Abstract: ZnS nanoparticles stabilized by cetyltrimethylammonium bromide were deposited on montmorillonite forming the ZnS-MMT nanocomposite. The nanocomposite was characterized by UV-Vis DRS, SEM-EDAX, FTIR, XRD and nitrogen physisorption and tested for N2O photocatalytic decomposition in an annular batch reactor illuminated with an 8 W Hg lamp (254 nm wavelength). Photolysis of N2O was tested at the same conditions. The N2O conversion in inert gas was 79% after 24 hours of illumination and was attributed to the simultaneous N2O photocatalytic and photochemical decomposition. The presence of water vapor inhibited photocatalytic reaction pathway while N2O photolysis was improved. Photocatalytic performance was higher with catalyst in fluidized bed than in fixed bed. The reason is that both mass and photon transfer to the photocatalyst was maximized. Better results were obtained with Zn-MMT compared to Evonic P25 catalyst.
Dr. Sixto Malato,
Managing Guest Editor
Catalysis Today “Special Issue SP4”

Dear Prof. Dr. Sixto Malato,

We are very pleased to learn from your letter about your recommendations for our manuscript entitled “Photocatalytic decomposition of N₂O on ZnS-MMT catalysts” (manuscript ID: CATTOD-D-13-00349).

The manuscript has been carefully revised and new data according reviews recommendation was added in the revised text. We appreciate the useful comments and suggestions from the reviewers. The point-by-point answers to the comments and suggestions were uploading as separate file.

With kind regards,

Lucie Obalová
Corresponding author

VSB - Technical University of Ostrava
17. listopadu 15
708 33 Ostrava
Czech Republic
E-mail:lucie.obalova@vsb.cz
Manuscript: L. Obalova, M. Sihor, P. Praus, M. Reli and K. Koci

**Photocatalytic decomposition of N\textsubscript{2}O on ZnS-MMT catalyst**

**List of reviewer’s comments and our actions**

**Reviewer 1**

<table>
<thead>
<tr>
<th>Reviewer’s note</th>
<th>Our reply</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. In the Fig. 3 please recalculate the X-axis in the (nm) scale because even in the manuscript you operate with nm rather than cm(-1).</td>
<td>The X-axis in the Fig. 3 was recalculated.</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Fig. 3 UV-Vis DRS spectra of ZnS nanoparticles and bulk particles on montmorillonite" /></td>
</tr>
<tr>
<td>2. In the end of section 3.1 the specific surface area of ZnS-MMT sample should be measured in the m\textsuperscript{2}/g.</td>
<td>Thank you, this mistake was corrected.</td>
</tr>
<tr>
<td>3. Please provide your experimental data with (a) - blank experiment without photocatalysts because N\textsubscript{2}O has probability to be decomposed photochemically under 254 nm irradiation especially if light source has additional spectral lines in shorter wavelengths (Cvetanovic R. J., J. Chem. Phys., 43, 1450 (1965)).</td>
<td>Thank you the Reviewer to this extremely valuable comment. We provided blank experiments without photocatalyst in N2O/N2, N2O+O2/N2, N2O+H2O/N2 and N2O+H2O+O2/N2 mixtures under 254 nm irradiation which documented significant contribution of photochemical decomposition of N2O. Blank tests are demonstrated in Fig. 5 and 7 and following comments were added to the manuscript: Moreover, photolysis of N2O was tested at the same conditions. Results showed that 34% of N2O was decomposed after 24 hours by photolysis, while the presence of ZnS-MMT and Evonik P25 catalyst caused a significant improvement of N2O conversion to the value of 75% and 60%, respectively. This is caused by the presence of a parallel reaction pathway of photocatalysis (Eq. 1) that co-exists with the direct photolysis (Eq. 3). N2O has is decomposed photochemically with ( \lambda \geq 240 \text{ nm} ) ([4]) and in our case the reaction was caused by additional spectral lines in shorter wavelengths of the UV lamp.</td>
</tr>
</tbody>
</table>
\[
\text{N}_2\text{O} \xrightarrow{h\nu} \text{N}_2 + \frac{1}{2}\text{O}_2 \quad (3)
\]

Fig. 5 Time dependence of \(\text{N}_2\text{O}\) conversion over ZnS-MMT and Evonic P25
Conditions: 0.1 g of catalyst spread on adhesive tape, 1000 ppm \(\text{N}_2\text{O}\) in \(\text{N}_2\), 8 W Hg lamp (\(\lambda = 254\ \text{nm}\)).

Fig. 7 Time dependence of \(\text{N}_2\text{O}\) conversion over ZnS-MMT and Evonic P25 photocatalysts in fluidized bed reactor.
Conditions: 0.1 g catalyst, 100 ppm \(\text{N}_2\text{O}\) (+ 6.5 mol% \(\text{O}_2\) + 0.6 mol% \(\text{H}_2\text{O}\)) in \(\text{N}_2\), 8 W Hg lamp (\(\lambda = 254\ \text{nm}\)).

