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Introduction

Natural clay minerals, due to their relatively low price and specific properties resulting from a layered structure, have attracted great attention in many various fields including catalysis.1 However, the catalytic application of clays demands the opening of their pore structure, which can be achieved, for example, by separation of adjacent layers by oxide nanoparticles (e.g. SiO₂, Al₂O₃, TiO₂, Fe₂O₃, ZrO₂) introduced into the interlayer space. Such a strategy of modification of the layered structure is used in the formation of pillared interlayered clays (PILCs) and porous clay heterostructures (PCHs).²⁻¹² PILCs are prepared by exchanging the charge-compensating cations present in the interlamellar space of clay with large oligomeric metal hydroxycations formed by hydrolysis of chosen metal salts. Upon calcination, these polyoxocations undergo dehydration followed by dehydroxylation, and are converted into the corresponding metal oxide clusters, so called pillars, which link permanently the clay layers. On the other hand, PCHs based on the clay layers pillared by a silica framework are synthesized

Physicochemical properties of hydrogel templatesynthesized copper(II) oxide-modified clay influencing its catalytic activity in toluene combustion

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CuO-modified montmorillonite was synthesized by the template-assisted route. Poly(acrylic acid) was intercalated into the interlayer gallery of natural clay. Subsequently, various amounts of Cu²⁺ cations were introduced into the prepared hydrogel-clay composite using adsorption in different volumes of aqueous Cu(NO₃)₂ solution at constant pH = 6. The resulting materials were finally calcined at 550 °C (chosen using the results of TGA-IR analyses) to transform them into thermally stable oxide systems. The changes in the structural properties of the clay during the progressive modification were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Moreover, porosity, reducibility and surface composition of the calcined materials were determined by means of low-temperature N₂ adsorption, temperature-programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS). It was shown that a high concentration of CuO nanoparticles, which were well-dispersed and protected against sintering between montmorillonite grains, and weak interaction between CuO and the clay support (resulting in easy reducibility of CuO) were the most important features influencing the catalytic activity of the synthesized materials in the total oxidation of volatile organic compounds (VOCs).

using the templating technique, which includes following steps: (i) the formation of micelle structure by a template intercalated in the clay interlayers, (ii) polymerization of a silica source on the micelle structures, (iii) removal of the template by calcination or extraction resulting in the exposition of interlamellar silica pillars.

The noble and transition metal-modified pillared clays have been studied as catalysts in a wide range of reactions, including air pollution control (mainly in selective catalytic reduction of NOx).^{2,4,5,8,10,13} Nevertheless, some examples of using of clay catalysts in the total oxidation of volatile organic compounds (VOCs) can be also found in the literature.¹⁴ VOCs, including various aliphatic/aromatic hydrocarbons and their derivatives, are emitted from both natural and anthropogenic sources. The processing and incomplete burning of fossil fuels as well as the use of solvents are considered as the main anthropogenic sources. VOCs present in the atmosphere contribute to photochemical reactions, which give products responsible for the smog phenomenon and the greenhouse effect.¹⁵ On the other hand, the increasing concentration of VOCs (containing many toxic and carcinogenic chemicals) has a harmful effect on the human and animal health. Methods for the reduction of VOCs emission based on recovery (e.g. membrane separation, condensation, sorption) as well as destruction operations (e.g. thermal, catalytic and photocatalytic oxidation) have been

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therefore developed.¹⁶⁻¹⁸ However, in the case of low concentration emission sources, the catalytic combustion seems to be the most effective approach to the VOCs elimination.

It was found that noble metals (especially Pt and Pd) supported on clays exhibit very high catalytic activity in the total oxidation of various organic compounds (*e.g.* aromatic hydrocarbons and ketones).^{18–20} A significant enhancement in the VOCs conversion was observed for Pd deposited on Al₂O₃-pillared clays modified additionally with cerium(*n*) oxide, which stabilizes the active phase at high oxidation state and good dispersion.^{21–24} It should however kept in mind that the noble metal-containing materials are expensive and characterized by a limited resistance to poisoning. Therefore, significantly cheaper pillared clays modified with transition metal oxides (*e.g.* Cr, Mn, Ce, Co, Cu, Ni, Fe) have been often studied.^{3,25–33} Li *et al.* showed that fine dispersion of active phase nanoparticles supported by mesoporosity nature of the modified material provide a good catalytic behavior in the VOCs combustion.³⁴

