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The Preparation and Catalytic Applications of Silica, Alumina, and Zirconia Supported Thermally Resistant Mono and Bimetallic Catalysts

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1. The Preparation of High Surface Area Pt/SiO_2 Catalysts.

Conclusions from this study are as follows (1): (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 m^2/g with microporous structures can be prepared at low pH (1). At intermediate values of the pH (3-8), BET surface areas ranging from 850 to 350 m^2/g can be obtained. Pore structures are mesoporous with pore diameters ranging from 4 to 25 nm at a preparative H_2O/TEOS ratio of 10. (2) Because of repulsive interactions, the use of H_2PtCl_6. xH_2O as the metal precursor results in poor dispersions (2). When $Pt(NH_3)_4(NO_3)_2$ 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 the formation of aerogels with high BET surface areas and large pore volumes. However, metal dispersions are unsatisfactory.

2. Stabilization and Sintering of Porous Pt/SiO_2 Catalysts

Matching the pore size to the metal particle diameter results in supported Pt/SiO_2 catalysts which have exceptional thermal stability (3). Conclusions from this study are as follows: (1) The average pore diameter of silica supported xerogel catalysts prepared by the sol-gel method can be varied from 3.5 nm to 7.5 nm by changing the H_2O/TEOS ratio during synthesis (Figure 1). (2) The pore diameter acts as a particle size template in that the metal particle increases as the pore diameter is decreased. This adjustment in particle size continues until a match between particle size and pore diameter is obtained (see Table 1). (3). Sintering in flowing O_2 at 675 °C had little effect on particle size over a period of 72 h. (4). Sintering at temperatures below 700 °C does not involve gas phase transport. Sintering in the 600-700 °C temperature range involves only surface diffusion.

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Table 1. Change in metal particle size and pore size distribution as a function of H_2O/TEOS ratios.

H_2O/TEOS	wt%(ICP)[(a)]	Average Pore Size (nm)	Average Particle Size (nm)	
			TEM	H-Chemisorption
10	0.5	7.5	1.7	1.6
20	0.6	7.0	2.0	1.5
40	0.6	5.0	2.8	2.7
60	0.65	3.5	3.3	2.5

(a) Measured using inductively coupled plasma (ICP).

