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# Preparation of Pt/Alumina Catalysts by the Sol–Gel Method

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A series of alumina-supported Pt catalysts were prepared by using the sol–gel method. The effect of the variables of preparation, the nature of solvent removal and pretreatment were investigated. The total surface area, pore size distributions, Pt dispersions, and catalytic reactivity were measured for the various samples. It was determined that a stoichiometric water/aluminum alkoxide molar ratio of 3.0 gave the sample with the highest surface area. These sol–gel samples were fairly active in the reactions of *n*-hexane and showed desirable selectivities. Xerogel samples were found to be superior in comparison to the corresponding aerogel samples as far as total surface area and metallic dispersions were concerned. Mixing of silica to the alumina (after a prehydrolysis step) to an extent of 5 wt%, in order to form a 1.0 Pt/(95% alumina–5% silica) mixed metal oxide sample, increased the sample total surface area and metallic dispersion by a small extent, in comparison to the 1.0 Pt/alumina sample.

## INTRODUCTION

Alumina-supported catalysts are widely used in the petroleum industry in reforming and hydrotreating processes (*1*). $Pt/Al_2O_3$ catalysts have been traditionally prepared by the impregnation method, in which a gamma alumina support is impregnated with an aqueous solution of $H_2PtCl_6$ acidified with HCl. In this study an attempt has been made to prepare Pt/alumina catalysts by a different procedure, namely, the sol–gel method. In this method porous gels having a very large surface area can be prepared. These gels are useful in preparing metallic catalysts or enzyme carriers, filters, adsorbants, or membranes (*2*). An application of the method to catalysis is that a solid can be prepared from a homogeneous solution which includes not only the metal precursor, but also the support precursor. The uniqueness of the method is that one starts with the molecular precursor of the support material and then goes all the way to the final catalyst. A greater degree of control over the catalyst preparation can be achieved in comparison to traditional methods of preparation (*3*). One can "tailor make" catalysts to fit particular applications using this method (*3*). Some of the advantages of using this method are: (a) superior homogeneity and purity, (b) better microstructural control of metallic particles, (c) higher BET surface area, (d) improved thermal stability of the supported metals, and (e) well-defined pore size distributions.

The high surface areas obtained by the sol–gel method are important from a catalysis point of view. A high support surface area is essential for reforming catalysts because it helps in the stabilization of metal dispersions and also helps in the retention of chloride by the support (*1*). The chloride in the support provides the acidity required to make the catalyst bifunctional in nature. Another significant advantage in the preparation of catalysts by the sol–gel method seems to be their superior mechanical resistance. This was illustrated by a recent study of $Ru/SiO_2$ catalysts prepared by the sol–gel method and their comparison to catalysts prepared by the ion-exchange method (*4*).

It is necessary to understand the chemistry (mechanisms of hydrolysis and condensation) and microstructure (aggregation and

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shrinkage) of sol–gel processing. There is considerable difference in the sol–gel chemistry of a support material such as alumina to that of silica (*5*). For this reason, it is important to study the effect of different preparation variables and types of solvent removal, on the nature of the sample produced. After preparation, the gel should be dried at temperatures in the range 100–180°C in order to remove physically adsorbed water (*6*). In sol–gel terminology, a xerogel is a product derived by solvent evaporation under normal conditions and involves the shrinkage of the gel network caused by capillary pressure. If the wet gel is placed in an autoclave and dried under hypercritical conditions, the product is called an aerogel. Aerogels have a low density and the gel network does not collapse during the removal of the pore liquid (*6*). The use of high surface area aerogels for catalyst supports has been described by Teichner and co-workers (*7, 8*).

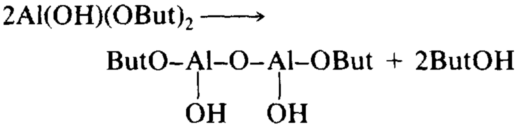
In the sol–gel process, the molecular precursors are metal alkoxides which have organic ligands attached to a central metal or metalloid atom. Examples include, aluminum tri-*sec*-butoxide (ATB), aluminum isopropoxide (AIP) and tetraethoxysilane (TEOS). The main reason for using these alkoxides is that they are very reactive. The addition of water readily leads to hydrolysis and condensation reactions (*3*). Another advantage is that molecular homogeneity of the reaction mixture can be easily achieved as alkoxides readily form homogeneous solutions in many solvents (*9*).

Starting with aluminum tri-*sec*-butoxide (ATB) the corresponding hydrolysis and polymerization reactions are as follows (*10*):

*Hydrolysis.*

$$\mathrm{Al(OBut)_3 + H_2O \longrightarrow Al(OH)(OBut)_2 + ButOH}$$

*Polymerization.*



$$\mathrm{2Al(OH)(OBut)_2 \longrightarrow ButO{-}\underset{\displaystyle OH}{\underset{|}{Al}}{-}O{-}\underset{\displaystyle OH}{\underset{|}{Al}}{-}OBut + 2ButOH}$$

Calcination at high temperatures is required to convert the pseudoboehmite structure obtained to gamma alumina (*11*). The high temperature (500°C) treatment also helps in stabilizing the gel due to the dehydroxylation of OH groups located within the pore structure (*6*). Silica, prepared by the sol–gel method was found to have a very high degree of thermal stability. Unlike silica prepared by sol–gel processing, the surface area of alumina is observed to decrease by about 50% following calcination (*12*).

The initial stages of this study were spent in the optimization of blank alumina with respect to BET surface area and pore size distribution. Following this optimization, monometallic Pt/alumina samples were prepared. These samples were shown to have large BET surface areas and also reasonably high metal dispersions. Mixed metal oxide samples were prepared by mixing the alumina with silica in order to observe whether the surface area of the support could be stabilized with respect to phase changes occurring in the alumina as the result of pretreatment at high temperatures. Test hydrocarbon conversion reactions using *n*-hexane as the probe hydrocarbon molecule were performed in order to study the reactivity of these catalysts. We hope to develop a new series of high surface area reforming catalysts using the sol–gel method. Recent work in our laboratory have shown that Pt/$SiO_2$ catalysts that are structurally stable and resistant to sintering in $O_2$ at temperatures up to 675°C could be prepared using the sol–gel method (*13*).

Catalysts prepared by the sol–gel method have been found to show good reactivity trends for several reactions. Ni/$SiO_2$ aerogel catalysts were used for the hydrogenation of toluene to methylcyclohexane (*14*). Willey *et al.* (*15*) studied the selective catalytic reduction of nitric oxide by ammonia over iron oxide–chromia–alumina aerogels. Armor *et al.* (*16*) found that $Pd/Al_2O_3$ aerogel catalysts were highly active hydrogenation catalysts for the complete and selective production of aniline from nitrobenzene. Foster and Keyes (*17*) compared the activities of several catalysts for the vapor-phase oxidation of acetaldehyde by air to acetic acid and found that the most suitable catalyst was a silica aerogel with 0.19% platinum oxide incorporated as a gel. This sample gave 85–90% yields of acetic acid. Other researchers have found that aerogel catalysts can be used for: the nitroxidation of toluene into benzonitrile (*18*); the synthesis of methanol from $CO_2/H_2$ mixtures (*19*); and the transformation of isobutane by NO into methacrylonitrile, acrylonitrile and acetonitrile (*20*). They are also good hydrogenation–dehydrogenation catalysts (*21*).

