

Synthesis of Nanocrystalline VO_x/MgO Aerogels and Their Application for Destructive Adsorption of CF₂Cl₂

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ABSTRACT

The developed method for synthesis of binary VO_x/MgO aerogels by hydrolysis of the V and Mg alkoxides mixed together followed by gelation and supercritical drying makes it possible to obtain aerogels with exceptionally high surface areas (~ 1200 m²/g) and uniform vanadium distribution. Their dehydration yields nanocrystalline VO_x/MgO with nanoparticle size ca. 5 nm. The synthesized nanocrystalline VO_x/MgO oxides were used as destructive sorbents for decomposition of halocarbons. The doping of MgO aerogels with a small amount of VO_x (1-2%) results in significant acceleration of the reaction with CF₂Cl₂ causing deeper MgO transformation to MgF₂ and shortening the induction period.

Keywords: aerogels, destructive sorption, halocarbons, nanocrystalline oxides, VO_x/MgO

1 INTRODUCTION

Aerogels are materials obtained by a sol-gel process followed by supercritical drying. Under supercritical conditions, the liquid-vapor interface that produces the collapse of the initial gel framework during conventional drying is eliminated. The obtained materials have high surface areas and pore volumes. The method is known to be versatile and allows controlling texture, composition and structural properties of the materials [1, 2].

The best known method for synthesis of nanocrystalline MgO aerogels with high surface area is the modified aerogel procedure developed by Klabunde et al. [3, 4]. Various nanocrystalline aerogel-prepared (AP) metal oxides prepared by this method have high surface areas, small crystallite sizes, unusual morphology, enhanced adsorption properties and have been extensively studied for their use as destructive adsorbents [4-6], decontamination of vegetative bacterial cells and spores [7] and in various catalytic and photocatalytic applications [8-10].

We have recently published first communications on the synthesis of the co-gelled VO_x/MgO aerogels and their catalytic performance in oxidative dehydrogenation of propane [11-13]. This paper is devoted to further elaboration and simplification of the synthesis of mixed V-Mg hydroxide and oxide aerogels and their application for

destructive sorption of CF₂Cl₂ known to be an ozone-depleting hazard.

2 EXPERIMENTAL

The method used for synthesis of mixed V-Mg(OH)_x hydroxide aerogels is generally similar to the one earlier used for preparation of nanocrystalline AP-MgO. Magnesium ribbon (Aldrich, 99.9%, 0.15 mm, 1 g), absolute methanol (30 ml), toluene (20 ml) and vanadium triisopropoxide oxide VOOCH(CH₃)₃ (Aldrich, 99%) were used as precursors. The amount of the vanadium precursor was varied depending on the desired vanadium concentration and was equal to 0.47 ml for the samples containing 10% V. All vanadium concentrations reported in this paper are normalized to V₂O₅. The concentrations were varied from 0 to 26 wt. %.

First, magnesium metal was dissolved in methanol to form magnesium methoxide solution. Then, a second solvent used as a gel stabilizer (toluene, ethanol) was added to the magnesium methoxide solution in methanol or just more methanol was added to give the same concentration of the solution. The obtained magnesium methoxide solution was slowly hydrolyzed with water (1.5 ml) to obtain a clear gel. Then, the desired amount of vanadium triisopropoxide oxide was added dropwise to the freshly prepared gel. The obtained mixed gel was placed into an autoclave (Parr Instruments) equipped with a stirrer and heated in nitrogen atmosphere to 260°C with 1.3 °C/min heating rate. The final pressure and temperature were varied to study their effect on the properties of the obtained aerogels. After reaching the desired temperature the solvents were vented and the autoclave was purged with nitrogen for 20 min. As our ultimate goal was to prepare catalysts operating at elevated temperatures, the obtained V-Mg(OH)_x hydroxide aerogels were calcined up to 550°C using different procedures to convert them to the corresponding binary oxides.

The CF₂Cl₂ reaction with nanocrystalline VO_x/MgO aerogels was studied in a TEOM (Tapered Element Oscillating Microbalance) microanalyzer. This instrument is based on the mass measurement using a relation between the oscillation frequency of the microreactor acting as a pendulum and the mass of the studied sample. The composition of gases at the outlet of the TEOM 150 PMA microanalyzer was analyzed using QMS-200 quadrupole mass spectrometer.

High-resolution transmission electron microscopy (HRTEM) images were obtained using JEM-2010CX instrument with 100 kV acceleration voltage and 1.4 Å resolution. The X-ray diffraction (XRD) patterns were registered using a X'TRA (Thermo ARL) diffractometer (Bragg-Brentano geometry, $\text{CuK}\alpha$ radiation, energy dispersed detector, step scan mode). Data registration was made in the 2θ angle range from 5° to 80° with step of 0.05° and accumulation time of 5 s in each point. The average crystallite sizes were calculated using the Scherrer equation.

