



Mesoporous Alumina

Photo-Cross-Linked Polydimethylacrylamide Hydrogels as Porogens for Mesoporous Alumina

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Abstract: Dimethylacrylamide-based hydrogels were utilized as porogenic matrices in the synthesis of mesoporous aluminum oxide (γ -Al₂O₃) with specific BET surface areas up to 360 m² g⁻¹. Polymers with molecular mass in the range 12000– 35000 g mol⁻¹ were synthesized from dimethylacrylamide and various comonomers by free-radical polymerization. Photocross-linking of the polymers and impregnation with aluminum nitrate $[Al(NO_3)_3]$ was carried out in a single step, followed by formation of $Al(OH)_3/AlO(OH)$ and subsequent calcination. Calcination led to the formation of mesoporous Al_2O_3 and simultaneous combustion of the hydrogel. The structural properties of the products were characterized by powder XRD, N_2 physisorption analysis, Hg intrusion porosimetry, and thermogravimetric analysis.

Introduction

Porous alumina (Al₂O₃) plays an important role in industry, mostly as a catalyst or catalyst support, due to its high specific surface area and pore volume.^[1-3] The pore size can be tuned by varying the synthesis conditions and by choice of the porogenic structure director. For example, rigid, porous structural matrices are frequently used for the synthesis of porous metal oxides by the so-called nanocasting method.^[4–6] This approach comprises the infiltration of precursor compounds (e.g., metal salts) into the pores of the matrix (e.g., porous silica or carbon) and conversion to the respective product (metal oxide). Removal of the matrix yields the porous product as a replica of the matrix pore system. For amphoteric metal oxides, such as alumina,^[7,8] magnesia,^[9] and zinc oxide,^[10,11] mesoporous carbon materials have proved to be suitable matrices, as they can be removed without chemical etching under harsh pH conditions.^[12] As an alternative to rigid matrices, hydrogels offer another versatile opportunity for structuring mesoporous metal oxides.^[13-15] Hydrogels are three-dimensional polymer networks that can absorb water and are well known for their application as super-absorbents, but they have also attracted great attention for tissue engineering, drug delivery, sensors, actuators, and catalysis.^[16–18] We have recently reported on using

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201601364. poly(dimethylacrylamide)-based hydrogels as porogenic matrices for mesoporous alumina.^[19] Here we extend this approach to using a variety of different photo-cross-linked hydrogels prepared by utilizing various building blocks in various ratios. By introducing the aluminum source (aluminum nitrate) prior to photo-cross-linking of the polymers, aluminum oxide can be formed conveniently in a one-pot synthesis approach.

Results and Discussion

Cross-linkable polymers were synthesized by free-radical polymerization of dimethylacrylamide (DMAAm) monomer and two comonomers (Scheme 1). The first comonomer was *N*-[2-(dimethylmaleimido)ethyl]acrylamide (DMIAAm; 5 or 10 %); it serves as the cross-linking unit in the subsequent photoinduced linking reaction (see below). The second comonomer was *tert*-butylacrylamide (*t*BuAAm) or *N*-[2-(dimethylamino)ethyl]acrylamide (DMAEAAm); its content varied between 5 and 15 %. The role of the second comonomer is to vary the hydrophilicity of the polymer by means of the hydrophobic *tert*-butyl group (in *t*BuAAm) and the more hydrophilic tertiary amino group (in DMAEAAm). The synthesis of DMIAAm has recently been described.^[19]

All synthesized polymers and their characterization are listed in Table 1. The molecular weights, dispersities, and yields of the polymers are typical for free-radical polymerization.^[18] Since the polymers are subsequently cross-linked to form hydrogels, the molecular weights and dispersities are of secondary importance. Polymer compositions calculated from NMR spectroscopic data (see Figure S1 in the Supporting Information) differ slightly from the feed compositions of the monomers. DMIAAm and DMAEAAm are less incorporated into the polymer.^[20,21] Specific reactivity ratios for those systems cannot be found in the literature, but at least a similar behavior was reported for

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Scheme 1. Synthesis of polymers by free-radical polymerization of DMAAm monomer and two comonomers (DMIAAm/tBuAAm or DMIAAm/DMAEAAm) in various ratios (see Table 1).

