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The Formation of Silica, Alumina and Zirconia Supported High Surface Area Monometallic and Bimetallic Catalysts

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Progress Report

During the current granting period, 12/01/92-11/30/93, studies have progressed along four fronts (1-4) : (1) Preparation of high surface area Pt/SiO₂ catalysts; (2) preparation of high surface area Pt/Al₂O₃ catalysts; (3) preparation of high surface area promoted zirconia superacid catalysts and, (4) stabilization and sintering of porous Pt/SiO₂ catalysts. In addition to these current studies a major review article on previously funded DOE research has been completed and will appear in Catalysis Reviews (5). The results of these studies are briefly described below.

The Preparation of High Surface Area Pt/SiO₂ Catalysts

Conclusions from this study are as follows (2-3): (1) Variables which control the microstructure of silica prepared by the sol-gel method using tetraethoxysilane as the silica precursor include: preparative pH, reactant stoichiometries and gelation temperature. High surface areas and well-defined pore diameters can be obtained using sol-gel processing. In particular, surface areas as high as 1000 m²/g with microporous structures can be prepared at low pH (1.3). At intermediate values of the pH (3-8), BET surface areas ranging from 850 to 350 m²/g can be obtained. Pore structures are mesoporous with pore diameters ranging from 4 to 25 nm at a preparative H₂O/TEOS ratio of 10. (2) Because of repulsive interactions, the use of H₂PtCl₆.x H₂O as the metal precursor results in poor dispersions. When Pt(NH₃)₄(NO₃)₂ is used, the precursor-support interactions become attractive and high dispersions are obtained. However, BET surface areas and pore volumes are difficult to control. The use of Pt (AcAc)₂ was found to be the most flexible metal precursor. Solubility in acetone is high, and surface areas and pore volumes are more easily controlled. (3) Solvent extraction under supercritical conditions lead to high BET surface areas and large pore volumes. However, metal dispersions are unsatisfactory.

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Pt/SiO₂ catalysts prepared by the sol-gel method were found to be at least as active in H₂/n-hexane reforming reactions as catalysts prepared by traditional ion-exchange methods. In addition to this high catalytic activity, these catalysts were found to be resistant to catalyst deactivation due to coke formation. They were also found to be more resistant to sintering than catalysts prepared by ion-exchange and impregnation methods.

The Preparation of High Surface Area Pt/Al₂O₃ Catalysts

Major conclusions from this study are as follows:

- (1) Pt/Al₂O₃ catalysts prepared by the sol-gel method using aluminum tertiary butoxide (ATB) as a starting material, result in high surface area materials (4). Surface areas in excess of 800 m²/g can be obtained. However, heat treatment at 600 °C results in a reduction in the surface area to 400 m²/g due to the formation of the γ-alumina phase.
- (2) A stoichiometric molar ratio of H₂O/ATB of 3 was found to be optimum in the preparation of highly dispersed Pt/Al₂O₃ catalysts.
- (3) A mixed metal oxide sample prepared by prehydrolyzing and then mixing 5 wt % silica with alumina resulted in a larger and more stable surface area than pure alumina.
- (4) The use of H₂PtCl₆·xH₂O as a metal precursor was found to lead to highly dispersed Pt/Al₂O₃ catalysts. These catalysts were observed to be active for the H₂/n-hexane reaction.

The Stabilization and Sintering of Porous Pt/SiO₂

It was found that when the average metal particle size was matched to the average pore size, sintering in flowing O₂ at 675°C for 72 h had little effect on particle size (1). However, if the wt % loading was higher than 0.2-0.3 wt %, some sintering did occur. This resistance to sintering is in marked contrast to catalysts prepared by ion-exchange or impregnation for which rapid sintering was observed at temperatures in excess of 600°C. These observations are consistent with previous studies using Ru and suggest that the preparation of supported metal catalysts by the sol-gel method can be structured to prepare materials which have a high degree of thermal stability.

The Preparation of High Surface Area Zirconia Catalysts

High surface area zirconia catalysts were prepared by the sol-gel method using zirconium tetra isopropoxide (ZrT-iP) as the starting material. Although the results obtained are still preliminary, the following conclusions are emerging:

- (1) High $\text{H}_2\text{O}/\text{ZrT-iP}$ lead to surface areas in excess of $200\text{m}^2/\text{g}$. However, a considerable loss in surface area occurs following heating at temperatures in excess of 400°C . Calcination at 200°C results in materials with a surface area of $370\text{m}^2/\text{g}$. When the temperature was increased to 500°C the surface area was observed to decrease to $160\text{m}^2/\text{g}$.
- (2) The preparation of mixed zirconium-titanium oxides resulted in materials having not only a higher surface area than zirconium or titania, but also materials with a much higher thermal stability.
- (3) A maximum surface area was observed for the mixed Zr-Ti oxide for which the molar ratio of ZrT-iP/TiT-iP was unity. Calcination temperatures in excess of 500°C were required to markedly reduce the surface area.
- (4) The zirconia and the mixed Zirconia-Titania oxides were promoted using both H_2SO_4 and $(\text{NH}_3)_2\text{SO}_4$. Surface areas appear to be slightly lower when $(\text{NH}_3)_2\text{SO}_4$ is used. The superacid properties of these materials will be studied during the next funding period.