3 RESULTS AND DISCUSSION

3.1 Synthesis of V-Mg(OH)_x and VO_x/MgO aerogels

Sol-gel synthesis of mixed oxide aerogels based on hydrolysis of either mixed alkoxides or a homogeneous solution of two or more individual metal alkoxides followed by supercritical drying in an autoclave allows excellent control of mixing yielding homogeneous materials with high surface areas and small crystallite size [14]. However, different hydrolysis rates of alkoxides of different metals often make it difficult to synthesize homogeneous aerogels without phase segregation. The approaches suggested to overcome this problem include selection of alkoxide precursors with matching reactivity, prehydrolysis or the less reactive alkoxide, chemical modification of a more reactive one, etc [14].

In our case, vanadium triisopropoxide oxide was hydrolyzed substantially faster than magnesium methoxide. So, when we added water to the mixture of the alkoxides, we obtained a precipitate consisting mostly of amorphous hydrated vanadia. Such precipitation could be avoided if magnesium methoxide was prehydrolyzed with a small excess of water before the vanadium precursor was added. This procedure yielded clear homogeneous gels and was used for synthesis of all aerogel materials described in this paper.

Previously it was shown that the surface area of magnesium hydroxide aerogels could be stabilized by adding aromatic solvents [6]. We found toluene to be a better second solvent for stabilization of the mixed 10% V-Mg(OH)_x gel than an alcohol. Typical surface area of the mixed aerogels obtained after supercritical drying was about 1150 m²/g. 10% V-Mg(OH)_x sample was even higher than that of the reference AP-Mg(OH)₂ prepared by a similar procedure. Even when the vanadium concentration was increased to 26%, the surface area of the hydroxide aerogel still exceeded 1000 m²/g.

As the final goal of this study was to prepare a nanocrystalline mixed VO_x/MgO oxide with high surface area, we explored the effect of dehydration conditions on the properties of obtained aerogels. Dehydration of Mg(OH)₂ aerogels is typically carried out by heating in vacuum to 500°C or higher temperatures [4-6]. When we

applied this approach to dehydration of AP V-Mg(OH)_x samples, the surface area of the synthesized mixed oxides never exceeded 300 m²/g. For example, dehydration of 10% V-Mg(OH)_x hydroxide aerogel by calcination under vacuum to 600°C led to the surface area decrease from 1100 to 220 m²/g. Also, heating in a vacuum installation is a complex procedure, and it was desirable to develop a simpler method that could yield samples with high surface area and small particle size. Therefore, we studied several other methods for dehydration of V-Mg(OH)_x hydroxide aerogels to nanocrystalline VO_x/MgO mixed oxides.

The same 10% V-Mg(OH)_x hydroxide aerogels with the surface area ca. 1100 m²/g was used for determination of the optimal dehydration conditions. By far the simplest dehydration method is calcination in air in a muffle furnace. Actually, this method proved to be rather efficient. The surface area of the mixed oxide prepared by such simple calcination of our hydroxide aerogel after calcination at 550°C was equal to 325 m²/g and was higher than the literature data on the VO_x/MgO materials prepared by impregnation even when AP-MgO with high surface area was used as the support [8].

To make further improvement of the dehydration procedure we studied the dehydration kinetics in a flow reactor with a spring balance using a linear heating with 1°C/min rate. There are two major weight loss regions between 100 and 200 °C and between 280 and 380°C. The first one corresponds to desorption of physically adsorbed water. The second peak corresponds to the decomposition of the mixed V-Mg(OH)_x hydroxide to the corresponding mixed oxide. So, our special attention was given to this temperature range because variation of the sample heating rate in this region could have a major effect on the properties of the final mixed oxide.

The developed procedure for dehydration of V-Mg(OH)_x hydroxide aerogels in a flow reactor with intense air flow and slow heating can be used for easily controlled and reproducible synthesis of nanoscale AP-VO_x/MgO mixed oxides with the surface area exceeding 400 m²/g. Actually, the absolute highest surface area of 10% VO_x/MgO mixed oxide aerogel equal to 470 m²/g after calcination at 550°C was obtained for the sample heated in air flow in a tubular flow reactor. This result exceeds the surface area of the sample prepared using the vacuum dehydration by more than a factor of two and appears to be the highest reported surface area for VO_x/MgO materials.