DMIAAm with reactivity ratios determined by the extended Kelen–Tüdös method for DMIAAm (r = 1.33) and a very similar monomer, namely, *N*-isopropylacrylamide (r = 1.45).^[22]

Table 1. Summary and characterization of the synthesized polymers.

	fe	ed comp	oosition	/ %	polymer composition [a] / %				÷	
sample	DMAAm	DMIAAm	DMAEAAm	<i>t</i> -BuAAm	DMAAm	DMIAAm	DMAEAAm	<i>t</i> BuAAm	yield / %	M _n ^[b] / g mol ⁻ D ^[b]
A1	90	5	5	-	91.4	4.3	4.3	-	80	12000 2.71
A2	85	5	10	-	88.6	4.6	6.8	-	88	23000 2.94
A3	80	5	15	-	84.1	3.9	12.0	-	80	16000 3.80
A4	85	10	5	-	87.6	8.1	4.3	-	66	30000 2.54
A5	80	10	10	-	83.6	8.2	8.2	-	62	25000 2.66
A6	75	10	15	-	79.4	7.6	13.0	-	52	14000 2.96
B1	90	5	-	5	90.6	4.3	-	5.1	76	35000 2.32
B2	85	5	-	10	84.7	4.7	-	10.6	82	29000 2.74
B3	80	5	-	15	81.3	4.4	-	14.3	76	18000 4.34
B4	85	10	-	5	87.0	8.8	-	4.2	44	27000 2.23
B5	80	10	-	10	83.7	8.2	-	8.1	46	12000 3.12
B6	75	10	-	15	78.0	8.0	-	14.0	64	33000 2.53
C1	90	10	-	-	94.3	5.7	-	-	50	20200 3.60

[a] Determined by ¹H NMR spectroscopy. [b] M_n : number-average molar mass; *D*: dispersity; both determined by gel permeation chromatography (GPC) in CHCl₃, calibrated with poly(methyl methacrylate) (PMMA) standards.

In the next step the as-prepared polymers were cross-linked by irradiation with UV light to build a cross-linked hydrogel matrix. For this purpose, the polymers were dispersed in a saturated aqueous solution of aluminum nitrate. The aluminum salt does not have any impact on the photo-cross-linking, and is used to prepare alumina in the hydrogel matrix afterwards; it is added at this stage for convenience, in order to avoid drying and re-swelling of the cross-linked hydrogel at a later stage. The DMIAAm in the polymer serves as the photo-cross-linker; after UV irradiation a three-dimensional polymer network is formed. The reaction mechanism is primarily a [2+2] cycloaddition, but other possible pathways have also been identified.^[23] In addition, the DMIAAm content in the polymer proved to be critical to prepare hydrogels and should be greater than 2–3 %.^[21] The thus-obtained aluminum-salt-containing hydrogels were then dried and exposed to ammonia steam at elevated temperature (60 °C) to form aluminum hydroxide/oxyhydroxide [Al(OH)₃/AlO(OH)] precursor species for alumina. This technique is well established in the nanostructure-directed synthesis of Al₂O₃.^[7,8] Constant contact times with ammonia steam are necessary for reproducible results, as this influences the crystallinity of the final product.^[8] The samples were finally dried and calcined at 500 °C. Calcination leads to the formation of Al₂O₃ from Al(OH)₃/AlO(OH); simultaneously, the porogenic hydrogel matrix is removed by thermal combustion.

All thus-prepared alumina materials show a rather low degree of crystallinity, comparable to that of mesoporous alumina prepared at similar temperature with other porogens.^[7,8] Figure 1 shows the powder XRD pattern of Al₂O₃ prepared by using hydrogel B1 [poly(DMAAm-*co*-DMIAAm-*co*-*t*BuAAm); 90.6:4.3:5.1 mol-%] as an example. Only two diffraction peaks are resolved; they can be indexed according to the defect spinel structure of γ -Al₂O₃ (JCPDS card No. 29-0063), which is the expected phase under these synthesis conditions.^[7,8] The XRD patterns of all other Al₂O₃ materials prepared with different hydrogels are very similar, and revealed no clear trend in crystallinity (Figure S2 in the Supporting Information).



Figure 1. Powder XRD pattern of γ -Al₂O₃ prepared by using hydrogel B1 as the porogenic structure director, after annealing.

Figure 2 shows the N₂ physisorption isotherm and corresponding BJH mesopore size distribution of the same AI_2O_3 sample as in Figure 1 (prepared with hydrogel B1). The isotherm exhibits a type IV(a) shape with H2 hysteresis,^[24] which confirms



