SUPERCRITICAL FLUID AIDED FUNCTIONALIZATION OF AEROGEL CATALYSTS

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The strength, thermal stability, and pore structure and morphology are key to success of wider deployment of aerogels. Furthermore, co or subsequent functionalization of the surfaces are equally if not more important. This paper addresses these issues through a new method. The path involves successful use of surfactant templating, supercritical drying, and supercritical fluid aided functionalization of the surface. Alumina supported nickel catalyst particles are used to evaluate the approach. Initially thermally stable surfactant alumina was synthesized. The surfactant was removed completely with the aid of a supercritical solvent mixture. The support, alumina, is subsequently impregnated with nickel. BET/pore measurements were used to follow the removal of solvents and templates as well as tracking the textural properties for the synthesized gel. EDAX and SEM were employed to study the distribution of the nickel on the alumina support and the percentage was compared with the starting mixture of the sol gels.

INTRODUCTION

The sol-gel method offers several advantages in making catalysts and catalyst supports. It provides production of aerogels, with favorable properties such as high purity, high porosity and homogeneity at molecular level (1). Controlled pore size distribution is another favorable property for catalysts. Recently, new pathways have been studied to prepare 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 (2). The basic advantage of the surfactant-templated porous material is high porosity and tunable unimodal nanoporosity (3). Also, removal of the solvent and surfactant using supercritical fluids ensures retaining the pore structure (4). In this paper, we present thermally stable surfactant-templated alumina aerogels and impregnation of nickel on the alumina supports including their synthesis, calcination and textural and morphological characterization and metal dispersion.

EXPERIMENTAL

Preparation of alumina support is summarized in Figure 1 and preparation of alumina and nickel-oxide/alumina catalysts is described in the sections below.
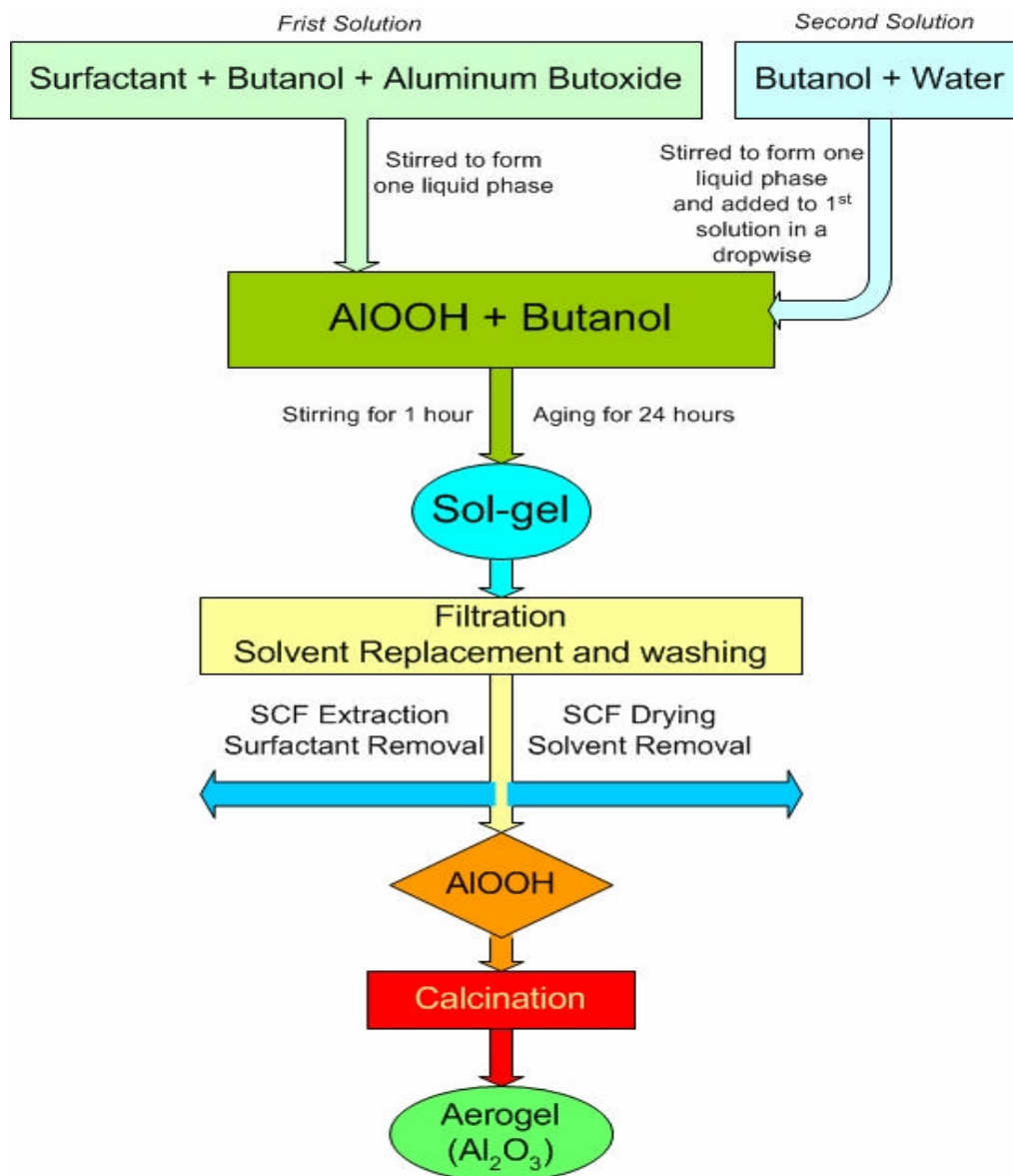
Figure 1. Preparation of Alumina Aerogel