Recently, a novel method of synthesis of clay catalysts based on using of clay–polymer composites, which is not limited to the introduction of metals forming stable oligomeric hydroxycations (PILCs) or condensed species on the interlamellar micelles (PCHs), has been proposed.^{35,36} In the first step of this procedure, hydrophilic monomers are intercalated into a clay gallery and subsequently *in situ* polymerized forming a clay– hydrogel composite, which exhibits enhanced swelling and metal cation adsorption capacities.^{35,37} Then, the obtained composite is modified with transition metal cations by adsorption performed at controlled conditions influencing the content and distribution of introduced species. Finally, the modified sample is calcined to remove the hydrogel template, and the oxide catalyst containing a highly dispersed active phase is formed.

In the presented paper, the clay–hydrogel composite based on natural montmorillonite and poly(acrylic acid) was synthesized and modified by sorption of various amounts of Cu^{2+} cations. The subsequent calcination resulted in the formation of thermally stable oxide-type catalysts for the total oxidation of chosen aromatic volatile organic compounds. We investigated the relationship between various physicochemical properties of the synthesized materials (including surface and bulk composition, structure, texture, and reducibility) and their catalytic activity in the above mentioned reaction.

Experimental

Synthesis

The clay-hydrogel composite was synthesized by the *in situ* polymerization method. The mixture containing natural Wyoming montmorillonite (10 wt%) and monomers (10 wt%) – acrylic acid (AA, Arkema) and N,N'-methylenebisacrylamide (NMBA, Sigma-Aldrich) at the NMBA/AA molar ratio of 1 : 100 – in water was agitated with a mechanical stirrer (400 rpm) at room temperature to obtain homogeneous suspension. Then, oxygen was removed from the slurry by purging with argon for 10 min, and ammonium persulfate (APS, Sigma-Aldrich) was added at the APS/AA molar ratio of 0.01. The suspension was

heated to 65 °C and kept at this temperature for 3 h to ensure the complete polymerization process. The synthesized composite was shredded in a cutting mill, dried at 60 °C and grinded to fine powder (<125 μ m).

In the next step, the obtained composite (MT-PAA) was modified by adsorption of Cu²⁺ ions from an aqueous of copper(II) nitrate solution (0.01 M). MT-PAA (2.0 g) was added to various volumes of Cu(NO₃)₂ solution (100, 200, 300, 400, 500, 600 or 700 mL) and kept at a constant temperature (30 °C) and pH = 6 (maintained by an addition of 0.1 M NaOH) on a magnetic stirrer (500 rpm). After 24 h, the material was separated from the solution by centrifugation (3000 rpm, 10 min) and washed with deionized water. The washing operation was repeated three times. Finally, the Cu2+-modified samples were dried in air at 65 °C overnight, and calcined in a tube furnace in an air flow (33 mL min⁻¹) at 550 °C for 8 h with a heating rate of 1 °C min⁻¹ in order to remove the hydrogel template. The studied materials were designated as MT-PAA CuY, where Y represents the volume (mL) of 0.01 M Cu(NO₃)₂ solution used during the modification.

Characterization

X-ray diffraction (XRD) patterns were recorded at room temperature with a Cu anode ($\lambda = 1.54184 \text{ Å}$) on a X-ray powder diffractometer (D2 Phaser, Bruker) in two ranges of $2\theta = 1-50^{\circ}$ and $33-41^{\circ}$ with a step size of 0.02° and two scan rates equal to 1 and 5 second per a step, respectively.

TGA-IR experiments were performed using a TA Instruments SDT Q600 thermoanalyzer coupled *via* a TGA-IR (Thermo Scientific) equipment with a FT-IR spectrometer (Nicolet 6700, Thermo Scientific). About 20 mg of a sample was heated from 30 to 1000 °C at a heating rate of 10 °C min⁻¹ in flowing air (20 mL min⁻¹). 2D FT-IR spectral maps of gaseous products evolved during decomposition were recorded with resolution of 4 cm⁻¹ collecting 8 scans for each spectrum.

