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Influence of the impregnation media on the catalytic properties of carbon-supported copper catalysts in NO reduction with CO

The role of organic media of impregnation on the catalytic activity of carbon-supported copper catalysts in NO reduction with CO was studied. The best activity possesses a catalyst prepared from methanol media. It was established a uniform disposition of the active phase on the surface and in the bulk of this catalyst. Large organic solvates hinder the deep penetration of the precursor molecules in the pores of the support and lead to formation of copper aggregates on the surface. The reduction of NO with CO on the catalyst prepared in methanolic media is assisted by the carbon support as an additional reducing agent.

Key words: carbon, copper catalyst, NO reduction with CO.

Introduction

The interest in active carbon's study as a support of catalysts was raised by the combination of different properties, which are expected to facilitate the decomposition of NO, namely a large specific surface area, highly developed micro (micro-meso) porosity and greater opportunities for modification of the surface by incorporation of heteroatoms (N, O) [1]. Transition metals (including Co, Ni, Cu, etc.) are widely used as active components for deposition on active carbon. Their choice is related to the fact that the oxide phases obtained by thermal decomposition exhibit high activity for catalytic reduction of NO [2].

Recently, it was shown [3, 4], that the activity of the supported catalysts is influenced not only by the specific surface area, pore texture parameters and the chemical nature of the support's surface but the type (aqueous or non-aqueous) of the solution of the precursor. It was found that the deposition of the active phase from aqueous solutions strongly depends on the chemical nature of the surface of the active carbons.

The influence of the different impregnation media and the chemical nature of the surface in preparation of carbon-supported catalysts on their catalytic properties are not elucidated completely. It was established for non-aqueous solutions that: 1) the electrolytic dissociation does not proceed or proceeds weakly via different mechanisms than in aqueous media; 2) the hydrated shell is replaced by solvated with larger size; 3) the role of IEP of the surface is minimized, i.e. of the surface oxygen groups; 4) the wettability of the surface is improved and the access to the various types of pores is facilitated. This assumes that the preparation of catalysts by impregnation from organic media leads to obtaining of highly dispersed active phase and its uniform distribution in the pore texture of the carbon support, ignoring the role of the surface oxygen and other heteroatom groups, minimal blocking and access of the pores.

Experimental/methodology

The active carbon support was prepared by pyrolysis of charcoal from Chukurovo [5]. Copper-active phase was deposited from solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) in organic media on the carbon. The solutions of Cu ~ 1.5 mass. % were prepared in methanol, dimethylformamide and dioxane. The deposition is made by incipient wetness technique- four-fold with a definite (concerning the total pore volume of the sample) vol-

ume of the solution. The samples were dried in a vacuum-drier for 2 h at 343 K. The thermal treatment was in vacuum for 2 h at 573 K.

The samples are denoted as: $\text{Cu}_{\text{Me}}/\text{AC}$ — prepared by methanolic solution; $\text{Cu}_{\text{DMF}}/\text{AC}$ — prepared by dimethylformamide solution; $\text{Cu}_{\text{DIO}}/\text{AC}$ — prepared by dioxane solution.

The characterization of the specific surface area and the porous texture of the samples under investigation were carried out by low-temperature adsorption of nitrogen (77.4 K) using a conventional volumetric apparatus with a outgassing of 453 K and up to a residual pressure $< 1.10^{-4}$ Torr.

The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following parameters. The specific surface areas (A_{BET}) were determined on the basis of the BET equation, the total pore volume (V_t) was estimated in accordance with the rule of Gurvich at a relative pressure 0.95. The volume of the micropores (V_{MI}) was evaluated in accordance with $n(C_{\text{BET}})$ -plots of Lecloux [6]. The volume of the mesopores (V_{MES}) was determined as the difference between V_t and V_{MI} . The average pore radius (r_p) was evaluated as the ratio between the doubled V_t and A_{BET} parameters of the samples assuming a cylindrical pore model [7]. The half-width for the micropore size distribution curve maximum (X_0) of the slit shaped pore model were determined according to the Simplified equation [8].

The chemical composition was determined by atomic absorption on SP-90B «Pye-Unicam».

X-ray diffraction (XRD) data were obtained using a Bruker D8 Advance diffractometer with $\text{Cu-K}\alpha$ radiation and SolX detector.