\(\text{N}_2\text{O}\) conversion during photocatalytic experiments as well as \(\text{N}_2\text{O}\) conversion caused by photolysis is depicted. The presence of oxygen in the reaction mixture (\(\text{N}_2\text{O} + \text{O}_2\)) did not cause significant changes in the rate of the photochemical and photocatalytic decomposition of \(\text{N}_2\text{O}\).

Water vapor affected the rate of photocatalysis and photolysis of \(\text{N}_2\text{O}\) quite differently. Photolysis of \(\text{N}_2\text{O}\) in wet gas proceeded faster than in inert gas and a further increase in its rate was caused by the addition of oxygen to \(\text{N}_2\text{O} + \text{H}_2\text{O}\). In contrast, photocatalytic decomposition of \(\text{N}_2\text{O}\) was strongly inhibited by water vapor and most of \(\text{N}_2\text{O}\) in mixture of \(\text{N}_2\text{O} + \text{H}_2\text{O}\) and \(\text{N}_2\text{O} + \text{O}_2 + \text{H}_2\text{O}\) was decomposed by photolysis.

Kinetic constants were used for the purpose of comparing the performance of fixed and fluidized catalyst beds, since different \(\text{N}_2\text{O}\) initial concentrations were used in these experiments. Assuming that both photocatalytic and photochemical \(\text{N}_2\text{O}\) decomposition proceeds parallel and can both be described by 1st order rate law, the total rate of \(\text{N}_2\text{O}\) disappearance is equal to the sum of the \(\text{N}_2\text{O}\) decrease by
photocatalytic and photochemical pathways and is also described by 1st order rate law:

\[-r_{N_2O} = k_1 \cdot c_{N_2O} + k_2 \cdot c_{N_2O} = k \cdot c_{N_2O}\]

Where \(c_{N_2O}\) is the concentration of \(N_2O\) (mol cm\(^{-3}\)), \(k = k_1 + k_2\) is the complex kinetic constant (cm\(^3\) h\(^{-1}\) g\(_{cat}\)^{-1}), \(-r_{N_2O}\) is rate of \(N_2O\) decrease (mol g\(_{cat}\)^{-1} h\(^{-1}\)).

Kinetic constants evaluated from experiments in fluidized bed in different reaction mixtures show following order: \(k(N_2O+O_2) > k(N_2O) > k(N_2O+H_2O+O_2) > k(N_2O+H_2O)\) which corresponds well to the conversion order in Fig. 7. However, if it is needed to reduce the concentration of \(N_2O\) in the mixture with water vapor and oxygen, the presence catalyst is practically unnecessary, because photolysis of \(N_2O\) prevails under these conditions.

4. I also recommend to check the reactor impermeability since you conduct rather long experiments. Please provide the 24 hr \(N_2O\) concentration profile in the dark along with the blank experiment.

Reactor impermeability was checked during every experiment by on-line pressure measurement. \(N_2O\) concentration profile in the dark during 24 hours was shown in new table (Table 1) with following comments:

In addition to the reaction experiments, a control experiment was conducted in the absence of UV light in which 100 ppm of \(N_2O\) in \(N_2\) and 0.1 g of ZnS-MMT catalyst was added to the reactor. The results in Table 1 showed that \(N_2O\) concentration profile during 25 hours is stable, i.e. there was no absorption to the sides of the reactor or on the catalyst surface.

### Table 1 Reproducibility of photocatalytic experiments of \(N_2O\) decomposition over ZnS-MMT and 24 hours \(N_2O\) concentration profile in dark in fluidized bed reactor.

<table>
<thead>
<tr>
<th>Reproducibility (^a)</th>
<th>(N_2O) concentration profile in dark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hours)</td>
<td>(N_2O) conversion (%)</td>
</tr>
<tr>
<td>15</td>
<td>62.8</td>
</tr>
<tr>
<td>15</td>
<td>58.5</td>
</tr>
<tr>
<td>22</td>
<td>75.8</td>
</tr>
<tr>
<td>22</td>
<td>75.2</td>
</tr>
<tr>
<td>23</td>
<td>77.7</td>
</tr>
<tr>
<td>24</td>
<td>78.8</td>
</tr>
</tbody>
</table>

\(^a\) 0.1 g catalyst, 100 ppm \(N_2O\) in \(N_2\), 8 W Hg lamp (\(\lambda = 254\) nm)

\(^b\) 0.1 g catalyst, 100 ppm \(N_2O\) in \(N_2\)

