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Obtaining of nanocatalizers for low-temperature conversion of oxide carbon (CuO/ZnO/Al_2O_3) with reduced copper content

The main goal of the work was to reduce the content of copper (in terms of copper (II) oxide) in the composition of the conversion catalyst, and to preserve high catalytic and physico-mechanical characteristics. As an alternative to the known technology for producing oxide catalysts from precursors of metal hydroxocarbonates, there have been selected a manner in which the precursor is copper/zinc hydroxocarbonate. It has been shown that of the many salts obtained from precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with an aurichalcite structure is most effective. The decomposition of these compounds results in the formation of nanosized metal copper clusters, which have a high specific surface area and high activity in the redox reaction of carbon monoxide conversion with water vapor to produce hydrogen. The coprecipitation conditions and the structure of copper/zinc hydroxocarbonate determine the subsequent activity of the oxide catalyst. A technology for producing nanocatalysts for low-temperature conversion of carbon monoxide with a low (up to 20 % — from 54 to 34 wt.%) copper content was proposed and the conditions for obtaining a precursor and catalyst were optimized.

Keywords: Aurichalcite, catalysts, conversion, copper content, low temperature, metal hydroxocarbonates.

Introduction

In recent years, the need for catalysts used in the production of hydrogen and hydrogen-containing gases by the method of hydrocarbon conversion has increased.

Existing methods for the preparation of copper-containing catalysts are based on the use of deposition processes and ammonia-carbonate technology. These preparation methods of copper-containing low-temperature catalysts are characterized by a complex, multi-stage and expensive main production scheme, which necessitates the improvement of existing technologies of catalysts' producing for the cost of low-temperature catalysts.

In the course of this work, a significant amount of sources on this issue was analyzed [1–3]. It has been established that the main condition for solving this problem is the formation of a certain structure of the corresponding metal hydroxides obtained by decomposition of ammonia-carbonate complexes of copper and zinc, followed by separation of the precipitate and heat treatment of the mass pressing.

As shown in [3], increased catalyst activity was achieved by chemical interaction of the catalyst components at an early stage of preparation, as well as by decomposition of ammonia-carbonate complexes. The completeness of the interaction was achieved by the processes in the kinetic mode (i.e., with intensive mixing of 150–500 rpm) at the solid — liquid interface.

Under these conditions, the aurichalcite phase $(CuZn)_5(CO_3)_2(OH)_6$ was detected in the obtained precursor. According to the differential thermal and x-ray phase analysis, the decomposition of the obtained precursor is accompanied by the formation of highly dispersed oxides of copper and zinc (6–7 nm and 8–10 nm, respectively).

It is shown that of the many salts obtained from precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with an aurichalcite structure, which has a high specific surface area and activity, is the most effective.

Based on this, the main attention is paid to the conditions for the formation of copper/zinc hydroxycarbonate with the structure of aurichalcite as a precursor of the oxide solid catalyst solution, as well as the conditions for the formation of the oxide catalyst itself.

In this regard, the main goal of the work is to improve the existing technologies by optimizing the conditions for their production and cheapening low-temperature catalysts by reducing the copper component in the catalyst, by creating a nanostructured morphology of a solid solution of copper/zinc oxides while maintaining its high catalytic and physicochemical characteristics.

Experimental

The copper/zinc hydroxocarbonate with an aurichalcite structure was prepared by precipitation from copper (II) nitrates and zinc, and sodium bicarbonate. It is shown that of copper/zinc hydroxocarbonate with the aurichalcite structure is formed both at a Cu:Zn ratio of 70:30 mol.% And at a ratio of 30:70 mol.%.

The wet weight of copper / zinc hydroxocarbonate after filtering the suspension and thoroughly washing from the concomitant salt of sodium nitrate was 271.00 g (of which 68.34 % moisture). The mass of dried (at 100 ºC, for 2.5 days, and then at 120–125 ºC, for 1 day) of copper/zinc hydroxocarbonate was 85.81 g (sample III.3).