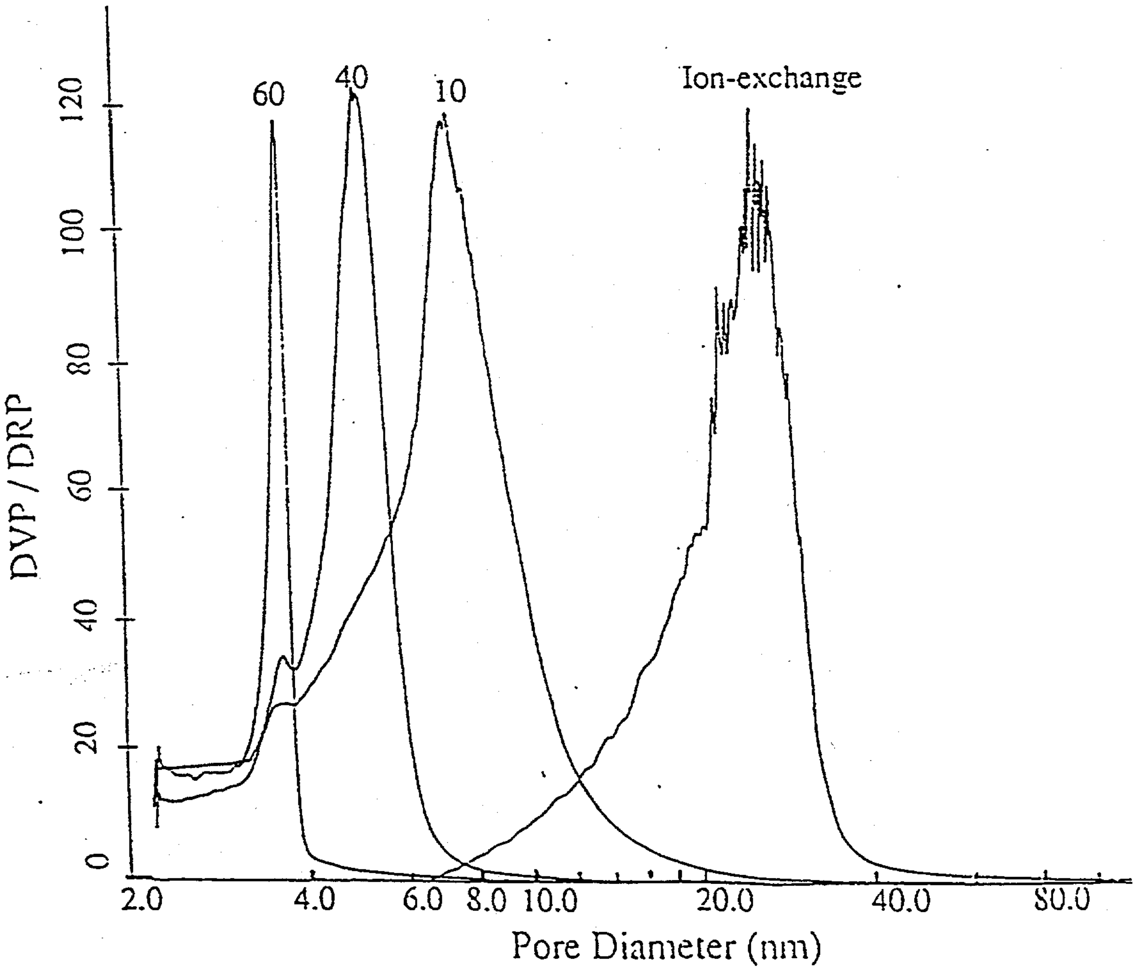

Figure 1.

3. Sintering of Porous Pd/SiO_2 Catalysts.

Supported Pd/SiO_2 xerogel catalysts prepared by the sol-gel method were thermally stable in an oxygen atmosphere at temperatures up to 700 °C for periods of up to 72 h. In these studies, catalysts having a high surface area (720 m^2/g) and a good match between pore size and metal crystallite diameter were prepared using $Pd(AcAc)_2$ and TEOS (3). Other conclusions from this study were: (1) Pd dispersions although stable in oxygen at 700 °C were unstable in hydrogen. (2) The sintering mechanism for Pd/SiO_2 catalysts in an oxidizing atmosphere at 650 °C occurs through the surface diffusion of PdO. (3) The reason behind the thermal instability of Pd in a H_2 atmosphere is unclear and requires further study. The formation of the Pd-β-hydride is a possibility. However, the formation of the hydride phase at high temperatures is not favored. It is more likely that Pd-Pd bonds are weakened due to the high solubility of H_2 in Pd. (4) The reforming reactions of n-hexane/H_2 over Pd/SiO_2 xerogel catalysts suggest that access of the reactants to the metal phase is not occluded by the pore structure of the support.

4. Preparation of Pt/Alumina Catalysts by the Sol-Gel Method.

Pt/Al_2O_3 xerogel catalysts were successfully prepared by the sol-gel method (4). Unlike silica supports, amorphous alumina undergoes a phase change to γ-alumina at about 500 °C. This phase change results in a loss in surface area in addition to the ability to control pore size distribution and microstructural features. Additional conclusions from this study are as follows: (1) Alumina-supported samples with BET surface areas in excess of 800 m^2/g can be prepared using the sol-gel method. During pretreatment, there is a reduction in the surface area to approximately 450 m^2/g due to a phase transformation to active γ-alumina. (2) Monometallic Pt/Al_2O_3 samples of reasonably high Pt dispersions (50-75%) can be prepared by this method. The samples are active for the reforming reactions of n-hexane. (3) The use of ATB (aluminum tri-sec butoxide) and a stoichiometric
H_2O/ATB molar ratio of 3 gave the best Pt/Al_2O_3 sample from a total surface area and Pt dispersion point of view. (4) Aerogel samples displayed a lower Pt metal dispersion when compared to xerogels of similar metal loading. (5) A mixed metal oxide sample prepared by prehydrolyzing and then mixing 5 wt.% silica with alumina resulted in a slightly higher and more stable surface area than pure alumina. The addition of a second oxide results in an increase in the resistance of the oxide to undergo a phase change. (6) Pt/Al_2O_3 catalysts prepared by the sol-gel method are more resistant to catalyst deactivation by coke formation. This deactivation can be related to the increase in the total surface area of the alumina. This increase in surface area has the effect of increasing the capacity of stored coke.

