

AEROGEL NANOSCALE ALUMINIUM OXIDES AS A DESTRUCTIVE SORBENT FOR MUSTARD GAS

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An autoclave hypercritical drying procedure has been used to prepare alumina (α -Al₂O₃) precursors from aluminium sec-butoxide C₁₂H₂₇AlO₃. Specific surface area was 1000 m²/g. The samples were characterized by X-ray diffraction, DTA-TG, scanning and transmission electron microscopy. The precursors were taken for experimental evaluation of their reactivity with Mustard Gas (Yperite, HD agents, Bis(2-chlorethyl)sulfid). Largest percentage of the conversion mustard into non-toxic products after the elapse of the reaction was 80 %.

INTRODUCTION

One of the methods used to detoxify corrosion-sensitive materials contaminated with highly toxic substances is the application of finely divided inorganic oxides of crystallite or crystal size of the order of tens or hundreds of nanometers (hereinafter referred to as "nano-dispersed oxides"). The ability of nano-dispersed metal oxides (MgO, CaO, ZnO, AlO_x(OH)_y, ZrO, TiO₂, etc.) to decompose certain very toxic substances, such as Sarin (GB, C₄H₁₀FO₂P), Soman (GD, C₇H₁₆FO₂P), Tabun (GA, C₅H₁₁N₂O₂P) or VX, C₁₁H₂₆NO₂PS into non-toxic products was studied in detail by Koper et al. [1,2] and Wagner et al [3-5]. Corresponding reaction products were identified and reaction mechanisms were postulated. Without exception all the toxic substances mentioned were demonstrated to decompose via heterogeneous chemical reaction involving proceeding predominantly on the surface of the metal oxide particles

The objective of this work was to study and acquire a procedure for preparing nano-dispersed aluminium oxide as well as to verify detoxification activity the product. Because the detoxification proceeds finally on the individual reactive sites on the particles surface, we attempted to find a method for accelerating the transport of the agent to the surface, namely using petroleum ether as a solvent improving mobility of the gas on the oxide surface.

According to the literature [8-10] aluminium oxide aerogels were prepared by the reaction of aluminium sec-butoxide with ethyl acetoacetate and dried in carbon dioxide under supercritical conditions. The products had the specific surface area of 400-600 m²/g. Another authors prepared alumina aerogels with specific surface

area 300-700 m²/g by sol-gel method using aluminium butoxide [11] or aluminium propoxide [12,13]. For the preparation of gel by drying under above-critical conditions carbon dioxide was most frequently used [1,2,8,14,15].

EXPERIMENTAL

Hydrolysis of aluminium sec-butoxide solution

Aluminium sec-butoxide (1g) was dissolved in butane-2-ol and resulting solution was placed in a cylindrical reaction vessel of 40mm diameter and 100 ml volume. Methanol and toluene were added in the volumes given in table 1. The solution was bubbled through with argon and subjected to ultrasonic waves of very high intensity, supplied by a ultrasonic generator (titanium horn, 25 kHz, 300 W/cm²). The cone was immersed in the solution 2 cm below its surface. In the course of sonification, solution temperature increased to 60°C. Distilled water (0.22 ml) was slowly added using a pipette to the solution during the ultrasonication. As soon as transparent gel-like solution was obtained after about 1-2 minutes, ultrasonic treatment was stopped.

Supercritical drying in the autoclave

A part of clear viscous solution (80 ml) was transferred into a stainless steel autoclave with inner volume 100 ml. The autoclave was flushed and then filled with nitrogen gas and heated to the temperature of 265°C at the rate of 3°C/min in a furnace fitted with a PID tem-

perature controller. Then, the pressure in the vessel was released to atmospheric pressure within approx. a minute. After cooling to the room temperature, the autoclave was flushed with nitrogen. The product was withdrawn and dried in an oven at the temperature of 120°C.

Annealing the precursors after above-critical drying

Subject to the corresponding results of DTA measurements (see figure 1) selected samples were annealed under dynamic vacuum conditions. Samples were put in quartz boats and placed in a tube of stainless steel, inserted in a PID controlled tubular furnace. There they were heated to the temperatures shown in table 2 at the rate of 1°C/min.

