

SUPERCritical FLUID AIDED SYNTHESIS OF SURFACTANT TEMPLATED AEROGELS

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Different kinds of alumina aerogels and xerogels (both regular and surfactant-templated) were synthesized. The problem of losing textural properties was greatly reduced in a new technique that is based on the surfactant-templated pathway for making the sol-gel for alumina and also, by further subsequent treatment for the sol-gel to extract the solvents and templates from the gel network by a technique that involves a supercritical drying method. For the first time, Surfactant-Templated Alumina Aerogel (STAA) was made and showed remarkable thermal stability and gave specific surface area of as high as 1000 m²/g for as-synthesized STAA and up to 700 m²/g for calcined STAA. Also, NiO/Al₂O₃ catalysts were prepared by co-precipitating the active metal and support. Nitrogen adsorption-desorption isotherms (NAD) were used to follow the evolution of the extraction of the pore solvents and templates and to follow the textural properties and XRD was used to follow the morphological properties and the structure phase change for the synthesized gels. SEM-EDS is utilized to study dispersion of nickel on alumina.

INTRODUCTION

Aerogel was invented by Kistler in 1931 [1] and is defined as gel dried at temperature and pressure higher than the critical point of the pore fluid. By eliminating capillary stress, the hypercritical drying process largely replaces the original pore liquids with air resulting in little associated shrinkage associated with drying, which gives rise to the highly porous materials referred to as aerogels. Aerogels show promise in many applications such as, catalysts, thermal insulations, chemical adsorbers, sensors, fuel storage, energy absorbers and aero capacitors [1-5]. Some of the remarkable properties for the aerogels are high porosity, large pore volume, high surface area and very good morphological stability during heat treatment at high temperatures [6]. The sol-gel method offers several advantages for making aerogels, such as high purity, microstructure, homogeneity at molecular level, and low temperature at preparation [5,7,8]. After the discovery of M41S family of solids by Beck et al. in 1992 [9], new pathways have been studied to extend the new technique to other porous base materials, such as alumina, and to have better control over the properties of the porous materials through the introduction of surfactants to the synthesis of the sol-gel [10]. Some of the advantages of the surfactant-templated porous materials include, high porosity and tunable unimodal nanoporosity. However, the main disadvantage of surfactant-templated xerogel is that they undergo 75% to 95% volume shrinkage during drying and calcination [11,12]. In this paper we present thermally stable surfactant-templated alumina aerogels and NiO/Al₂O₃ catalysts including their synthesis, calcination and textural and morphological characterization and metal dispersion. For comparison purposes xerogels made of the same materials were prepared and characterized.

EXPERIMENTAL

2.1. Sol-Gel Synthesis

2.1.A. Preparation Of Regular Alcogels

Preparation of Alumina gel

Aluminum sec-butoxide ASB (Aldrich) was dissolved in sec-butanol was mixed with the required amount of distilled water with continuous stirring for one hour at room temperature. Then the gel was stored in its own solvents at room temperature for two days for aging.

Preparation of Nickel-Alumina gel

Aluminum sec-butoxide ASB (Aldrich) was dissolved in sec-butanol. Nickel acetate was dissolved in methanol and was mixed with the required amount of distilled water. The first solution was added to the second one with continuous stirring for one hour at room temperature. Then the gel was stored in its own solvents at room temperature for two days for aging.

2.1.B. Preparation of Templated Alcogels

Preparation of Alumina gel

The required amount of the surfactant Triton X-114 (Sigma) was dissolved into one half of the required amount of the sec-butanol (Aldrich) then Aluminum sec-butoxide ASB (Aldrich) was added to the solution. The other half of the required sec-butanol was mixed with the required amount of distilled water. The later solution was added to the former drop wise (so as to prevent sudden precipitation) with continuous stirring of the mixture. The mixture was then further stirred for one hour at room temperature. Then the gel was stored in its own solvents at room temperature for two days for aging. The aged sol-gel sample was then washed with ethanol (Aldrich) before it was extracted in a Soxhlet extractor with ethanol for 12 hours. The molar ratio for making the sol-gel was ASB:sec-butanol:X:H₂O are 1:20:0.1:2 respectively, where, X is surfactant triton X-114. However, other surfactants concentrations were also used (Figure 4).

