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AEROGEL DERIVED CATALYSTS

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ABSTRACT

Aerogels are a class of colloidal materials which have high surface areas and abundant mesoporous structure. SiO_2 aerogels show unique physical, optical and structural properties. When catalytic metals are incorporated in the aerogel framework, the potential exists for new and very effective catalysts for industrial processes. Three applications of these metal-containing SiO_2 aerogels as catalysts are briefly reviewed in this paper -- NO_x reduction, volatile organic compound destruction, and partial oxidation of methane.

INTRODUCTION

Aerogels are a special class of open cell foams which have ultrafine pore or cell sizes of usually up to 1000 Å, and high surface areas of 200 to 1000 m^2/g or more. The physical structure is basically a colloidal matrix composed of interconnected colloidal type particles or polymeric chains of diameters of 10 to 50 Å units. This gives a nanostructure that is responsible for the unusual optical, thermal, and acoustic properties of these materials, and should make them ideal for catalysis. SiO_2 aerogels have been known for sometime, but not until recently have the metal-containing SiO_2 aerogels received attention for use in catalytic processes.

Aerogels can be made by several methods. We have been employing sol-gel hydrolysis-condensation methods which utilize mixing Si alkoxides with metal complexes in various forms, such as alkoxides, acetates, and nitrates. Typically, metal and Si alkoxides, such as Zr *tetrakis* ethoxide and Si *tetrakis* ethoxide, are mixed with limited amounts of water. One to four ethoxides are replaced with hydroxides, the number depending on the amount of water. The hydroxylated species then condense to form oxo-bridged oligomers. Because this is a somewhat random step, some Si-Si and Zr-Zr and the desired Zr-Si species will be formed in a one to three dimensional framework.

This condensation causes gelation upon setting. The drying method determines the porosity. Supercritical drying methods give extensive porosity (90+%), called aerogels, while simple evaporative drying gives minimum porosity (50% or lower) called zerogels. Transmission electron microscopy show the nanostructure and overall porosity consistent with adhered colloidal particles in a 3-dimensional cross-linked array. These materials generally have extensive micropores, with very finely dispersed metals. If done properly, and with a cooperative metal, minimum crystallite formation will occur.

The following is a brief review of three applications where we have used metal-containing SiO_2 aerogels as catalysts: 1) NO_x reduction, 2) volatile organic compound (VOC) oxidation, and 3) methane partial oxidation. These topics will not be covered in detail, nor the best catalysis results will be highlighted. The attempts here are to give useful insights into the potential of these materials as catalysts and the behavior when applied to industrial processes.

NO_x REDUCTION CATALYSTS

Background. The Clean Air Act of 1991 has set a course of regulations which will continue to require decreasing emission levels of certain products during combustion. By 2004, the following emission levels from an automobile exhaust will have to be met (g/mi) -- hydrocarbons (HCs), 0.125; CO, 1.7; and NO_x 0.2. With current engines and catalytic converters, the auto manufactures have been targeting lean-burn type systems to meet the low HC and CO requirements. This is partially accomplished by increasing the air to fuel ratio in combustion. Although useful for HC and CO reduction, this can increase NO_x production.

Unfortunately, NO_x abatement using HCs as the reductant is not a particularly easy. Currently three-way catalysts are essentially state of the art, but are probably not going to be sufficient to meet all new emission standards under the lean burn scenario. We have examined Cu- and V-containing SiO_2 aerogels to deal with this problem.¹² Precedence comes from: 1) selected Cu zeolites having NO_x removal activity in the presence of HCs, and 2) V on titania being well established for stationary source NO_x removal in the presence of ammonia as the reductant.

Results. The Cu- SiO_2 aerogel was synthesized by mixing a stock solution of *tetrakis* methoxy silane (TMOS) in methanol with Cu acetate and ammonia in methanol using nitric acid as the catalyst. The V- SiO_2 aerogel was synthesized by mixing the same stock solution with V *tris* isopropoxide in methanol and adding small amounts of HBF_4 .

Table 1 shows the Cu- SiO_2 aerogel (CuSiAP) has a high surface area of over $500 \text{ m}^2/\text{g}$ and a micropore diameter of around 60 Å. Oxidative pretreatment (CuSiOxy) at 400°C to remove organics changes the properties very little, indicating the organics are not involved in the structural stability of the materials. The stability of these materials is further evident because the after reaction (CuSiAR) properties only change slightly.