Methods of characterisation

The specific surface area of samples was measured by means of a Coulter SA 3100 instrument with the nitrogen isotherm at the temperature of liquid nitrogen and sample degassing. X-ray powder diffraction measurements were carried out by means of a Siemens D5005 instrument fitted with a secondary monochromator, using CuK α radiation (40 kV, 30 mA). For the related qualitative analyses the Bede ZDS software for Windows, version 1.99 and JCPDS PDF-2 database were employed [17].

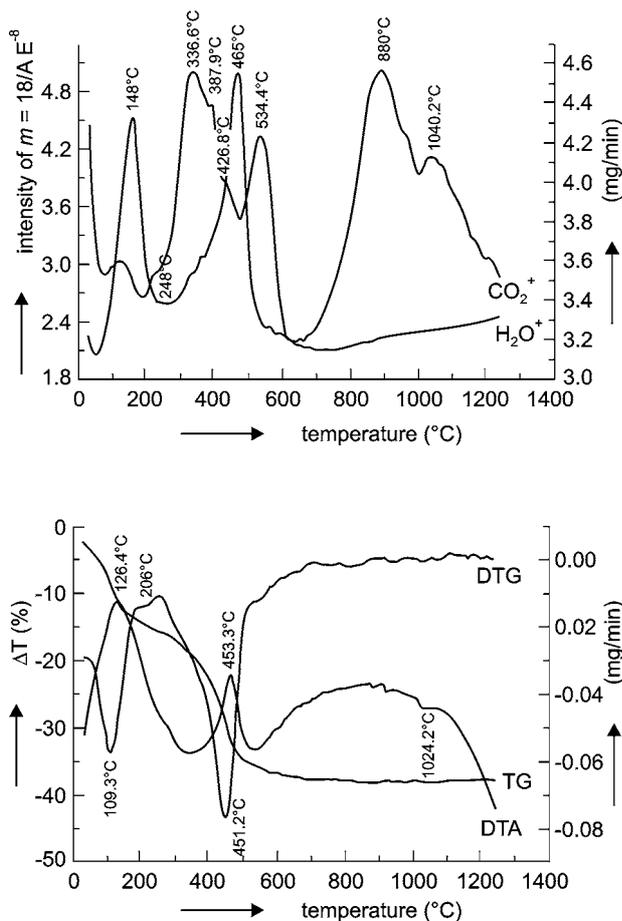


Figure 1. DTA - TG of sample A17.

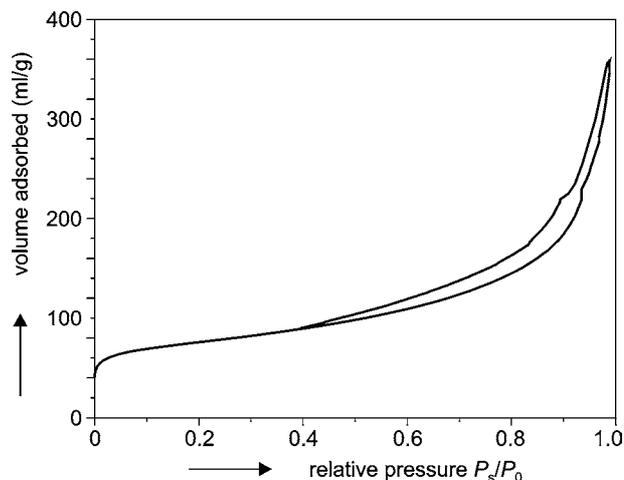


Figure 2. Nitrogen adsorption-desorption isotherm of sample A17.