Preparation of Nickel-Alumina gel

The required amount of the surfactant Triton X-114 (Sigma) was dissolved in the required amount of the *sec*-butanol (Aldrich) then Aluminum sec-butoxide ASB (Aldrich) was added to the solution. Nickel acetate was dissolved in methanol and was mixed with the required amount of distilled water. The first solution was added to the second one with continuous stirring for one hour at room temperature. The mixture was then further stirred for one hour at room temperature. Then the gel was stored in its own solvents at room temperature for two days for aging. The aged sol-gel sample was then washed with ethanol (Aldrich) before it was extracted in a Soxhlet extractor with ethanol for 12 hours. The molar ratio for making the sol-gel was ASB:*sec*-butanol:X:H₂O are 1:20:0.1:2 respectively, where, X is surfactant triton X-114. However, other surfactants concentrations were also used.

2.2. Drying Of Alcogels

2.2.A. Preparation Of Xerogels

For making xerogel, the alcogel was allowed to dry at ambient pressure and 313K for three days.

2.2.B. Preparation Of Aerogels

For making aerogel, the alcogel was loaded into the autoclave for CO₂ supercritical drying. The autoclave is heat-jacketed and the temperature was set to 333K. CO₂ at 1800 psi pressure, was pumped to the autoclave in a continuous mode during the entire supercritical drying process. An auxiliary recycle pump was used to make the gas mixture running fast through the sol-gel sample during the drying process to help make the supercritical drying process fast and efficient.

2.3. Calcination

For calcining the xerogels and aerogels, samples were heat treated at different temperatures 773K, 873K, 973K in a flowing air atmospheric pressure.

2.4. Characterization of Samples

Samples are analyzed on a Nova 3000 apparatus for determination of surface area, porosity and adsorption and desorption isotherms. XRD is used to analyze alumina and aluminum hydroxide phases. Bulk densities are determined gravimetrically. SEM-EDS analysis is used to determine Nickel distribution on alumina.

3. RESULTS

3.1 BET Specific Surface Area

The effect of calcination temperature on specific surface area of the alumina aerogel and xerogel is shown in Figure 1 for both surfactant-templated (ST) and regular (prepared without use of any surfactant) aerogels and xerogels. ST aerogel shows high surface area and high thermal stability. ST xerogel has considerable less specific surface area than ST aerogel, yet, the area is still higher than surface areas of both regular aerogel and regular xerogel. Table 1 shows the textural properties for the prepared samples including specific surface area values of about 1000 m²/g and 600 m²/g for as synthesized ST aerogel and ST xerogel respectively.

3.2 Pore Volume and Pore Size Distribution

The pore volumes as determined from the nitrogen desorption part of the NAD isotherms using BJH method and are shown in Table 1. Unlike all other samples, ST xerogel showed a consistent trend of gaining pore volume when it was calcined at the first temperature (773K), which suggests that ST xerogel still has considerable amount of the templates within the pore mesostructure before calcinations, even though it was Soxhlet extracted and dried for several days. On the other hand, in the case of the ST aerogel, there was no gain in the pore volume after calcination, which suggests that supercritical CO₂ drying removes additional amount of the templates left after the Soxhlet extraction. The pore size distribution measured by NAD is shown in Figure 2. ST aerogel has the largest average pore size. ST xerogel and regular aerogel have average pore size close to the ST aerogel. Regular xerogel has a pore size distribution closer to micropores (Figure 2).

3.3 XRD Phase Characterization

Figure 3 shows the phase progress for the ST aerogel. The as-synthesized ST aerogel shows a diffraction pattern that was assignable to boehmite alumina structure. Sample calcined at 973K mainly had an amorphous diffraction pattern plus a little diffractions that could be assigned to gamma phase alumina.