Temperature-programmed reduction (H₂-TPR) experiments were conducted using the same thermoanalyzer. The measurements were carried out using 10 mg of a sample placed in a corundum crucible in a flow of mixture containing 10 vol% H₂ in argon (60 mL min⁻¹). The sample was heated from 30 to 1000 °C at a rate of 10 °C min⁻¹.

 N_2 adsorption isotherms were collected using a Micromeritics ASAP 2020 instrument. Prior to the measurements, samples were degassed at 350 $^\circ \rm C$ for 6 h under vacuum.

X-ray fluorescence (XRF) analyses were carried out on an ARL Quant'x analyzer (Thermo Scientific) for 300 mg of each sample in a powder form.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Prevac spectrometer equipped with a hemispherical VG Scienta R3000 analyzer. Samples were introduced through a load lock (where pressure better than 3×10^{-7} mbar was achieved) into an ultrahigh vacuum analytical chamber with the base pressure of 5×10^{-9} mbar. The XPS experiments were carried out using a monochromatized aluminum source AlK α (E = 1486.6 eV) and a low energy electron flood gun (FS40A-PS) to compensate charge on the surface of nonconductive samples. Photoelectron peaks were recorded with constant pass energy of 100 eV for the survey and high resolution spectra. The scale of the binding energy value was adjusted by the position of Si 2p peak at 103.0 eV. The composition and chemical surrounding of sample surface were investigated on the basis of the areas and binding energies of Cu 2p, Si 2p, Al 2p, O 1s, Na 1s, Mg 2p and C 1s photoelectron peaks. Fitting of the high resolution spectra was provided through Casa XPS software.

Transmission electron microscope (Tecnai G2 F20) equipped with a field emission gun operating at 200 kV was used. Before TEM analyses, samples in a powder form were placed on a nickel grid.

Catalytic tests

The obtained oxide materials were tested as catalysts in the total oxidation of VOCs (benzene, toluene, o-xylene, m-xylene and pxylene). Prior to a catalytic run, a catalyst (0.1 g with a sieved particle fraction of 160-315 µm) was placed in a central position of quartz flow microreactor on a quartz wool plug and outgassed at 500 °C for 30 min in the flow of air (100 mL min⁻¹). Then, the reactor was cooled down to 200 °C and VOCs dosing started by passing air through a saturator (kept at a selected temperature) to achieve the VOCs vapor concentration of 1000 ppm in the reaction mixture. The catalytic tests were carried out at 200, 250, 275, 300, 325, 350, 400, 450 and 500 °C. The reactor was kept at each temperature (reached at a heating rate of 10 °C min⁻¹) for 80 min with three 25 minutes lasting analyses of reaction products conducted using a Bruker 450-GC gas chromatograph equipped with three columns (molecular sieve 5A for separation of O₂, N₂ and CO, Porapak S - CH₄, CO₂ and H₂O, and Chromosorb WAW-DMCS - aromatic compounds), a thermal conductivity detector, two flame ionization detectors as well as a methaniser.

Results and discussion

Structure and thermal stability of Cu²⁺-modified MT-PAA composite

The XRD patterns of MT, MT-PAA and MT-PAA CuY materials after adsorption of Cu²⁺ ions are shown in Fig. 1. In the case of raw clay (MT), the diffraction lines at 9.1, 19.9, 27.9 and 35.2° are attributed to (001), (111), (003) and (211) planes, respectively [PDF 00-060-0315]. The interlayer distance (d_{001}) for this sample, calculated according to the Bragg's equation $(n\lambda =$ $2d\sin\theta$ based on the position of (001) peak, is equal to 0.98 nm. The determined value of d_{001} parameter is typical of dried natural montmorillonite, in which sodium and calcium cations are located in the ditrigonal cavities between the adjacent layers of clay.38 Moreover, in the studied mineral small amounts of crystalline impurities, mainly in the form of quartz, are present as confirmed by the (101) diffraction line at 26.6° [PDF 00-001-0649]. An increase in the $d_{(001)}$ value to 1.76 nm is observed after the successful intercalation of poly(acrylic acid) into the interlayer gallery of MT (MT-PAA sample). What is surprising, the further modification of MT-PAA by the Cu²⁺



