Sorption characteristics of paper produced from sepiolite

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Paper laboratory-produced from sepiolite, Goleš-Serbia was studied to determine its sorption characteristics for nitric oxides, water vapor, and ammonia. The paper adsorbed high percentages of nitric oxides and ammonia was stoichiometrically chemisorbed on paper saturated with NO₂ and H₂O. Infrared spectroscopy showed that the sorption of nitric oxides and ammonia does not destroy the crystal lattice of sepiolite, which was confirmed by XRD-analysis. Sorption of both nitric oxides and ammonia occurred by zeolitic water inside the structural channels of sepiolite. Pressure swing adsorption (PSA) or temperature swing adsorption (TSA) cycles can be repeated many times, in the case of NOₓ and NH₃.

Keywords: ammonia, IR, nitric oxides, sepiolite, sorption, XRD.

The mineral sepiolite has an idealized unit half-cell Mg₁₈Si₆O₉(OH)₄(OH₂)₄nH₂O, where n = 6–8. It has a fibrous morphology related structurally to Mg-Si bands with narrow channels of specified widths on the fiber surface and contains zeolitic, bonded and constitutive water molecules, which are released at different temperatures.¹ Owing to its channels with dimension 0.6–0.9 nm, sepiolite can be classified as a molecular sieve. Miller and Kollermann² found that at 293 K and atmospheric pressure CO₂, SO₂, n-C₄H₁₀, CCl₃NO₂, and n-C₄H₉OH are adsorbed on sepiolite, whereas CO and N₂ are not adsorbed. Dandy³ investigated the adsorption of CH₃NH₂, C₂H₅NH₂, and NH₃ and concluded that ammonia molecules enter into the channels, not only because of the molecular diameter of about 0.4 nm, but also because of strong interaction with the channel walls.

Barrer and Mackenzie⁴ suggested that the accessibility of sepiolite channels may depend more on the polarity of a substance than on the dimensions of the molecules. Both polar and nonpolar molecules can enter the channels, with a negative free energy change for polar molecules and a positive one for nonpolar molecules. If the adsorbed cations or water molecules are distributed within the sepiolite channels, the diffusion of nonpolar molecules is suppressed. Thus, the adsorption of substances such as N₂, O₂, and CO₂ occurs at or near the channel entrance. From ESR measurements of ammonia
adsorption on sepiolite, Hasashi and Makiyo\textsuperscript{5} concluded that the sepiolite changes its electron-spin state when ammonia is adsorbed. The adsorption compensates the charge produced by the polarization of the planes of Mg, O and OH in the sepiolite crystal lattice. The OH− and O− planes are accessible to adsorbed gases, so the positive charges of an oxygen plane are neutralized. In this case, the electrostatic potential of a negatively charged Mg-plane is increased and a free electron moves into a cavity, so ammonia is adsorbed as NH$_3^+$. In this way, adsorbed molecules, although they are not in direct contact with a negatively charged Mg-plane, compensate the charge by the positive charge of an oxygen plane.

Aznar \textit{et al.}\textsuperscript{6} Serna \textit{et al.}\textsuperscript{7} and Gonzales-Roman \textit{et al.}\textsuperscript{8} used infrared spectroscopy (IR) to investigate the structure of sepiolite. According to Gonzales-Roman \textit{et al.}\textsuperscript{8} the main IR vibration region is between 4000 cm$^{-1}$ to 3000 cm$^{-1}$, and in this range are OH-extended bands of some important groups. The absorption at 3720 cm$^{-1}$ corresponds to free SiO-H groups, and occurs only when samples have many external silanol groups; at 3680 cm$^{-1}$ the sharp band of the Mg$_3$OH group appears; the absorption of structurally bonded water is at 3580 cm$^{-1}$; and the bands, attributable to zeolitic water are at 3440 cm$^{-1}$ and 3640 cm$^{-1}$. There is another vibration band at 1655 cm$^{-1}$, which is attributable to bonded water, while the shoulder at 1700 cm$^{-1}$ is attributable to zeolitic water. The lattice vibrations are between 1200 cm$^{-1}$ and 400 cm$^{-1}$; the connecting SiO bands are at 1200 cm$^{-1}$, 1080 cm$^{-1}$ and 980 cm$^{-1}$, the Si-O-Si bands are at 1020 cm$^{-1}$ and 470 cm$^{-1}$, the Si-O-Mg bands are at 440 cm$^{-1}$; and the Mg$_3$OH bands are at 655 cm$^{-1}$.