The X-ray photoelectron spectroscopy (XPS) measurements were done in the UHV chamber of ESCALAB-Mk II (VG Scientific) electron spectrometer with a $\text{Al K}\alpha_{1,2}$ radiation ($h\nu = 1486.6$ eV).

Scanning Electron Micrographs (SEM) were taken with a JSM-5510 JEOL scanning electron microscope in order to characterize the morphological structure of the used materials and the dispersion state. Before analysis, samples were metallized with gold.

The copper content were determined by atomic absorption using Pye Unicam SP 90B spectrometer.

The catalytic experiments were carried out in catalytic flow apparatus in an isothermal flow reactor (quartz tube, i.d. 8 mm). NO reduction with CO was investigated in the temperature range 298–573 K. The catalytic tests were performed with a gas mixture: $\text{NO} + \text{CO} + \text{Ar}$, containing 1200 ppm NO and 1200 ppm CO, gas hourly space velocity (GHSV) was $26\,000\text{ h}^{-1}$. The outlet concentrations of NO, CO and CO_2 were controlled by infrared gas analyzers «UNOR 5-Maihak» (Germany). N_2O was measured spectrophotometrically and a thermal converter was used for the total analysis of NO_x ($\text{NO} + \text{NO}_2$). The concentrations of NO, NO_x ($\text{NO} + \text{NO}_2$), N_2O , CO, and CO_2 were continuously measured. Based on the experiment, we can calculate the nitrogen balance ($[\text{N}_2] = \text{inlet} [\text{NO}] - \text{outlet} [\text{NO}] - [\text{N}_2\text{O}] - [\text{NO}_2]$).

Results and discussion

Figure 1 represents in a normalized way the adsorption isotherms of the initial activated carbon and of the supported catalysts whereas the main texture parameters calculated on their base are shown in Table 1.

Table 1

Main texture parameters and Cu content of the AC and of impregnated samples

Sample	$A_{\text{BET}}, \text{m}^2 \cdot \text{g}^{-1}$	$V_t, \text{ml} \cdot \text{g}^{-1}$	$V_{\text{MI}}, \text{ml} \cdot \text{g}^{-1}$	$V_{\text{MES}}, \text{ml} \cdot \text{g}^{-1}$	X_0, nm	r_p, nm	Cu content, mass %
AC	387	0.35	0.13	0.22	0.71	1.8	-
$\text{Cu}_{\text{Me}}/\text{AC}$	362	0.32	0.13	0.19	0.96	1.8	3.9
$\text{Cu}_{\text{DMF}}/\text{AC}$	295	0.26	0.10	0.16	0.88	1.8	3.3
$\text{Cu}_{\text{DIO}}/\text{AC}$	317	0.30	0.10	0.20	0.91	1.9	3.2

The comparison of normalized isotherms of Cu catalysts and that of AC as well between themselves reveals the influence of the nature of media of the precursor solution on the location of Cu phase inside the initial porous carbon (AC) texture matrix.

Fig. 1 leaves the impression of affinity between the isotherms of the samples AC, $\text{Cu}_{\text{Me}}/\text{AC}$ and $\text{Cu}_{\text{DIO}}/\text{AC}$ within the interval (P/P_0 : 0.6–0.85) characteristic of capillary condensation, while there is practically merging of the isotherms of AC and $\text{Cu}_{\text{DMF}}/\text{AC}$ within the interval P/P_0 : 0.18–0.23 as well as $\text{Cu}_{\text{Me}}/\text{AC}$ and $\text{Cu}_{\text{DIO}}/\text{AC}$ within the interval P/P_0 : 0.47–0.85.

The observed affinity has been explained based on the presence of regions of similar (or discretely changing) pore's size, with close content of Cu phase, as well that the sample isotherm affinity with that of

initial AC testifies probability Cu phase to be more uniformly distributed inside the corresponded porous texture regions.

