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Autoreduction of Copper on Silica and Iron-Functionalized Silica Nanoparticles with Interparticle Mesoporosity

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Copper-supported catalysts are of industrial importance in many catalytic processes. Mesoporous silica materials are of particular interest as green heterogeneous catalyst supports. In the present study we demonstrate the nature and reduction properties of copper oxide species, which are influenced by the peculiarity of the silica nanoparticles with interparticle mesoporosity (KIL family) and the presence of a second metal (iron) in the silica matrix. The copper-containing KIL-2 and FeKIL-2 samples are prepared by incipient wetness impregnation. The reduction of copper oxide species is easier on the

Introduction

Copper-supported catalysts are of industrial importance in many important processes: catalytic oxidation of volatile organic compounds (VOCs) as an air-cleaning method, the synthesis of cyclohexanone from cyclohexanol, the steam reforming of methanol, the synthesis of methanol, the selective catalytic reduction of nitrogen oxide, and so forth.^[1-8] Their catalytic properties depend on the oxidation and the coordination states of the copper ions. Particular interest has been paid to the preparation of a copper catalyst in a specific oxidation state with copper(I) prevailing over copper(II). The copper(II) ions that are supported on microporous aluminosilicate zeolite ZSM-5 are well known to be thermally reduced to copper(I) under vacuum or in an inert gas flow at high temperature (the reducing agent is the Brønsted acid sites, which are formed because of the presence of aluminum).^[9] The thermal autoreduction process can be explained by the dehydrogenation of Cu(II)-(OH) species and the bridging extra-lattice oxygen atoms, which are desorbed as oxygen molecules; this is accompanied by reduction of copper(II) to copper(I) ions.^[9-16] The copper(II) species dispersed on aluminosilicates that have a lower Si/Al ratio are prevented from autoreduction.^[12] During the last few decades, mesoporous silica materials, with their uniform mesoporous channel structure and high specific surface area, have been of particular interest as green heteroge-

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Ljubljana (Slovenia) F-mail: natasa novak tusar@ki si FeKIL-2 supported sample in comparison to its KIL-2 supported analogue, whereas the copper-containing KIL-2 sample shows higher catalytic activity in total toluene oxidation. The presence of iron in the FeKIL-2 structure leads to autoreduction of copper followed by the redispersion and oxidation of metallic copper in the reaction medium; this results in the formation of different types of finely dispersed copper oxide species (<100 nm). The later species possess lower catalytic activity in toluene oxidation in comparison to species that are 100 nm in size and formed on KIL-2.

neous catalyst supports.^[17-20] The interparticle mesoporosity of the new KIL family of silicates gives a new opportunity for the preparation of highly active catalysts.^[21] The KIL family is related to mesostructured silicate families with textural or interparticle porosities (HMS, MSU, NBS).^[21] Our recent results clearly demonstrate that silicates with interparticle mesoporosity are highly promising catalysts for the decomposition of organic pollutants in a liquid phase.^[22] The conditions for the formation of catalytically active metal oxides and their transformations during the reaction as a result of KIL-support peculiarity are important topics that have not been investigated yet. The nature and dispersion and reduction properties of copper oxide species can be influenced by the peculiarity of the nanosized KIL structure and the presence of a second metal in the silica matrix (to form Brønsted acid sites as a reducing agent in the structure). Our previous investigations $^{\scriptscriptstyle [23,\,24]}$ showed that the modification of mesoporous silica with two metals simultaneously leads to high metal oxide dispersion, which positively influences their catalytic behavior in toluene oxidation. The modification by copper and chromium also results in a high copper dispersion of CuCr/SBA-15 materials and stabilizes the formed copper oxide species in copper chromates and bichromates.

In this study, we demonstrate for the first time the nature and reduction properties of copper oxide species that are influenced by the peculiarity of the silica nanoparticles with interparticle mesoporosity (KIL-2 structure from KIL family) and the presence of a second metal (iron) in the silica matrix. The catalytic behavior of copper-modified KIL-2 and FeKIL-2 samples, pretreated in different conditions, is studied in total toluene oxidation (oxidation of toluene as a model air pollutant to CO_2 and H_2O).