Fernandez-Montreal and De Sande-Moreno\textsuperscript{9} used sepiolite in the form of sepiolite ceramics as a sorbent, catalyst, catalysts support, or a reagent for ethylene oxidation. Its corresponding use in the form of sepiolite paper is advantageous for the following reasons:

– paper can be used either for sorption during filtration through a sorbent layer or with a flow parallel to the paper sheets.

– for filtration through the paper, the diffusion paths are short and the flow resistance is high. For flow parallel to the paper sheets, the diffusion paths are longer and the flow resistance is negligible. In both cases, the sorption dynamics are better than when sorbent granules are used;

– for industrial or small-scale applications, paper sheets have some advantages in regard to equipment construction and exploitation;

– if sepiolite is used as a catalyst or a catalyst support, paper sheets can be applied as either membrane catalysts or ordinary catalysts;

– sepiolite paper is also easy and inexpensive to produce in any quantity;

– because paper is produced at a temperature of 105 °C, the sepiolite structure is not affected. Also, paper based on organic or mineral fibers can be produced, thus the sorption or catalytic elements can be used over a broad temperature range;

– finally, sepiolite paper can be used to produce corrugated paper board, Ishida \textit{et al.}\textsuperscript{10} or honeycomb structures, which are advantageous for many applications.
The purpose of this paper is to present the results of an investigation of the sorption characteristics of sepiolite paper made from sepiolite from the magnesite and sepiolite mine, Goleš - southern Serbia. NO\textsubscript{x}, NH\textsubscript{3} and H\textsubscript{2}O were used as adsorptives and temperature swing adsorption (TSA) cycles were used for sorption and paper regeneration. XRD analysis and IR spectrometry were employed to determine if structural OH groups at the sepiolite surface are excited by sorption of nitric oxides and ammonia, as well as other functional groups bonded to the sepiolite crystal lattice. Also, both techniques can be used to determine whether irreversible loss of crystallinity occurs during regeneration of the sepiolite paper. These data on sorption and desorption of NO\textsubscript{x} and NH\textsubscript{3}, on possible structural changes of the sepiolite, and on the conditions for the TSA cycles are useful for the design of filters for gas purification.

**EXPERIMENTAL**

*Preparation of sepiolite paper sheets*

Several grades of sepiolite paper were prepared in the laboratory and tested:

The papers were prepared: (1) with bleached conifer cellulose pulp (30 % to 80 % sepiolite); (2) with borosilicate glass fibers (30 % to 60 % sepiolite, 5 % sodium silicate), and (3) on borosilicate glass paper with a thin layer of pure sepiolite. In the preparation of the first two types of paper, sepiolite pink from a trace of Fe oxides was used, whereas the third paper was prepared with white sepiolite (as is used for thin-layer chromatography where the color is important). Papers with 60 % sepiolite were used for most experiments. The pink sepiolite has the following chemical constitution (wt. %): 38.56 SiO\textsubscript{2}, 3.42 CaO, 27.57 MgO, 0.04 Fe\textsubscript{2}O\textsubscript{3}, 0.07 NiO, 0.29 Na\textsubscript{2}O, and 28.61 loss on ignition. The sepiolite was ground to an average particle size of 5.8 \(\mu\text{m}\) (particles from 2.1 \(\mu\text{m}\) to 17 \(\mu\text{m}\)), mixed with pulped cellulose fibers in deionized water (suspension with 1 % dry matter), and circular paper sheets were made on a laboratory paper-making set. The paper disks were dried at 105 °C. To increase the surface area, some disks were corrugated before drying. Detailed preparation procedures have been presented by Mitrović et al.\textsuperscript{11} Each disk was 250 0.5 mm with a weight of 250 g/m\textsuperscript{2}. Results of scanning electron microscopy (SEM) of sepiolite paper, obtained using a JEOL 4-JSM-840a instrument, are presented in Fig. 1.