Outline for studies to be Completed During the Next Funding Period

Continuing Studies on the Preparation of $\text{Pt}/\text{Al}_2\text{O}_3$ Catalysts

Studies to date have been focussed on preparative variables aimed at maximizing BET surface areas and metal dispersions. These studies have been completed and the activity of the resulting materials compare favorably with $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts prepared by ion-exchanged and impregnation methods. However, attempts to compare the catalytic properties of $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts prepared by the sol-gel method to commercial reforming catalysts is sort of like comparing apples to oranges. To make valid comparisons we will need to chlorinate the $\text{Pt}/\text{Al}_2\text{O}_3$ sol-gel catalysts in order to modify the acid properties of the support. Sulfiding of the resultant catalysts is also a necessary step. We have recently initiated such studies in order to make valid comparisons. The addition of a second metal (i.e., Ir, Sn or Re) is also under study.

Attempts to ion-exchange or impregnate metals on large surface area aerogels or xerogels has not been very successful. In general rather poor metal dispersions were obtained using this approach. In order to understand why this is so an infrared study of the resulting aerogels and xerogels will be performed. What I suspect is happening is that the surface hydroxyl groups are undergoing esterification by solvent molecules and inhibiting the ion-exchange process. If this can be reversed, a second method of preparing high surface area supported metals with high dispersions may result.

Continuing Studies on the Preparation of Pt/SiO₂ Catalysts

Comments similar to those made for the preparation of Pt/Al₂O₃ catalysts by the sol-gel method also apply to SiO₂ catalysts. In other words high surface area aerogels and xerogels can be impregnated or ion-exchanged using either organic or inorganic metal precursors with difficulty. Hopefully, this matter can be resolved by performing an infrared study.

The sharp dependence of metal dispersion on precursor is puzzling. H₂PtCl₆·xH₂O and Pt(NH₃)₄Cl₂ have been disappointing. However, the use of Pt(NH₃)₄(NO₃)₂ resulted in high dispersions. Pt(AcAc)₂ is also acceptable and has an advantage over Pt(NH₃)₄(NO₃)₂ in that its solubility in acetone is higher. We suspect that the problem that we have encountered may be due to the presence of chloride. We plan to undertake a study of the adsorbed species using diffuse UV reflectance spectroscopy. Interference of the resultant UV spectra due to silica bands and solvent molecules has been troublesome in the past. However, new subtractive software which we have recently installed will alleviate the problem. Care must be taken in the interpretation of spectral results.

A significant new finding in our current studies is the observation that when the metal particle size is matched to the pore diameter, a high degree of thermal stability is achieved. Unfortunately this thermal stability can only be achieved for rather low loadings (< 0.4 wt %). We most certainly want to pursue this observation. High thermal stability of supported metals in such applications as automotive exhaust catalysts are badly needed. An extension of our Pt studies to include Rh, Ru and Pd is planned.

Continuing Studies on High Area Superacid Catalysts

We regard our current observations on the thermal stability of sulfate promoted Zr-Ti oxide catalysts to be very encouraging. Because superacidity is very difficult to measure with solid indicators, we are approaching the problem using an infrared study combined with a

catalytic study using the isomerization of n-butane as a probe reaction.

As shown in Figure 1, the adsorption of pyridine results in a change in the bond order of both the S-O and the S=O bond. For M=Zr or Ti, the shift in the position of the S=O bond following the adsorption of pyridine is 50 cm⁻¹. For M=Fe, the shift is 46cm⁻¹ and for M=Al it is 33 cm⁻¹. For M=Si or Bi, no shift is observed. Perhaps the S=O bond shift can be related to the superacid properties obtained by measuring n-butane isomerization rates.

Personnel

The current level is appropriate. Two graduate students will be supported. Additionally, two undergraduate students will perform honors research during the academic year and will be incorporated into the group during the Summer. Each undergraduate will receive a summer stipend of \$3,000. It is anticipated that this research experience will be of value to them.

Budget

It is anticipated that the funds originally set aside for this project will be satisfactory. A second gas chromatograph which is essential to our catalytic studies will be added with funds supplied by a DOE supplement.

Equipment

The current inventory in the Catalysis laboratory includes:

A Coulter Omnisorb Gas Sorption Analyzer.

A Coulter Delsa instrument to perform zeta potential measurements

A Digilab FT 40 FTIR

An on-line Balzer's quadrupole mass spectrometer

A Perkin Elmer UV visible spectrophotometer interfaced to a remote integrating sphere through fiber optics cables

A Perkin Elmer Differential Scanning Calorimeter

Three on-line reaction systems for performing catalytic studies

Two Hewlett Packard gas chromatographs

Access to a scanning transmission electron microscope and an ICP is available.

* Proposed Structure of sulfur-promoted metal oxides

* S = O stretching frequency shift by pyridine adsorption

Figure 1

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