Fig. 1 XRD patterns of raw montmorillonite and MT–PAA composite before and after deposition of Cu^{2+} cations.

deposition results in a decrease in the distance between the clay layers, which depends on the volume of copper(II) nitrate solution used. For the sample modified in the solution containing the lowest Cu amount (100 mL) the $d_{(001)}$ value is 1.23 nm, whilst for the material obtained by the contact with the highest $Cu(NO_3)_2$ solution volume (700 mL) the *d*-spacing increases to 1.68 nm, and is only slightly lower than for MT-PAA. Obviously, Cu²⁺ cations migrate into the interlayer space of composite and interact with COO⁻ groups of PAA. Crosslinking of PAA chains by transition metal ions cannot be excluded. This effect could explain the decrease in the d_{001} value observed after the Cu²⁺ deposition. On the other hand, the introduction of MT-PAA composite in the raising volume of copper(II) nitrate solution results in more effective swelling of modified material and growing basal spacing is observed. As is shown by the XRF analysis (Table 1), higher volumes of $Cu(NO_3)_2$ solution enable to introduce more Cu²⁺ cations into the MT-PAA structure. It should however be kept in mind that a part of PAA macromolecules is most likely deposited on the external clay surface. This hydrogel also participates in adsorption of Cu²⁺ cations, which thereby remain outside of the MT interlayers.

The thermal stability of the MT–PAA composite before and after the introduction of Cu²⁺ cations was studied by TGA. The gaseous products evolved during the measurements were additionally analyzed by FT-IR. The recorded TG, DTG and DTA curves and corresponding 2D FT-IR spectral maps for the MT–PAA, MT– PAA Cu100 and MT–PAA Cu500 samples are presented in Fig. 2.

For the unmodified composite, the decomposition of polymer begins at temperature as low as 180 °C just after the

Table 1 Cu content as well as textural, structural and redox properties of the calcined materials

| | | N ₂ adsorption | | XRD | H ₂ -TPR | | |
|-------------------|---------------------|---|--|-----------------------|--|---|--|
| Sample | Content of Cu [wt%] | $S_{ m BET} \left[m^2 \ g^{-1} ight]$ | $V_{\text{total}} \left[\text{cm}^3 \text{ g}^{-1} \right]$ | D _{CuO} [nm] | $T_{\rm red} \left[^{\circ} \mathbf{C}\right]$ | H _{2,consum.} /H _{2,theor.} | |
| MT | _ | 31.0 | 0.09 | _ | _ | _ | |
| MT-PAA Cu100 calc | 3.8 | 23.5 | 0.135 | 19 | 267 | 1.10 | |
| MT-PAA Cu200 calc | 8.8 | 28.2 | 0.158 | 15 | 253 | 0.97 | |
| MT-PAA Cu300 calc | 15.5 | 37.4 | 0.209 | 15 | 250 | 0.90 | |
| MT-PAA Cu400 calc | 19.3 | 42.5 | 0.194 | 14 | 250 | 0.79 | |
| MT-PAA Cu500 calc | 22.2 | 50.8 | 0.220 | 12 | 241 | 0.83 | |
| MT-PAA Cu600 calc | 27.2 | 43.4 | 0.164 | 13 | 289 | 0.75 | |
| MT-PAA Cu700 calc | 28.7 | 55.4 | 0.190 | 14 | 305 | 0.81 | |

dehydration step. Up to 350 °C the emission of gaseous, organic decomposition products containing carboxyl groups is manifested by the FT-IR bands in the ranges of 1760–1780 cm⁻¹ and 1135–1190 cm⁻¹, assigned to the vibrations of C=O and C–O, respectively. Acrylic acid can be the main product of decomposition at this step. Nevertheless, Chen *et al.*, who studied the thermal degradation of acrylate–methacrylate copolymers by TG-FT-IR, suggested that the band at 1767 cm⁻¹ observed above 310 °C can also correspond to the formation of acid anhydride.³⁹ Simultaneously, above 260 °C the oxidation of