## EXPERIMENTAL

### (*a*) *Catalyst Preparation*

*Method A.* This method was initially used to prepare the blank alumina samples. Important variables that influence the hydrolysis–polymerization reactions in sol–gel processing for a given system are: the degree of hydrolysis and the pH (*2*). Blank alumina samples were prepared in order to study the effect of the pH of the hydrolyzing solution and the effect of the water/Al alkoxide molar ratio (water ratio), on the physical properties of the sample produced. On a stoichiometric basis, a molar ratio of 3 corresponds to complete conversion of the Al alkoxide to Al hydroxide. In our experiments some samples were prepared with substoichiometric as well as more than stoichiometric amounts of water. These samples were compared with a sample prepared with stoichiometric amounts of water in order to better determine the effect of the amount of water used for hydrolysis on the nature of sample produced. The blank alumina samples were prepared by diluting both the ATB and the water separately with ethanol and was based on the work of Yoldas (*22*). To 49.914 g of ATB 70.648 g of ethanol was added and mixed thoroughly. Then separately, 10.634 g of water was added to 70.209 g of ethanol. The solution was mixed and the pH was found to be 7.6 when $NH_4OH$ (0.6 ml) was added to the water + ethanol solution. Small amounts of acid or base were sometimes added during sol–gel processing. The acid or base acts as a catalyst and may also have an influence on the nature of polymeric particles that are formed (*23*). The pH of the hydrolyzing solution was found to be 10.3 following $NH_4OH$ addition. The ATB + ethanol mixture was placed in a flask in a rotavapor system. The hydrolyzing solution was added drop by drop to the ATB + ethanol mixture with continuous stirring over a period of 2 hr and 15 min. The sample was kept under these conditions for approximately 15 min and the pH was measured. The sample was heated to 50°C in the rotavapor system while keeping one of its ends open to the atmosphere. The sample was kept at 50°C for 30 min and then heated to 100°C where it was kept for an additional 30 min. The sample was then removed from the rotavapor system, placed in an oven, and dried at 120°C for 24 hr.

*Method B.* A more elaborate sol-gel method was used to prepare Pt/alumina samples with satisfactory Pt dispersions. This method was adapted from the work of Armor *et al.* (*16*). In a typical preparation of a Pt/alumina sample (in this case 2.0-wt% Pt/alumina), 49.814 g of ATB was added to 100 cm of *sec*-butanol followed by thorough mixing. The reason for this procedure was to prevent rapid hydrolysis as a result of the direct addition of water to the alkoxide. Uncontrolled hydrolysis may even result in phase separation (*23*). A second solution consisting of 0.527 g of $H_2PtCl_6 \cdot xH_2O$ dissolved in 10 $cm^3$ of warm acetone was prepared. This Pt salt solution was added to the ATB–alcohol mixture and the solution was stirred thoroughly. A solution consisting of 10.602 g of $H_2O$ dissolved in 100 $cm^3$ of methanol was added to the previous mixture containing ATB and the Pt salt. The resultant mixture was stirred at room temperature for 10 min in a rotavapor. The sample was heated to 45°C and maintained at that temperature with continual stirring for 10 min. The temperature was then reduced to 40°C and stirring continued for 1 hr more. At this point two separate solvent removal schemes were used.

In the case of the xerogel the solvent removal process was carried out in a rotavapor system. One end of the system was left open to the atmosphere and the sample was maintained at 60°C for 20 hr with continuous stirring. The temperature was then raised to 80°C and maintained at that temperature for 1 hr. Finally, the temperature was increased to 100°C and the solvent allowed to evaporate over a 30 min period. The sample was then dried in an oven at 120°C for 24 hr.

In the case of the aerogel, the sample was placed in the autoclave together with 250 cm$^3$ of excess methanol. The autoclave was flushed with $N_2$ at room temperature and then heated in order to reach the hypercritical conditions of the solvents. These conditions ($T$ = 295°C and $P$ = 1250 psig) were obtained 2 hr and 45 min following the start of heating. The sample was kept under hypercritical conditions for 30 min. The vapor was then bled off and the pressure was lowered. The heat was turned off and the autoclave was pumped for 30 min using a mechanical pump to further remove the solvent vapors. During this pumping period the temperature was above the critical temperature for the solvents. The autoclave was cooled to room temperature under flowing $N_2$ before the sample was removed. The sample was then dried at 120°C for 24 hr.

The dried samples were pretreated in a flow system using the following sequence of steps. The sample was heated in flowing He at the rate of 10°C/min to a final temperature of 500°C. Heating in He at a flowrate of 30 cm$^3$/min was continued for 15 min at 500°C followed by heat treatment in $O_2$ at the same temperature for 2 hr. The $O_2$ was replaced by He flow for 15 min followed by reduction in $H_2$ at 500°C for 3 hr at a flow rate of 30 cm$^3$/min. The $H_2$ was again replaced by He and the temperature increased to 520°C for 1 hr. Finally, the sample was cooled to room temperature in flowing He. The pretreatment was necessary in order to convert the dry alumina gel to active alumina, and also to reduce the Pt. Portions of the pretreated samples were sent for ICP analysis in order to determine the actual Pt loading. In this paper catalyst loadings reported as wt% refer to designed metal loadings. Actual metal loadings as determined by ICP are given in Table 1.

### (*b*) *Total Surface Area and Pore Size Measurements*

Total surface area and pore size measurements were performed using a Coulter Omnisorb 100 instrument. A small amount of sample (0.1–0.15 g) was weighed out and placed in the sample holder. It was then inserted into the pretreatment port of the machine. The sample was heat treated under vacuum at 200°C until the pressure in the sample holder was $\sim 10^{-5}$ Torr (1 Torr = 133.3 Pa). The sample was isolated by means of a stopcock and exposure to air was avoided. The sample holder was then placed in the measurement port of the machine. Total surface areas were obtained by physical adsorption of nitrogen at its saturation pressure. Pore size distributions were obtained from the desorption branch of the isotherm. Pore widths are defined by IUPAC to categorize the nature of pores in the following way: micropores, <2 nm diameter, mesopores, 2–50 nm diameter, and macropores, >50 nm diameter. The BET plot and equation, when applicable, was used to calculate the total surface area of the samples. The Langmuir isotherm was used in the case of highly microporous samples.

### (*c*) *Hydrogen Chemisorption Studies*

Pulsed hydrogen chemisorption was used to determine the Pt metal dispersion. Approximately 0.2 g of pretreated sample was placed in a glass microreactor. The sample

TABLE 1

Catalyst Composition

| Alumina precursor | Platinum precursor | Alumina content (wt%) | Silica content (wt%) | Water/alkoxide molar ratio | Gel type | Pt loading (designed wt%) | Pt loading (actual wt%, ICP) |
|---|---|---|---|---|---|---|---|
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 1.5 | Xerogel | 1.0 | 0.59 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 3.0 | Xerogel | 1.0 | 0.54 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 9.0 | Xerogel | 1.0 | 0.65 |
| ATB | $Pt(C_5H_7O_2)_2$ | 100 | — | 3.0 | Xerogel | 1.0 | 0.63 |
| AIP | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 3.0 | Xerogel | 1.0 | 0.52 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 3.0 | Xerogel | 2.0 | 1.14 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 3.0 | Aerogel | 1.0 | 0.60 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 100 | — | 3.0 | Aerogel | 2.0 | 1.38 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 95 | 5 (with prehydrolysis) | 3.0 | Xerogel | 1.0 | 0.50 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 95 | 5 (no prehydrolysis) | 3.0 | Xerogel | 1.0 | 0.52 |
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 90 | 10 (no prehydrolysis) | 3.0 | Xerogel | 1.0 | 0.52 |

was heated to 500°C in Ar. The sample was then reduced in flowing $H_2$ at 500°C for 2 hr. Adsorbed $H_2$ was removed by flushing with Ar at 520°C for 1 hr. The sample was cooled to room temperature and the chemisorption was performed by pulsing hydrogen into the Ar carrier gas. The hydrogen was detected using a thermal conductivity detector of an HP 5890 gas chromatograph after passing through a separation column (60/80 Carboxen 1000 from Supelco, Inc.).