Table 1. Experimental conditions and resulting specific surface areas, S_{BET} , and total pore volume, V_p , of Al-aerogels prepared from aluminium sec. butoxide.

sample	aluminium sec. butoxide	sec.butanol (ml)	methanol (ml)	toluene (ml)	S_{BET} (m ² /g)	V_p (cc/g)
A15	1g	10	-	50	225	1.52
A16	1g	5	5	50	786	2.66
A17	1g	10	10	50	1004	2.15
A110	1g	10	15	50	776	1.98
A111	1g	10	20	50	767	2.02
A112	1g	10	10	60	844	1.28

Table 2. Specific surface areas S_{BET} , total pore volume, V_p , and XRD of heating samples.

sample	T (°C)	S_{BET} (m ² /g)	V_p (cc/g)	XRD
Al7/1	470	562	2.06	Amorphous
Al7/2	650	475	1.38	Amorphous
Al7/3	1000	192	0.92	Amorphous
Al7/4	1200	80	0.63	α -Al ₂ O ₃

Table 3. Average residual content of the yperite after reaction, sample marked AL7.

average residual content of the yperite ($\mu\text{G}/50 \text{ MG}$ charge of Al reagent)	149.7	49.3
standard deviation of the average	2.5	3.4
percentage of the yperite conversion after the elapse of the reaction (%)	70.1	80.3

TEM micrographs were obtained from a Philips 201 transmission electron microscope. The micrographs were taken at the voltage of 80 kV and 1500-200 000 \times magnification. Measurement samples were prepared on Formvar 1595E membranes (Merck) with copper grids (400 mesh). SEM micrographs come from a Philips XP 30 CP scanning electron microscope fitted with EDX, Robinson, SE a BSE detectors.

DTA-TG measurements were carried out with a Netzsch STA 409 instrument at the helium flow-rate of 10 cm³ per min. and heating rate of 10 K per min.

Activity measurement of Mustard decomposition

24 hours before verifying its activity, the powdered sample was dried in a vacuum oven at the temperature of 100°C. The oxide preparation (50 mg) was weighed in a reaction vessel (i.e. a sealable vial of CRS-33 type, supplied by Supelco) and on its layer yperite solution in petroleum ether (100 μl) was metered. With this solvent volume the entire powder layer was soaked and yperite could get into an effective contact with its whole surface. The weight ratios of oxide to yperite of 100:1 and 200:1 (with surface load with yperite reduced by 50 %) and the reaction time of 1 hour were chosen. The observed oxide reactivity was expressed as the conversion rate of yperite (wt.%) decomposed by the reaction with aluminium oxide under experimental conditions. The residual content of toxic substance in the nano-dispersed preparation was determined after its extraction

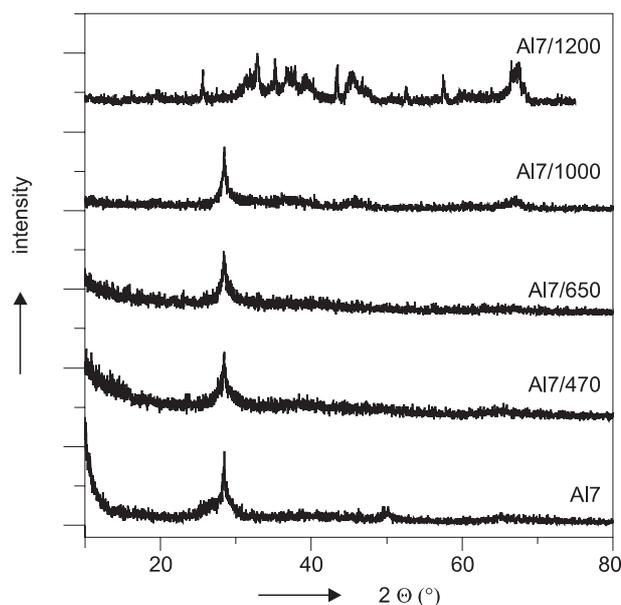


Figure 3. XRD patterns of the sample Al7 and samples Al7/470 - Al7/1200.

by isopropanol. The extraction was made by metering the extraction agent in the reaction vessel after the reaction time has expired. This operation terminated the reaction effectively, as an independent experiment demonstrated that the reaction did not continue at a measurable rate after an excess alcohol had been added to the reaction mixture. The mixture was homogenised by shaking and after one minute at rest it was centrifuged at 9000 r.p.m. for three minutes. An aliquot portion of the extract was withdrawn for chemical analysis. Yperite concentrations were determined by the method described by Franke [7].