The XRD analysis of VO_x/MgO samples with different vanadium concentrations showed the presence of nanocrystalline MgO phase with the average crystallite size 5-6 nm together with some Mg(OH)₂. The latter can be due to partial rehydration of MgO nanoparticles exposed to the atmosphere after the heat treatment. It is remarkable that no vanadium oxide or magnesium vanadate phase was observed even in the sample with the highest vanadium concentration 26%.

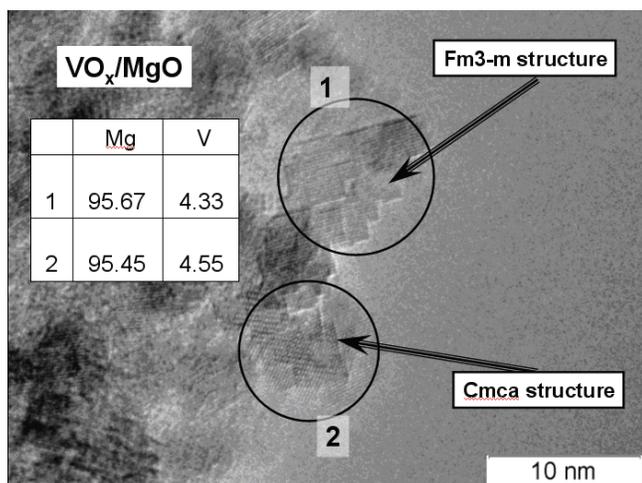


Figure 1. HRTEM image of 5% VO_x-MgO aerogel (1 – Fm3m structure, 2 – Cmca structure).

Figure 1 presents high-resolution TEM image of 5% VO_x/MgO aerogel. The image clearly shows that the sample is nanocrystalline and consists of interconnected nanocrystals with typical dimensions below 5 nm. However, the analysis of electron diffraction images showed that the structure is changed after the vanadium introduction. The observed structure of VO_x/MgO nanocrystals can be attributed to two different crystalline groups denoted as 1 and 2 in Figure 1:

- 1 – Face-centered cubic lattice – Fm3m;
- 2 – Orthorhombic lattice – Cmca.

These data suggest that the growth of the vanadium concentration in VO_x/MgO aerogels is accompanied by gradual transformation of the face-centered cubic lattice (Fm3m) typical for MgO into the structure with orthorhombic symmetry (Cmca) typical for magnesium vanadate Mg₃(VO₄)₂.

The chemical composition in different regions of the sample marked in Figure 1 was studied using an EDX attachment. The data shown in Figure 1 and obtained for other aerogels clearly show that the vanadium concentrations in atomic per cents measured by EDX match the calculated bulk concentrations for all nanoparticles in all studied aerogel samples. So, the vanadium distribution in VO_x/MgO aerogels is homogeneous independent of the vanadium concentration in the studied concentration range. This proves that the aerogel preparation procedure yields samples where vanadium is evenly distributed in the structure of the MgO aerogel matrix.

3.2 CF₂Cl₂ destructive sorption over VO_x/MgO aerogels

The investigation of the weight gain kinetics using a TEOM microanalyzer with 100% contact of the sample with the halocarbon allowed us to obtain more detailed information on the reaction mechanism. The data on the reaction of AP-MgO with CF₂Cl₂ obtained in the TEOM

microanalyzer (Fig. 2) are presented for comparison. One can see that at 350°C fast MgO conversion begins in 15 minutes after the reaction start. Meanwhile, this induction period is shortened to 11 min for 1% VO_x/MgO.

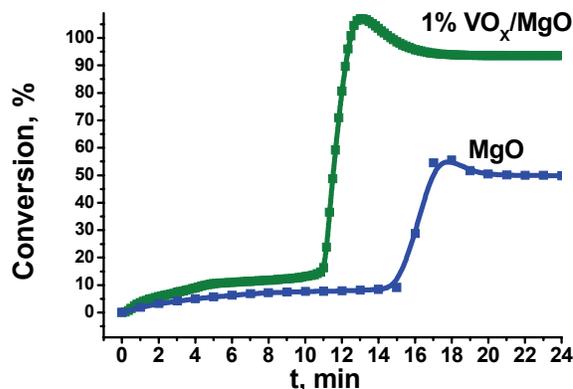


Figure 2. Kinetics of CF₂Cl₂ reaction with MgO and 1% VO_x/MgO aerogels at 350 °C.