Fig. 2 TG, DTG and DTA curves as well as FTIR maps recorded during decomposition of MT–PAA, MT-PAA Cu100 and MT-PAA Cu500 in flowing air.

the PAA backbone intensifies and the formation of huge amounts of carbon dioxide (identified by the bands at 670-750 cm⁻¹ attributed to the bending vibrations, and at 2250-2400 cm^{-1} – the asymmetric stretching vibrations of CO_2) and water (the bands at $3450-3750 \text{ cm}^{-1}$ and $1250-2000 \text{ cm}^{-1}$ corresponding to the symmetric and asymmetric stretching vibrations and the bending vibrations of H₂O, respectively) together with traces of carbon monoxide (the bands at 2110 and 2200 cm⁻¹ related to the stretching vibrations of CO) is detected.^{39,40} Both the DTG curve and the FT-IR map exhibit an additional, high-temperature step of the sample decomposition observed in the range of 575-710 °C, which is related to two processes running simultaneously: (i) the combustion of carbon deposit formed due to incomplete oxidation of the polymer present in the clay interlayers, and (ii) dehydroxylation of MT layers. These two independent transformations are reflected in the FT-IR map as the intensive bands characteristic of carbon dioxide (at 670- 750 cm^{-1} and $2250-2400 \text{ cm}^{-1}$) and the weak absorption peaks attributed to water vapour (at 3450-3750 cm⁻¹ and 1250-2000 cm^{-1}).

For the Cu²⁺-adsorbed composites, thermal decomposition of polymer matrix occurs at significantly lower temperatures compared to MT–PAA. The decomposition process undergoes in the temperature range of 200–525 °C with the emission of carbon dioxide and water solely. It could be discerned that the temperature of complete oxidation of polymer template strongly depends on the Cu content and decreases from 575 °C for MT– PAA to 525 °C and 430 °C for MT–PAA Cu100 and MT–PAA Cu500, respectively. This accelerating effect of Cu species in the removal of the organic template causes the transformation of Cu²⁺-modified composites into the final oxide-type catalysts possible at the temperature as low as 550 °C. Therefore, this temperature was selected as appropriate to eliminate hydrogel from the prepared precursors avoiding the destruction of the montmorillonite structure by the dehydroxylation of layers.

Structural, textural and surface properties of calcined MT-CuO materials

In the XRD patterns of the calcined copper-containing samples (Fig. 3A) the diffraction lines typical of the montmorillonite structure are still present. Nevertheless, a shift of the (001) peak to higher 2θ values (8.9–9.2°), compared to that position detected for the samples before the thermal treatment, is observed. Moreover, a gradual increase in the intensity of (001) diffraction line in relation to the intensity of (111) reflection is found at the increasing Cu loading. Obviously, the highly ordered layered clay structure remains after the performed modification.

The behavior of various cations (*e.g.* Li⁺, Cu²⁺, Cd²⁺) in the clay interlayers upon thermal treatment has been previously studied by many researchers. Zhu *et al.* observed the collapse of layered structure of Cu-modified montmorillonite already slightly above 200 °C.⁴¹ On the other hand, the EPR and DTA study of the Cu-modified montmorillonite calcined at different temperatures revealed that below 400 °C Cu²⁺ cations are located mainly in the ditrigonal cavities in the Si–O sublayers, whereas an increase of temperature above 460 °C leads to the



Fig. 3 XRD patterns of calcined MT–PAA and Cu-containing MT–PAA materials measured in the 2θ ranges of 1–50° (A) and 33–41° (B).

partial dehydroxylation of clay layers and the penetration of octahedral vacancies by some ${\rm Cu}^{2+}$ ions. $^{42-44}$