### Reviewer 2

<table>
<thead>
<tr>
<th>Reviewer’s note</th>
<th>Our reply</th>
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</thead>
<tbody>
<tr>
<td>1. I recommend adding some data concerning the reproducibility into manuscript as a figure or a table.</td>
<td>Regarding to this comment, we added table documenting the reducibility of photocatalytic experiments: The reproducibility of photocatalytic experiments was...</td>
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<tr>
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<tr>
<td>verified by repeated tests (Table 1).</td>
<td></td>
</tr>
<tr>
<td>2. I am not sure that it is possible to write: &quot;and a relatively high catalyst surface&quot; (in conclusion) for catalyst with the surface area only 3.7 m²/g, which is mentioned at the page 9 without per gram.</td>
<td>Thank you for reviewer comment. We corrected this discrepancy: The catalyst in suspension showed better results of N₂O photocatalytic decomposition than the catalyst spread on adhesive tape. This was due to more efficient contact between the catalyst and N₂O molecules, lower mass transfer resistance and higher catalyst surface which was exposed to UV radiation.</td>
</tr>
<tr>
<td>3. Manuscript includes also another mistyping and English is not as the sufficient level. It should be corrected.</td>
<td>The revision of English was accomplished.</td>
</tr>
</tbody>
</table>
07 July 2013

Dear Colleague,

Your paper of draft title “Photocatalytic decomposition of N2O on ZnS-MMT catalyst” has been selected to be part of the Catalysis Today-Special issue SELECTED CONTRIBUTIONS OF THE 4th INTERNATIONAL CONFERENCE ON SEMICONDUCTOR PHOTOCHEMISTRY (SP4). We need you to please strictly follow the instructions and dates attached.

The articles should be written according to journal instructions (available at journal web pages http://www.elsevier.com/wps/find/journaldescription.cws_home/500857/authorinstructions). Article should be through with Elsevier Editorial System (EES) service (http://ees.elsevier.com/cattod/).

Please, specify in the STEP 1 (“Select an Article Type”) that the article is for the “Special Issue of 4th INTERNATIONAL CONFERENCE ON SEMICONDUCTOR PHOTOCHEMISTRY (SP4)”.

In your cover letter you should also include:
- 2 contact authors per article with correct e-mail address.
- 4 possible “referees” per article that you think are sufficiently capable of reviewing your article (name, e-mail and complete address).

You should also include in the last step this letter as “letter of invitation of the guest editors”.

The maximum length of each article is 7000 words (including abstract, text, figures, tables and references). A figure or table is equivalent to 400 words. Beyond this amount, the paper will be rejected.

The deadline for receiving manuscripts is June 28th, 2013. We are going to be completely inflexible on this point, since we have committed ourselves with the editor in chief of the journal.

Do not hesitate to contact us if you have any question.

Petr Kluson
kluson@icpf.cas.cz
Sixto Malato
Sixto.malato@psa.es

Prof. Josef Krýsa
krysaj@vscht.cz

Guest Editors: CATALYSIS TODAY-Special issue SELECTED CONTRIBUTIONS OF THE 4th INTERNATIONAL CONFERENCE ON SEMICONDUCTOR PHOTOCHEMISTRY (SP4)
Highlights

- ZnS nanoparticles deposited on montmorillonite forming ZnS-MMT nanocomposite
- Catalyst for photocatalytic decomposition of N₂O
- Better catalytic performance in fluidized bed than fixed bed
- Presence of water vapor inhibited N₂O decomposition by photocatalysis
- Presence of water vapor improved N₂O photolysis
UV light

ZnS-MMT

N_2O → N_2
O_2 → O_2

Graphical Abstract (for review)
http://dx.doi.org/10.1016/j.cattod.2013.09.047
Photocatalytic and photochemical decomposition of N\textsubscript{2}O on ZnS-MMT catalyst

L. Obalová*, M. Šihor, P. Praus, M. Reli, K. Kočí

VŠB - Technical University of Ostrava, 17. listopadu 15, Ostrava, Czech Republic

*Corresponding author. Phone: +420 596991532, e-mail: lucie.obalova@vsb.cz

Abstract

ZnS nanoparticles stabilized by cetyltrimethylammonium bromide were deposited on montmorillonite forming the ZnS-MMT nanocomposite. The nanocomposite was characterized by UV-Vis DRS, SEM-EDAX, FTIR, XRD and nitrogen physisorption and tested for N\textsubscript{2}O photocatalytic decomposition in an annular batch reactor illuminated with an 8 W Hg lamp (254 nm wavelength). Photolysis of N\textsubscript{2}O was tested at the same conditions. The N\textsubscript{2}O conversion in inert gas was 79 % after 24 hours of illumination and was attributed to the simultaneous N\textsubscript{2}O photocatalytic and photochemical decomposition. The presence of water vapor inhibited photocatalytic reaction pathway while N\textsubscript{2}O photolysis was improved. Photocatalytic performance was higher with catalyst in fluidized bed than in fixed bed. The reason is that both mass and photon transfer to the photocatalyst was maximized. Better results were obtained with Zn-MMT compared to Evonic P25 catalyst.