### (*d*) *n-Hexane Reaction Studies*

Reactions of *n*-hexane and hydrogen were performed in a continuous flow reactor. About 0.2 g of a previously pretreated sample was weighed and placed in a glass microreactor. The sample was reduced at 500°C for 2 hr in flowing hydrogen prior to cooling to the reaction temperature in order to commence the reaction of *n*-hexane. The hydrogen gas used was UHP grade obtained from Lincoln Big Three, Inc. The liquid hexane (Fluka Chemicals) was placed in a saturator through which the hydrogen gas was bubbled during reaction. The temperature of the *n*-hexane saturator was maintained at 273 K with the help of an ice bath. The total gas flow rate ($H_2$ + *n*-hexane) was 18.5 SCCM. The *n*-hexane flow rate was 1.1 SCCM. The hydrogen to *n*-hexane molar ratio was 15.5.

The reaction products and the unreacted *n*-hexane were separated in an HP 5890 gas chromatograph using a $\frac{1}{8}''$ o.d., 3-m-long GC column obtained from Alltech Associates. A flame ionization detector was used to detect the hydrocarbon products. An HP 3393A integrator provided the integrated area counts corresponding to the various components. Response factors for various hydrocarbons were obtained by using Scotty Analyzed gas mixtures. Deactivation studies were performed at a reaction temperature of 400°C by allowing the reaction to run and collecting data points following various times on stream. Reaction runs were also performed at lower temperatures so that the conversion could be kept reasonably low (<20%). The catalytic selectivity towards dehydrocyclization, isomerization and hydrogenolysis products was obtained.

## RESULTS

### (*a*) *Surface Area Measurements*

Surface areas were determined using: (1) the physical adsorption of $N_2$ at its saturation temperature to give the total surface area, pore volume, and pore size distribution of the sample and (2) by room temperature chemisorption of $H_2$ to obtain the Pt metal surface area and dispersion. Either the BET or the Langmuir equation were used for surface area calculations depending

TABLE 2

Effect of the Hydrolysis Solution pH for Unpretreated Blank Alumina Samples Prepared with Water/ATB Ratio = 3.0

| pH | BET surface area ($m^2/g$) | Avg. pore diameter (nm) |
|---|---|---|
| 0.8 (added 0.6 ml HCl) | 932 | 4 |
| 5.0 (no acid or base added) | 878 | 4 |
| 10.3 (added 0.6 ml $NH_4OH$) | 924 | 4 |

on which was appropriate for the given data. Nitrogen desorption isotherms were used to calculate mesopore size distribution by applying a method based on the BJH (Barrett, Joyner, and Hallender) method (*24*). The micropore volume was obtained by the *T*-plot analysis method.

*Blank alumina samples*. Three blank alumina samples were prepared in order to study the effect of pH (Table 2). The water + ethanol mixture used for hydrolysis had a pH of 5.0 and the resulting BET surface area was 878 $m^2/g$. On adding 0.6 ml HCl the pH of the hydrolyzing solution decreased to 0.8, while the addition of 0.6 ml $NH_4OH$ resulted in an increase in the pH to 10.3. The BET surface area was not a strong function of acid or base addition. The average mesopore size remained constant at about 4 nm. These results show that the pH of the hydrolyzing solution does not affect the properties of the alumina formed to any significant extent.

Table 3 shows the effect of water/ATB molar ratio on the unpretreated blank alumina xerogel samples at pH ~10. A comparison of the $N_2$ adsorption isotherm plots obtained in going from a substoichiometric amount of water (water/ATB molar ratio = 1.5) to a stoichiometric amount (water/ATB molar ratio = 3.0) is shown in Fig. 1. The dried samples were pretreated using the procedure given earlier. During pretreatment the dried alumina gel is converted to active alumina. Figure 2 shows the effect of pretreatment on a typical blank alumina xerogel sample.

The effect of the water/ATB molar ratio on the nature of the alumina sample produced is interesting (Fig. 1 and Table 3). When a water/ATB molar ratio of 1.5 is used an isotherm similar to the so-called Type I isotherm is obtained which is indicative of the small size of the pores in the sample. The Langmuir plot and calculations can be applied to a Type I isotherm (*24*). For this sample (water/ATB ratio = 1.5) the micropore volume was large (0.3197 ml/g) while

TABLE 3

Effect of Water/ATB Molar Ratio for Unpretreated Blank Alumina Samples Prepared with Hydrolysis Solution pH ~10

| Water/ATB ratio | Total surface area ($m^2/g$) | Avg. pore diameter (nm) |
|---|---|---|
| 1.5 | 1137 (Langmuir) | 3 |
| 3.0 | 924 (BET) | 4 |
| 4.5 | 772 (BET) | 5 |
| 6.0 | 625 (BET) | 7 |
| 15.0 | 352 (BET) | 7 |

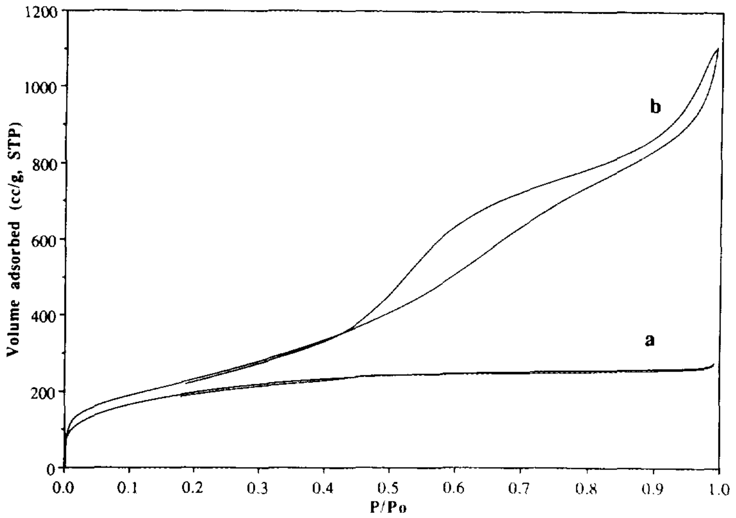


Fig. 1. $N_2$ adsorption isotherms for unpretreated blank alumina xerogel samples prepared using the following water/ATB molar ratios: (a) 1.5, and (b) 3.0.

the mesopore volume was small (0.2088 ml/g). The Langmuir surface area was found to be 1137 $m^2/g$. Because the total surface area of the meso- and macropores was only 105 $m^2/g$ a significant fraction of the surface area was in the micropores. When a water/ATB molar ratio of 3.0 or higher is used one obtains isotherms for which the BET equation can be used to obtain the total surface areas. These are the so-called Type IV isotherms for which the BET surface area plot and calculations must be carried out over a linear region in the sample data between usually 0.05 and 0.25 $P/P_0$ (*24*).