that the material exhibits mesopores of a somewhat uniform size of about 4 nm (although the BJH method regularly underestimates the size of small mesopores by up to 20 %). Thus, the hydrogel matrix has a porogenic impact, as previously discussed.^[19] Al₂O₃ is formed between bundles of polymer strands in the continuous hydrogel network; removal of the hydrogel by combustion leaves behind disordered, tubular mesopores. Comparison of the physisorption data of all prepared Al₂O₃ materials shows that the choice of porogenic hydrogel matrix has only little impact on the porosity, that is, on the mesopore size distribution, specific mesopore volume, and specific BET surface area. Table 2 shows the respective values for all samples (for data, see Figure S3 in the Supporting Information). On average, the pore volumes and BET surface areas tend to be slightly larger in the samples prepared with hydrogels containing the hydrophilic DMAEAAm comonomer than in those prepared with the hydrophobic tBuAAm comonomer. Likewise, the width of the mesopore size distribution peak tends to be slightly narrower. Both effects are very weak, and more data will be necessary to confirm that the observed trends are statistically significant. Such findings would suggest that the more hydrophilic hydrogels have a slightly more favorable structure-directing, porogenic impact on alumina synthesis. Stronger attractive interaction between the aluminum salt and the polymer strands may result in more uniform mesopores. No clear trend was observed concerning the impact of the ratio of the comonomers in the hydrogel networks.



Figure 2. N_2 physisorption isotherm and mesopore distribution (inset) of the same Al_2O_3 sample as in Figure 1.

In addition to the uniform mesopores, the materials also contain macropores, as evidenced by mercury intrusion porosimetry. Figure 3 shows the pore size distribution of an alumina sample prepared by the same procedure with a poly(DMAAmco-DMIAAm) containing 5.7 mol-% cross-linker as the porogenic matrix.^[19] The distribution curve of the as-synthesized material exhibits three maxima: a narrow peak occurs in the mesopore



Table 2. Specific surface areas A_{BET} and specific mesopore volumes V_{pore} of the alumina materials prepared by using hydrogels of various cross-linked polymers as porogens.

Polymer porogen ^[a]	$A_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_{\rm pore}/{\rm cm}^3~{\rm g}^{-1}$
A1	312	0.45
A2	336	0.36
A3	345	0.36
A4	367	0.51
A5	306	0.41
A6	332	0.47
B1	341	0.46
B2	273	0.39
B3	314	0.50
B4	342	0.49
B5	356	0.50
B6	253	0.37
C1 ^[18]	362	0.44

[a] For designation of polymers, see Table 1.

regime at about 5 nm, which is consistent with the above-presented findings from N₂ physisorption analysis. In addition, two more, very broad peaks are observed in the macropore regime around 1.4 and 100 µm. The specific volumes of the three types of pores are 0.32, 1.94, and 4.60 cm³ g⁻¹, corresponding to the respective peak areas in the pore size distribution curve. The first value is consistent with the results obtained by N₂ physisorption analysis (0.46 cm³ g⁻¹; see Figure S4 in the Supporting Information). The macropores may originate from an inhomogeneous distribution of the polymer during cross-linking (clustering of polymer bundles) and from inhomogeneous shrinking of the solid Al₂O₃ material on calcination. The macropores may therefore be considered to be "textural pores", that is, basically voids between adjacent (intrinsically mesoporous) alumina particles. This is consistent with the observation that grinding of the porous alumina sample in a mortar drastically reduces the



Figure 3. Meso- and macropore size distribution of Al_2O_3 before and after grinding in a mortar, measured by Hg intrusion porosimetry.





macroporosity (Figure 3). The larger mesopores (ca. 100 μ m) completely collapse under the mechanical stress; they no longer exist after 2 min of grinding. The peak of the smaller macropores (ca. 1.4 μ m) drastically decreases in intensity by 56 % after grinding for 2 min and by a total of 67 % after 20 min. [Grinding also has a slight impact on the mesopores, which is in line with the observations from N₂ physisorption analysis (see Figure S4 in the Supporting Information)].

To confirm that the hydrogel is quantitatively removed from the alumina during the calcination procedure in the final part of the synthesis, thermogravimetric analysis (TGA) was carried out. Figure 4 shows the results for the calcined Al₂O₃ sample from Figure 1 (prepared by using hydrogel B1). A weight loss of about 19 % is observed in the entire temperature range from 25 to 1000 °C, most of which takes place below about 250 °C. Since the calcination temperature was 500 °C (for 4 h) the mass loss is apparently attributable to desorption of water taken up by the calcined porous sample from air during storage. This water may be physisorbed or chemically bound to coordinatively unsaturated Al sites in the (poorly crystallized) material (either as H₂O or as OH⁻ with protonation of adjacent Al-O-Al bridges, that is, reverse oxolation). TGA of all other prepared alumina samples gave very similar results (see Figure S5 in the Supporting Information). The fact that no considerable mass change occurs above 500 °C (i.e., above the calcination temperature) confirms that the calcined materials do not contain any residual organic moieties.