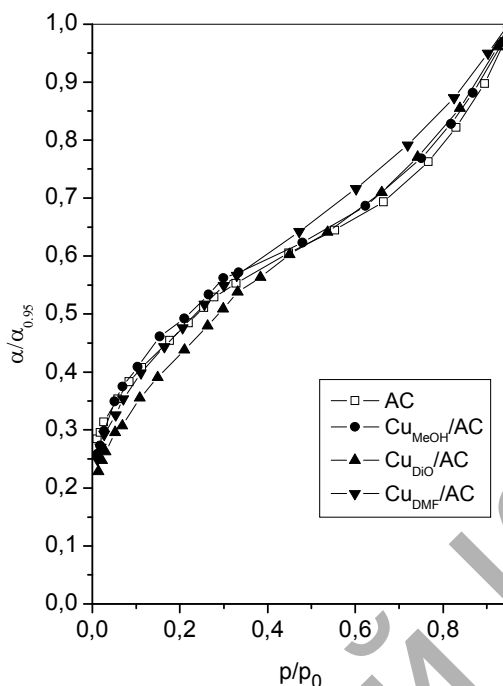


Figure 1. Normalized nitrogen isotherms (77.4 K) of the initial activated carbon and of the supported Cu catalysts

On the other hand the coincidence of the isotherms of the samples AC and $\text{Cu}_{\text{DMF}}/\text{AC}$ within the interval P/P_0 : 0.18–0.23 as well as $\text{Cu}_{\text{Me}}/\text{AC}$ and $\text{Cu}_{\text{DiO}}/\text{AC}$ within the interval P/P_0 : 0.47–0.85 indicates the fact that in dependence of the type of organic media Cu phase does not influence substantially the all pore size ranges of porous texture (including supermicro- and mesopores).

The elemental analysis of the active carbon shows that it is characterized by high carbon content (91.8 mass. %). The sulphur content is 0.66 mass. %, but it does not affect the copper phase in this preparation procedure. It is established that on the active carbon acidic surface oxygen groups prevail.

The activated carbon support is characterized by relatively low specific surface area, small micropore volume and better developed mesoporous (i.e. transport) porous texture, where the ratio $V_{\text{MES}}/V_{\text{MI}} \approx 1.7$.

AC is assigned to the type of meso- microporous activated carbons, appropriate for catalytic phase support.

From the value of parameter X_0 (≈ 0.71 nm) is obvious that according to the slit shaped microporous model the main part of micropores belongs to the typical (ultra) microporous and/or to fine supermicropores. On the other hand the average mesopore radius ($r_p \approx 1.8$ nm) is characteristic of lignite base activated carbons prepared by steam activation with not too high burn off.

The texture parameters of the supported copper catalysts and their Cu phase content are shown in Table 1.

It may be noted from the Table 1 that the less is the diminution in the A_{BET} for the sample $\text{Cu}_{\text{Me}}/\text{AC}$ in comparison to that of the initial supports despite of its high copper content. The decreasing of V_{MES} towards the same parameter of AC (~ 14 %) as well considerable increasing of X_0 (up to 0.96 nm) (Table 1) demonstrates that Cu phase ($\text{Cu}_{\text{Me}}/\text{AC}$) is located first of all inside the range of fine mesopores.

As mentioned above the affinity between the isotherms of the samples AC and $\text{Cu}_{\text{Me}}/\text{AC}$ within the interval P/P_0 : 0.47–0.85 (Fig. 1) testifies for the uniform distribution inside the mesopore part of the porous texture of $\text{Cu}_{\text{Me}}/\text{AC}$ sample.

With the rest catalysts a diminution of A_{BET} is relevant to the content of the copper active phase deposited. The factors that affect the disposition of the active phase — wetting the surface of the carbon matrix and the sorption of the solvents, along with the copper ions are different for the used types of copper solutions. They influence the disposition of the copper active phase in the porous texture. The diminution in the

specific surface areas of $\text{Cu}_{\text{DMF}}/\text{AC}$ and $\text{Cu}_{\text{DiO}}/\text{AC}$ compared to the initial carbon with $\sim 24\%$ and 18% could not be explained with fine pores filling only, but with blocking admission pore entrances in particular by the copper phase and giving rise to a bottle neck effect [9] inside the pores in that case.

Because of worse wetting of the carbon surface in the case of dioxane solution of the precursor Cu aggregates are formed to a considerably extent as compare to methanol and dimethylformamide (Fig. 2b) and additional pore entrance blocking is observed in this case. An important alternation of the porous texture type of $\text{Cu}_{\text{DiO}}/\text{AC}$ (Fig. 1) observes as compare to other samples.

