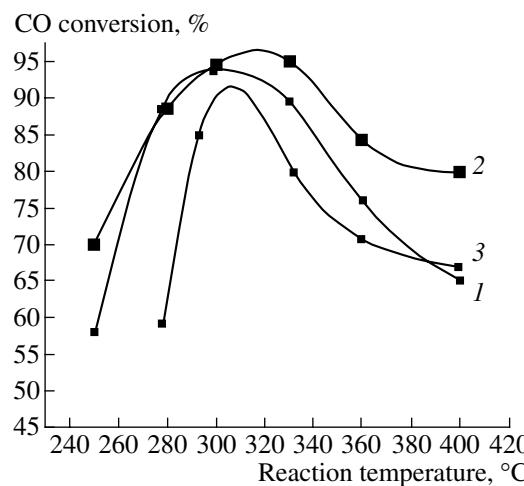


Fig. 4. CO conversion versus temperature for the WGS reaction over catalysts prepared by the mechanical activation of a $\text{CuO} + \text{Fe}_2\text{O}_3$ mixture in a vibrating mill for (1) 15, (2) 30, and (3) 45 min. $T_{\text{calcin}} = 450^\circ\text{C}$; $\text{CuO} : \text{Fe}_2\text{O}_3 = 1 : 1$.

the 16 M^{3+} cations occupy octahedral sites. In an inverse spinel, eight M^{3+} cations occupy the eight tetrahedral sites and the other eight M^{3+} cations and the eight M^{2+} cations occupy the 16 octahedral sites in a random way [8, 9, 15]. The normal and inverse spinels are the limiting cases. Most spinels are mixed. Knowing the coordinates of the Cu and Fe atoms, we calculated, using a PC, the degree of inversion of the resulting spinels, which appeared to be ~75%. Therefore, most of the copper cations occupy octahedral sites and some of the Fe^{3+} cations pass into tetrahedral holes. The activity of copper ferrite catalysts in the WGS reaction depends strongly on the activation time and heat-treatment temperature. The highest activity is exhibited by the sample ground in a vibrating mill for 30 min. The

activity maximum is observed at reaction temperatures of 300–340°C, at which the CO conversion is ~95%. Lengthening the activation time to 45 min reduces the CO conversion to ~92% (Fig. 4).

The copper ferrite synthesized does not need high-temperature treatment: the CO conversion decreases from 94.8 to 92.0 and 91.2% as the heat-treatment temperature is raised from 400 to 500 and 600°C. Because copper oxide, like iron oxide, can form amorphous hydrocarbonates during mechanical activation, low-temperature copper ferrite specimens are anion-modified, as in the case of calcium ferrite.

All catalysts lose activity and selectivity and disintegrate as they are used. The problem of extending the lifetime of the high-reactivity structure acquired by the catalyst during mechanical activation is of particular significance. Thermal stability studies have demonstrated that the thermal stability coefficient of calcium ferrite at 360°C is 98.8% and that of copper ferrite is 95.3% (Table 1). Therefore, these catalysts are thermally very stable.

Note that, besides activity, selectivity is another very significant property of a catalyst. The point is that the steam condensate resulting from ammonia synthesis should be recycled. The condensate returned to the evaporation system provides a cheap means of saving raw materials and energy. Returning the condensate reduces the expenditures for preliminary water treatment and desalination, shortens the purging time, and diminishes the heat losses. As a rule, the recycled condensate improves the quality of process water, thereby enhancing the service reliability of the boilers. However, the concentration of organic impurities, such as methanol, in the condensate should not exceed 15 mg/l.

Acetaldehyde, methyl acetate, methanol, ethanol, propanol, and butanol (Table 2) have been identified

Table 1. Thermal stability of calcium and copper ferrites in the WGS reaction

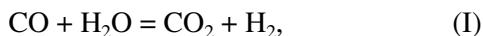
System	Experimental conditions*	Temperature, °C					
		250	280	300	330	360	400
$\text{Ca}_2\text{Fe}_2\text{O}_5$, vibrating mill, 45 min, $T_{\text{calcin}} = 450^\circ\text{C}$	Before overheating	–	78.40	84.93	87.89	88.96	82.53
	After overheating	–	77.38	81.36	85.52	87.49	80.38
		–	98.7	98.5	97.3	98.8	97.4
	Before overheating	70.20	88.48	94.48	94.94	84.15	79.73
	After overheating	68.40	83.90	90.20	91.40	80.20	70.50
		97.7	94.8	95.4	96.3	95.3	88.4

* See Experimental.