Three compositions of copper/zinc hydroxocarbonate were obtained, which differ in color. The pronounced light blue color is expressed for the sample — II.2; bluish-green for the sample — I.1 and dark blue — for the sample of copper/zinc hydroxocarbonate No. III.3, and during the drying process at a temperature of 100 ºC it darkens, which indicates that a certain proportion of malachite is formed, decaying at temperatures of 80–100 ºC. It was also noted that the sample of copper/zinc hydroxocarbonate — III.3 is characterized by a rather large size of well crystallized particles of a flat shape, in comparison with the two previous samples of copper/zinc hydroxocarbonate. The color of samples I.1 and II.2 after drying in the temperature range of 100–110 ºC is stable.

Results and Discussion

This study examined the industrial conditions for the preparation of the catalyst used in the process of low-temperature conversion of carbon monoxide with water vapor: CuO — 54 %, Cr_2O_3 — 24 %, ZnO — 11 %, Al_2O_3 — 19.5 % by weight.

The main role of the catalyst is the conversion of CO to CO_2 in the presence of water vapor at 270 ºC with the formation of hydrogen for the synthesis of ammonia.

We present the probable redox reactions of CO conversion on a copper-zinc-chromium catalyst:

$$CO + H_2O \rightarrow CO + H_2 \text{ (conversion process);}$$
$$Cu + H_2O \rightarrow CuO + H_2 \text{ (copper oxidation);}$$
$$CuO + CO \rightarrow CO_2 + Cu \text{ (copper recovery).}$$

It has been shown that under industrial conditions occurs a formation of a catalyst with a zinc-malachite structure, which has low thermal stability.

In this regard, the main solution to the problem is to search for conditions for the formation of a specific structure of catalyst precursors — copper/zinc hydroxocarbonate; obtained by co-precipitation of nitrates of the corresponding metals in a precipitating medium, the preparation of which is shown in Figure 1.

The mixture contains various amorphous compounds, the structure of which depends on the dosage rate, the concentration of the base or precipitant. Depending on the change in conditions, precursors of various structures are formed. The reaction of the formation of hydrozincite (E) or aurichalcite (D) realizes by substitution from $Na_2Zn_3(CO_3)_4$.

Figure 1. Formation of precursors and their structure

The catalytic activity of oxide catalysts was studied with varying the content of components in it (Tables 1 and 2). It has been shown that both the alumina content and the mass ratio of copper (II) oxide to zinc oxide (obtained under various conditions for the synthesis of copper/zinc hydroxocarbonate), as well as the total fraction of the latter in the composition of the catalyst, determine its properties (Table 1).

Table 1

Activity, specific surface area and chemical composition of four-component oxide catalysts for low temperature conversion CO/H_2O

Catalyst	A_{mean}, %	S_{unit}, m^2/g	w[CuO], mass.%	w[ZnO], mass.%	$w[Cr_2O_3]$, mass.%	$w[Al_2O_3]$, mass.%
Normative (Technical specifications of Rep. of Uzb. 6.3–57–95)	80 (no less)	–	54.0	11.0	14.0	19.5
$CuO/ZnO/Al_2O_3$	84.00	43.16	42.7	44.5	–	8.8
	91.00	68.50	41.3	39.2	–	17.8
	86.31	105.38	35.0	35.4	–	27.4
	76.54	123.93	30.6	29.7	–	38.0

As can be seen from the Table 1, the alumina content, as well as the mass ratio of copper (II) oxide to zinc oxide (obtained under various conditions for the synthesis of copper/zinc hydroxocarbonate), as well as the total fraction of the latter in the composition of the catalyst, determine its properties.