This is also evident from the micrographs taken by the transmission electron microscopy (TEM) presented in Fig. 2. The comparison between the images (the contrast in the images representative of the type of located Cu phase) confirms the conclusions made from the physical adsorption studies. Sample $\text{Cu}_{\text{DiO}}/\text{AC}$ differs from $\text{Cu}_{\text{Me}}/\text{AC}$ and $\text{Cu}_{\text{DMF}}/\text{AC}$ by its higher Cu phase content onto the external surface. The latter is connected with the forming of aggregates to a considerably extent as compare to other two samples.

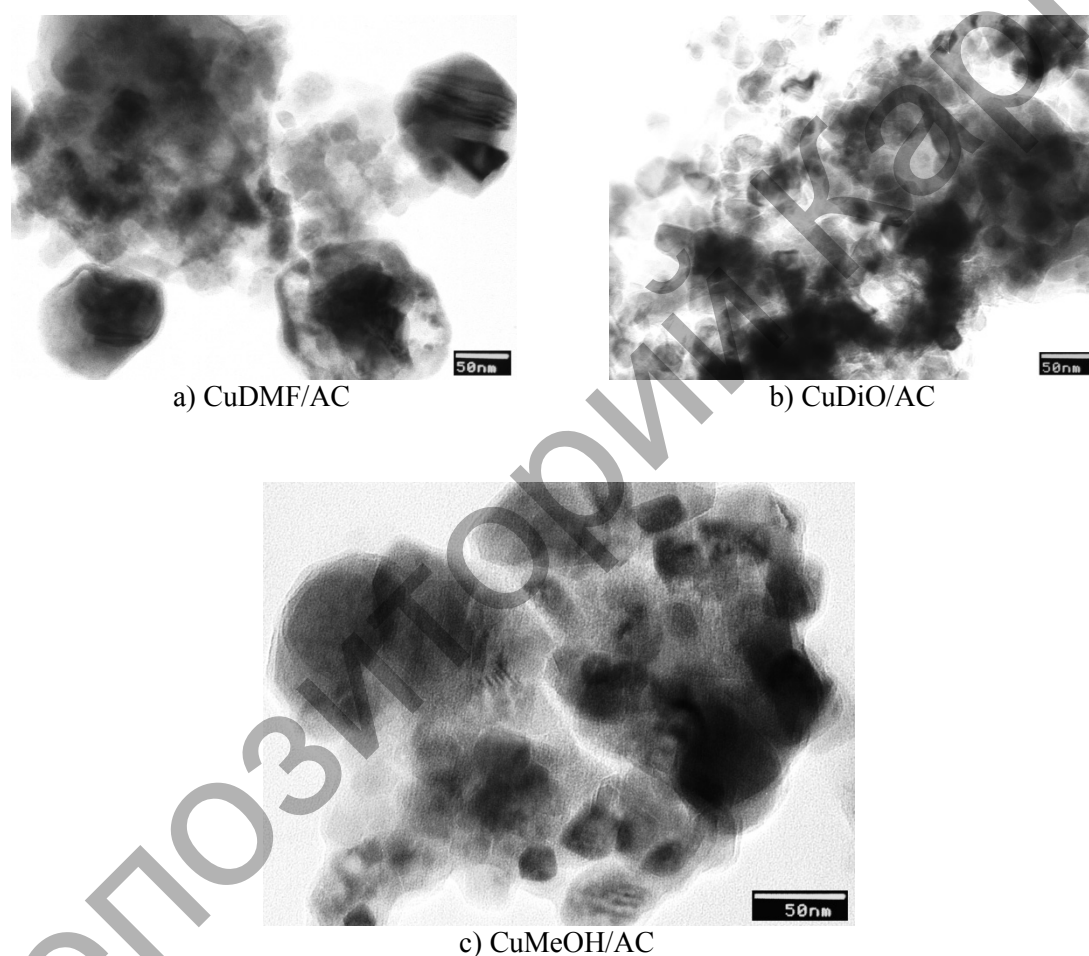


Figure 2. TEM micrograph images

The composition of the active phase and its location on the surface of the support are essential for the elucidation of the activity of the every catalyst in the reaction of NO reduction with CO. Table 2 presents the XRD and XPS data on the studied catalysts.