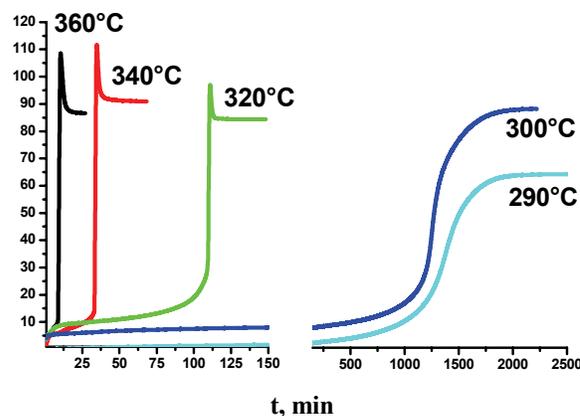


Figure 3. Kinetics of 1% VO_x/MgO reaction with CF₂Cl₂ at different temperatures.

Two temperature ranges can be distinguished for the kinetic curves of the CF₂Cl₂ destructive sorption on 1% VO_x/MgO (Fig. 3). At high temperatures (320-360° C) the reaction is characterized by a prolonged induction period when the sample weight does not change much. After the induction period ends, fast reaction accompanied by the weight takes place followed by some weight loss after reaching the maximum weight. At lower temperatures the induction period becomes longer, whereas the reaction rate remains approximately constant. At even lower temperature it is impossible to distinguish the induction period because the sample weight grows slowly, and the weight growth kinetics has the S-shape typical for many solid-state reactions. For AP-MgO such behavior is observed at 325°C or lower temperatures. After the vanadium introduction this

temperature is decreased. For instance, for 1% VO_x/MgO this change is observed at 300°C.

Figure 4 illustrates the dependence of the induction period length on the vanadium concentration in the sample. At 1% vanadium concentration the induction period is equal to 11-12 minutes at 350°C. Further increase of the vanadium concentration makes the induction period several times shorter. Most likely, such dependence results from the fact that vanadia both participates in the halocarbon decomposition and acts as a catalyst initiating the reaction with MgO matrix.

The complete mass-spectrum of the reaction products was analyzed to select the main representative peaks of the products that were continuously monitored during the reaction. These selected peaks included the peaks with $m/z = 63$ (COCl₂), 44 (CO₂), 84 (CF₂Cl₂) and 117 (CCl₄). The results obtained by the mass-spectrometric analysis show that CCl₄ and CO₂ were the main products obtained over VO_x/MgO. After the end of the induction period intense CF₂Cl₂ absorption by the sorbent takes place with the evolution of water, CO₂, CCl₄ and a small amount of phosgene. The kinetic data (Fig. 4) indicate that the CO₂ evolution takes place at the same time as the main changes of the sample weight. Meanwhile, the CCl₄ is released somewhat later, and the length of this delay grows with the increase of the vanadium concentration in the sample. The obtained data prove substantial participation of added vanadium in the halocarbon decomposition.

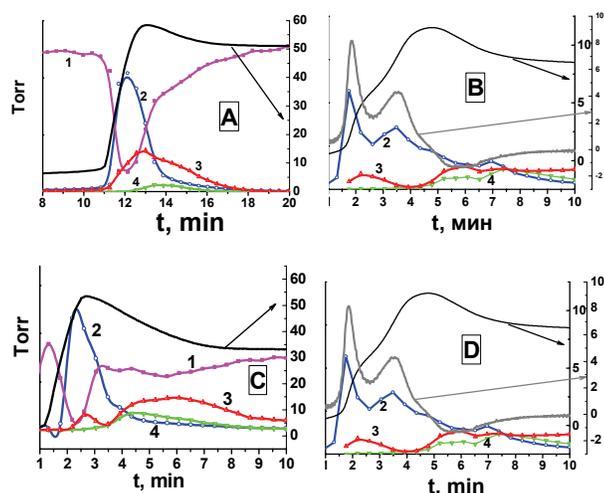


Figure 4. Kinetics of the product formation during reaction of X%VO_x/MgO aerogels with CF₂Cl₂ at 350°C. A) X = 1; B) X = 8; C) X = 15; D) X = 26. Gaseous products: 1 – CF₂Cl₂, 2 – CO₂, 3 – CCl₄, 4 – COCl₂.

4 CONCLUSIONS

The developed aerogel method for synthesis of binary vanadium-magnesium oxides and hydroxides yields nanocrystalline materials in a wide range of vanadium concentrations. The conditions used for the aerogel hydroxide dehydration and conversion to binary oxide were

optimized to obtain materials with the surface area as high as 450 m²/g. Unlike the traditional impregnation methods, the aerogel synthesis method leads to materials with a homogeneous vanadium distribution in the MgO structure according to the EDX data.

No magnesium vanadate phase was observed in the samples with the vanadium concentration 26% or lower. Vanadium ions are introduced into the MgO nanocrystals changing their symmetry from the initial cubic (Fm3m) to orthorhombic (Cmca). Samples with introduced vanadium showed substantially higher activity in the destructive sorption of CF₂Cl₂.

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