In the case of the studied materials, calcination performed at 550 °C results in the complete elimination of hydrogel template. In a consequence, a significant part of Cu^{2+} ions locates in the interlamellar ditrigonal cavities or even infiltrates the MT layers, especially in the samples with the relatively high amounts of Cu^{2+} introduced into the PAA chains. Thus, the negative charge of MT layers is partly neutralized by Cu^{2+}

cations leading to the stabilization of the layered structure. On the other hand, at the increasing amount of Cu²⁺ ions they are mainly adsorbed by the hydrogel located outside of the MT galleries. After the thermal treatment the introduced species form CuO nanoparticles highly dispersed on the external surface of MT. The presence of crystalline CuO phase in the calcined samples is confirmed by three distinct diffraction lines at 35.6°, 38.8° and 48.8° (Fig. 3A and B), which correspond to (-111), (111), (-202) planes, respectively [AMCSD 0018812]. Since the (-111) reflection is overlapped by the (211) reflection attributed to MT, the average crystallite size of $CuO(D_{CuO})$ in the studied samples was calculated according to the Scherrer equation based on the (111) line broadening at half the maximum intensity (FWHM) (Table 1). The D_{CuO} values below 20 nm may suggest that poly(acrylic acid), acting as the complexing agent of Cu²⁺ cations, separates them and prevents the formation of larger metal oxide crystals during the thermal treatment.

The presence of nanocrystalline CuO phase was additionally confirmed by the TEM measurements (Fig. 4). The collected images clearly show the existence of CuO crystallites with the average particle size corresponding to the D_{CuO} values calculated from the XRD data, highly dispersed between the MT particles, which evidently protect them against agglomeration.

The textural parameters of the calcined materials were determined by means of N_2 adsorption-desorption measurements at 77 K. The specific surface area (S_{BET}) and total pore volume (V_{total}) calculated based on the BET and single point methods, respectively, are demonstrated in Table 1. The obtained results show a slight growth in the specific surface area and total pore volume with the increasing Cu content. These textural changes should be attributed to the appearance small grains of CuO, which located between MT particles, forming interparticle porosity.

The surface composition and the state of the Cu species in the catalysts were studied by X-ray photoelectron spectroscopy. The XPS spectrum of the Cu $2p_{3/2}$ region was deconvoluted into two peaks at 933.2 \pm 0.1 eV (peak I) and 935.1 \pm 0.1 eV (peak II) (cf. Fig. 5), that suggest the existence of at least two chemical environments of Cu2+ cations in the MT-CuO materials. Moreover, the presence of intense satellite peaks (at 941.7 eV and 944.0 eV) and the lack of peak at about 932.6 eV confirm an absence or a presence of negligible amounts of Cu₂O.43,45,46 The peak at the binding energy of 933.2 \pm 0.1 eV is characteristic of Cu²⁺ in the CuO phase.^{43,47} The binding energy of another fitted peak (935.1 \pm 0.1 eV) indicates the existence of Cu²⁺ ions connected to the -OH groups, which were formed on the surface of CuO particles during an exposure of the samples to a humidified atmosphere.⁴⁵ On the other hand, the interaction of Cu²⁺ cations with -OH groups from the clay layers is also possible. As shown in Table 2, the increasing participation of peak I (at 933.2 eV) in relation to peak II (at 935.1 eV) as well as the increasing Al/Si atomic ratio, attributed to the deposition of Al₂O₃ particles on the external surface of MT, are observed with the raising Cu content in the MT-PAA CuY samples. These findings confirm the migration of Cu²⁺ cations into the ditrigonal cavities and/or the partial replacement of the Al³⁺ cations by Cu²⁺ ions in the



Fig. 4 TEM images of calcined MT–PAA Cu400: (A) bright field mode, (B) HR image, and (C) SAED pattern.

sublayers, and are also supported by differences in the catalyst composition determined by XRF (Table 1) and XPS (Table 2), which show slightly lower Cu contents on the surface than in the bulk.^{41,43}

 H_2 -TPR experiments were carried out to recognize reducibility of the copper species formed in the thermally treated materials. As presented in Fig. 6, the profiles recorded for the studied samples show one main reduction peak, which finishes at temperature below 340 °C. Obviously, Cu^{2+} species distributed in the modified materials are reduced to metallic Cu under the applied H_2 -TPR process conditions in two overlapping processes:^{32,48}

$$2CuO + H_2 \rightarrow Cu_2O + H_2O$$
$$Cu_2O + H_2 \rightarrow 2Cu + H_2O.$$





Fig. 5 Cu 2p XPS spectra of selected calcined Cu-containing MT–PAA materials.