*Fig. 1. SEM of the sepiolite – cellulose paper (60 % : 40 %).*

*Fig. 2. SEM of crystallized NH\textsubscript{4}NO\textsubscript{3} in the sepiolite paper.*

*Determination of the sorption equilibrium characteristics*

Cellulose-based sepiolite paper disks 60 mm in diameter were activated by heating at 160 °C for two hours. In the initial experiments, NO\textsubscript{x}, CO\textsubscript{2}, NH\textsubscript{3}, HCl, and H\textsubscript{2}O were adsorbed at room temperature (22 2 °C) by placing paper disks over aqueous solutions of each gas for 24 h. The adsorbed quantities were measured gravimetrically.
As the equilibrium quantity of sorbed NO\textsubscript{x} was much greater than for the other investigated gases, additional experiments were performed with NO\textsubscript{x} and H\textsubscript{2}O only. Ammonia was used to neutralize NO\textsubscript{x} by subsequent sorption of NH\textsubscript{3} on paper saturated with NO\textsubscript{x}. These sorption experiments were performed in the same way as described above. The ammonium nitrate formed at the surface of the paper was either desorbed by heating to 160 ºC or leached with distilled water. Sorption experiments were repeated thirty times on each disk. The disks were activated at 160 ºC for two hours after each adsorption desorption cycle.

**Determination of non-equilibrium-sorption characteristics**

The same kind of sepiolite-cellulose paper disks and experimental techniques as described above were applied to measure the influence of temperature on the sorption of NO\textsubscript{x} and H\textsubscript{2}O (temperatures of 30–80 ºC and sorption steps of 30 min). Desorption was performed at 160 ºC.

The potential of sepiolite paper or paper structures to remove NO\textsubscript{x} from industrial waste gases by the use of TSA requires good regeneration efficiency, and high mechanical stability after many adsorption desorption cycles. At a specified adsorption temperature (80 ºC, the temperature of waste gases from the nitric fertilizer factory in Pančevo, Serbia, was used) and a desorption temperature of 160 ºC, the regeneration efficiency is expressed as the ratio of sorbed quantities: \( S_i / S_j \) where \( i = 1 – n \) is the number of sorption cycles, and the stability is the ratio of corresponding tensile strengths: \( F_a / F_0 \). \( F_0 \) and \( F_a \) are the initial tensile strength and the tensile strength after \( n \) cycles, respectively.

To measure the regeneration efficiency and the mechanical stability of the sepiolite-cellulose paper, cycling adsorption and desorption of NO\textsubscript{x} and H\textsubscript{2}O in the temperature interval of 80 – 160 ºC was repeated thirty times.

To ensure that only the sepiolite is the effective adsorbent for NO\textsubscript{x} and not the basic, cellulose fibers, a series of parallel experiments with adsorptions and desorptions of NO\textsubscript{x} and H\textsubscript{2}O were performed using paper disks based on glass fibers (60 % sepiolite).

**IR spectrometry and X-ray diffraction (XRD) analysis**

Disks 60 mm in diameter and composed of 60 % sepiolite and 40 % cellulose fibers were placed in sealed glass vessels in atmospheres of water vapor over water or vapor over 90 % aqueous nitric acid or 25 % aqueous ammonia solution for 24 h at room temperature. Then, the disks were exposed for 24 h to open air. Subsequently, IR spectra were recorded with a Specord 75 IR spectrometer (Carl Zeiss, Jena) in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using the K\textsubscript{Br} pellet technique. To discern the effects of regeneration, one sample with adsorbed NO\textsubscript{x} was heated for two hours at 180 ºC and another sample at 160 ºC before recording the IR spectra.

To determine how NO\textsubscript{x} sorption changes the crystallinity of sepiolite, untreated sepiolite paper, paper after activation at 160 ºC, and paper regenerated at 160 ºC after several NO\textsubscript{x} sorption–desorption cycles were examined by XRD.

The XRD data were obtained using a Philips PV Automated Powder Diffractometer system with a TTK Temperature Attachment Unit (Anton Paar K.G.) on a Philips PW Vertical Goniometer (820, CuK\textsubscript{α} radiation, 35 kV, 50 mA, scanning rate of 1.5 °2 /min).