Key words: N\textsubscript{2}O, Photocatalysis, Photolysis, Decomposition, ZnS, Montmorillonite

1. Introduction

Nitrous oxide (N\textsubscript{2}O) is a compound that during the last decade has been recognized as a contributor to the destruction of the ozone in the stratosphere and acknowledged as a
relatively strong greenhouse gas. The continuous increase of its concentration, both due to
natural and anthropogenic sources (use of synthetic fertilizers, adipic acid production, nitric
acid production, fossil fuels and biomass burning) and long atmospheric residence time
(150 years), entails the need of developing efficient method for its abatement. N$_2$O
decomposition into nitrogen and oxygen offers simple solution for its conversion to natural
components of air. The thermal catalytic decomposition of N$_2$O requires temperatures higher
then approximately 200 °C, because the produced molecular oxygen is tightly bound to the
catalyst surfaces at temperatures lower than 200 °C [1]. Thermal catalytic N$_2$O catalytic
decomposition has been extensively investigated during last decades and nowadays, first large
scale installations are tested e.g. for N$_2$O abatement from HNO$_3$ plants [2]. However,
catalysts often suffer from oxygen, water vapor or NOx inhibition, deactivation or low
selectivity. Therefore, a need for further research in this area still exists.

Relatively little attention has been paid to the N$_2$O decomposition initialized by UV
light. Both photochemical [3-5] and photocatalytic decomposition [6] have been reported.
While thermal catalytic decomposition of N$_2$O is suitable mainly for N$_2$O abatement from
waste gases from industry and combustion, N$_2$O photoinduced decomposition might help to
reduce its concentration also in indoor and outdoor environments [6]. Compared to N$_2$O
thermal catalytic decomposition, photoinduced reactions are suitable for treatment of low-
concentration gases and have some advantages: the reaction proceeds at ambient temperature,
and if sunlight was utilized, it would lead to energy savings.

N$_2$O photocatalytic decomposition (Eq. 1) under wavelength higher than 254 nm has
been reported on Cu and Ag ion-exchanged powder zeolite [8, 9], Cu$^+$ ion anchored on
various oxides (SiO$_2$.Al$_2$O$_3$, Al$_2$O$_3$, SiO$_2$) [10, 11], un-modified TiO$_2$ [10] or TiO$_2$
doped by Pt [12] and Ag [13 - 16]. Trapping of the photoformed electron by the N$_2$O molecule to form
N$_2$O$^-$ ion is believed to be key process in N$_2$O photocatalytic decomposition over semiconductor catalysts [7].

$$\text{N}_2\text{O} \xrightarrow{h_v, \text{catalyst}} \text{N}_2 + 1/2 \text{O}_2$$ (1)

It is important to mention, that although N$_2$O photolysis is known process, none of the above cited papers dealing with N$_2$O photocatalytic decomposition (including our previous papers) took it into account or distinguished between N$_2$O conversion caused by photolysis and photocatalysis.

Photocatalysts for N$_2$O decomposition were typically tested as a powdered material which was simply placed on the bottom of the reactor [13, 17], spread on adhesive tape [14] or immobilized in the form of a thin film on a glass tube [16]. Especially the spreading of powdered catalyst does not guarantee that all particles are illuminated to the same extent and that no aggregation occurs and that the reaction rate is not influenced by transport phenomena. Another possible arrangement of photocatalytic experiment in the gas phase is to put fine powdered catalyst into suspension. For sufficiently intensive mixing uniform light distribution without the influence of external and internal diffusion limitation can be assumed. Fluidized bed photocatalytic reactor can then be used to obtain intrinsic kinetic data. Fluidized bed reactors were used e.g. for photocatalytic oxidation of volatile organic compounds [18], but never for photocatalytic decomposition of N$_2$O.

In our previous papers we investigated the preparation of ZnS nanoparticles stabilized by the cationic surfactant cetyltrimethylammonium bromide (CTAB) and montmorillonite (MMT) was used as an inorganic support [19 - 21]. Montmorillonite and the ZnS nanoparticles formed the ZnS-MMT nanocomposite that exhibited promising photocatalytic activity for CO$_2$ reduction [19] and phenol decomposition [20].

The aim of this work is to verify the catalytic performance of ZnS-MMT nanocomposite for N$_2$O photocatalytic decomposition and compare it with commercial
photocatalyst Evonic P25. To simulate real conditions, the effect of oxygen and water vapor on N₂O conversion was also tested as it has been only rarely studied in literature. The contribution of photochemical reaction to observed N₂O conversion during photocatalytic experiments was evaluated too. Two reactor configurations were compared - a catalyst fixed on adhesive tape and a catalyst in a fluidized bed.