3.4 Bulk Densities

Figure 4 shows the bulk density as a function of the surfactant (X-114) concentration used in the sol gel initial concentration. It is apparent that ST aerogel poses the lowest bulk density. The calcined ST aerogel showed more stable density after calcination at X-114 concentration of 0.1 and seems to undergo more volume shrinkage for the other surfactant concentrations. The sample processing steps (drying and calcination) account for volume shrinkage of 5 and 75% and porosity was 98 and 81% for the ST aerogel and ST xerogel respectively.

3.5. Nickel Dispersion

SEM-EDS analysis of co-precipitated NiO/Al₂O₃ samples show good dispersion of nickel on the alumina support. Ni/Al mass ratio on the surface is higher than 9%, as determined by SEM/EDS. The mass of Nickel introduced per mass of Aluminum is 10.

CONCLUSION

Thermally stable alumina supports are synthesized using surfactant templating and supercritical drying. Co-precipitation permits even and high dispersion of the metal on the support when NiO/Al₂O₃ catalysts are prepared using surfactant templating and supercritical drying.

REFERENCES:

- [1] KISTLER, S.S., Nature, Vol. 127 **1931**, p.741
- [2] HRUBESH, L.W., Journal of Non-Crystalline Solids, Vol. 225, **1998**, p.335
- [3] KNOZINGER, H., RATNASAMY, P., Catal. Rev. Sci. Eng, Vol. 17 (1), **1978**, p.31
- [4] BRINKER, C.J., SCHERER, G.W. "Sol-Gel Science The Physics and Chemistry of Sol-Gel Processing", **1990**, Academic Press.
- [5] SUH, D.J., Journal of Non-Crystalline Solids, Vol. 225 **1998**, p.168
- [6] JANOSOVITS, U., ZIEGLER, G., SCHARF, U. WOKAUN, A., Journal of Non-Crystalline Solids, Vol. 210, **1997**, p.1
- [7] ERTL, G., KNOZINGER, H., WEITKAMP, J., "Preparation of solid catalysts", **1999** Wiley-VCH
- [8] BAGWELL, R.B., MESSING, G.L., Key Engineering Materials, Vol.115 **1996**, p.45
- [9] BECK, J.S., VARTULI, C., ROTH, W.J., LEONOWICZ, M.E., KRESGE, C.T., ACHMITT, K.D., CHU, C.T-W., OLSON, D.H., SHEPPARD, E.W., MCCULLEN, S.B., HIGGINS, J.B., SCHLENKER, J.L., J. Am. Chem. Soc. Vol.114, **1992**, p.10834.
- [10] GONZALEZ-PENA, V., DIAZ, I., MARQUEZ-ALVAREZ, C., SASTRE, E., PEREZ-PARIENTE, J., Microporous and Mesoporous Materials Vol. 44-45, **2001**, p.203
- 11- MARK T. ANDERSON, PATRICIA S. SAWYER, THOMAS RIEKER, Microporous and Mesoporous Materials Vol. 20, **1998**, p.53-65.
- 12- MARK .T. ANDERSON, J.E. MARTIN, J.G. ODINCK, P.P. NEWCOMER, J.P. WILCOXON, Microporous Mater. Vol.10, **1997**, p.13

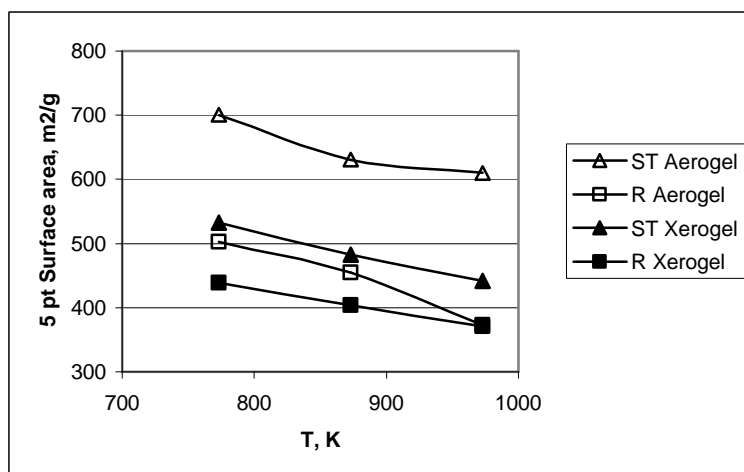


Figure 1: Effect of calcination temperature on the specific surface area measured with 5-pt. BET method.