Results and Discussion

Physicochemical characterization of the samples

XRD patterns show reflections that are typical of copper oxide for Cu/KIL-2 (Figure 1a), but not for the Cu/FeKIL-2 sample, probably because of the formation of small copper oxide nanoparticles. Copper oxide with a particle size of approximately 100 nm is determined for Cu/KIL-2 (Figure 1a) with calculations from the Scherrer equation, which is based on the selected diffraction peaks of the corresponding XRD pattern.

Gas physisorption is extensively used in the characterization of porous solids, particularly for evaluation of their specific sur-



Figure 1. a) XRD patterns with a 01-080-1916 reference for copper oxide, b) nitrogen physisorption data, and c) UV/Vis spectra for the studied samples.

face area, total pore volume, pore size distribution as well as surface properties. The shape of the isotherm obtained from these adsorption measurements is important because it can reveal the kind of porosity (micro, meso, or macroporosity) present in the sample. Nitrogen adsorption isotherms for KIL-2, FeKIL-2 and Cu/FeKIL-2 materials are shown in Figure 1 b, whereas structural parameters determined on the basis of these isotherms are listed in Table 1. KIL-2 and FeKIL-2 samples

Table 1. Structural parameters of the catalysts determined from nitrogen adsorption isotherms.						
Sample	Copper oxide [wt %]	$S_{BET}^{[a]}$ [m ² g ⁻¹]	$V_{T}^{[b]}$ [cm ³ g ⁻¹]	$V_{meso}^{[c]}$ [cm ³ g ⁻¹]	w _{BJH} ^[d] [nm]	
KIL-2	-	545	1.480	1.392	19.9	
Cu/KIL-2	6	359	0.732	0.648	14.8	
FeKIL-2	-	556	1.459	1.326	21.6	
Cu/FeKIL-2	6	407	1.105	1.004	16.1	
[a] BET surface area. [b] Total pore volume evaluated from the adsorption						

isotherm at the relative pressure of \approx 0.98. [c] Primary mesopore volume evaluated by using the α_s -plot method. [d] Mesopore diameters at the maximum of the BJH pore size distribution.

exhibit adsorption isotherms typical for KIL-2 and FeKIL-2 materials, $^{\scriptscriptstyle [30-32]}$ that is, with relatively narrow hysteresis loops of type IV.^[26] The FeKIL-2 sample undergoes a capillary condensation step at higher relative pressures than the KIL-2 sample, which indicates that larger mesopores are present in the FeKIL-2^[32] material compared to the KIL-2 support. It can be clearly observed that the presence of copper oxide nanoparticles in KIL-2 and FeKIL-2 supports leads to a marked change in the shape of the hysteresis loop. The hysteresis loop of copper(II) oxide loading samples is widening, less intensive and closing down at lower p/p_0 values compared to the original supports, which indicates that the pores are partially narrowed with copper oxide nanoparticles. The loading of copper oxide nanoparticles into KIL-2 and FeKIL-2 supports also leads to a decreased specific surface area, pore volume and pore diameter (Table 1). Therefore, it can be concluded that the copper oxide nanoparticles are dispersed inside the KIL-2 and FeKIL-2 matrices.

Pore size distribution of the different mesoporous materials was determined by using the Barrett–Joyner–Halenda (BJH) model, which is widely used for this type of samples.^[28] Although this model often underestimates pore sizes,^[29] it is appropriate for comparative purposes. The pore size distributions determined from the adsorption isotherms are displayed in Figure 2b (inset). It can be observed that the maxima characteristics of the mesopores of KIL-2 and FeKIL-2 supports are more intense and broader in comparison to their copper oxide loaded samples. They show average pore diameters of 19.9 and 21.6 nm, respectively. The maxima characteristics of copper oxide impregnated materials are shifted to lower pore size values (14.8 nm for Cu/KIL-2 and 16.1 nm for Cu/FeKIL-2).