2. Experimental

2.1 Preparation and characterization of ZnS and MMT nanocomposite

The ZnS nanoparticles were precipitated by zinc acetate and Na₂S in the presence of the stabilizing cationic surfactant cetyltrimethylammonium bromide [19]. The nanocomposite of ZnS nanoparticles and montmorillonite was prepared by adding montmorillonite into the ZnS nanodispersion and shaking for 24 hours. The solid part was filtered out, dried at 105°C and stored for further experiments.

Various techniques were used to characterize the prepared photocatalyst. The scanning electron microscope (SEM) Philips XL30 equipped with a Robinson backscattered electron (BSE) detector was used for examination of the ZnS morphology and zinc and sulphur distribution on the montmorillonite surface. The powdered samples were coated with gold and palladium in an ionization chamber before the examination. The elemental analysis of ZnS-MMT was performed by an EDAX detector.

The UV diffuse reflectance spectra (UV-Vis DRS) of granulated ZnS-MMT (diameter of 0.25-0.50 mm) were recorded using a GBC CINTRA 303 spectrometer equipped with a spectralon-coated integrating sphere against a spectralon reference. The Kubelka-Munk function was calculated from the reflectance by the following formula: \( F(R) = \frac{(1-R)^2}{2R} \), where \( F(R) \) is the Kubelka-Munk function and \( R \) is the reflectance.
FTIR spectra were obtained by the KBr (mid IR) and polyethylene (far IR) tablet methods using a Nicolet NEXUS 470 Fourier transform spectrometer (ThermoNicolet, USA). For each spectrum, 64 scans were obtained with the resolution of 8 cm\(^{-1}\). The recorded FTIR spectra were normalized for the same weight of MMT and processed by means of the program OMNIC 7.3.

The nitrogen adsorption–desorption measurements at −196°C were performed using Sorptomatic 1990 (Thermo Electron Corporation, USA). The specific surface area was calculated by the Advance Data Processing software according to the BET isotherm for ratio \(p/p^0\) up to 0.3 [21].

2.2. UV light induced experiments

\(\text{N}_2\text{O}\) decomposition induced by UV light was carried out in a homemade apparatus depicted in Fig. 1 with or without the catalyst (photocatalysis and photolysis, respectively).

In photocatalytic experiments, the catalyst was placed in the batch annular reactor (volume of 450 ml) in two ways (i) catalyst powder (0.135 g) was spread on adhesive tape placed on the bottom of the reactor, (ii) catalyst powder (0.05 – 0.15 g) was simply placed on the bottom of the reactor and a magnetic stirrer was used for fluidization.

In both phochemical and photocatalytic experiments, the reactor was filled with \(\text{N}_2\text{O}/\text{N}_2\) mixture (100 or 1000 ppm) and illuminated by an 8 W Hg lamp with a peak light intensity at 254 nm. Water vapor (0.6 mol %) and oxygen (6.5 mol %) were added to the reaction mixture in some experimental runs. Pressure and temperature inside the reactor were monitored during the reaction. Gas chromatograph with thermal conductivity detector (GC/TCD) equipped with the Molsieve and the HP Poraplot Q column was used for the analysis of \(\text{N}_2\text{O}\) and \(\text{O}_2\). The \(\text{N}_2\text{O}\) concentration level was measured before switching on a UV lamp, and during the irradiation.
The N$_2$O conversion was determined according to Eq. 2 provided that the total pressure in the reactor could be considered as constant due to low N$_2$O concentration and low amount of sample withdrawn for analysis. Therefore, the experiments with photocatalyst were performed such that maximum of three samples were removed for analysis from one batch. After that, the reactor was flushed with nitrogen, filled with fresh catalyst and refilled with reaction mixture. During photochemical experiments, only three gaseous samples were also withdrawn from the same batch.

$$X_{N_2O} = \frac{x_{N_2O}^0 - x_{N_2O}}{x_{N_2O}^0}$$  (2)

Where $x_{N_2O}^0$, $x_{N_2O}$ is the N$_2$O molar fraction at the beginning of reaction ($t = 0$) and at different times during the photocatalytic reaction, respectively.

The reproducibility of photocatalytic experiments was verified by repeated tests (Table 1). In addition to the reaction experiments, a control experiment was conducted in the absence of UV light in which 100 ppm of N$_2$O in N$_2$ and 0.1 g of ZnS-MMT catalyst was added to the reactor. The results in Table 1 showed that N$_2$O concentration profile during 25 hours is stable, i.e. there was no absorption to the sides of the reactor or on the catalyst surface.