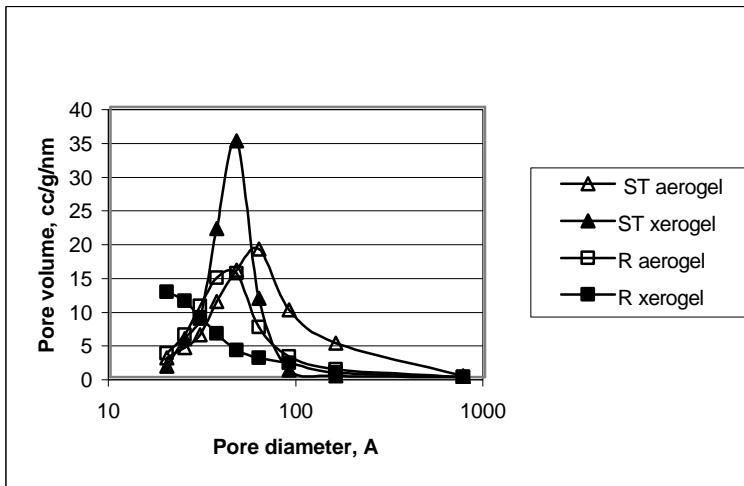


Figure 2 Pore size distribution measured by nitrogen adsorption-desorption method (NAD).

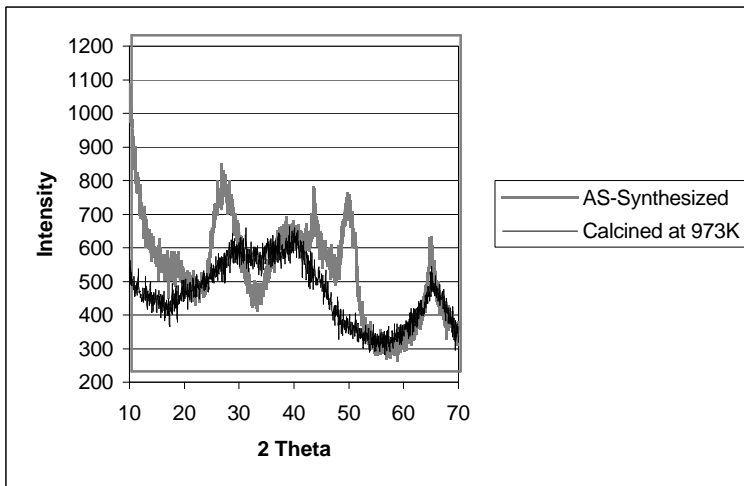


Figure 3 X-ray diffraction patterns for ST aerogel, as-synthesized and calcined at 973K.