RESULTS AND DISCUSSION

Characterisation of alumina aerogels

The specific surface area of a particular sample was determined by measuring the sample adsorption and desorption isotherms at the temperature of liquid nitrogen. All the measured samples showed a hysteresis curve (see figure 2) characteristic for mesoporous substances. The specific surface area and pore distribution (size and volume) were calculated using the BET and BJH methods, respectively. The values of specific surface area and total pore volume for particular samples are shown in table 1 and 2. The sample identified as Al 7 of the highest specific surface area ($\approx 1000 \text{ m}^2/\text{g}$) was gradually annealed in a furnace up to the temperature of 1200°C. The specific surface area of all precursors showed a steady decrease with increased annealing temperature.

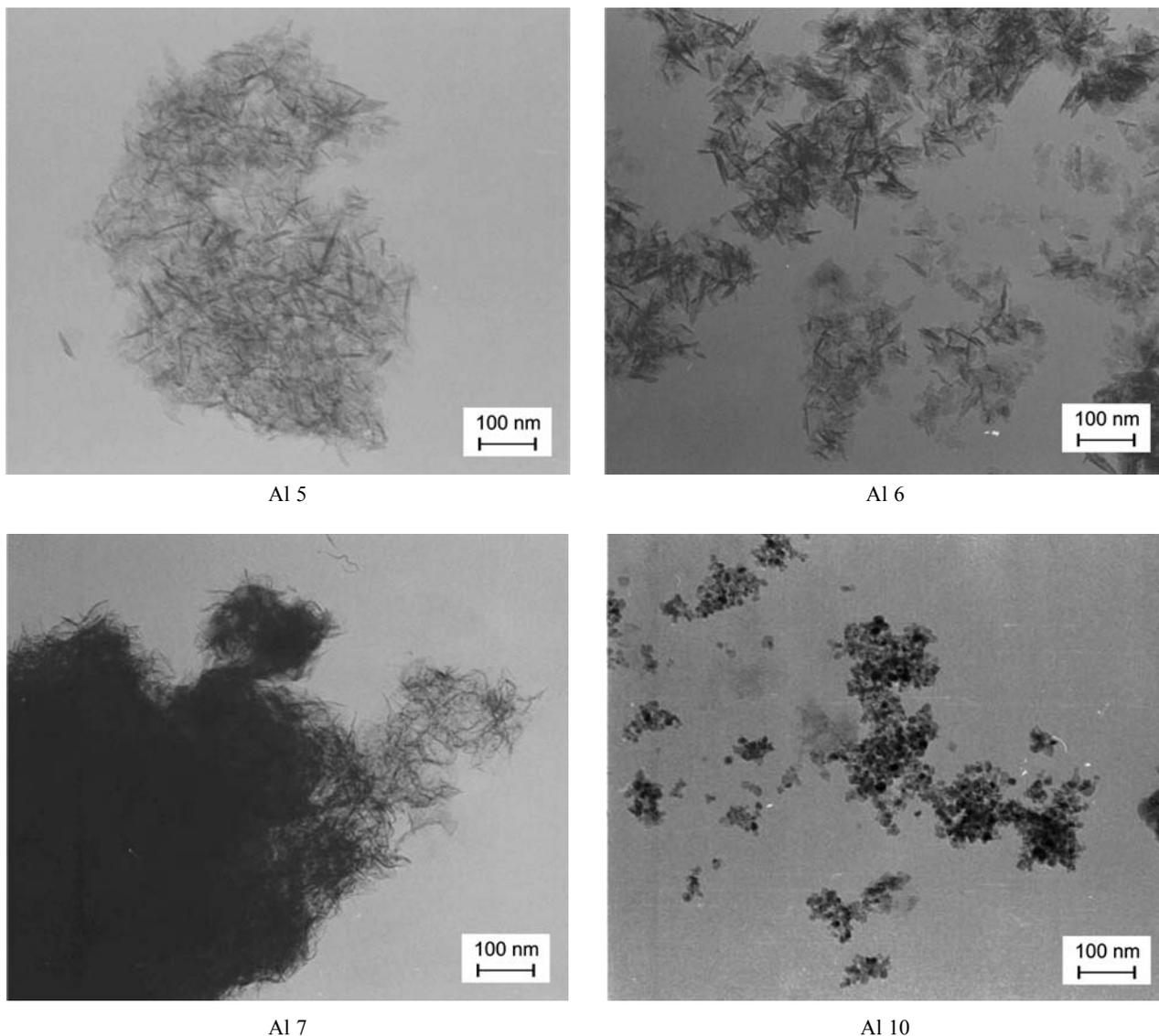


Figure 4. TEM micrographs of samples Al 5, Al 6, Al 7 and Al 10.