A TEM micrograph of the Cu/KIL-2 sample shows a porous texture with interparticle porosity typical for KIL-2 silica materi-

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Figure 2. TEM micrographs of a) Cu/KIL-2 and b) Cu/KIL-2 with copper oxide crystallites (dark spots) located on the surface of the KIL-2 silica matrix, c) SAED pattern of Cu/KIL-2 with selected reflections with the corresponding marked crystal lattices, d) close-up TEM micrograph of Cu/KIL-2, e) TEM micrograph of Cu/FeKIL-2 with copper oxide crystallites (dark spots) located on the surface of the FeKIL-2 silica matrix, f) close-up TEM image of Cu/FeKIL-2.

als (Figure 2 a). Agglomerated silica nanoparticles with an estimated size of 10 nm form voids and cavities with a broad size distribution. The porous silica matrix contains individual crystallites of copper oxide. The relatively large thickness of the crystallites makes the TEM observation somewhat difficult, however an approximate size of 100 nm could be estimated (Figure 2 b). This is in agreement with the calculations from the Scherrer equation, which is based on the selected diffraction peaks of the corresponding XRD pattern.

The presence of the monoclinic copper oxide phase (*Cc*, a = 4.69 Å, b = 3.43 Å, c = 5.13 Å, $\beta = 99.65^{\circ}$) in the CuKIL-2 sample, which is already indicated by XRD analysis, is finally confirmed by the selected area electron diffraction method (SAED). The SAED pattern of the copper oxide crystallites with the selected maxima and their corresponding crystal planes are shown in Figure 2*c*, whereas a comparison of measured and referenced *d* values of selected crystal planes are shown in Table 2.

The sizes of the copper oxide crystallites indicate that they are located exclusively on the surface of the KIL-2 silica matrix.

Table 2. Comparison of measured and referenced d values of corresponding crystal planes.					
	Crystallographic plane	Measured [nm]	PDF ^[a] (No. 01-080-1917) [nm]		
<i>d</i> ₁	[110]	2.79	2.75		
d2	[002]	2.56	2.52		
d ₃	[202]	1.60	1.58		
[a] Powder diffraction file.					

The observations at higher magnification did not reveal the presence of any smaller metal oxide nanoparticles that could be located within the voids of KIL-2 matrix(Figure 2d).

TEM analysis of the Cu/FeKIL-2 sample shows similar textural properties as for the Cu/KIL-2 sample. The FeKIL-2 silica matrix is inhomogenously covered with the copper oxide phase, however individual metal oxide nanoparticles are somewhat smaller (100 nm) and seem to be agglomerated into larger clusters (Figure 2 e). Similarly, as in the case of the Cu/KIL-2 sample, the observations at higher magnification do not reveal the presence of any smaller metal oxide nanoparticles (Figure 2 f).

Diffuse reflectance UV/Vis spectroscopy was used to investigate the nature of the iron and copper ions in the Cu/KIL and Cu/FeKIL-2 samples (Figure 1 c). The UV/Vis spectrum of the FeKIL-2 sample reveals two peaks at $\lambda = 240$ and 285 nm. The same peaks can be found in the UV/Vis spectrum of the Cu/ FeKIL-2 sample. These peaks are assigned to the charge transfer between the iron(III) ions and the oxygen of the Fe-O-Si in the network of FeKIL-2,^[33] which indicates the presence of tetrahedrally and octahedrally coordinated iron(III) species.^[34] The peak at $\lambda = 240$ nm can be attributed to copper(II) ions, and oxygen charge transfer transitions in Cu/KIL-2 and Cu/FeKIL-2 are observed as well.^[35] No contribution at greater than $\lambda =$ 300 nm is observed in FeKIL-2, which excludes the occurrence of an oligonuclear iron complex and iron oxide particles in this sample. A broad absorption peak from $\lambda = 400$ to 800 nm can be observed in the Cu/KIL-2 and Cu/FeKIL-2 UV/Vis spectra, which owes to d-d transitions of copper(II) with the octahedral environment in copper oxide particles.^[35] The additional shoulder at approximately $\lambda = 340$ to 360 nm can be seen in Cu/FeKIL-2, but not in the Cu/KIL-2 sample, which corresponds to the presence of [Cu–O–Cu]_n surface species.^[35] The differences in the nature of copper species, which are formed on the modified samples, can be ascribed to the presence of iron in the silica matrix.