Sol-Gel Procedure for Preparation of Templated Alumina

The non-ionic surfactant used was Triton X-114 (Sigma) (polyoxyethylene (5) isooctylphenyl ether). The sol gel procedure was as follows: The required amount of the surfactant and aluminum sec-butoxide (ASB) were dissolved in *sec*-butanol. The required amount of distilled water was mixed with sec-butanol. The later solution was added to the former drop-wise 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 24 hours for aging. The aged sol-gel sample was then washed with ethanol (Aldrich) and excess alcohol was filtered.

**Supercritical Extraction of the Solvent and Surfactant /
Impregnation of Nickel with the Aid of Supercritical Fluids**

The supercritical extraction / impregnation system used to extract the solvent (alcohol) and surfactant from the wet gel matrix is shown in Figure 2. The surfactant is removed with supercritical ethanol-carbon dioxide mixture and the remaining alcohol is removed with supercritical carbon dioxide. Nickel is impregnated from nickel acetate and nickel nitrate. Precursor to alumina weight ratio used was 2:1 or 1:1. Extraction and impregnation conditions are given in Table 1. Samples are calcined in air for three hours at 500°C after preparation. Impregnation was performed on previously calcined alumina and alumina that was not calcined.
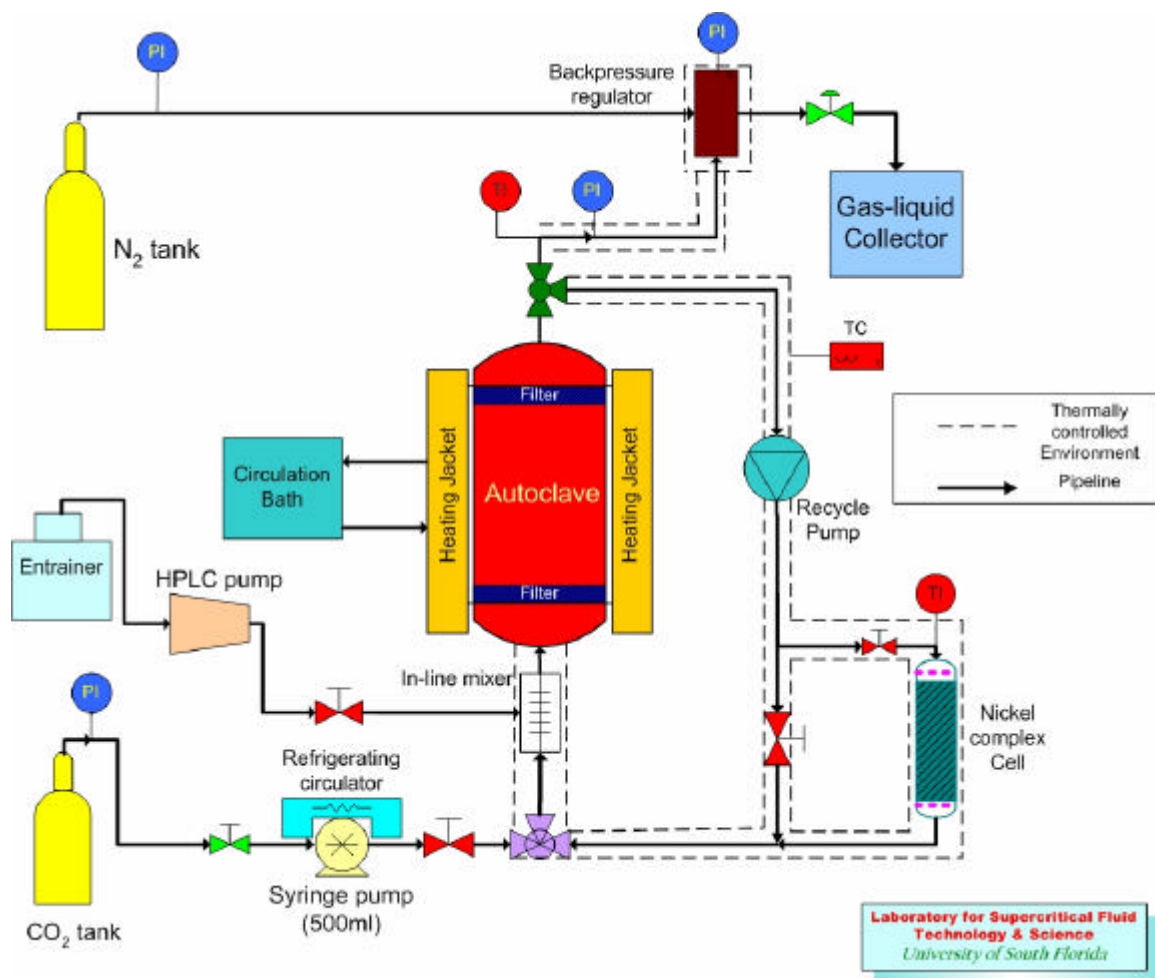
Figure 2. Supercritical Extraction and Impregnation System