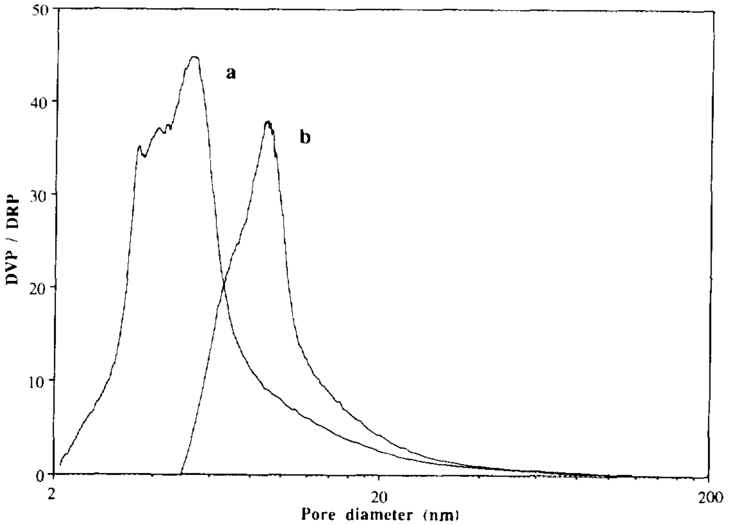


Fig. 2. Effect of pretreatment on a blank alumina xerogel sample. (a) before pretreatment and (b) after pretreatment.

The BET surface area for the sample prepared with a stoichiometric water/ATB molar ratio of 3.0 was found to be 924 $m^2/g$. The total mesopore volume was 1.7243 ml/g. Almost all of the area was present in the mesopores and macropores and the micropore volume was not significant. This was quite different from the sample prepared with a substoichiometric amount of water (water/ATB molar ratio = 1.5). As the water/ATB molar ratio was increased above the stoichiometric amount it was found that the BET surface area dropped and larger average mesopore sizes were obtained. For the sample prepared with excess water (water/ATB molar ratio = 15.0) the BET surface area was 352 $m^2/g$. The total mesopore volume was found to be 0.7895 ml/g. Some micropores were present (micropore volume = 0.01994 ml/g). However, a large fraction of the surface area was located in the meso and macropores (total area of meso + macropores = 297 $m^2/g$). A similar result of decreasing BET surface areas with increasing water/ATB molar ratio above a value of 3.0 was obtained by Teichner *et al.* (*25*).

*Pt/alumina samples.* The effect of pretreatment on the alumina xerogel BET surface area and average pore size is shown in Fig. 2. The BET surface area was observed to decrease from 982 $m^2/g$ prior to pretreatment to 469 $m^2/g$ after pretreatment. The average pore diameter was observed to increase from 5 to 9 nm following pretreatment. A comparison of the effects of pretreatment on a xerogel and an aerogel are interesting. In the case of the 1.0 wt% Pt/Alumina xerogel the BET surface area decreased from 876 $m^2/g$ before pretreatment to 490 $m^2/g$ after pretreatment. The average mesopore size of this sample increased from 6 to 9 nm as a result of the pretreatment. On the other hand, in the case of the 2.0 wt% Pt/alumina aerogel sample, pretreatment seems to have very little effect on the nature of the sample. The BET surface area decreased by very little (319 to 309 $m^2/g$), while the average mesopore size remained the same (~19 nm). This is because the sample has already been treated to high enough temperatures in the autoclave (hypercritical conditions) leading to the formation of active alumina and the decrease in surface area occurs prior to pretreatment step.

The effect of the addition of Pt on the properties of pretreated xerogel samples are

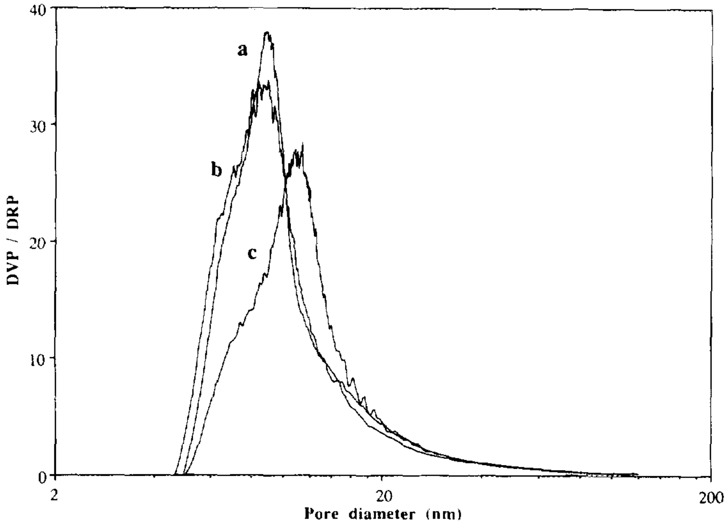


Fig. 3. Effect of platinum metal addition (pretreated xerogel samples). (a) blank alumina, (b) 1.0-wt% Pt/alumina, and (c) 2.0-wt% Pt/alumina.

TABLE 4

The Effect of the Addition of Platinum on the Surface Properties of Pretreated Xerogel Samples

| Sample | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Av. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|
| Blank $Al_2O_3$ | 469 | 2.1781 | 9 | — |
| 1-wt% $Pt/Al_2O_3$ | 490 | 2.1302 | 9 | 74 |
| 2-wt% $Pt/Al_2O_3$ | 398 | 2.0531 | 11 | 82 |

shown in Fig. 3 and Table 4. The 1.0-wt% Pt/alumina sample had a BET surface area of 490 $m^2/g$ and a total mesopore volume of 2.1302 ml/g. The total surface area and pore size distribution for the 1.0-wt% Pt/alumina sample were not significantly different than the corresponding values obtained for the blank alumina sample. The 2.0 wt% Pt/alumina xerogel sample had a BET surface area of 398 $m^2/g$ and a total mesopore volume of 2.0531 ml/g. The main difference between the 1-wt% Pt/alumina and the 2-wt% Pt/alumina samples is a decrease in the BET surface area. However, Pt dispersions were not significantly different. In fact, the dispersion increased from 74% in the case of the 1-wt% Pt sample to 82% for the 2-wt% sample. A higher designed metal loading than 1 wt% may not be desirable from a BET surface area point of view but there was no undesirable effect on the Pt dispersion.

The effect of the water/ATB molar ratio on pretreated 1-wt% Pt/Alumina xerogel samples is quite significant (Table 5 and Fig. 4). It is evident that the best Pt/Alumina sample, from both the total surface area and Pt dispersion viewpoints, was obtained by using a stoichiometric water/ATB molar ratio of 3.0. When a substoichiometric amount of water was used (water/ATB molar ratio = 1.5) the BET surface area dropped from 364 $m^2/g$ to 222 $m^2/g$ while the dispersion decreased from 74 to 53%. When excess amounts of water were used (water/ATB molar ratio = 9.0) the BET surface area dropped from 490 to 363 $m^2/g$ while the dispersion decreased from 74 to 61%.