Table 2

The activity, specific surface area and chemical composition of three-component oxide catalysts for low temperature conversion CO/H_2O

Catalyst	w[CuO], mass.%	w[ZnO], mass.%	$w[Al_2O_3]$, mass.%	S_{unit}, m^2/g	$P_{unit}\times10^{-2}$, cm^3/g	A_{mean}, %
$CuO/ZnO/Al_2O_3$	36.80	58.60	2.80	147.89	6.40	92.22
	34.20	56.10	8.80	145.15	6.30	81.30
	31.70	49.90	17.10	160.38	6.90	76.00

As shown in the Table 2, copper/zinc hydroxocarbonate with an aurichalcite structure is formed both at a Cu:Zn ratio of 70:30 mol.% and at a ratio of 30:70 mol.%. It is shown that copper/zinc hydroxocarbonate with the aurichalcite structure was obtained by precipitation from copper (II) nitrates and zinc, and sodium bicarbonate.

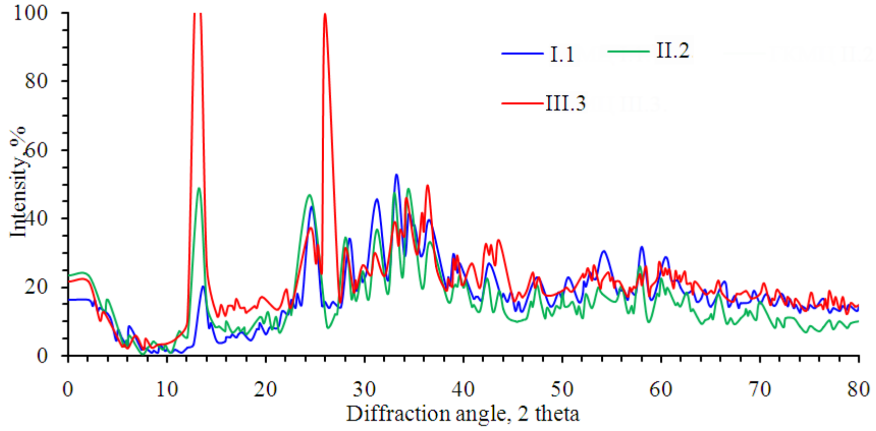

Figure 2. X-ray diffraction patterns of hydroxocarbonate samples copper/zinc obtained in three syntheses

The diffraction patterns of three samples of copper/zinc hydroxocarbonate, similar to the structure of aurichalcite are depicted in the Figure 2. According to the presented curves, three samples of copper/zinc hydroxocarbonate-HC Cu/Zn are characterized by the intensity of reflexes. The position of reflexes in all three samples remains almost constant.

In the spectrum of sample No. III.3, an intense reflection is observed in the range of 27º, the prevalence of the individual phase of copper (II) oxide in which, apparently, affects the structure and properties of the catalyst as a whole.

It has been revealed that the content of composing catalysts, the main part occupied a solution based on a zinc oxide lattice with copper (II) oxide clusters embedded in it during calcination of copper/zinc hydroxocarbonate with an aurichalcite structure.

All three catalysts obtained by varying the ratio Cu:Zn from copper/zinc hydroxocarbonate with the structure of aurichalcite have different properties, because a continuous series of solid solutions of copper/zinc hydroxocarbonate with the structure of aurichalcite is formed.

It has been noted that for an oxide low-temperature catalyst, the ratio Cu:Zn = 30:70 mol% is optimal. Violation of stoichiometry in the composition of copper/zinc hydroxocarbonate inevitably affects the structure and properties of the oxide catalyst. The coprecipitation conditions and the structure of copper/zinc hydroxocarbonate determine the subsequent activity of the oxide catalyst.