Figure 4. TGA (black line) of the same AI_2O_3 sample as in Figure 1. The differential thermogravimetric (DTG) curve (gray line) is the first derivative of the TGA curve.

It is interesting to compare the TGA data of the Al(OH)₃/ hydrogel composites (after ammonia treatment, before annealing) with those of the pure (aluminum-free) hydrogels. Figure 5 shows the TGA curve of poly(DMAAm-*co*-DMIAAm-*co*-*t*BuAAm) (before cross-linking) with composition of 90.6/4.3/5.1 mol-% (sample B1) with and without the Al(OH)₃/AlO(OH) species. A steep mass loss of about 40 % occurs in the composite material at approximately 220 °C, attributable to the conversion ("dehydration") of Al(OH)₃/AlO(OH) to Al₂O₃. This is immediately followed by further a mass loss of about 20 % in the temperature range from 220 °C to 550 °C, corresponding to the decomposition of the polymer. For the pure polymer, by contrast, a first weight loss of about 7 % occurs below 170 °C, which can be attributed to the loss of physisorbed water from the polymer network. A further mass loss of 93 % is observed between 170 and 630 °C. (TGA data for all other prepared polymers show very similar results; see Figure S6 in the Supporting Information). Hence, a higher temperature is necessary to decompose the polymer completely when Al₂O₃ is absent. The presence of Al₂O₃, finely dispersed in the hydrogel, reduces the combustion temperature, which indicates that the decomposition of the polymer is catalyzed by Al₂O₃. Such a catalytic effect has been observed before for the combustion of porous carbon serving as a structure matrix for various mesoporous metal oxides, including Al₂O₃.^[12b]



Figure 5. DTA (TGA; solid lines) of the $AI(OH)_3/AIO(OH)$ -hydrogel composite and of the pure hydrogel [poly(DMAAm-*co*-DMIAAm-*co*-tBuAAm), polymer B1]. The DTG curves (dashed lines) are the first derivatives of the TGA curves.

Conclusions

Poly(dimethylacrylamide)-based hydrogels are suitable as porogenic structure matrices for the synthesis of mesoporous Al_2O_3 . The products exhibit mesopore sizes in the range from 3 to 8 nm, large specific BET surface areas up to 360 m² g⁻¹, and specific pore volumes up to 0.50 cm³ g⁻¹. Variation of the polymer composition has only little impact on the structural properties of the products. The calcination of the hydrogel/alumina composite materials (i.e., the final step of the synthesis) comprises the annealing of Al_2O_3 and simultaneous combustion of the hydrogel. This procedure benefits from the fact that hydrogel decomposition is catalyzed by the freshly formed Al_2O_3 .

Experimental Section

Chemicals: Acryloyl chloride (Alfa Aesar, 96 %), aluminum nitrate nonahydrate [Al(NO₃)₃•9H₂O, Sigma-Aldrich, \geq 98.0 %], 25 % ammonia solution (Stockmeier), *N*,*N*-dimethylethylenediamine (Aldrich, \geq 98.0 %), 2,6-di-*tert*-butyl-4-methylphenol (BHT, Fluka, 99 %), sodium carbonate (99.5 %), and *tert*-butylacrylamide (*t*BuAAm, Acros, 97 %), were used as received. *N*,*N*-Dimethylacrylamide (DMAAm, TCI, 99 %) was distilled under reduced pressure. Azobisisobutyronitrile (AlBN, Fluka, > 98 %) was recrystallized from methanol. Diethyl ether (Hanke+Seidel), ethyl acetate (Stockmeier), and methanol (Stockmeier) were of technical grade and used as received. 1,4-Dioxane (Carl Roth, \geq 99.5 %) and THF (BASF) were distilled under





reduced pressure. Dichloromethane (Stockmeier) was distilled and dried with CaCl₂.