Table 1. Physical Properties of Aerogels

Sample	Description	Metal, wt %	BET Surface Area m^2/g	Total Pore Volume (cc/g)	Ave. Pore Diameter (Å)
CuSiAP	As prepared ^a	3.1	591	1.06	61.5
CuSiOxy	Oxidized at 400°C	2.8	583	1.03	59.9
CuSiAR	After reaction ^b	3.2	565	0.97	57.8
VSiAP	As prepared ^a	3.8	530	1.18	78.7
VSiOxy	Oxidized at 400°C	3.9	501	1.12	76.7
VSiAR	After reaction ^b	4.3	462	1.09	73.8

- a) After CO_2 extraction
b) See ref for conditions
c) Gas adsorption analysis (micrometrics ASAP 2000)

Figure 1. Pore volume (cm^3/g) versus pore diameter (Å) for a) V- SiO_2 aerogels and b) Cu- SiO_2 aerogels.

Figure 2. NO , C_3H_6 and C_3H_8 conversions for a) VSiOxy and b) CuSiOxy.

The V-SiO₂ aerogel shows less surface area and larger pore size than the Cu-SiO₂ aerogel, and exhibits more change upon oxidation and reaction. These changes are not dramatic, however, indicating the true stability of these two catalyst materials.

Figure 1 shows the pore volume as a function of the pore size for both catalysts before and after seasoning, and after reaction. Commensurate with behaviors seen in the Table 1, the pores change little upon pretreatment and use for both the Cu-SiO₂ and V-SiO₂ aerogels.

Figure 2 shows the NO_x removal performance for the Cu-SiO₂ aerogel using a synthetic gas mixture to simulate a lean-burn engine exhaust (175 ppm propane, 130 ppm H₂, 400 ppm CO, 525 ppm propylene, 7.0 vol % CO₂, 230 ppm NO, 8.0 vol % O₂, balance He, 200 ml/min, MS and NO_x meter detection). NO_x reduction begins around 100°C at the same time as propylene removal. NO_x removal continues to improve until about 300°C where 100% propylene conversion is seen. Little improvement is seen at higher temperatures even though propane begins to convert around 300°C. The NO_x removal begins to decrease after 600°C. The maximum NO_x conversion under these conditions is around 20%. The V-SiO₂ aerogel has similar behavior to the Cu-SiO₂ aerogel except that the overall NO_x reduction is slightly lower and activity does not start until 300°C.

The catalysts before and after use were characterized by several methods in attempts to assess the catalytic sites. Figure 3 shows the Raman spectra of the V-SiO₂ aerogels and related materials. The top spectrum is of pure V₂O₅. Several bands are evident, but the characteristic band for surface V=O is at about 1040 cm⁻¹. This band is shifted but evident to some extent in the VSiAP spectrum and to a much greater extent in the VSiOxy and VSiAR spectra. This band has been seen in isolated monomer surface species and has been assigned as a surface V=O species.³⁻⁵ The other bands seen for V₂O₅ are absent in the V-SiO₂ catalysts indicating crystalline V₂O₅ is not present.

Figure 3. Laser Raman spectra of selected V-containing materials.

Figure 4. Near-edge structure of V-SiO₂ aerogel as prepared (solid line) and after oxidation (dotted line).

This assignment is further confirmed in the x-ray absorption near edge spectra (XANES) shown in Figure 4. Comparing these spectra with those of model compounds⁶, the following features indicate the V is in a mixed-metal oxide environment: 1) The pre-edge at 5.8 eV is a forbidden 1s to 3d transition. This transition is seen in V₂O₄ and V₂O₅ also. The intensity of the transition for the catalyst appears to be a weighted average of the transition for the two model compounds. 2) The broader feature is a 1s to 4p transition and in V₂O₅ occurs at 30.1 eV and in

V_2O_4 around 26.6 eV. For the samples, the feature is around 28.8 eV. 3) Little structural change is observed between the prepared and oxidized materials.

Figure 5. Comparison of Cu-SiO₂ aerogel as prepared (solid line) with CuO (dotted line) near-edge structures.

Figure 5 shows the Cu-SiO₂ aerogel XANES. The CuSiOxy, CuSiAR and (not shown) CuSiAP spectra are identical. Clearly, the spectrum does not match CuO perfectly. Combining the XANES and EXAFS (not shown) indicate the species is probably a Cu-O-Si type structure. Laser Raman and temperature programmed reduction support these analyses.