Irrespective to the complex composition of the active phases on the supported catalysts, XRD and XPS data reveal the existence of CuO , $\text{Cu}(\text{OH})_2$ and $[\text{Cu}(\text{NO}_3)_2]$. $\text{Cu}(\text{OH})_2$ on $\text{Cu}_{\text{Me}}/\text{AC}$. For the other two samples $\text{Cu}_{\text{DMF}}/\text{AC}$ and $\text{Cu}_{\text{DiO}}/\text{AC}$, according to data from XPS only CuO can be established, although there are some deviations from the binding energies characteristic of CuO , which means the composition of the phase in any case has a complex character.

According to XRD CuO is observed only for the samples, prepared by methanolic solution. For all rest samples, due to the high dispersity of the copper phase probably, no copper phase is detected.

The methanolic solution is rapidly evaporated thus resulting in formation of copper oxide aggregates and registered by XRD. XPS data refer to CuO [10] for all samples, but some deviations from the binding energies characteristic for Cu^{2+} in CuO do not exclude additional Cu^+ or even Cu^0 availability. The XPS data show that the copper phase is mainly located on the surfaces of the both supports, that favours the catalytic

Table 2

XRD and XPS data

Sample	XRD	Binding energy, EV		Cu_s , %	Cu_b , %	Cu_s/Cu_b
		$\text{Cu}2p_{3/2}$	$\text{O}1s$			
$\text{Cu}_{\text{Me}}/\text{AC}$	CuO	934.6	531.8 533.7	4.3	3.9	1.1
$\text{Cu}_{\text{DMF}}/\text{AC}$	–	933.8 934.7	529.7 533.3	5.3	3.3	1.6
$\text{Cu}_{\text{DiO}}/\text{AC}$	–	934.1	530.1 531.7	4.2	3.2	1.3

The ratios $\text{Cu}_{\text{surf}}/\text{Cu}_{\text{bulk}}$ show that for $\text{Cu}_{\text{DiO}}/\text{AC}$ and $\text{Cu}_{\text{DMF}}/\text{AC}$ they are more than 1, evidencing the disposition of the copper phase rather on the surface, while the copper phase is practically uniformly distributed on the surface and in the bulk of $\text{Cu}_{\text{Me}}/\text{AC}$.

Catalytic activity of different catalysts as a function of temperatures in NO reduction with CO is shown in Fig. 3. The catalytic performance over all catalysts monotonically increase with temperature, but the discrepancy of reactivity for the catalysts prepared by different media is obvious. All catalysts prepared by different solution media possess higher activity in the temperature interval investigated (Fig. 3). The samples could be arranged by the activity as $\text{Cu}_{\text{DiO}}/\text{AC} < \text{Cu}_{\text{DMF}}/\text{AC} < \text{Cu}_{\text{Me}}/\text{AC}$.

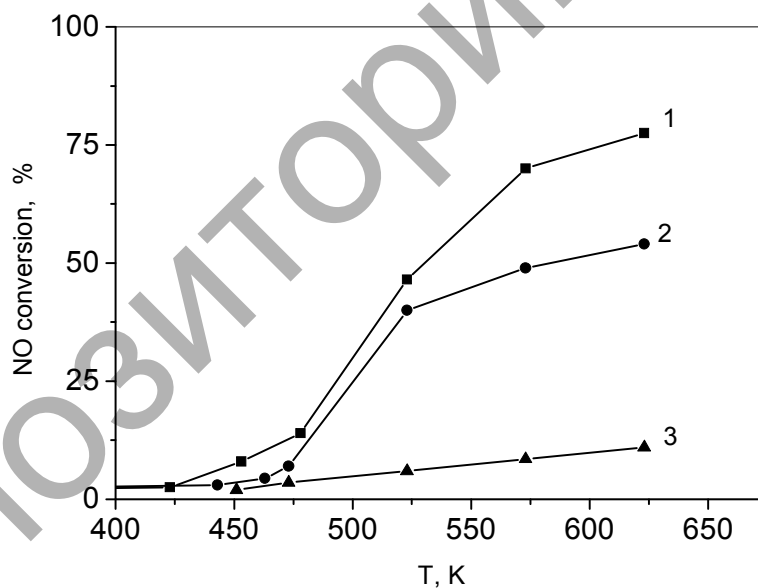


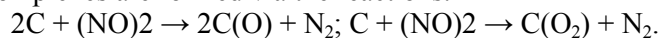
Figure 3. Catalytic reduction of NO with CO on carbon supported copper catalysts prepared from 1) methanol, 2) DMF and 3) dioxane media

$\text{Cu}_{\text{Me}}/\text{AC}$ is the only catalyst active below 473 K and possesses high nitrogen selectivity.