3. Results and discussion

3.1. Characterization of ZnS-MMT photocatalyst

Since detail characterization of ZnS-MMT catalysts has been already published in our previous publications [19 - 21], only summary of results are shown here. The content of ZnS in the nanocomposite determined by chemical analysis of zinc and sulphur was about 7 wt % and the CTAB content was 30 wt % [21]. The scanning electron micrograph demonstrates morphology of ZnS-MMT and the location of ZnS nanoparticles on MMT (Fig. 2). The EDAX analysis found the presence of zinc, sulphur and carbon confirming the presence of
ZnS nanoparticles and CTAB. Other detected elements (Mg, Na, Al, Fe, Si) were the components of montmorillonite.

The UV absorption spectra of the ZnS-CTAB dispersions were shown in our previous paper [19]. In these dispersions the ZnS nanoparticles exhibited the absorption edge at 320 nm. The DRS spectra of the ZnS-MMT nanocomposite and bulk ZnS precipitated without the CTAB stabilization and deposited on MMT (ZnS(bulk)-MMT) were used to estimate the ZnS band-gap energies (Fig. 3). The band-gap energies of the ZnS nanoparticles and bulk ZnS particles supported on MMT were 6.69 eV and 3.59 eV, respectively.

The presence of ZnS nanoparticles in the ZnS-MMT nanocomposite was confirmed by the far IR spectra (Fig. 4). Weak vibration bands at 280 cm$^{-1}$ of ZnS were identified recorded. Other vibrations bands belong to lattice vibrations of montmorillonite.

X-ray powder diffraction was used to recognize where the ZnS nanoparticles were located in the nanocomposite. The MMT interlayer distance increased from 1.23 nm to 1.83 nm as a result of intercalation of CTAB. Therefore, the ZnS nanoparticles with the mean size of 5 nm had to be located on the MMT external surface in its mesopores. The specific surface area of ZnS-MMT was 3.7 m$^2$ g$^{-1}$ due to blinding the micro- and mesopores of MMT by adsorbed CTAB.

3.2. UV light induced decomposition of N$_2$O

First test was the photocatalytic decomposition of N$_2$O in inert gas in the presence of ZnS-MMT or commercial Evonik P25 catalyst, which was spread on adhesive tape (Fig. 5). Moreover, photolysis of N$_2$O was tested at the same conditions. Results showed that 34% of N$_2$O was decomposed after 24 hours by photolysis, while the presence of ZnS-MMT and Evonik P25 catalyst caused a significant improvement of N$_2$O conversion to the value of 75% and 60%, respectively. This is caused by the presence of a parallel reaction pathway of
photocatalysis (Eq. 1) that co-exists with the direct photolysis (Eq. 3). N₂O has is decomposed photochemically with λ < 240 nm [4] and in our case the reaction was caused by additional spectral lines in shorter wavelengths of the UV lamp.

\[ \text{N}_2\text{O} \xrightarrow{hv} \text{N}_2 + \frac{1}{2}\text{O}_2 \]  

(3)

The test also showed that the ZnS-MMT catalyst is more active than the commercial Evonic P25, which is commonly used for photocatalytic efficiency comparisons.

Then the N₂O photocatalytic decomposition tests with catalysts in fluidized bed were performed and the contribution of N₂O decomposed by photolysis was also evaluated. First, it was necessary to determine a suitable amount of catalyst. Three experiments with various ZnS-MMT catalyst weights were carried out in a mixture of 100 ppm N₂O and N₂ (Fig. 6). It can be seen that first there was an increase in conversion of N₂O with an increase of the catalyst weight and the optimum amount of catalyst in terms of maximum conversion of N₂O was 0.1 g. Higher sample amount caused a decrease in conversion probably due to light scattering. The catalyst weight of 0.1 g was then used for all subsequent experiments in fluidized bed.

Figure 7 shows the effect of irradiation time on the N₂O conversion in different gas mixtures over ZnS-MMT and Evonic P25 catalysts. N₂O conversion during photocatalytic experiments as well as N₂O conversion caused by photolysis is depicted. The gradual increase in N₂O conversion with increasing reaction time was observed in all cases. The highest N₂O conversion of 79 % was reached after 24 hours in the mixtures of N₂O and N₂O+O₂ in N₂.