The effect of the type of alumina and platinum precursor used in the catalyst preparation on the nature of Pt/Alumina xerogel samples formed are reported in Table 6 and Fig. 5. The first two samples were prepared using identical Pt precursors, namely chloroplatinic acid hydrate. However, the alumina precursors were different. The sample prepared with aluminum tri-*sec*-butoxide (ATB) results in a higher Pt dispersion (74%) compared to the sample prepared with aluminum-isopropoxide (AIP). The BET sur-

TABLE 5

Effect of the Water/ATB Molar Ratio on the Surface Properties of Pretreated 1.0-wt% $Pt/Al_2O_3$ Xerogel Samples

| Water/ATB ratio | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Avg. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|
| 1.5 | 222 | 0.7079 | 5 | 53 |
| 3.0 | 490 | 2.1302 | 9 | 74 |
| 9.0 | 363 | 2.6191 | 15 | 61 |

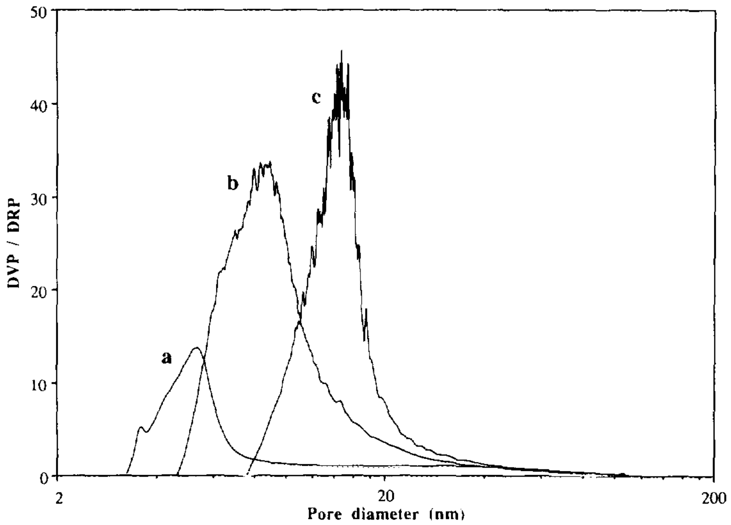


Fig. 4. Effect of water/ATB molar ratio on pretreated 1.0-wt% Pt/alumina xerogel samples. (a) water ratio = 1.5, (b) water ratio = 3.0, and (c) water ratio = 9.0.

face areas of both samples, on the other hand, were quite similar (450–500 $m^2/g$). This is probably because as the ATB is initially in the form of a viscous liquid and it is likely that a more homogeneous mixture could be obtained with the Pt salt compared to the sample prepared with AIP which is initially in the form of a solid powder. On using the same alumina precursor, namely ATB, and changing the Pt precursor from the inorganic $H_2PtCl_6 \cdot xH_2O$ to the organic $Pt(C_5H_7O_2)_2$ resulted in a sample having BET surface area that was not very different (450–500 $m^2/g$). However, the Pt metal dispersion is much lower for the sample prepared using the organic precursor. The interactions between the $(PtCl6)^{2-}$ ion and the alumina surface could account for the better dispersion observed in the case of the sample prepared with the inorganic chloride precursor. It was decided to use ATB as the primary alumina precursor and $H_2PtCl_6 \cdot xH_2O$ as the main Pt precursor for this work. Comparisons between xerogel and aerogel samples are shown in Table 7 and Fig. 6.

*Alumina-silica mixed metal oxide samples.* Mixed metal oxide samples were prepared in order to observe whether or not dilution of the alumina with a second metal oxide such as silica leads to a stabilization of the support with respect to surface area reduction during sample pretreatment. Mixed metal oxides in the form of cordierite ceramics ($2MgO–2Al_2O_3–5SiO_2$) are used as

TABLE 6

Effect of Precursor on the Surface Properties of Pretreated 1.0-wt% $Pt/Al_2O_3$ Xerogel Samples

| Alumina precursor | Platinum precursor | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Avg. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|---|
| ATB | $H_2PtCl_6 \cdot xH_2O$ | 490 | 2.1302 | 9 | 74 |
| ATB | $Pt(C_5H_7O_2)_2$ | 447 | 1.9774 | 9 | 33 |
| AIP | $H_2PtCl_6 \cdot xH_2O$ | 453 | 2.5983 | 9 | 61 |

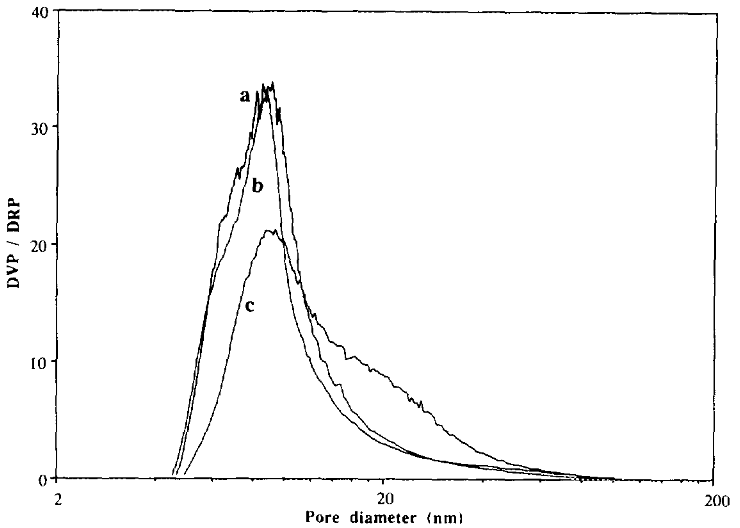


Fig. 5. Effect of alumina and platinum precursor on pretreated 1.0-wt% Pt/alumina xerogel samples. (a) aluminum tri-*sec*-butoxide and chloroplatinic acid hydrate, (b) aluminum isopropoxide and chloroplatinic acid hydrate, and (c) aluminum tri-*sec*-butoxide and *bis*-(acetylacetonato) platinum (II).

monolithic supports in automobile catalytic converters. They are also used as heat exchangers for gas turbine engines, industrial furnaces, or as an alternative to alumina in integrated circuit substrates due to their excellent thermal properties (*26*). Monolithic cordierite aerogels which are hydrophilic, have a high microporosity and a specific surface area of 400 $m^2/g$ have been prepared before.

In the case of mixed metal oxide samples it is important to check the effects of prehydrolysis on the nature of the sample produced. This is because different metallic alkoxides display different chemical reactivity towards nucleophilic reactions depending primarily on two parameters, namely, the electrophilic character of the alkoxide and their degree of unsaturation (*3*). It was found that the silicon alkoxide was much less reactive in comparison to the corresponding transition metal, rare earth and aluminum alkoxides (*3*).