**RESULTS AND DISCUSSION**

The experiments showed that paper based on either cellulose of borosilicate glass fibers is easy to produce with 60 % ground sepiolite, and that such paper has a satisfactory structure and sepiolite fiber distribution, thickness (0.5 mm), and tensile strength (4.5 N/15 mm). Such paper may be produced on standard continuous paper machines.

The initial set of equilibrium sorption experiments (Table I) indicated that sepiolite paper at room temperature is not an outstanding sorbent for any of the used vapours
SORPTION ON SEPIOLITE PAPER

The quantities of NH₄NO₃ desorbed by heating at 160 °C in 8 cycles are 35 %, or by leaching at 22 °C in 8 cycles are 27.5 %. Four possibilities of utilizing sepiolite paper with sorbed ammonium nitrate were considered:

1. Direct consumption of ground paper as a low grade fertilizer.
2. Leaching the NH₄NO₃ and drying and activating the paper (dry NH₄NO₃ is a high-grade fertilizer).
3. Repulping the paper, leaching ammonium nitrate, and producing new paper from the pulp.
4. Catalytic destructive desorption of NH₄NO₃ by heating the paper at 160 °C. Chemical analysis confirmed that only NH₄NO₃ was leached by distilled water. Thermal desorption probably proceeds by catalytic destruction with sepiolite as the cat-

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TABLE I. Sorption equilibrium characteristics for humid gases

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>% Sorbed</th>
<th>Desorption (temperature) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>32.7</td>
<td>160</td>
</tr>
<tr>
<td>H₂O</td>
<td>6.0</td>
<td>100</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.8</td>
<td>70</td>
</tr>
<tr>
<td>NH₃</td>
<td>5.8</td>
<td>70</td>
</tr>
<tr>
<td>HCl</td>
<td>6.7</td>
<td>64</td>
</tr>
</tbody>
</table>

Sorption equilibriums of NOₓ + H₂O after 8 cycles for the same sorbent were higher (3.8 6 %), with a desorption temperature of 160 °C.

Samples with adsorbed NOₓ were neutralized with vapor phase NH₃. The produced NH₄NO₃ remains in the structure of the paper and crystallizes inside it if the samples are left in sealed vessels (Fig. 2).

Fig. 3. Sorption-desorption of NOₓ on sepiolite paper as a function of the sorption temperature (desorption at 160 °C).

Fig. 4. Sorption-desorption of water vapor on sepiolite paper as a function of the sorption temperature (desorption at 160 °C).
2 NH₄NO₃  2N₂ + 4H₂O + O₂ where O₂ reacts with the cellulose in the paper. This may explain the higher values obtained by thermal desorption.

The non-equilibrium measurements of the sorption capacity vs. temperature of the paper based on cellulose fibers (sorption steps of 30 min) are presented in Table II for NOₓ and water vapor.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Temperature/°C</th>
<th>Sorp. - Desorp.</th>
<th>Average/%</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ</td>
<td>30</td>
<td>Sorp. 10.1 0.9</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 10.1 0.6</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Sorp. 13 2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 14 1</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Sorp. 16 2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 16.3 0.9</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Sorp. 16.3 0.5</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 16.3 0.5</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Sorp. 17.0 2.0</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 17.0 0.3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Sorp. 18 1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 18 1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>30</td>
<td>Sorp. 6.2 0.2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 6.2 0.2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Sorp. 5.5 0.4</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 5.5 0.4</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Sorp. 6.2 0.2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 6.2 0.1</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Sorp. 5.3 0.2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 5.3 0.2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>Sorp. 4.6 0.0</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 4.6 0.1</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Sorp. 4.4 0.1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desorp. 4.5 0.1</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sorption capacity of the sepiolite paper for NOₓ increases with temperature (Fig. 3).

These results and the logarithmic dependence of the sorbed NOₓ on temperature suggest a chemisorption mechanism for NOₓ sorption.

The linear decrease of the sorption capacity for water on sepiolite (Fig. 4) confirms the results of other research on the physical adsorption of water on sepiolite.
Cycling TSA experiments between 80 °C and 160 °C under non-equilibrium conditions are presented in Table III.