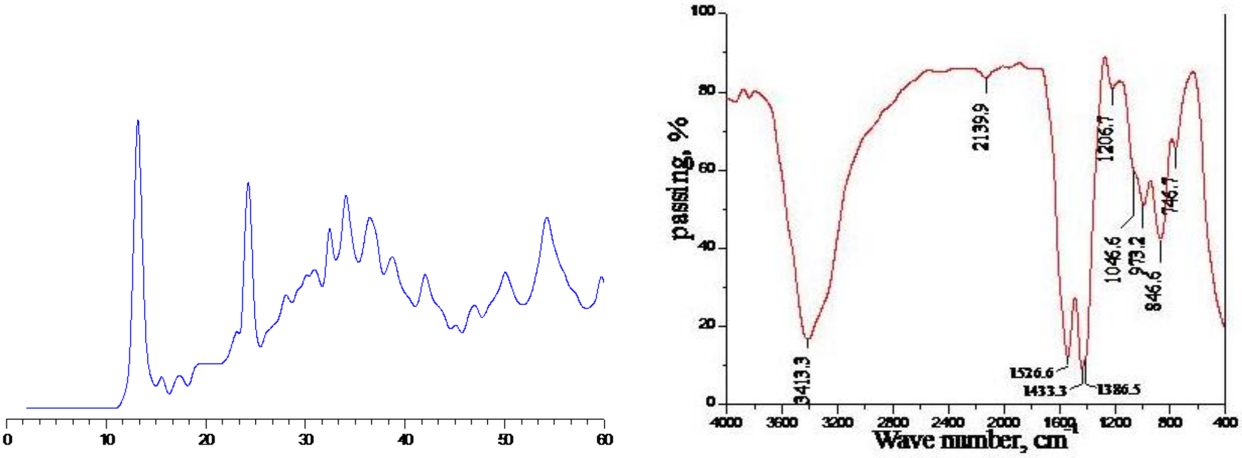

Figure 3. X-ray diffraction pattern and IR-spectrum of copper/zinc hydroxocarbonate
{aurichalcite $(Cu_{5-5x}Zn_{5x})(CO_3)_2(OH)_6$}

During the calcination of copper/zinc hydroxocarbonate with the aurichalcite structure $(Zn_xCu_{1-x})_5(CO_3)_2(OH)_6$ (Fig. 3), a solid solution of copper/zinc oxides is formed with a maximum distortion of the crystal lattice of copper (II) oxide. After preliminary activation of the catalyst (hydrogen reduction), there were formed the clusters of metallic copper with a high active surface area.

The aurichalcite spectra are characterized by: strong absorption vibrations at 1415 and 1340 cm^{-1} of nitrate groups in gerhardit; georgite is characterized by weak absorption vibrations below 1350 cm^{-1}, except for carbonate groups at 838 cm^{-1}; hydroxyl groups at 3407, 3317 cm^{-1} for malachite. Also, a slight difference is observed in the spectra of hydrozincite and aurichalcite, which makes impossible to distinguish which was monophase.

DSC can also be used as a method of identifying a mixture of phases and allows to determine the degree of homogeneity of zinc/copper. It is important that hydrozincite and aurichalcite have different destruction maxima of 241 ºC and 325 ºC, respectively, which makes it quite easy to identify hydrozincite present in the aurichalcite sample or vice versa. Thus, the optimal conditions for obtaining a catalyst with aurichalcite structure are established.

The formation of catalyst precursors — hydroxocarbonate salt of copper and zinc with the structure of aurichalcite

Under the action of mechanochemical activation of metals in a gaseous environment, copper and zinc ammonia are formed, which subsequently form a double hydroxocarbonate salt of copper and zinc with the structure of aurichalcite in the next stage of steam treatment:

$$10Cu(NH_3)_2CO_3 + 10Zn(NH_3)CO_3 + 6H_2O \rightarrow 2(Cu, Zn)_5(CO_3)_2(OH)_6 + 30NH_3\uparrow + 16CO_2\uparrow + 5O_2\uparrow$$

The decomposition of such a precursor allows one to obtain copper and zinc oxides, the crystal lattices of which are distorted as much as possible, while after hydrogen reduction of such a solid solution, nanosized metal copper clusters are formed that have a high specific surface and high activity in the redox reaction of carbon monoxide conversion with water steam to produce hydrogen.

This technology is of significant interest as catalysts in the production of hydrogen and hydrogen-containing gases by the conversion of hydrocarbons, in the production of ammonia, methyl alcohol, etc.