Conclusions. The study of these aerogels as NO_x reducing catalysts has shown that the materials are structurally very stable to pretreatment and reaction conditions. They can be synthesized with high surface area and extensive porosity. The Cu environment is probably Cu-O with Si possibly in the second coordination sphere, and the V environment is probably a mixture of V oxides.

AEROGELS FOR CATALYTIC OXIDATION OF VOCs

Background. In 1992 over 22 MM tons of VOCs were emitted to the atmosphere in this country alone. Because VOCs are considered to cause ozone production in the lower atmosphere, there have been efforts to decrease emissions. Catalytic oxidation could be a desirable approach. Aerogels show promise for this type of catalysis because of the high porosity, high permeability, high metal dispersion, and the benign nature of the materials. To understand this utilization of aerogels, several metal-containing SiO₂ aerogels were examined for oxidation capabilities.⁷ Methanol was selected as a surrogate test material.

Table 2. Measured Properties of Aerogels

Aerogel	% Metal (wt %)	Crystallinity (from EBD)	Chain Diameter (Å)	Surface Area (m ² /g)
Silica	0.0	amorphous	30-50	650
Zr-Silica	8.3	amorphous	30-70	780
V-Silica	5.1	amorphous	30-70	735
Zirconia	74.0	orthorhombic	50-100	250

Results. Table 2 shows some of the physical properties of the aerogels examined in detail. All have high surfaces areas as well as chain sizes around 30 to 70 Å. A Zr aerogel was also compared for activity. The SiO₂ aerogels have obviously much lower metals loading than the Zr aerogel. In addition, all are amorphous except the Zr aerogel. The aerogels were tested in lab scale plug flow reactor (0.3g catalyst, 30-50 mesh) where a mixture of O₂ and He was bubbled through room temperature methanol at 40 cm³/min flow rate (O₂:CH₃OH of 6.3:1; 75% He). Detection was by GC and MS. The main products observed were CO₂, formaldehyde, water and sometimes CO.

Figure 6 shows the selectivity of the aerogels for oxidation of methanol to CO₂. The empty reactor shows no conversion or activity below 500°C, which increases above that temperature. The SiO₂ aerogel exhibits good methanol conversion (not shown) reaching 100% at 400°C. However, this conversion does not show good selectivity to CO₂ as seen in Figure 6. V-

SiO₂ aerogel (not shown) exhibits even poorer conversion of methanol, never reaching 100% in the entire temperature range. The selectivity was surprisingly low towards CO₂ also.

Figure 6. Selectivity to CO₂ of selected aerogels towards oxidation of methanol.

The Zr-SiO₂ aerogel also exhibited excellent conversion (~100% at >400°C) of the methanol, just as the SiO₂ aerogel. But unlike the SiO₂ aerogel, the Zr-SiO₂ aerogel shows excellent selectivity to CO₂ reaching 100% at 400°C, as seen in Figure 6. The Zr aerogel exhibits by far the best activity showing 100% conversion of methanol (not shown) at even 300°C. The selectivity to CO₂ is excellent being above 80% in the entire temperature range studied.

Conclusions. Pure Zr aerogel is extremely effective for the incineration of methanol. Mixtures of Zr-SiO₂ aerogels show promise, even though the temperature where complete methanol conversion occurs is higher. However, the Zr-SiO₂ aerogel has a much reduced concentration of Zr.

AEROGELS AS METHANE PARTIAL OXIDATION CATALYSTS

Background. There are over 3900 TCF of proven reserves of natural gas. Converted to liquids, this resource could power our transportation needs for at least 100 years. Simple, inexpensive technology does not exist which can accomplish extensive utilization of this resource. Part of the problem is that much of the natural gas is in remote locations, away from population centers where the fuel can be easily accessed.

Methods are known which can convert natural gas (primarily methane) to usable products.⁸⁻¹⁰ Indirect routes are known which convert the methane to synthesis gas (syn-gas) first. The Fischer-Tropsch process eventually yields high molecular weight waxes and alcohols. The Mobil MTG process converts the syn-gas to methanol, then to other products.