Only weak shoulder at lower temperatures appears, which can be attributed to the reduction of surface Cu²⁺. Nevertheless, an influence of Cu(NO₃)₂ solution volume used during the modification on the position of H₂-TPR maximum (*T*_{red}) is clearly observed for the MT–PAA Cu*Y* materials (Table 1). This peak is centered at 267 °C for MT–PAA Cu100, and subsequently shifts to lower temperatures with the increasing Cu content up to MT–PAA Cu500 (*T*_{red} = 241 °C). The further increase in the Cu loading results in harder reducibility of Cu²⁺ species attributed to stronger interaction of formed CuO nanoparticles with the MT platelets.

In the collected $\rm H_2\text{-}TPR$ profiles, the broad peak in the temperature range of 550–750 $^{\circ}\rm C$ is additionally identified. This



Fig. 6 Temperature-programmed reduction profiles of calcined Cucontaining MT–PAA materials.

mass loss is mainly attributed to the dehydroxylation of aluminosilicate support. However, the reduction of Cu^{2+} ions located in the clay layers and the interlayer ditrigonal cavities at so high temperatures cannot be also excluded. The values of $H_{2,consum}/H_{2,theor.}$ ratio between the real amount of consumed H_2 in the temperature range up to 340 °C and the theoretical one (Table 1), calculated assuming the reduction of CuO to metallic Cu, confirm this supposition. The increase in the amount of introduced Cu results in the decreasing $H_{2,consum.}/$ $H_{2,theor.}$ values exhibiting the existence of part of Cu^{2+} species which are very highly stabilized in the structure of the formed catalysts.

Catalytic activity of calcined MT-CuO materials in toluene combustion

The Cu-containing clay catalysts were synthesized to be used in the total oxidation of volatile organic compounds.

| Sample | Cu ²⁺ in CuO (peak I) | | Cu²⁺–OH− (peak II) | | | Sum | | Atomic ratio | | |
|-------------------|-------------------------------------|-------|-----------------------|-------|----------------|-------|--------------------------|-----------------|-------|-------|
| | BE [eV] | % at. | BE [eV] | % at. | Peak I/peak II | % at. | $I_{\rm sat}/I_{\rm mp}$ | Cu/Si | Al/Si | Na/Si |
| MT | _ | _ | _ | _ | _ | _ | _ | _ | 0.36 | 0.08 |
| MT-PAA Cu100 calc | 933.3 | 0.89 | 935.1 | 0.76 | 1.17 | 1.65 | 0.43 | 0.04 | 0.45 | 0.80 |
| MT-PAA Cu200 calc | 933.1 | 1.47 | 935.0 | 1.36 | 1.08 | 2.83 | 0.45 | 0.07 | 0.48 | 0.58 |
| MT-PAA Cu300 calc | 933.3 | 2.01 | 935.2 | 1.99 | 1.01 | 4.00 | 0.55 | 0.10 | 0.53 | 0.40 |
| MT-PAA Cu400 calc | 933.2 | 3.10 | 935.2 | 2.56 | 1.21 | 5.66 | 0.54 | 0.13 | 0.54 | 0.31 |
| MT-PAA Cu500 calc | 933.1 | 4.77 | 935.2 | 3.17 | 1.50 | 7.94 | 0.44 | 0.18 | 0.75 | 0.23 |
| MT-PAA Cu600 calc | 933.1 | 4.54 | 935.2 | 3.33 | 1.36 | 7.87 | 0.48 | 0.18 | 0.71 | 0.15 |
| MT-PAA Cu700 calc | 933.1 | 4.16 | 935.2 | 2.91 | 1.43 | 7.07 | 0.45 | 0.15 | 0.72 | 0.09 |

Table 2 Surface composition of the calcined materials determined by XPS

In Fig. 7A the conversion of toluene achieved over the studied materials in the temperature range of 200–550 °C are shown. In addition, T_{50} (the reaction temperature required for 50% conversion of toluene) is used to evaluate the catalytic activity of the catalysts (Fig. 7B). It should be noted that carbon dioxide and water were the main products formed during the toluene combustion in the presence of investigated samples. Only traces of benzene, a by-product formed with selectivity lower than 0.05%, were detected.