More information on the oxidation state of copper oxide species and their reducibility was obtained by temperatureprogrammed oxidation-reduction thermogravimetric analysis (TPO/TPR-TG) experiments (Figure 3). Pretreatment in different media (air and argon) was applied before the TPR experiments. The samples showed different behavior during the pretreatment procedure, which depended on the pretreatment media and the used support (Figure 3).

There were no significant changes in the weight of both samples Cu/KIL-2 and Cu/FeKIL-2 during the pretreatment in air. A low intensity peak is registered at 870 K for both samples; this is probably due to silica matrix dehydroxylation. In contrast, the pretreatment in argon results in significant weight changes, which correspond to 100% reduction of copper(II) ions to metallic copper on the FeKIL-2 sample. Reduction peaks at 595 and 770 K are registered for Cu/FeKIL-2 pretreated in argon. For the first time the copper autoreduction process is determined on mesoporous materials. We ascribe the copper autoreduction process to the influence of iron(III) ions and the formation of weak Brønsted acid sites in the sample as a result of iron incorporation into the silica structure. The predominant formation of copper(II) ions on this sample is







Figure 3. TPO/TPR-DTG profiles of a, b) Cu/FeKIL-2 and c, d) Cu/KIL-2 samples.

due to the presence of Brønsted acid sites in the iron-containing KIL-2 support and their interaction with the copper precursor during the impregnation process. These copper(II) species can be easily reduced to metallic copper during evacuation at high temperature or under an inert atmosphere [Eq. (1)].

$$Cu^{2+} \rightarrow Cu(OH)^{+} \rightarrow [Cu-O-Cu]^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$$
(1)

Kuroda et al^[13] also found that the presence of Brønsted acid sites in the sample that has a high Si/Al ratio is a necessary condition for the formation of copper(I) ions. The reduction profiles of the copper-containing catalysts depend on the support material used and the pretreatment procedure. The copper-containing KIL-2 and FeKIL-2 samples pretreated in air possess clearly defined low-temperature reduction peaks at 530 and 440 K, respectively, which can be attributed to copper(II) to metallic copper reduction. The extent of reduction is 89.33% for Cu/KIL-2 and 100% for Cu/FeKIL-2. The narrow reduction peak with a maximum at 430 K, registered for Cu/KIL-2 after pretreatment in argon (Figure 3d), is related to the more homogenous distribution of copper oxide species on the supports. There are no peaks in the TPR-TG profile of the Cu/KIL-2 sample after pretreatment in argon at 773 K (Figure 3 c), which is due to total copper autoreduction during the pretreatment under an inert atmosphere.

By summarizing the above observations we can conclude that the reduction of copper oxide species is easier on the

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FeKIL-2 supported sample in comparison to its KIL-2 supported analogue. It is probable that the formation of different types of copper oxide species on the two applied supports and the influence of iron in FeKIL-2 are responsible for the different reduction behavior. This assumption is also supported by diffuse reflectance UV/Vis data, in which the formation of different copper species is registered.

Catalytic activity for total toluene oxidation

The catalytic activities versus the temperature and versus the time on a stream of copper-containing materials that were pretreated in an inert gas or air at 723 K in total toluene oxidation are presented in Figure 4. The pretreatment in different media (air or argon) does not lead to a different catalytic activity with a temperature increase for Cu/FeKIL-2 (Figure 4b). It is the opposite for Cu/KIL-2, the increase in the temperature leads to a higher catalytic activity in toluene oxidation for this sample after the pretreatment in air at 773 K (Figure 4a). The use of KIL-2 as a support has a positive effect on the catalytic performances of the Cu/KIL-2 sample. The Cu/FeKIL-2 catalyst shows stable catalytic activity at 653 K after pretreatment in different reaction media (air and argon) (Figure 4d), whereas the Cu/KIL-2 sample shows stable catalytic activity only in the pretreatment with air, and a trend towards deactivation in the pretreatment with argon (Figure 4c). The physicochemical characteristics (UV/Vis and TPR data) of the catalysts show the

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Figure 4. Catalytic activity versus temperature on a) Cu/KIL-2 and b) Cu/FeKIL-2 samples and versus time on stream at 653 K on c) Cu/KIL-2 and d) Cu/FeKIL-2 samples after pretreatment in argon or air.