### TABLE III. Cyclic sorption-desorption quantities, for the mixture water vapor-NO\textsubscript{x} (repeated cycles with the same sepiolite paper)

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Number of measurements</th>
<th>T/ ºC</th>
<th>max. %</th>
<th>min. %</th>
<th>Aver. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>30 Sorp.</td>
<td>80</td>
<td>25.0</td>
<td>10.2</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>24.4</td>
<td>9.7</td>
<td>13.2</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>30 Sorp.</td>
<td>80</td>
<td>6.1</td>
<td>3.5</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>160</td>
<td>6.1</td>
<td>3.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

The results show that the adsorbed and desorbed quantities of NO\textsubscript{x} decrease after several cycles to a near constant value of approximately 12 % (Fig. 5).

The regeneration efficiency for NO\textsubscript{x} is: $S_{30}/S_1 = 0.55$ and $S_{30}/S_6 = 0.1$ which indicates that sepiolite paper may be useful as a high-capacity sorbent for a few cycles, or as a somewhat lower-capacity sorbent for a greater number of cycles. The chemisorption mechanism (Fig. 3) and the decrease in sorption capacity after several cycles is explained by partial irreversible binding of NO\textsubscript{x} to sepiolite while the remaining NO\textsubscript{x} is reversibly adsorbed. This was also confirmed by IR-analysis.

The sorption capacity of sepiolite paper for water slowly decreases: $S_{30}/S_1 = 0.84$.

As water adsorption on sepiolite is completely reversible between 80 °C and 160 °C, this decrease is attributed to the deterioration of the cellulose during desorption at 160°C.

Measurements of the tensile strength of sepiolite paper strips show that the paper is partially damaged during 30 TSA cycles with NO\textsubscript{x} because: $F_{30}/F_0 = 0.47$.

Also, the paper samples are discolored after 30 cycles, showing partial carbonization of the cellulose fibers. However, the integrity of the paper is sufficient for handling.

The measurements presented in Table IV show that approximately the same amount of NO\textsubscript{x} is adsorbed on sepiolite paper based on borosilicate glass fibers as on...
paper based on cellulose fibers: $S_{av(1-3)} = 17.2\%$ (160 ºC/80 ºC). However, smaller quantities of water vapor are adsorbed and desorbed than on cellulose-based paper under the same conditions: $S_{av(1-3)} = 3.6\%$ (160 ºC/80ºC). These measurements show that only the sepiolite in a paper adsorbs NO\textsubscript{x}, whereas a portion of H\textsubscript{2}O is adsorbed on the cellulose in papers with cellulose fibers.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Number of measurements</th>
<th>$T$ºC</th>
<th>% Sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>3</td>
<td>Sorp.</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Desorp.</td>
<td>160</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>3</td>
<td>Sorp.</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Desorp.</td>
<td>160</td>
</tr>
</tbody>
</table>

After three NO\textsubscript{x} TSA cycles, the glass fiber-based sepiolite paper appears unchanged. It is to be expected that even after a very large number of TSA cycles the mechanical strength of the paper will not have changed.

The IR spectra of a cellulose-based sepiolite paper with adsorbed water and NO\textsubscript{x} after regeneration at 180 ºC and after regeneration at 160 ºC, and after it is allowed to reach equilibrium with adsorbed water in a laboratory environment are presented in Fig. 6. Fig. 6a presents the spectrum of the sepiolite paper submitted to water vapor.

The Si–O–Mg band is at 440 cm\textsuperscript{-1}, the Si–O–Si group is at 470 cm\textsuperscript{-1}, and the vibrations of Mg\textsubscript{3}OH are at 655 cm\textsuperscript{-1}. The vibrations at 750 cm\textsuperscript{-1} and 880 cm\textsuperscript{-1} are from CO\textsubscript{3}\textsuperscript{2–} since sepiolite contains some MgCO\textsubscript{3} (confirmed by recording the IR spectrum of MgCO\textsubscript{3}). The vibrations of the Si–O bonding bands appear at 980 cm\textsuperscript{-1} and 1080 cm\textsuperscript{-1}, and the Si–O–Si vibrations are present at 1020 cm\textsuperscript{-1}.