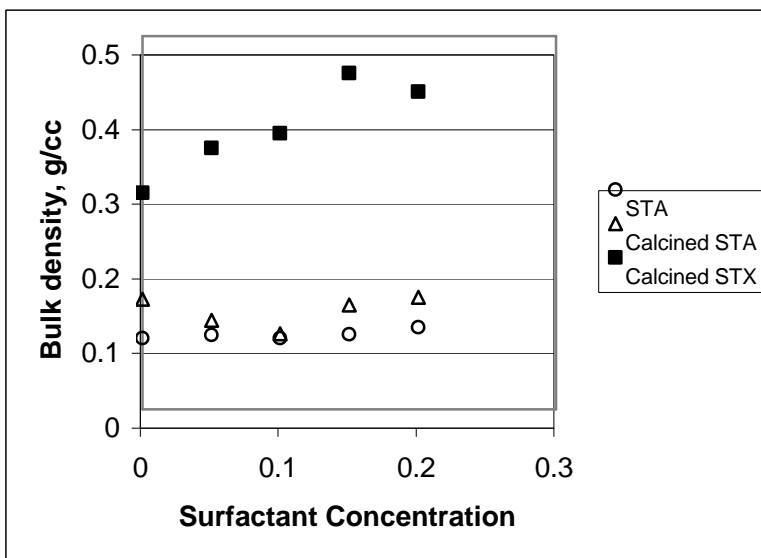


Figure 4 Bulk densities.

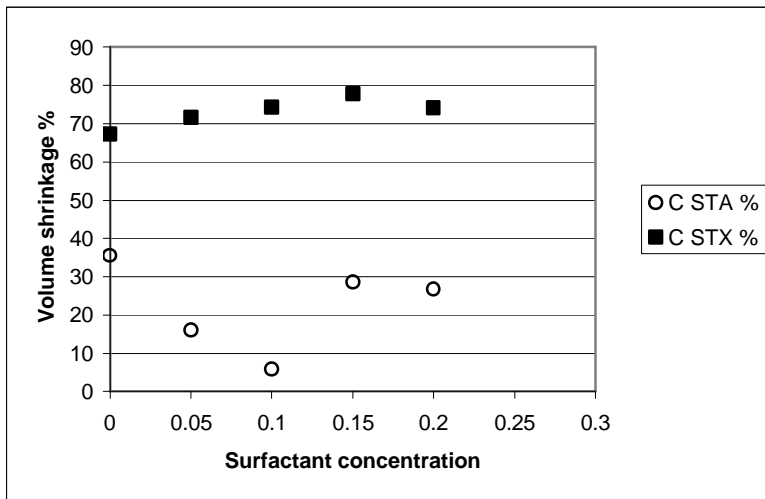


Figure 5 Volume shrinkage

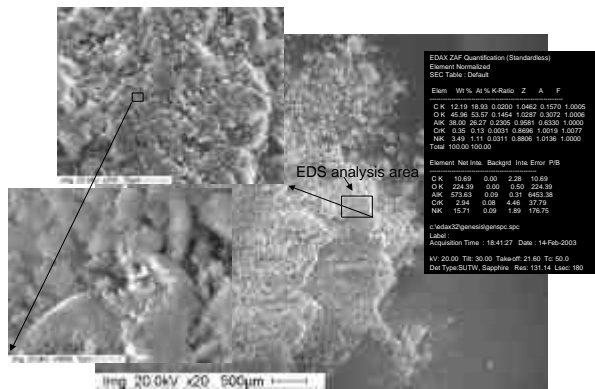


Figure 6. SEM images of NiO/Al₂O₃ catalysts

Table 1 Textural properties for templated and regular gels

Temperature, K	ST Aerogel			ST Xerogel			Regular Aerogel			Regular Xerogel		
	Sa, m ² /g	Vp, cc/g	Dp, A	Sa, m ² /g	Vp, cc/g	Dp, A	Sa, m ² /g	Vp, cc/g	Dp, A	Sa, m ² /g	Vp, cc/g	Dp, A
As-Synthesized	997	2.56	103	587	0.61	41	763	0.77	40	535	0.82	61
773	701	2.15	123	533	0.94	71	503	0.62	50	439	0.81	74
873	631	1.94	123	483	0.79	65	455	0.53	47	404	0.75	75
973	610	1.63	107	442	0.77	69	373	0.44	48	371	0.66	71

Table 2 Aerogel and xerogel porosities as a function of Surfactant mole ratio in the sol-gel.

Surfactant mole ratio	STA Porosity	STX Porosity
0.00	0.91	0.83
0.05	0.96	0.82
0.10	0.98	0.81
0.15	0.92	0.80
0.20	0.93	0.81