reaction. Redispersion of the copper oxide phase during the reaction on both samples (Cu/ KIL-2 and Cu/FeKIL-2) was observed after pretreatment in inert gas. The copper autoreduction in argon on FeKIL-2 results in the formation of more finely dispersed copper(I) and copper (II) species (not detectable by XRD, Figure 5) in the oxidative reaction medium, which are less active. The pretreatment in air of Cu/KIL-2 results in the formation of copper oxide that is 100 nm in size; this possesses the highest catalytic activity in toluene oxidation but lower stability compared to the Cu/FeKIL-2 and Cu/KIL-2 samples pretreated in argon. Our experiments show that finely dispersed copper species are less active, and the formation of nanosized crystalline copper oxide is responsible for the high catalytic activity in total toluene oxidation. The Cu/KIL-2 and Cu/FeKIL-2 catalysts after

formation of finely dispersed copper oxide species on both supports, which determine their high catalytic activities. Kim^[19] also found that the presence of highly-dispersed copper species had a positive effect on the catalytic activity in toluene oxidation. The catalytic activity of bulk copper oxide is presented in Figure 4 as a reference. All supported samples show much higher catalytic activity in comparison to bulk copper oxide. The easier oxygen release is an essential step in the oxidation reaction according to the Mars-van-Krevelen mechanism^[19] and

in this relationship the reduction properties of the samples can be used for the interpretation of their catalytic performance. However, the higher extent of copper reduction at lower temperature observed for Cu/FeKIL-2 (Figure 3) does not lead to higher catalytic activity in toluene oxidation. We did not find a direct relationship between the reduction properties and the catalytic activity of the catalysts, which could be assumed from the mechanistic point of view. Additional XRD experiments of the spent catalysts (Figure 5) were applied to indicate the changes of the oxidation state of copper oxide species during the the pretreatment in argon keep their catalytic activity in 3 reaction cycles. A trend to deactivation is observed only for Cu/ KIL-2 after pretreatment in air most probably because of the agglomeration of the formed copper oxide on the KIL-2 support after pretreatment (Figure 5 a (2)). The pretreatment in air of the Cu/FeKIL-2 catalyst doesn't have a negative influence on its catalytic stability, which can be related to the formation and stabilization of finely dispersed copper(II) oxide and copper(I) oxide species.





On the basis of the presented catalytic data we conclude that copper supported on KIL-2 pretreated in air is the better catalyst compared to the copper-supported FeKIL-2 sample with a Fe/Si molar ratio of 0.01 for total toluene oxidation. The presence of iron in the KIL-2 structure leads to autoreduction of copper followed by the redispersion and oxidation of metallic copper in the reaction medium; this results in the formation of finely dispersed copper oxide clusters. The latter species possess low catalytic activity in toluene oxidation.

Conclusions

The copper-containing KIL-2 and FeKIL-2 samples with interparticle mesoporosity are prepared by incipient wetness impregnation. The relationship between the type of copper oxide species generated and the stabilized copper oxide species, the KIL-2 support and the presence of iron as a second metal are studied. The type of the generated and stabilized copper oxide species depends on the presence of iron in the KIL-2 support and the pretreatment procedure. The formation of copper oxide nanoparticles that are smaller than 100 nm in size and are 100 nm in size for FeKIL-2 and KIL-2 respectively, is registered. The copper-containing KIL-2 sample shows higher catalytic activity in total toluene oxidation if compared to coppercontaining FeKIL-2, whereas copper autoreduction is easier on FeKIL-2. The presence of iron in the KIL-2 structure leads to the redispersion and oxidation of metallic copper in the reaction medium, which results in the formation of finely dispersed copper oxide clusters (< 100 nm). Further investigations on the optimal relationship between iron content and the particle size of copper oxide species for optimal catalytic activity of the supported catalysts are in progress.

Experimental Section

Catalyst preparation

We prepared porous silica with interparticle mesoporosity, which is denoted as KIL-2 and iron-modified KIL-2 with Fe/Si molar ratios of 0.01, which is denoted as FeKIL-2, under procedures already reported in the literature.^[21,22]

An incipient wetness impregnation technique with copper nitrate was applied for loading of 6 wt% copper oxides and the samples were designated as Cu/FeKIL-2 and Cu/KIL-2.