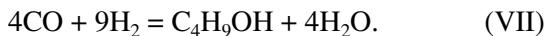
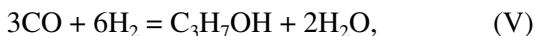
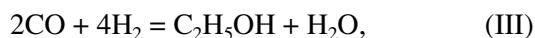
Table 2. By-products in the condensate

System	T, °C	By-product concentrations in the condensate, mg/l						
		acetaldehyde	methanol	methyl acetate	ethanol	propanol	butanol	
CuFe_2O_4 , vibrating mill, 45 min, $T_{\text{calcin}} = 450^\circ\text{C}$	300	0.16	0.31	7.81	0.60	0.35	0.06	9.39
	330	0.19	0.41	9.35	0.65	0.54	0.09	11.23
	360	0.20	0.43	11.60	0.70	0.56	0.10	13.89
$\text{Ca}_2\text{Fe}_2\text{O}_5$, vibrating mill, 30 min, $T_{\text{calcin}} = 450^\circ\text{C}$	300	0.10	1.09	1.80	0.25	—	—	3.24
	330	0.14	2.41	2.10	0.28	—	—	4.93
	360	0.18	2.52	2.38	0.34	—	—	5.42

chromatographically in the WGS product mixture along with the main reaction products (CO_2 and H_2). Therefore, under carbon monoxide conversion conditions, the main reaction,



is accompanied by the following carbon monoxide hydrogenation reactions:



These reactions yield undesired products, contaminating the condensate.

According to chromatographic data, the total by-product concentration in the condensate resulting from CO conversion at 330–360°C on calcium ferrite is 3.2–5.4 mg/l, much lower than is observed with copper ferrite (9.4–13.9 mg/l). In the case of calcium ferrite, methyl acetate and methanol are the most abundant by-products and ethyl acetate and ethanol are minor by-products. The catalytic conversion of CO over copper ferrite yields propanol and butanol along with the above compounds.

Based on the above results, we prepared mixed catalysts and studied their activity in the WGS reaction. A catalyst containing 93% Fe_2O_3 and 7% Cr_2O_3 (specimen 1) was prepared using a commercial technology, and a catalyst containing 90% $\text{Ca}_2\text{Fe}_2\text{O}_5$ and 10% CuFe_2O_4 (specimen 2) was prepared mechanochemically. Catalytic tests have demonstrated that the mixed catalyst consisting of calcium and copper ferrites is far superior to the conventional catalyst. For example, at $T = 300^\circ\text{C}$, the CO conversion is 42.0% for specimen 1 and 81.2% for specimen 2. At 400°C, the CO conversion over these catalysts is 63.7 and 84.1%, respectively.

Thus, our study has demonstrated that copper and calcium ferrites can be mechanochemically synthesized in a medium-energy-intensive apparatus (vibrating mill). The mechanochemical activation of a mixture of anhydrous calcium and iron oxides (2–1.5 : 1 mol/mol) results in amorphous anion-modified calcium ferrite, whose thermolysis above 700°C yields braunmillerite. The mechanochemical activation of a mixture of iron and copper oxides (1 : 1 mol/mol) affords an amorphous hydrocarbonate, which yields the mixed spinel CuFe_2O_4 with a degree of inversion of ~75% upon heat treatment at 400–600°C. The heat treatment of spinels at $T = 400$ –900°C makes their structure more perfect owing to sintering, the removal of anions, and crystal growth, causing a decrease in the CO conversion. Calcium ferrite exhibits a high catalytic activity in the temperature range 320–360°C, in which the CO conversion is 80–88%. Copper ferrite is most active at lower temperatures of 280–320°C, at which the CO conversion is 81–95%. The selectivity of the catalysts in the WGS reaction has been studied. The by-products of this reaction are acetaldehyde, methyl acetate, propanol, butanol, etc. Calcium ferrite is more selective than copper ferrite. The data characterizing the catalytic properties of copper and calcium ferrites may be of use in the development of a new-generation of catalysts for medium-temperature CO conversion.

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