Figure 3 shows the X-ray diffractograms of samples prepared by annealing the Al7 sample. The precursor and samples Al7/1 through Al7/3 are X-ray-amorphous. Diffraction lines characteristic for corundum (Al_2O_3 , PDF 46-1212) begin to appear with sample Al7/4, annealed at 1200°C . The diffraction line at $2\theta = 28^\circ$ corresponds to silicon from silicon paste used for sample fixation.

Figure 4 shows the TEM micrographs of precursors Al5, Al6, Al7 and Al10. The comparison of the two micrographs suggests the effect of methanol on the reduction of particle size and, consequently the increase of the specific surface area of the product. The micrographs of samples Al7/1000 and Al7/1200 are shown in figure 5. According to those photos, any additional increase in annealing temperatures has no effect on particle size.

The course of DTA-TG curves for sample Al7 is illustrated in figure 1. The curves show a maximum at 148°C , for adsorbed moisture and other maxima at temperature 465°C , $336,6^\circ\text{C}$, 534°C , 889°C and 1040°C for carbon dioxide, corresponding to the decomposition of residual $-\text{OCH}_3$ groups of organic solvents.

Reactivity of alumina aerogels

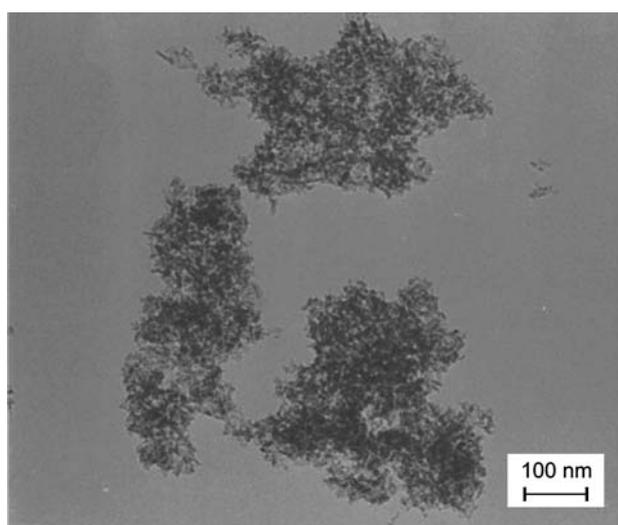
The work of Wagner et al. [6] is devoted to the properties, structure and reactivity of aluminium oxides and oxide hydroxides (hereinafter referred to as "oxides"). Among metal oxides studied up to now, particularly aluminium oxide features a sufficiently high detoxifying activity that makes it, together with its negligible corrosiveness, especially suitable for practical

application in the decontamination of sensitive technological components and materials. Detailed study of the structural analogues of aluminium oxide, γ -alumina and η -alumina, revealed that a few structures differing one another in the type of coordination of surface aluminium atoms (either tetrahedral or octahedral coordination) could be detected on their surface, subject to the temperature, degree of oxide surface hydration, etc. The hydroxyl groups bound to tetrahedrally coordinated aluminium atoms are comparably more basic, while those bound to octahedrally coordinated atoms are relatively more acidic. Therefore, the condition and character of aluminium oxide surfaces may influence its chemical properties. It was also found that the activity of oxide surfaces is not evenly distributed, being higher at the edges and various shape dislocations of microcrystals. That is why observed kinetics of heterogeneous surface reactions features two main phases, i.e. an initial fast phase followed by a subsequent slower phase. The first phase corresponds to the reaction of the toxic substance (substrate) at more active centres of nano-dispersed powdered agent. The second phase is rather governed by the rate of surface transport of the substrate from the points of low surface activity to chemically more active centres. In general, substrate transport is dependent on its rate of evaporation and subsequent transport of its vapour by diffusion or convection. However it may be influenced also by the capillary lift of its liquid phase along the solid agent surface, governed by such factors as substrate viscosity and angle of contact. The rate of evaporation was determined as the partial controlling process that influences required surface transport.