Shoulders from the Si–O group appear at 1200 cm\textsuperscript{-1}, a shoulder from CO\textsubscript{3}\textsuperscript{2–} at 1450 cm\textsuperscript{-1} and vibrations from bonded water occur at 1620 cm\textsuperscript{-1}, vibrations from zeolitic water at 1660 cm\textsuperscript{-1}, and vibrations from CO\textsubscript{3}\textsuperscript{2–} at 2880 cm\textsuperscript{-1}. There is a broad extended band at 3400 cm\textsuperscript{-1} (zeolitic water) with a smaller band at 3550 cm\textsuperscript{-1}, (bonded water), which suggests that the surface of the sepiolite fibers is covered by a compact layer of zeolitic and adsorbed water. For this reason, vibrations of Si–OH and Mg\textsubscript{3}OH at 3600 cm\textsuperscript{-1} to 3700 cm\textsuperscript{-1} are not visible.

The IR spectrum of sepiolite paper on which NO\textsubscript{2} is sorbed is presented in Fig. 6b. Compared to Fig. 6a, it is clear that the lattice vibrations between 400 cm\textsuperscript{-1} and 500 cm\textsuperscript{-1} are very weak; Mg\textsubscript{3}OH group vibrations at 655 cm\textsuperscript{-1} are not visible, and carbonate bands are absent. The lattice band from the Si–O group at 1060 cm\textsuperscript{-1} is evident, and the bands from zeolitic water at 1630 cm\textsuperscript{-1} and from zeolitic and bonded water at 3550 cm\textsuperscript{-1} are strong. Also, new bands appeared, one at 600 cm\textsuperscript{-1}, and at 830 cm\textsuperscript{-1}, and a very strong band at 1380 cm\textsuperscript{-1}.

The IR spectrum of sepiolite paper after both regeneration at 180 ºC and NO\textsubscript{2} sorption is presented in Fig. 6c. Compared to Fig. 6b, the bands attributable to zeolitic water are much weaker (1630 cm\textsuperscript{-1} and 3350 cm\textsuperscript{-1}), as is the band at 1380 cm\textsuperscript{-1}. The shoulder attributable to CO\textsubscript{3}\textsuperscript{2–} appears at 1340 cm\textsuperscript{-1}, the lattice vibrations at 1060 cm\textsuperscript{-1}.
Fig. 6. a) IR spectrum of sepiolite paper submitted to water vapor; b) IR spectrum of sepiolite paper with NO2 sorbed; c) IR spectrum of sepiolite paper regenerated at 180 °C; d) IR spectrum of sepiolite paper regenerated at 160 °C; and kept in air for about 100 days.
are the same, and a band at 1220 cm\(^{-1}\) is visible. Vibrations at 600 cm\(^{-1}\) and 830 cm\(^{-1}\) are much weaker.

Sepiolite paper regenerated from NO\(_2\) sorption at 160 °C and then kept in laboratory air for \(100\) days showed the IR spectrum presented in Fig. 6d. Bands attributable to zeolitic and bonded water are visible, as are carbonate bands at 2880 cm\(^{-1}\), 1447 cm\(^{-1}\), 880 cm\(^{-1}\) and 760 cm\(^{-1}\), lattice vibrations between 400 cm\(^{-1}\) and 500 cm\(^{-1}\) are clear, as are vibrations at 655 cm\(^{-1}\) and the band at 1380 cm\(^{-1}\) remained, although much weaker than the corresponding band in Fig. 6b.

The IR results indicate that a portion of the nitric oxides bonds to the sepiolite lattice by removing OH groups of the constitutive water and occupying its place (vibrations at 655 cm\(^{-1}\) attributable to Mg\(_3\)OH are probably covered by a new peak). This produces new bands at 1380 cm\(^{-1}\) and 600 cm\(^{-1}\), which probably result from NO\(_x\) bonded to the oxygen of the Mg–O–Si group (450 cm\(^{-1}\)). This bond is not strong, since NO\(_x\) was desorbed as a result of heating and the resulting IR intensity decreased. The strongest bonds with NO\(_x\) are within the sepiolite structure, where some OH groups of constitutive water are exchanged by the NO\(_x\), since the band at 1380 cm\(^{-1}\) remains after heating the paper or by placing it in air for a long period of time. This fact can explain the decrease in the quantity of NO\(_x\) sorbed on the paper, which has a constant value of about 12 % after several sorption-desorption cycles. A portion of the sorbed NO\(_x\) is strongly bonded to the sepiolite crystal lattice (a little weaker at the edges of sepiolite cells, where, also, constitutive OH groups are bonded to Mg ions), and, therefore, only a portion of the nitric oxide bonded to the zeolitic water inside the sepiolite channels are sorbed and desorbed.