It is interesting to notice that N_2 formation for the samples (at temperatures above 473–523 K) is related to less CO consumed than needed for the stoichiometry, more pronounced with HS(HSm)/CuAm and HS(HSm)/CuDiO. This confirms the presumption that NO reduction in this temperature interval is assisted by the free (unbound active carbon) of the both unmodified and modified hybrid supports. In this case, although rather formally, the results can be explained by the mechanism for NO reduction proposed by Teng and Suuberg [11, 12]. According to this mechanism (for the temperature range 323–523 K) two routes for the process are possible.

The first is a reversible hemi-sorption, accompanied by formation of nitric-oxide surface complexes via the reaction: $C + NO \leftrightarrow C(NO)$, where $C(NO)$ is an intermediate stage in the process leading to the decomposition of NO .

The second is irreversible adsorption with formation of oxygen complexes $C(O)$ and $C(O_2)$ and nitrogen release. $C(O)$ and $C(O_2)$ complexes are formed via the reactions:



The formation of $C(O)$ and $C(O_2)$ is associated with intermediate formation of NO -dimers in the finest pores of the carbon material [13]. In our case the role of CO (at temperatures ≥ 473 – 523 K) will be limited to the regeneration of active centers on carbon fragments, without taking direct part in the reaction.

Rather lower activity in the studied reaction NO with CO for Cu_{DMF}/AC and Cu_{DiO}/AC compared to Cu_Me/AC and stoichiometric NO and CO consumptions show that in these cases the role of the carbon support in the reaction is neglected. It could be suggested that in the case of uniform distribution of the active phase (by methanolic solution in our case) on the surface and in the bulk the conditions are favorable for the participation of the carbon atoms as an additional reducing agent along with CO .

Conclusions

The role of the organic media of impregnation on the catalytic activity in NO with CO reduction of carbon-supported copper catalysts was studied. The best activity possesses catalyst prepared from methanolic media. It was established uniform disposition of the active phase on the surface and in the bulk of this catalyst. Large organic solvates hinder the deep penetration of the precursor molecules in the pores of the support and leads to formation of copper aggregates on the surface. The reduction of NO with CO on the catalyst prepared in methanolic media the carbon support assisted the reaction as additional reducing agent.

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NO-ны көміртек монооксидімен тотықсыздандыру процесінде белсендірілген көміртек негізді мыс катализаторларының каталитикалық қасиеттеріне импрегнационды ортаның ықпалы

Көміртек монооксидімен тотықсыздандыру процесінде белсендірілген көміртек негізді мыс катализаторларының каталитикалық қасиеттеріне әр түрлі органикалық ортаның ықпалы зерттелді. Жоғары белсенділік қасиетті мыс нитратының метанолды ерітіндісімен сіңдірілген катализатор көрсетті. Катализатордың бетінде және көлемінде белсенді фазаның біртекті таралуы байқалды. Тәжірибе жүзінде үлкен органикалық сольваттар мыс нитратының енуіне қарсылық етіп, мыс агрегатының түзілуіне әкелетіні анықталды. Көміртекті тасымалдағыш мыс нитратының метанолды ерітіндісінде дайындалған катализатордың әсерін көміртек монооксидімен NO тотықсыздандыруда қосымша тотықсыздандырғыш агент ретінде арттырды.

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Влияние типа импрегнационной среды на каталитические свойства медных катализаторов на основе активированного угля в процессе восстановления NO монооксидом углерода

Исследована роль различных органических сред пропиточных растворов при получении медных катализаторов на основе активированного угля на их активность в процессе восстановления NO монооксидом углерода. Отмечено, что самая высокая активность имеется у катализатора, приготовленного пропиткой метаноловым раствором нитрата меди. У катализатора наблюдается самое однородное распределение активной фазы на внешней поверхности и в объеме пор. Опытным путём установлено, что большие органические сольваты препятствуют проникновению молекул нитрата меди в тонкие поры носителя и помогают формированию медных агрегатов на его поверхности. Определено, что углеродный носитель способствует действию катализатора, приготовленного в метаноловом растворе нитрата меди, как дополнительный восстанавливающий агент при восстановлении NO монооксидом углерода.