Since oxygen and water vapour are always present in atmosphere together with N₂O, we focused on the evaluation of their effect on the rate of N₂O photochemical and photocatalytic decomposition. The presence of oxygen in the reaction mixture (N₂O + O₂) did not cause significant changes in the rate of the photochemical and photocatalytic decomposition of N₂O. However, a new reaction route in photocatalytic decomposition of N₂O cannot be excluded:
Oxygen could react with emerging electrons forming •O⁻ radical according to Eq. 6. The resulting radical then reacts further with N₂O to give nitrogen and oxygen (Eq. 7).

\[
\begin{align*}
\text{O}_2 + 2 \text{e}^- & \rightarrow 2 \text{•O}^- \\
\text{N}_2\text{O} + \text{•O}^- & \rightarrow \text{N}_2 + \text{O}_2 + \text{e}^-
\end{align*}
\]  

(6)  

(7)

Water vapor affected the rate of photocatalysis and photolysis of N₂O quite differently. Photolysis of N₂O in wet gas proceeded faster than in inert gas and a further increase in its rate was caused by the addition of oxygen to N₂O+H₂O. In contrast, photocatalytic decomposition of N₂O was strongly inhibited by water vapor and most of N₂O in mixture of N₂O+H₂O and N₂O+O₂+H₂O was decomposed by photolysis. Water vapor was likely adsorbed on the catalyst surface, causing less light penetration and thus reducing the efficiency of photocatalytic decomposition of N₂O.

Quite different results were observed in our recent work dealing with N₂O photocatalytic decomposition on Ag-modified TiO₂ nanocomposite thin film immobilized on a glass tube [16]. The presence of water vapor and oxygen caused an increase in the rate of N₂O decomposition in comparison with the reaction in inert gas. It was caused by reduction of N₂O by atomic hydrogen formed by the photoreduction of water on an Ag-TiO₂ photocatalyst. These different results confirmed that the effect of water vapor presence is dependent on the photocatalyst type and on its properties.

Kinetic constants were used for the purpose of comparing the performance of fixed and fluidized catalyst beds, since different N₂O initial concentrations were used in these experiments. Assuming that both photocatalytic and photochemical N₂O decomposition proceeds parallel and can both be described by 1st order rate law, the total rate of N₂O disappearance is equal to the sum of the N₂O decrease by photocatalytic and photochemical pathways and is also described by 1st order rate law:

\[ \text{(4)} \]
Where $[N_2O]$ is the concentration of $N_2O$ (mol cm$^{-3}$), $k = k_1 + k_2$ is the complex kinetic constant (cm$^3$ h$^{-1}$ g$_{cat}^{-1}$), $r$ is rate of $N_2O$ decrease (mol g$_{cat}^{-1}$ h$^{-1}$). An integral form of material balance of batch reactor with ideal mixing working in isothermal isobaric regime was used for data processing:

$$\ln \frac{1}{1 - X} = k \frac{m_{cat} t}{V}$$

(5)

Where $t$ is reaction time (h), $V$ is volume of reactor (cm$^3$), $m_{cat}$ weight of catalyst (g) and $X$ is $N_2O$ conversion (-). Evaluation of the kinetic data (Fig. 8) confirmed that the reaction kinetics can be described by 1$^{st}$ order rate law.

The values of complex kinetic constant $k$ are listed in the Table 2. The kinetic constants over both photocatalysts (Evonic P25 and ZnS-MMT) were lower in fixed bed than in fluidized bed. Assuming the same contribution of photolysis, the reason is that both mass and photon transfer to the photocatalyst was maximized. Kinetic constants evaluated from experiments in fluidized bed in different reaction mixtures show following order: $k(N_2O+O_2) > k(N_2O) > k(N_2O+H_2O+O_2) > k(N_2O+H_2O)$ which corresponds well to the conversion order in Fig. 7.

ZnS nanoparticles immobilized on montmorillonite were tested for $N_2O$ photocatalytic decomposition for the first time. It can be said that they showed significantly better results than commercial Evonic P25. Moreover, the catalyst does not contain expensive precious metals. However, if it is needed to reduce the concentration of $N_2O$ in the mixture with water vapor and oxygen, the presence catalyst is practically unnecessary, because photolysis of $N_2O$ prevails under these conditions.

4. Conclusions
ZnS catalyst was successfully immobilized on montmorillonite forming the ZnS-MMT nanocomposite and tested for N\textsubscript{2}O photocatalytic decomposition in fixed bed and fluidized bed annular reactor. Photolysis of N\textsubscript{2}O was tested at the same conditions.

The N\textsubscript{2}O conversion in inert gas was 79\% after 24 hours of illumination and was attributed to the simultaneous N\textsubscript{2}O photocatalytic decomposition and to N\textsubscript{2}O photolysis. The presence of water vapor inhibited photocatalytic reaction pathway while N\textsubscript{2}O photolysis was improved. Further increase in photolysis reaction rate was caused by the simultaneous presence of water vapor and oxygen. Reaction kinetics was well described by pseudo 1\textsuperscript{st} rate law. The catalyst in suspension showed better results of N\textsubscript{2}O photocatalytic decomposition than the catalyst spread on adhesive tape. This was due to more efficient contact between the catalyst and N\textsubscript{2}O molecules, lower mass transfer resistance and higher catalyst surface which was exposed to UV radiation.