Fig. 6d also shows that sorbed nitric oxides do not destroy the CO\(_3^{2-}\) group, since the band appears after the water and NO\(_x\) are desorbed.

The IR-spectrum of paper placed in an ammonia atmosphere and released in air is shown in Fig. 7. There are no great differences between this spectrum and the spectrum presented in Fig. 6a, although the vibrations of bonded water are weaker (at 1620 cm\(^{-1}\) and 3550 cm\(^{-1}\)). These results, and the fact that only 5 % of NH\(_3\) is sorbed, indicate that ammonia is adsorbed by zeolitic water.

Fig. 7. IR spectrum of paper with sorbed ammonia.
The X-ray diffractograms of paper before NO\textsubscript{x} sorption and of the same paper after NO\textsubscript{x} sorption and desorption by heating at 160 °C are shown in Fig. 8a and b, respectively. The letters S and Mg denote sepiolite and magnesite, respectively. Also present are two nonidentified peaks (Fig. 8a). One of these peaks does not occur in Fig. 8b and can possibly be ascribed to the cellulose in the paper.

**CONCLUSIONS**

- Sepiolite is an excellent material for the production of sorbent, or catalytic papers with either cellulose or glass fibers due to its fibrous structure, affinity for basic fibers, and the properties of sepiolite as a sorbent, a carrier of catalysts, or a catalyst.

  - Sorbents in the form of paper have many advantages over powders and granules, such as the accessibility of the surface, pressure losses, and regeneration ability, as well as in production processes and in the construction of adsorption units.

  - Sepiolite paper shows good characteristics for the sorption of NO\textsubscript{x} and chemisorption of NH\textsubscript{3} when NO\textsubscript{x} is already sorbed.

  - TSA cycles between 80 °C and 160 °C and with 30 regenerations show that the capacity of a paper for NO\textsubscript{x} decreases after several cycles, but remains constant after that (about 12 % adsorbed and desorbed). Paper based on cellulose fibers is not seriously damaged, and it can be expected that paper based on borosilicate glass fibers will not be damaged at all.

  - NH\textsubscript{4}NO\textsubscript{3} was removed from the paper by leaching or destroyed by heating.

  - Infrared spectrometry shows that the structure of sepiolite is not destroyed by the sorption of NO\textsubscript{x} and regeneration of the paper, but a portion of the NO\textsubscript{x} is irreversibly bonded to the sepiolite.
ИЗВОД

СОРПЦИОНЕ КАРАКТЕРИСТИКЕ ХАРТИЈЕ ПРОИЗВЕДЕНЕ ОД СЕПИОЛИТА
МИРОСЛАВ ДОЈИНОВИЋ, МИЛАН МИТРОВИЋ, МИЈЕНКО МАРИЋ, ВЕРА ВУЧЕЛЛИЋ и
ДУНАН ВУЧЕЛЛИЋ

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Лабораторијски произведена хартија од сепиолита из рудника Голељ (Србија) је испитивана да се одреде ради одређивања њених сорпционих карактеристика за азотове оксиде, водну пару и амонијак. Хартија је адсорбовала велике проценте азотових оксиде, а амонијак је стехиометријски хемисорбован на хартији засићеној са NO2 и H2O. Инфрацрвена спектроскопија је показала да сорпција азотових оксиде и амонијака не разара кристалну решетку сепиолита, што је потврђено XRD-анализом. Сорпција азотових оксиде и амонијака се одиграва у зеолитској води унутар структурних каналова сепиолита. Адсорпција са варијацијама притиска (PSA) или температуре (TSA) може се применити на десорпцију азотових оксиде великих броја чита. Амонијум-нитрит настао сукцесивном адсорпциом NO2 и NH3 се може из хартије уклонити уврстан или термичком разграђењем. Такође ова хартија може да се користи као вештачко ђубриво.

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