It is clear that the presence of CuO species significantly enhanced the catalytic activity of MT. The value of T_{50} decreases with the increasing Cu content from 427 °C (MT–PAA Cu100) to 310 °C (MT–PAA Cu500), and then grows slightly for the materials with the highest Cu loadings (MT–PAA Cu600 – 313 °C and MT–PAA Cu700 – 317 °C). Thus, correlation between the



Fig. 7 Conversion of toluene (A) and values of $T_{\rm 50}$ (B) determined over calcined MT–PAA and Cu-containing MT–PAA materials.

catalytic performance and the Cu content (especially the surface concentration of Cu species determined by XPS) is found. Nevertheless, it should be kept in mind that dispersion of CuO phase also plays an important role influencing the catalytic activity. For all synthesized catalysts, the mean crystallite size of CuO is very similar and mainly nanoparticles lower than 20 nm are identified. However, at the higher CuO concentrations, the interaction between CuO active phase and aluminosilicate support becomes too strong. In a consequence, the materials with the highest Cu loadings show harder reducibility and lower activity (due to the most probable Mars-van Krevelen mechanism involving lattice oxygen), compared to the materials containing relatively lower Cu amounts. Moreover, it should be kept in mind that Cu²⁺ species built-in the interlayers and sublayers are catalytically inactive being inaccessible for the reacting molecules.

Among the studied samples, the calcined MT-PAA Cu500 material with an optimal content and high dispersion of easily reducible CuO active phase appeared to be an ideal catalyst for the toluene abatement. Kim49 showed that among various transition metal oxides, CuO supported on γ-Al₂O₃ was found to be the most promising catalyst in the aromatic VOCs combustion. Nevertheless, those results ($T_{50} \sim 265 \ ^{\circ}\text{C}$) were achieved in the presence of higher amount of catalyst (0.5 g) compared to the present study (T_{50} \sim 310 °C). The T_{50} values of 303–307 °C over 0.1 g of a catalyst at toluene concentration of 1000 ppm were observed for the CuO-Al₂O₃ systems containing more than 50 wt% of Cu.50 In order to increase in the catalytic activity of CuO-based materials, they were promoted by other various components (e.g. MnOx,⁵¹⁻⁵³ CeO2,^{53,54} ZrO2 ⁵⁵). Thus, the main advantage of the materials developed in this study is high catalytic activity at a relatively low CuO content and absence of expensive additives.

The activity of the MT–PAA Cu500 catalyst was tested in the total oxidation of other aromatic VOCs (benzene, *o*-xylene, *p*-xylene and *m*-xylene) as well. The collected results are presented in Fig. 8. Only CO_2 and H_2O were formed as the products of these reactions. It was found that the activity with respect to the VOC molecule follows the sequence: toluene > xylenes >



Fig. 8 Conversion of various aromatic volatile organic compounds determined over calcined MT-PAA Cu500.

benzene. The similar sequence was previously reported by Kim⁴⁹ for 5 wt% Cu/ γ -Al₂O₃. Obviously, benzene with the highest ionization potential is the most stable molecule, which demands using higher temperatures to be oxidized.

Conclusion

The hydrogel template-assisted route, based on (i) the intercalation of poly(acrylic acid) into the interlayers of montmorillonite, (ii) the subsequent modification of the formed composite with Cu²⁺ cations using adsorption in an aqueous solution of $Cu(NO_3)_2$ at constant pH = 6, and (iii) finally calcination at elevated temperature of 550 °C, allowed us to synthesize CuO-containing clay catalysts. It was shown that the increasing Cu content introduced into the material resulted in a higher order of layered clay structure attributed to the migration of part of Cu²⁺ cations into the clay interlayers and/or even incorporation of these ions in the montmorillonite sublayers. Furthermore, a majority of adsorbed Cu²⁺ formed CuO nanoparticles, highly dispersed between montmorillonite grains, after the thermal treatment. The produced MT-CuO composites showed the open pore structure and high stability of transition metal oxide phase. They also appeared to be excellent catalysts in the total oxidation of VOCs. The toluene combustion was the most effectively catalyzed by the materials characterized by the highest surface concentration of CuO and the weak interaction between active phase and clay support, which promoted the reaction based on the Mars-van Krevelen mechanism.

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