Table 1. Extraction and Drying Conditions

Condition	Extraction	Impregnation
Temperaure (^{o}C)	62.5	50
Pressure (psi)	1800	1500
Flow	Solvent: CO_2 Rate: 10 ml/min Time: 2hrs.	Solvent: CO_2 + MeOH Rate: 2 + 0.1 ml/min Time: 6 hrs.
	Solvent: CO_2 + EtOH Rate: (10 + 2) ml/min Time: 4 hrs.	Solvent: CO_2 Rate: 10 ml/min Time: 2hrs.
	Solvent: CO_2 Rate: 10 ml/min Time: 2hrs.	

RESULTS AND DISCUSSION

Total specific surface area, specific pore volume and average pore diameter of the samples are given in Table 2.

Table 2. Pore Structure Analysis

Sample	SSA(m^2/g)	TPV(cc/g)	APD(?)
Al_2O_3 (not calcined) (A)	567	0.759	53.58
Al_2O_3 (calcined) (B)	434	0.722	66.53
NiO/Al_2O_3 (impregnated from $Ni(NO_3)_2$ on B) (uncalcined) (C) Ni:Al=2:1	384	0.697	72.66
NiO/Al_2O_3 (impregnated from $Ni(NO_3)_2$ on B) (calcined) (D)	376	0.676	71.98
NiO/Al_2O_3 (impregnated from NiAc on B) (uncalcined) (E) Ni:Al=2:1	432	0.784	72.56
NiO/Al_2O_3 (impregnated from NiAc on B) (calcined) (F)	411	0.748	72.77
Al_2O_3 (not calcined) (G)	405	0.854	84.26
NiO/Al_2O_3 (impregnated from $Ni(NO_3)_2$ on G) (uncalcined) (H) Ni:Al=1:1	439	0.919	83.79
NiO/Al_2O_3 (impregnated from $Ni(NO_3)_2$ on G) (calcined) (I)	390	0.723	74.20
NiO/Al_2O_3 (impregnated from NiAc on G) (uncalcined) (J) Ni:Al=1:1	435	0.835	76.83
NiO/Al_2O_3 (impregnated from NiAc on G) (calcined) (K)	366	0.766	83.68

During the preparation of samples C-F, nickel was impregnated on alumina B that was calcined a priory. When nickel was impregnated from the nitrate on calcined alumina, the total surface area decreased from $434 m^2/g$ (for calcined alumina) to $376 m^2/g$ (after calcination of the impregnated sample). For impregnation from the acetate, the decrease in surface area was less (from $434 m^2/g$ to $411 m^2/g$). During the preparation of samples H-K, nickel was impregnated on alumina G that was not calcined a priory. After calcining the impregnated sample the surface area decreased to $390 m^2/g$ and $366 m^2/g$ for impregnation from the nitrate and acetate respectively. Impregnated samples had an average pore size diameter of approximately 8nm.

SEM-EDAX analysis was performed in order to determine nickel to aluminum ratio in the impregnated samples. The results show that the samples contain up to 4% weight of nickel. Results are given in Table 3.

Table 3. EDAX Analysis Results

Element	O wt%	Al wt%	Ni wt%
Sample D	49.06	47.21	3.73
Sample F	52.04	4.45	0.5
Sample G	52.48	47.38	0.13
Sample K	48.47	50.55	0.98

CONCLUSIONS

High surface area alumina catalysts supports (surface areas above $400 m^2/g$) were prepared using sol-gel synthesis. Mesopores with uniform pore sizes of diameter equal to 7-8 nm were obtained through use of a non-ionic surfactant template. The non-ionic surfactant was removed with supercritical ethanol – carbon dioxide mixture. The solvent used in the sol-gel process (alcohol) was removed with supercritical carbon dioxide. Impregnation of nickel onto the alumina support was successfully realized through impregnation of the metal using the nitrate and acetate precursors with the aid of supercritical methanol – carbon dioxide mixtures.

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