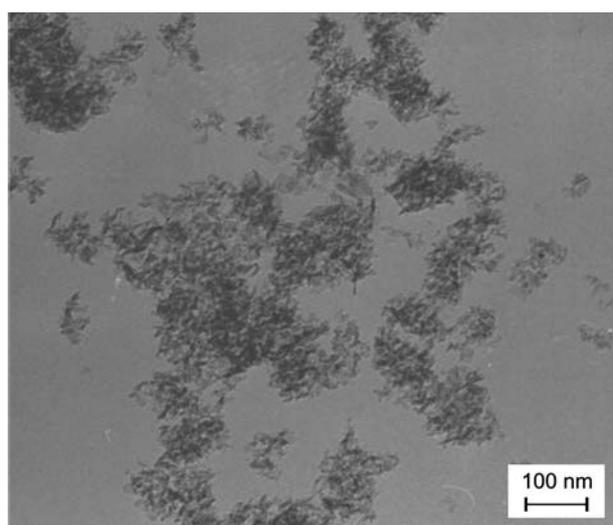
Mustard (Bis(2-chlorethyl)sulphide) was intentionally chosen for evaluating the reactivity of obtained preparations. It is known as the substance that features comparably highest resistance on the solid surface of most oxides of concern [3]. In general, its reaction with oxides results in divinyl sulphide as the final product of the eliminating dehalogenisation, or in thio-diglycol produced by a substitution reaction, or in sulphonium salts that are formed on nano-dispersed oxide surface by the reaction of ethylsulphonium intermediates of the substitution reaction with Mustard itself.

Out of the prepared air-gel samples, sample A17 was singled out for measuring yperite decomposition activities due to its highest specific surface area values. Other obtained samples featured specific surface area lower by 300 m²/g at least. With the preparations obtained by annealing under vacuum the reduction in surface area was still more significant (even down to 80 m²/g). For sample A17 the average contents of residual yperite and yperite conversion data at the end of reaction time are shown in table 3. Each figure was obtained as the arithmetic mean of six separate measurements.

Aluminium oxide showed a high activity of yperite decomposition, as comparably high degrees of conversion (70 or even 80 %) were achieved after the reaction time of one hour. From the comparison of the yperite conversion data obtained for the powdered agent in question it ensued that higher degrees of conversion and higher yields of reaction resulted in case that surface loads with yperite had been reduced under the same reaction conditions.



A1 7/1000



A1 7/1200

Figure 5. Tem micrographs of sample A1 7 heated at 1000 and 1200°C showing a stability of nano-dispersed oxide particle size on heating.

CONCLUSION

To the above-cited literature, nano-dispersed aluminium oxides (or hydroxides) are prepared by drying aluminium sec-butoxide mixed with ethyl acetate under supercritical conditions. The process can yield precursor materials of specific surface area as high as 600 m²/g. By modifying the procedure for preparing nano-dispersed magnesium oxides [16] it is possible to obtain precursors of specific surface area in excess of 1000 m²/g. According to available literature, the latter procedure has not been described up to now. The high specific surface area of final products is subject to the appropriate process of homogeneous hydrolysis that may be ensured only by the application of ultrasonic waves of high intensity. As soon as the ultrasonic generator power output is reduced by surface cavitation, the specific surface area of the prepared sample will decrease significantly due to imperfect hydrolysis of alkoxides.

Acknowledgement

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NANODISPERSNÍ AEROGELY OXIDU HLINITÉHO JAKO DESTRUKTIVNÍ SORBENTY PRO YPERIT

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Metodou nadkritického sušení v autoklávu byly připraveny prekurzory oxidu hlinitého z aluminium sekundárního butoxidu. Specifický měrný povrch prekurzorů byl cca 1000 m²/g. Připravené vzorky byly charakterizovány pomocí RTG práškové difraktometrie, DTA-GT a skenovací a transmisní elektronovou mikroskopií. Připravené prekurzory byly použity k rozkladu yperitu. Stupeň konverze yperitu na netoxické produkty dosáhl maximální hodnoty 80 %.