Direct conversion to higher hydrocarbons is not thermodynamically favorable. Alternatively, oxidative coupling, utilizing the formation of water as the driving force, presents a pathway by which conversion could possibly be attained:

In this case, ethylene is a useful product ($\Delta G = -68.7$ kcal/mol). However, the limiting aspect is the control of over oxidation to CO and CO₂. Because of this reasonable thermodynamic argument, many heterogeneous materials have been tested for catalytic activity: Li/MgO, Li/BeO, Na/CaO, lanthanides, Se, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Ag, Cd, W, Pt, Sn, Pb, Sb, Bi, Tl, Sn, Ge and others. Because of the high surface area, good gas permeability, and wide selection of metals, metal-containing SiO₂ aerogels were tested for methane conversion and for selectivity to C₂+ species.¹¹

Results. Several catalysts were tested in the same reactor system as for the VOC oxidation. The feed was a composition of CH₄, O₂ (ratio of 2 to 1) and was run either at full concentration or in He or Ar at a 75% dilution. Three operating temperatures were selected -- 750, 800, and 850°C. Best conversion/selectivity was observed at 800°C. However, the chemistry was clearly easier to follow at 750°C. Over oxidation was observed at 850°C. Best results were also observed with the diluted feed streams.

Figure 7 shows activity of several metal-SiO₂ aerogels for methane conversion and C₂+ selectivity at the 800°C reaction temperature and dilute gas feed. The spread and behavior is typical of most methane conversion catalysts for partial oxidation -- the more methane conversion, the less selectivity for C₂+ species. These catalysts have conversions which fit into the

patterns established for almost all methane conversion catalysts and perform neither better nor worse than any others.

Figure 7. CH₄ conversion vs C₂⁺ selectivity for selected aerogels.

Figure 8. Effects of V loading on conversion and selectivity to C₂⁺ of CH₄ oxidation.

Figure 8 shows the performance of V-SiO₂ aerogels at different V loadings at 750°C reaction temperature and dilute feed. V was selected because it exhibits the highest methane conversion (Figure 7). The oxidative capabilities of V is clearly evident, where selectivity to C₂⁺ is almost absent compared to the selectivity of pure SiO₂ aerogel. The product composition was almost exclusively CO₂, with minute amounts of CO (not shown). More V does not assist C₂⁺ selectivity.

Figure 9 shows the performance of La-SiO₂ aerogels at different La loadings at the same conditions as for the V. La was selected because it exhibited high C₂⁺ selectivity (Figure 7). Note the completely different behavior. As the La loading increases, selectivity towards C₂⁺ increases also. At 44% La, the selectivity is as high as 65%. However, there is almost no methane conversion.

Figure 9. Effects of La loading on conversion and selectivity to C₂⁺ of CH₄ oxidation.

Figure 7 also shows Ti-SiO₂ aerogel performed very similarly to the V-SiO₂ aerogel. To understand the chemistry of these aerogels better, the Ti-SiO₂ aerogel as made, oxidized before processing, and after 8 hours of processing at 800°C was examined by XANES. Figure 10 shows the Ti spectra for the catalyst as made and after processing. Clearly there have been some changes, both in the pre-edge and edge features. Comparing this with model compounds Ti(OiPr)₄, Ti(OSi(CH₃)₃)₄, tyzor, rutile and anatase (not shown) show that the changes in the pre-edge are due to a structural change from octahedral (pure or distorted) to tetrahedral coordination of the Ti site, and that Si could be in the second coordination sphere. This is envisioned as occurring by the Ti center loosing both hydroxyls and methoxides while still retaining the siloxy coordination.

Figure 10. XANES spectra for Ti-SiO₂ aerogels and related compounds.

Conclusions. Relative to SiO₂ aerogel, V, Ti, W, Zr, Nb, and Ta promote and La, Sm, and Y reduce the oxidation of methane. Zr, Nb, W, and Ta promote CO formation, Ti and V promote CO₂ formation. Metal-containing SiO₂ aerogels retain about 1/2 the original surface area in reactions at 800°C (still very high surface area materials around 500 m²/g). The Ti center in Ti-SiO₂ aerogel appears to go from octahedral to tetrahedral coordination (by possibly losing hydroxyls and methoxides) in this process.

FINAL CONCLUSIONS

Metal-containing SiO₂ aerogels show potential as catalysts because they can be made with high surface areas and with extensive porosity. They have been used as catalysts for NO_x reduction, hydrocarbon oxidation, and methane activation. Used for these applications, the many of the metal-containing SiO₂ aerogels retain some or most structural integrity.

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