5. Preparation of Bimetallic Pt-Sn/Alumina Catalysts.

Because Pt-Sn/Alumina catalysts are important in naphtha reforming, it was decided to study whether the sol-gel synthesis of these bimetallic catalysts might lead to a noticeable improvement in the performance of these catalytic materials in reforming reactions (5). An important characteristic of these bimetallic catalysts is that they display better stability during reaction in comparison to monometallic Pt catalysts. The reason for this improved stability is believed to be due to a change in the catalytic selectivity that leads to a suppression of coke-forming reactions in comparison to reforming reactions.

Table 2. Catalytic Selectivity at a total of n-Hexane Conversion ~10%

catalyst	temperature (^{0} C)	conversion(%)	selectivity (%)		
			dehydrocyclization	isomerization	hydrogenolysis
1.0 Pt/Al_2O_3	300	12.2	6.3	46.2	47.5
1.0 Pt-0.3 Sn/Al_2O_3	333	11.4	7.6	62.7	29.7
1.0 Pt-0.9 Sn/Al_2O_3	355	9.1	2.4	95.2	2.4
1.0 Pt-1.5 Sn/Al_2O_3	390	12.6	2.0	96.3	1.7

It is interesting to compare results on sol-gel Pt/Al_2O_3 catalysts to a study performed on Pt-Sn catalysts prepared by traditional methods of coimpregnation (6). Catalytic selectivity at a constant conversion of approximately 10% for the reforming reactions of n-hexane conversion is shown in Table 2. Constant conversion was maintained by increasing the temperature.

As in the case of traditionally prepared samples, there was an increase in the isomerization selectivity and a decrease in the hydrogenolysis selectivity with increasing amounts of tin in the sample. However, there is one very important difference. In the case of traditionally prepared samples it was found that when the Pt loading was kept constant at 1 wt.% and the amount of Sn was increased gradually, then for small amounts of tin addition (up to a loading of 0.5 wt.%), the isomerization selectivity did not increase by a very large amount. When the metal loading was increased beyond 0.5 wt.% to 1.0 wt.%, there was a large increase in the isomerization selectivity, from 39.6% to 95.5%. In the case of the sol-gel samples, a gradual increase in the isomerization selectivity is observed (Table 2). A possible reason for this could be that in the case of the traditionally prepared samples at low loadings of Sn, the platinum and tin are, in all likelihood, segregated on the alumina surface. In the case of the bimetallic catalysts prepared from a homogeneous solution in a one step synthesis, Pt and Sn are more intimately mixed and form bimetallic particles at low Sn loadings.

6. Sol-gel Synthesis of Thermally Stable Sulfate Promoted Zirconia Catalysts.

Sulfate promoted zirconia catalysts have been prepared by the sol-gel method using zirconium iso-propoxide as the alkoxide precursor. Unpublished results to date lead to the following conclusions: (1) Sulfated zirconium catalysts prepared by the sol-gel method are at least as active as the MEI commercial catalysts. (2) Catalyst deactivation occurs at about the same rate on both sets of catalysts. (3) Catalyst deactivation is highest when there is no hydrogen added to the feed. (4) A feed consisting of n-butane in a gas mixture consisting of N_2-H_2 in a 3 to 1 ratio was optimum in reducing the deactivation rate in the isomerization reaction. (5) BET surface areas are a maximum (~175 m^2/g following activation at 600 °C in O_2) when H_2SO_4 impregnation was performed using 0.5 N H_2SO_4. High acid strengths result in a sharp decrease in BET surface area. (6) Mixed sulfate promoted zirconia-titania catalysts prepared by a one-step sol-gel method result in materials which are less active than zirconia.

Although progress is being made to obtain a more complete understanding of the deactivation process, we clearly have a long path ahead of us.

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