In order to determine whether or not prehydrolysis affects the total surface area and the metallic dispersion, the 1.0-wt% Pt/(95-wt% alumina–5-wt% silica) sample was prepared both with and without the prehydrolysis step. The sample without prehydrolysis was prepared in a manner similar to that

TABLE 7

Comparison of Xerogel with Aerogel (Pretreated Samples)

| Sample | Gel type | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Avg. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|---|
| 2-wt% Pt/$Al_2O_3$ | Xerogel | 398 | 2.0531 | 11 | 82 |
| 2-wt% Pt/$Al_2O_3$ | Aerogel | 309 | 2.5534 | 19 | 37 |
| 1-wt% Pt/$Al_2O_3$ | Xerogel | 490 | 2.1302 | 9 | 74 |
| 1-wt% Pt/$Al_2O_3$ | Aerogel | 306 | 2.4640 | 19 | 40 |

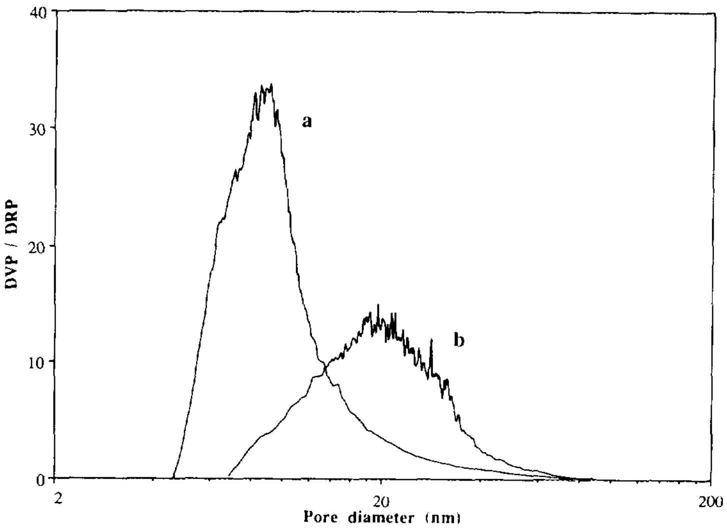


Fig. 6. Comparison of xerogel with aerogel (pretreated 1.0 wt% Pt/alumina samples). (a) xerogel sample and (b) aerogel sample.

used for the 1.0 Pt/alumina sample. The only difference was that the required amount of the silica precursor, namely $Si(OCH_3)_4$ or TMOS, was dissolved in methanol and mixed with ATB dissolved in *sec*-butanol. The sample with prehydrolysis was prepared by prehydrolyzing the TMOS dissolved in methanol by mixing it with the water + methanol solution. The rest of the sample preparation was similar to that used in the case of the 1.0 Pt/alumina sample. A blank 95-wt% alumina–5-wt% Silica xerogel sample was also prepared. This sample was found to have a higher BET surface area after pretreatment (576 $m^2/g$) compared to the blank alumina xerogel sample consisting only of alumina (469 $m^2/g$). The effect of prehydrolysis is shown in Table 8. It appears as though prehydrolysis does not have a significant influence on the total surface area of sample produced. The BET surface area and pore size distribution are similar for both samples. However, the sample which had been prehydrolyzed shows a higher Pt metal dispersion. For this reason the silica precursor prehydrolysis step results in mixed metal oxide samples with more desirable properties and may be a recommended step in the preparation of alumina–silica mixed metal oxide samples. The comparison of mixed metal oxide samples containing a designed Pt metal loading of 1 wt% are given in Table 9 and Fig. 7. The three samples were 1.0 Pt/alumina, 1.0 Pt/(95-wt% alumina–5-wt% silica), and 1.0 Pt/(90-wt% alumina–10-wt% silica), respectively.

TABLE 8

Effect of Prehydrolysis for Pretreated 1-wt% Pt/(95% alumina–5% silica) Mixed Metal Oxide Samples

| Prehydrolysis | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Avg. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|
| No | 529 | 1.641 | 8 | 61 |
| Yes | 538 | 1.9579 | 7 | 89 |

TABLE 9

Comparison of Pretreated 1.0-wt% Pt Mixed Metal Oxide Xerogel Samples

| % alumina | % silica | BET area ($m^2/g$) | Pore volume ($cm^3/g$) | Avg. pore diameter (nm) | Dispersion (%) |
|---|---|---|---|---|---|
| 100 | — | 490 | 2.1302 | 9 | 74 |
| 95 | 5 | 529 | 1.6410 | 8 | 61 |
| 90 | 10 | 512 | 1.4541 | 4 | 58 |

Both the mixed metal oxide samples were prepared without the prehydrolysis step in order to obtain consistent data. It was found that dilution of alumina with small amounts of silica does stabilize the support to a certain extent and decreases the pretreatment induced loss in total surface area though not by a very significant amount. The sample containing 5 wt% silica has a higher BET surface area (529 $m^2/g$) than the sample containing no silica (490 $m^2/g$). On increasing the silica content further (10 wt%) the BET area was found to be 512 $m^2/g$.

*(b) Catalytic Reactivity*

All Pt containing samples seem to be fairly active for the *n*-hexane conversion reactions. Initially a series of data points were collected at low conversions of *n*-hexane in order to maintain differential reactor conditions. This was through small increases in the reaction temperature. The reaction data analysis was performed using the method recommended by Ponec and Sachtler (*27*). The reaction products were categorized as dehydrocyclization products (methylcyclopentane, benzene and cyclohexane), as isomerization products (2-methylpentane and 3-methylpentane) or as hydrogenolysis products (methane, ethane, propane, isobutane, butane, 2-methylbutane, and *n*-pentane). The catalysts that were used for the reaction studies were: 1.0-wt% Pt/alumina xerogel (water/ATB molar ratio = 1.5), 1.0-

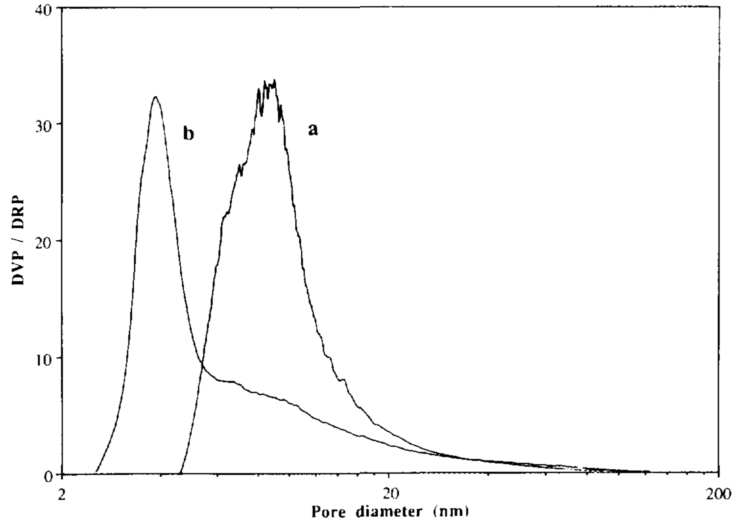


Fig. 7. Effect of mixing the alumina support with silica for pretreated 1.0-wt% Pt xerogel samples supported on the following supports: (a) 100% alumina and (b) 90% alumina–10% silica.