Characterization: ¹H and ¹³C NMR spectra were recorded with a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. Solvent signals at δ = 7.26 and 2.56 ppm were used as reference for spectra in CDCl₃ and [D₆]DMSO. The monomer contents of the polymers were calculated from NMR spectra by using the ratios of the methyl proton signal of DMIAAm at about 1.94 ppm, the methyl proton signals of DMAAm in the range of 2.77-3.22 ppm, the methyl proton signal of tBuAAm at about 1.33 ppm, and the methyl proton signal of DMAEAAm at about 2.16 ppm. GPC was performed with a Jasco 880-PU Liquid Chromatograph with a Waters RI Detector 2410 in chloroform at 30 °C and a flow rate of 0.75 mL min⁻¹. The instrument was equipped with a PSS-GRAM 10⁶ Å, a PSS-GRAM 10⁵ Å, a PSS-GRAM 10³ Å, and a PSS-GRAM 10² Å column. All samples were calibrated with PMMA standards. TGA was conducted under synthetic air at a heating rate of 10 °C min⁻¹ by using a Mettler Toledo TGA/SDTA 851e balance. N₂ physisorption analysis was performed at 77 K with a Quantachrome Autosorb 6B instrument; samples were degassed at 120 °C for 12 h at a rate of 5 °C min⁻¹ prior to measurement. Specific surface areas were determined by multipoint BET analysis^[25] in the range of $0.1 \le p/p_0 \le 0.3$. Pore volumes were calculated at $p/p_0 = 0.99$. Pore size distributions were calculated by BJH analysis^[26] from the desorption branches of the isotherms. Powder XRD was performed with a Bruker AXS D8 Advance diffractometer with Cu- K_{α} (λ = 0.154 nm) radiation (40 kV, 40 mA), a step size of 0.02°, and a counting time of 3 s per step. Mercury porosimetry was performed with a Quantachrome Poremaster 60 instrument with a contact angle of 140° for intrusion und extrusion. The surface tension of mercury is 0.48 N m⁻¹. The measurement was performed at 25 °C in the pressure range between 0.05 and 4100 bar.

Monomer Synthesis: *N*-[2-(dimethylmaleimido)ethyl]acrylamide (DMIAAm) was synthesized as described in the literature.^[19] N-[2-(dimethylamino)ethyl]acrylamide (DMAEAAm) was prepared by stirring N,N-dimethylethylenediamine (7.3 mL, 0.07 mol), anhydrous sodium carbonate (10.59 g, 0.10 mol), and a small amount of BHT in dichloromethane (100 mL) under argon atmosphere. The mixture was cooled with an ice bath and the temperature was kept always lower than 3 °C while acryloyl chloride (8.1 mL, 0.1 mol) was added slowly. The reaction mixture was warmed to room temperature and stirred for a further 4 h. The precipitate was filtered off and the solution was concentrated under reduced pressure. The product was purified by flash column chromatography with silica gel as the stationary phase and gradient elution with ethyl acetate/methanol (3:1 to 1:1). The pure product was obtained as a slightly yellow oil (4.35 g, 46 %). ¹H NMR (500 MHz, CDCl₃): $\delta = 2.18$ [s, 6 H, N(CH₃)₂], 2.39 (t, ³J = 6.04 Hz, 2 H, NCH₂), 3.34 (m, 2 H, NHCH₂), 5.55 (dd, ²J = 1.65, ³J = 10.22 Hz, 1 H, =CH₂), 6.08 (dd, ³J = 10.22, ³J = 17.04 Hz, 1 H, =CH), 6.21 (dd, ²J = 1.65, ³J = 17.04 Hz, 1 H, =CH₂), 6.43 (br. s, 1 H, NH) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 36.8 (NHCH₂), 45.1 (CH₃), 57.7 (NCH₂), 125.9 (=CH₂), 131.0 (=CH–), 165.6 (C=O) ppm.

Polymer Synthesis: Polymers were prepared by free-radical polymerization initiated with AIBN in an analogous fashion to that described in the literature:^[21] Various amounts (see Table 1) of DMAAm, DMIAAm, tBuAAm, or DMAEAAm and about 0.002 mol-% AIBN relative to the total amount of monomer were dissolved in 1,4-dioxane and the solution was purged with argon for 20 min. The total monomer concentration was 0.55 mol L⁻¹. The polymerization was carried out at 70 °C for 7 h under argon atmosphere. Afterwards, the polymer was precipitated in diethyl ether and reprecipitated from THF into diethyl ether for further purification. The

polymers were dried under high vacuum. All polymers were characterized by NMR spectroscopy and GPC (see Table 1).

Photo-Cross-Linking and Alumina Formation/Hydrogel Removal: A solution of the respective polymer (196 mg) in a saturated solution of Al(NO₃)₃·9H₂O in water (800 µL, 1.9 mol L⁻¹) was irradiated for 4 h with a 100 W high-pressure mercury vapor arc lamp equipped with an IR filter (FSUV1, HEBO Spezialglas) and water cooling in the light path. The sample solution was cooled by a water bath and covered with a glass plate to prevent solvent evaporation. After cross-linking, the samples were dried and treated at 60 °C with the vapor of an aqueous ammonia solution (12.5 %) for 3 h to convert Al(NO₃)₃ to Al(OH)₃/AlO(OH) and then dried overnight at 60 °C. The material was calcined in a tube furnace under air for 4 h at 500 °C at a rate of 1 °C min⁻¹ to simultaneously form Al₂O₃ and degrade the polymer matrix.

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