Characterization

X-ray diffractograms were recorded on a PANanalytical X'Pert PRO high-resolution diffractometer by using CuK_a radiation ($\lambda =$ 1.5406 Å) in the 2 θ range from 0.5 to 5° (100 s per step of 0.034°) and from 5 to 60° (100 s per step of 0.016°) for the samples and from 10 to 90° (100 s per step 0.016°) for the sample holder by using a fully opened X'Celerator detector.

Morphology and surface properties of the samples were observed by SEM on a Zeiss Supra 3VP microscope. Elemental analysis of all samples was performed by the energy-dispersive X-ray spectroscopy (EDX) method with an INCA Energy system attached to a Zeiss Supra 3VP microscope. Nitrogen physisorption measurements were performed at 77 K by using an ASAP 2020 Micromeritics volumetric adsorption analyzer. Before the adsorption analysis, the samples were outgassed under vacuum for 2 h at 473 K in the port of the adsorption analyzer. Nitrogen adsorption measurements were measured at 77 K on a Tristar 3000 Micromeritics volumetric adsorption analyzer. Before the adsorption analysis, the samples were outgassed under vacuum for 2 h at 473 K in the port of the adsorption analyzer. The BET specific surface area^[25] was calculated from adsorption data in the relative adsorption data in the relative pressure range from 0.05 to 0.2. The total pore volume was estimated on the basis of the amount adsorbed at a relative pressure of 0.98.^[27] The mesopore volume V_{meso} was determined by using the $\alpha_{\rm s}\text{-plot}$ method $^{\text{[26]}}$ from the adsorption data in the range of the standard reduced adsorption from 2.1 to 3.0. In the α_s -plot calculations, a macroporous silica material Li-Chrospher Si-1000 ($S_{BET} = 22.1 \text{ m}^2 \text{g}^{-1}$) was used as a reference adsorbent.^[19] The pore size distributions (PSDs) were calculated from nitrogen adsorption data by using an algorithm based on the BJH method.^[27] The maxima on the PSD were considered as the primary mesopore diameters for the given samples.

The mesostructure characteristics and presence of copper oxide was investigated by using high-resolution transmission electron microscopy (HRTEM) on a 200 kV field-emission gun (FEG) microscope JEOL JEM 2100. Dispersed samples in ethanol were placed on a carbon-coated Cu grid. The specimens were additionally coated with carbon to prevent excessive charging of the samples under the electron beam.

The TPO/TPR-TG investigations were performed in a Setaram TG92 instrument. Prior to the TPR experiments the samples (40 mg) were treated in situ in an air or argon flow (temperature increase rate of 5 Kmin⁻¹) up to 773 K, followed by a hold-up of 1 h. In a typical TPR measurement, the sample was heated in a flow of 50 vol% H_2 in Ar (flow rate of 100 cm³min⁻¹) up to 773 K at 5 Kmin⁻¹ and a final hold-up of 1 h.

Diffuse reflectance spectra of the samples in the UV/Vis region were registered by using a Jasco V-650 UV/Vis spectrophotometer equipped with an integrated sphere. All spectra were recorded under ambient conditions.

Catalytic activity tests

Prior to the catalytic test the samples were pretreated for 1 h in air or argon up to 723 K Toluene oxidation was studied at atmospheric pressure by using a fixed-bed flow reactor, air as carrier gas and the sample (30 mg, particle size 0.2–0.8 mm) diluted with glass beads (60 mg) of the same diameter, which was previously checked to be inactive. The air stream passed through a saturator filled with toluene and equilibrated at 273 K ($p_{toluene}$ =0.9 kPa). The activity was determined in the temperature interval of 550–750 K at a weight hourly space velocity of 1.2 h⁻¹. On-line analysis of the reaction products was performed by using high pressure gas chromatography (HPGC) with a PLOT Q capillary column (25 m). The turnover frequency (TOF) was calculated as the converted number of toluene molecules per metal atoms per second.

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