TABLE 10

Catalytic Selectivity for the Reactions of *n*-Hexane at 325°C after 0.5 hr on Stream

| Catalyst | Dispersion (%) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|---|
| | | | Dehydro-cyclization | Isomerization | Hydrogenolysis |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 53 | 8.4 | 9.7 | 54.2 | 36.1 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 74 | 10.8 | 9.9 | 56.0 | 34.1 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 61 | 14.7 | 10.4 | 51.6 | 38.0 |
| 1.0 Pt/$Al_2O_3$ (aerogel) | 40 | 11.4 | 10.4 | 61.9 | 27.7 |
| 1.0 Pt/(90% $Al_2O_3$–10% $SiO_2$) (xerogel) | 58 | 6.7 | 10.4 | 60.6 | 29.0 |

wt% Pt/alumina xerogel (water/ATB molar ratio = 3.0), 1.0-wt% Pt/alumina xerogel (water/ATB molar ratio = 9.0), 1.0-wt% Pt/alumina aerogel, and a 1.0-wt% Pt/(90% alumina–10% silica) xerogel. All the catalysts were prepared using $H_2PtCl_6 \cdot xH_2O$ as the platinum precursor. Reactions were also studied over a blank alumina xerogel sample and its reactivity was found to be insignificant in comparison to the Pt containing catalysts. Table 10 gives selectivity values over the various catalysts at a reaction temperature of 325°C. The selectivities are compared at a total conversion of *n*-hexane not greater than 15% in order to prevent the complications arising from secondary reactions that occur at higher conversions. In addition to the low conversion runs, reactions were also performed at 400°C also in order to compare the catalytic activity and selectivity at higher conversions (Table 11 and Fig. 8). Figure 8 is a plot of the total conversion of *n*-hexane as a function of time on stream at 400°C. Turnover frequencies determined from hydrogen chemisorption results are listed in Table 12. In order to distinguish between the activity trends for the various catalysts, deactivation rate constants ($k_d$) were calculated assuming first-order reaction and first-order deactivation which was concentration independent (*28*). These values, which are listed in Table 13, are approximations of the actual deactivation rate constants.

## DISCUSSION

The differences between pretreated xerogel and aerogel Pt/alumina samples are of

TABLE 11

Catalytic Selectivity for the Reactions of *n*-Hexane at 400°C after 0.5 hr on Stream

| Catalyst | Dispersion (%) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|---|
| | | | Dehydro-cyclization | Isomerization | Hydrogenolysis |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 53 | 30.3 | 35.1 | 46.7 | 18.2 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 74 | 37.9 | 34.8 | 45.3 | 19.9 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 61 | 46.9 | 32.2 | 43.4 | 24.4 |
| 1.0 Pt/$Al_2O_3$ (aerogel) | 40 | 41.0 | 31.4 | 45.8 | 22.8 |
| 1.0 Pt/(90% $Al_2O_3$–10% $SiO_2$) (xerogel) | 58 | 22.9 | 31.4 | 49.7 | 18.9 |

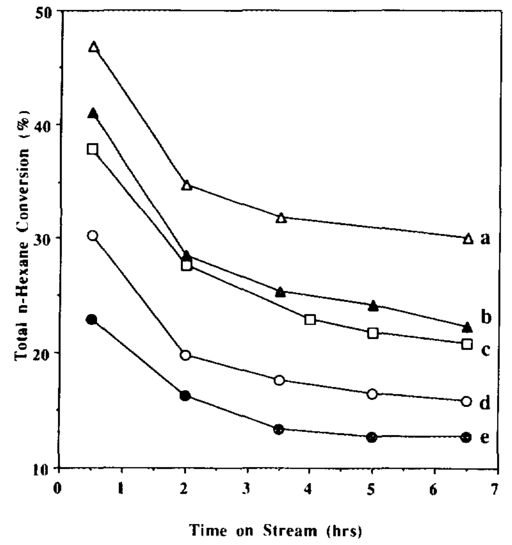


FIG. 8. Change in total *n*-hexane conversion as a function of time on stream for the various sol–gel catalysts at 400°C. (a) 1.0 Pt/Alumina, xerogel, average pore diameter = 15 nm, (b) 1.0 Pt/alumina, aerogel, average pore diameter = 19 nm, (c) 1.0 Pt/alumina, xerogel, average pore diameter = 9 nm, (d) 1.0 Pt/alumina, xerogel, average pore diameter = 5 nm, and (e) 1.0 Pt/(90% alumina–10% silica), xerogel, average pore diameter = 4 nm.

interest (Table 7 and Fig. 6). For both designed Pt metal loadings, namely 1 wt% and 2 wt%, the results show similar trends. The BET surface areas are lower for the aerogel samples in comparison to the xerogel samples. The average mesopore diameter and total mesopore volume are larger for the aerogel than the xerogel samples. It is clear that by changing the way that the solvents are removed from the gel one can change the pore structure of the catalyst sample. In the case of the aerogel samples, solvent removal under hypercritical conditions lead to an increase in the average pore diameter.

Another result is that irrespective of the designed metal loading, the Pt metal dispersion in the case of the aerogel samples is around 40–50% of the values obtained for the corresponding xerogel samples. One reason for this could be that as excess alcohol is added to the aerogel sample when it is placed in the autoclave, esterification reactions may occur during the autoclaving process which may then lead to rehydrolysis. Rehydrolysis could lead to the occlusion of the Pt particles due to the formation of a layer of alumina on top of the Pt. This, in turn, may lead to a final product which has a lower Pt metal dispersion as compared to the xerogel sample prepared without adding excess alcohol during the drying step. This reason was rejected because in a parallel study on silica-supported Pt catalysts (*29*) it was found that in the case of aerogel samples, there was agreement between chemisorption and transmission electron microscopy data. This meant that Pt occlusion was not taking place and hence the lower Pt dispersion in the case of the aerogel samples is not likely due to rehydrolysis. There is another more likely explanation for the observed decrease in Pt dispersion in the case of aerogels as compared to xerogels (*29*). In

TABLE 12

Turnover Frequencies for the Reactions of *n*-Hexane at 325°C after 0.5 hr on Stream

| Catalyst | Dispersion (%) | Conversion (%) | Average pore diameter (nm) | TOF × $10^3$ ($sec^{-1}$) |
|---|---|---|---|---|
| 1.0 Pt/(90% $Al_2O_3$–10% $SiO_2$) (xerogel) | 58 | 6.7 | 4 | 23.1 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 53 | 8.4 | 5 | 26.5 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 74 | 10.8 | 9 | 28.6 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 61 | 14.7 | 15 | 36.6 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 40 | 11.4 | 19 | 44.4 |

TABLE 13

First-Order Deactivation Rate Constants for the Reactions of *n*-Hexane at 400°C

| Catalyst | Conversion (%) | BET surface area ($m^2/g$) | $k_d$ ($hr^{-1}$) |
|---|---|---|---|
| 1.0 Pt/(90% $Al_2O_3$–10% $SiO_2$) (xerogel) | 22.9 | 512 | 0.255 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 37.9 | 490 | 0.256 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 46.9 | 363 | 0.264 |
| 1.0 Pt/$Al_2O_3$ (aerogel) | 41.0 | 306 | 0.301 |
| 1.0 Pt/$Al_2O_3$ (xerogel) | 30.3 | 222 | 0.329 |

the case of aerogels, the substitution of the OH groups in the samples by OR groups due to reactions with excess alcohol in the autoclaving step, could lead to a decrease in the interactions between the metal precursor and the support. This could in turn lead to growth of Pt crystallites (*29*). The Pt crystallite size was calculated using a method suggested previously (*30*). In the case of the l-wt% Pt/alumina xerogel sample it was found to be 1.5 nm. For the corresponding aerogel sample with the same designed Pt metal loading it was 3.5 nm.