Photocatalytic activity of Zn-MMT was significantly better in comparison with Evonic P25, which shows that the ZnS-MMT nanocomposite is, besides CO\textsubscript{2} photocatalytic reduction and phenol decomposition, also promising for N\textsubscript{2}O photocatalytic decomposition.

\textbf{Acknowledgements}

Financial support of EU projects No. CZ.1.05/2.1.00/03.0069 „ENET“ and No. CZ.1.05/2.1.00/03/0100 “IET”, Grant Agency of the Czech Republic (P107/11/1918) and project SP2013/41 is gratefully acknowledged.

\textbf{References}


Table 1 Reproducibility of photocatalytic experiments of N$_2$O decomposition over ZnS-MMT catalyst and N$_2$O concentration profile in dark in fluidized bed reactor.

<table>
<thead>
<tr>
<th>Reproducibility$^{1)}$</th>
<th>N$_2$O concentration profile in dark$^{2)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (hours)</td>
<td>N$_2$O conversion (%)</td>
</tr>
<tr>
<td>15</td>
<td>61.8</td>
</tr>
<tr>
<td>15</td>
<td>58.5</td>
</tr>
<tr>
<td>22</td>
<td>75.8</td>
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<tr>
<td>22</td>
<td>75.2</td>
</tr>
<tr>
<td>24</td>
<td>77.7</td>
</tr>
<tr>
<td>24</td>
<td>78.8</td>
</tr>
</tbody>
</table>

1) 0.1 g catalyst, 100 ppm N$_2$O in N$_2$, 8 W Hg lamp ($\lambda = 254$ nm)

2) 0.1 g catalyst, 100 ppm N$_2$O in N$_2$
Table 2 The pseudo-first-order rate constant ($k$) for N$_2$O photocatalytic decomposition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gas mixture</th>
<th>$k$ (cm$^3$ h$^{-1}$ g$_{cat}^{-1}$)</th>
<th>Catalyst</th>
<th>Gas mixture</th>
<th>$k$ (cm$^3$ h$^{-1}$ g$_{cat}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evonic P25</td>
<td>100 ppm N$_2$O</td>
<td>199.2 ± 3.3</td>
<td>Evonic P25</td>
<td>1000 ppm N$_2$O</td>
<td>138.0 ± 2.3</td>
</tr>
<tr>
<td>ZnS-MMT</td>
<td>100 ppm N$_2$O</td>
<td>282.3 ± 3.3</td>
<td>ZnS-MMT</td>
<td>1000 ppm N$_2$O</td>
<td>201.3 ± 3.3</td>
</tr>
<tr>
<td>ZnS-MMT</td>
<td>100 ppm N$_2$O + O$_2$</td>
<td>300.7 ± 4.3</td>
<td>ZnS-MMT</td>
<td>100 ppm N$_2$O + H$_2$O + O$_2$</td>
<td>209.4 ± 2.4</td>
</tr>
<tr>
<td>ZnS-MMT</td>
<td>100 ppm N$_2$O + H$_2$O</td>
<td>166.2 ± 2.9</td>
<td>ZnS-MMT</td>
<td>100 ppm N$_2$O + H$_2$O</td>
<td>166.2 ± 2.9</td>
</tr>
</tbody>
</table>
Figure captions

**Fig. 1** Block scheme of the apparatus for N₂O photocatalytic decomposition

**Fig. 2** SEM micrograph of ZnS-MMT

**Fig. 3** UV-Vis DRS spectra of ZnS nanoparticles and bulk particles on montmorillonite [18]

**Fig. 4** Far IR spectrum of ZnS-MMT

**Fig. 5** Time dependence of N₂O conversion over ZnS-MMT and Evonic P25
Conditions: 0.1 g of catalyst spread on adhesive tape, 1000 ppm N₂O in N₂, 8 W Hg lamp (λ = 254 nm).

**Fig. 6** Dependence of N₂O conversion on the amount of ZnS-MMT photocatalyst.
Conditions: catalyst in fluidized bed, 100 ppm N₂O in N₂, 8 W Hg lamp (λ = 254 nm), 24 hours of irradiation

**Fig. 7** Time dependence of N₂O conversion over ZnS-MMT and Evonic P25 photocatalysts in fluidized bed reactor. Conditions: 0.1 g catalyst, 100 ppm N₂O (+ 6.5 mol% O₂ + 0.6 mol% H₂O) in N₂, 8 W Hg lamp (λ = 254 nm).

**Fig. 8** Evaluation of kinetic constants (1st rate law) for N₂O photocatalytic decomposition in fixed (a) and fluidized bed (b) reactor by integral method.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8