Conclusions

It was shown that of the many salts obtained from the precursors — metal hydroxocarbonates, copper/zinc double hydroxocarbonate with the aurichalcite structure is the most effective as a catalyst for the low-temperature conversion of carbon monoxide with water vapor.

The technology of producing nanocatalysts of low-temperature conversion of carbon monoxide with the aurichalcite structure was proposed, and the conditions for producing a precursor and catalyst with a reduced copper content of up to 20 % (from 54 to 34 wt.%) were optimized.

The conditions for obtaining a solid solution of copper/zinc oxides with an aurichalcite structure with a maximum distortion of the crystal lattice of copper oxide and the formation of nanoscale clusters of metallic copper with a high specific surface and activity in the redox reaction of carbon monoxide conversion with water vapor were determined.

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Мыс құрамы төмендеген ($CuO/ZnO/Al_2O_3$) көміртегі оксидінің төмен температуралы конверсиясында нанокатализаторларды алу

Жұмыстың негізгі мақсаты конверсиялық катализатор құрамындағы мыс құрамын төмендету ((II) мыс оксидіне қайта есептегенде) және жоғары каталитикалық және физика-механикалық сипаттамаларды сақтау болды. Металдардың гидроксокарбонаттарынан оксидті катализаторларды алудың белгілі технологиясына балама ретінде мыс/мырыш гидроксокарбонаты болып табылатын әдіс таңдалды. Түзілуден алынған көптеген тұздардың — метал гидроксокарбонаттары, аурихальцит құрылымы бар мыс/мырыш қос гидроксокарбонаты ең тиімді болып табылады, олардың ыдырауынан кейін металл мен мыстың наноөлшемді кластерлері пайда болады,үстіңгі беті бар және көміртегі оксидінің су буында сутекке айналу конверсиясының тотығу — қалпына келтіру реакциясында белсенділікке ие. Мыс/мырыш гидроксокарбонатының тұндыру жағдайлары мен құрылымы, оксидті катализатордың келесі белсенділігін анықтайды. Төмен температуралы конверсиясының нанокатализаторын алу технологиясы ұсынылды (20 %-ға дейін 54-тен, 34-ші массаға дейін) және прекурсор мен катализаторды алу шарттары оңтайландырылған.

Кілт сөздер: төмен температуралы, катализаторлар, металдардың гидрооксокарбонаттары, көміртегі оксиді конверсиясы, аурихальцит, мыс құрамы.

М.М. Усманова, В.В. Долгов, Н.Р. Ашуров, С.Ш. Рашидова, Т. Дадаходжаев

Получение нанокатализаторов низкотемпературной конверсии оксида углерода ($CuO/ZnO/Al_2O_3$) с пониженным содержанием меди

Основной целью работы ставилось снижение содержания меди (в пересчете на оксид меди (II)) в составе катализатора конверсии и сохранение высоких каталитических и физико-механические характеристик. В качестве альтернативы известной технологии получения оксидных катализаторов из предшественников гидроксокарбонатов металлов был выбран способ, в котором предшественник представлял собой гидроксокарбонат меди/цинка. Показано, что из многих солей, полученных из предшественников — гидроксокарбонатов металлов, двойной гидроксокарбонат меди/цинка со структурой аурихальцита является наиболее эффективным, после разложения которого образуются наноразмерные кластеры металла и меди, которые имеют высокую удельную поверхность и активность в окислительно-восстановительной реакции конверсии оксида углерода водяным паром с образованием водорода. Показано, что условия соосаждения и структура гидроксокарбоната меди/цинка определяют последующую активность оксидного катализатора. Предложена технология получения нанокатализаторов низкотемпературной конверсии оксида углерода с пониженным (до 20 % — с 54 до 34 масс.%) содержанием меди и оптимизированы условия получения прекурсора и катализатора.

Ключевые слова: низкотемпературный, катализатор, гидрооксокарбонаты металлов, конверсия оксида углерода, аурихальцит, содержание меди.

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