The pretreatment induced decrease in total surface area could be reduced only slightly through the addition of small amounts of silica. The addition of silica in excess of this amount does not appear to have further beneficial effects with respect to the total surface area. Secondly, by adding large amounts of silica it is very likely that the chemical nature of the sample could be changed significantly. This is not desirable because the primary reason for the addition of the second metal oxide is to stabilize the BET surface area and not to change the chemical properties of the support. With respect to the metal dispersion it was found that all three samples had Pt dispersions in the 55–75% range. It was found that a 5% silica mixed metal oxide prepared by reacting boehmite alumina with TEOS was much more stable with respect to surface area loss following calcination at 1223 K compared to the boehmite alumina sample (*31*). Johnson (*1*) found that the addition of elements such as Ba, Sr, La, Sn, $SiO_2$, or $PO_4$, lead to a marked increase in the stability of the surface area during steaming.

Another point to note is that with the addition of silica the mesopore size distribution tends to shift towards smaller pore values (Fig. 7 and Table 9). The average mesopore size for the 1.0 Pt/Alumina sample was 9 nm. In the case of the mixed metal oxide sample (1.0 Pt/90% alumina–10% silica) the average mesopore size was observed to shift to 4 nm. It is clear that incorporation of silica into the alumina matrix can have a noticeable effect on the nature of pores present in the support which could, in turn, effect the nature of Pt particles formed during the sample pretreatment step.

The main advantage of the sol–gel method is that it allows us to prepare alumina-supported Pt samples having different support and metal particle morphologies. By using a stoichiometric amount of water during the hydrolysis step a sample having an average pore diameter of 9 nm and a Pt dispersion of 74% was obtained. Now by changing the water/ATB molar ratio one can change the average pore diameter of the support and also influence the Pt dispersion. By using a substoichiometric amount of water during the hydrolysis step one can obtain a sample having a smaller average pore diameter (5 nm). On the other hand, the use of a higher than stoichiometric amount of water gives a sample having a larger average pore diameter (15 nm). Apart from changing the water/alkoxide molar ratio other methods can also be used to change the nature of pores. The average pore diameter can also be increased by changing the method of solvent removal. By removing the solvent under hypercritical conditions an aerogel is obtained which has a larger average pore diameter (19 nm) in comparison to the corresponding xerogel (9 nm). On the other hand, the average pore diameter can also be decreased by preparing a mixed metal oxide support. By mixing in silica to an extent of 10 wt% along with alumina a sample which has a smaller average pore diameter (4 nm) is obtained. The Pt metal dispersion also was effected by the different preparative variables used. A xerogel sample prepared with a stoichiometric amount of water during hydrolysis seems to have the highest Pt dispersion.

The catalytic selectivity towards dehydrocyclization, isomerization, and hydrogenolysis products were quite similar at 325°C and at 400°C (Tables 10 and 11). The differences in selectivity for the various catalysts was not significant at either reaction temperature. On increasing the reaction temperature to 400°C there was an increase in the dehydrocyclization selectivity for all the catalysts as larger amounts of benzene were produced. As a function of time on stream at 400°C the catalytic activity decreased but the selectivity did not change very much. It is clear from Table 11 that the catalysts display a high selectivity toward the desirable components from a reforming standpoint, namely, dehydrocyclization and isomerization and the selectivity for the undesirable hydrogenolysis products is the lowest. In this paper comparisons between samples prepared by the sol–gel method and samples prepared by more traditional methods, namely impregnation and ion exchange, have not been made. The main reason for this is that as the sol–gel samples have been prepared without the use of HCl, any comparison between the reactivity of these catalysts and the reactivity of traditionally prepared industrial catalysts would not be meaningful. HCl is generally added to traditionally prepared bifunctional catalysts in order to provide the necessary support acidity and hence modify the catalytic reactivity. In the future, we plan to prepare sol–gel catalysts with varying amounts of chlorine in order to compare them to industrial catalysts. This would make the reactivity comparison between samples prepared by different methods more meaningful.

The size of the pores in the samples does seem to have an effect on the conversion of *n*-hexane as determined from the variations in turnover frequencies (TOF) as a function of average pore diameter which are listed in Table 12. It is clear that there is an increasing trend noticeable in the TOF values as the average pore diameter is increased. The largest TOF was obtained in the case of the 1.0 Pt/alumina aerogel sample that had the largest average pore diameter. The mixed metal oxide sample which has the smallest average pore diameter also shows the lowest TOF value. The values for the three 1.0 Pt/alumina xerogels lie in between the values obtained for the aerogel and mixed metal oxide sample. The advantage of having larger pores could be that pore blocking by carbonaceous deposits is less likely to occur in larger pores as compared to smaller pores during the reactions of *n*-hexane. Even though the aerogel sample had a lower Pt dispersion than the corresponding xerogel, the predominance of larger pores made it less susceptible to pore mouth plugging during reaction as compared to the xerogel sample. The xerogel sample had smaller pores and hence these pores could more easily be plugged by the carbonaceous deposits during reaction. This is a likely reason for the observed higher value of the TOF for the aerogel sample. Of course, one cannot rule out other effects like a metal-support interaction effect, for instance, that could have lead to this particular trend in the TOF.

From Fig. 8 it is clear that all the 1.0-wt% Pt sol–gel samples display similar trends in activity as a function of time on stream during the reactions of *n*-hexane with hydrogen at 400°C. There is an initial rapid drop in activity but after 4 hr on stream the catalytic activity does not change much. The first-order deactivation rate constants ($k_d$) were calculated for the initial region in the plots listed in Fig. 8 wherein there was maximum deactivation. Table 13 shows that there is a correlation between the BET surface area of the sample and the $k_d$ value. A decrease in the BET surface area results in a greater rate of deactivation because there is less surface area to accommodate carbonaceous residues. Under these conditions, the Pt sites are more easily poisoned. A higher BET surface area appears to be beneficial for activity maintenance.

This work suggests that the sol–gel method offers an interesting and potentially useful method of preparing supported metal samples because of the several preparative variables that can be changed as a means to alter the structure of the sample. Future directions of research using sol–gel catalysts should focus on the following:

(a) Preparation of Pt/alumina samples with HCl added during the synthesis and their comparison to samples prepared by more traditional methods.

(a) Preparation of bimetallic Pt–Re/alumina and Pt–Sn/alumina samples using various deposition techniques, in order to increase the exposed surface area of the active metal, while at the same time maintaining high total surface areas.

(c) Preparation of mixed metal oxide samples using metal oxides other than silica to stabilize the alumina surface.

## CONCLUSIONS

The following are the main conclusions that can be drawn from this study:

(1) The sol-gel method provides a convenient means of preparing alumina-supported Pt catalysts having different support and metal particle morphologies.

(2) 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 total surface area to around 450 $m^2/g$ due to active alumina formation.

(3) 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 reactions of *n*-hexane.

(4) Use of ATB as the alumina precursor and a stoichiometric water/ATB molar ratio of 3 gave the best $Pt/Al_2O_3$ sample from a total surface area and Pt dispersion point of view but not necessarily from a reactivity point of view.

(5) Aerogel samples displayed a lower Pt metal dispersion in comparison to xerogels of similar metal loading.

(6) 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.

(7) $Pt/Al_2O_3$ catalysts prepared by the sol–gel method are more resistant to catalyst deactivation by coke formation. This deactivation can be related to the total BET surface area.

## ACKNOWLEDGMENT

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