Preparation, Characterization, and Acidity of a Silica Gel/Tungsten Oxide Solid Acid

Nicholas Kob, Russell S. Drago,* and Vaneica Young

Catalysis Center, Department of Chemistry, University of Florida, Gainesville, Florida 32611

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Solid acidity is measured by simultaneously solving data from a calorimetric titration and an adsorption isotherm measurement to provide the amount, equilibrium constant, and enthalpy for each acid site. The utility of this procedure, referred to as cal-ad, in the synthesis of solid acids is illustrared with the preparation and characterization of a new hydrated tungsten oxide−silica-supported acid catalyst, referred to as SG-W. Cal-ad shows that SG-W, prepared from WCl_6, is a stronger acid with more Bronsted sites per gram than tungsten oxide, tungstic acid, or silica-supported WO_3 prepared by thermal decomposition of ammonium tungstate (SG-WO_3). Surface studies show a much better dispersion of tungsten in SG-W than in SG-WO_3. SG-W adds to a growing series of reproducible, characterized solid acids of varying strengths. A quantitative cal-ad series of solid acid strengths is given to provide a new scale for correlating acidity with catalytic activity and to establish acidity thresholds for different acid-catalyzed transformations. Solid acids with varying acidities are compared as catalysts for alcohol dehydration, light paraffin isomerization, and the alkylation of phenol with methanol to illustrate this approach.

Introduction

Solid acids are the most important catalysts used in the petroleum industry.[1] This fact coupled with environmental demands to replace liquid acids[2] in alkylation and other process has motivated study of the synthesis, characterization, and measurement of the acidity of solid acids.

Our interest in this area follows an earlier report of the synthesis and characterization of the strongest supported solid acid prepared to date, silica-supported aluminum chloride.[3] The material is prepared by refluxing a slurry of silica gel and Al_2Cl_6 in CCl_4. Evolution of 2 mol of HCl/mol of Al_2Cl_6 that reacted led to the formulation of this material as SG-$OAlCl_2$ (where SG refers to silica gel). Coordination of aluminum to neighboring surface Si−OH groups of SG leads to strong Bronsted acids. The SG-$OAlCl_2$ catalyst cracks hydrocarbons and alkylates at room temperature[4] but slowly loses HCl and deactivates during the course of the reaction. In an attempt to circumvent this mode of decomposition, non-halogen-containing Lewis acids supported on silica gel are being investigated.

This article describes the addition of tungsten (VI) oxide onto silica gel. A novel preparation of this material from WCl_6 affords a material, referred to as SG-W, in which an excellent dispersion of the tungsten oxide results. Data from a combined calorimetric titration and adsorption isotherm measurement, cal-ad, on this solid are simultaneously solved to produce equilibrium constants, enthalpies, and numbers of different types of acid sites.[5−8] SG-W is found to be a moderately strong acid some 19 kcal/mol weaker than SG-$OAlCl_2$ but 19 kcal/ mol stronger than silica gel.

Very strong solid acid catalysts are not required for all acid-catalyzed reactions. For example, if too strong a solid acid is used for dodecane isomerization, cracking to light hydrocarbons occurs. The long-term goal of establishing a scale of solid acid strength is to gain sufficient understanding of solid acid catalysis to tailor the catalyst acidity to the needs of the reaction. SG-W adds to those solid acids that have been investigated by cal-ad, providing one of moderate strength.

The correlation of catalytic activity with cal-ad acidity can be used to establish the threshold acidity and optimum solid acidity needed for acid-catalyzed reactions. These preliminary results indicate that correlations between acid strength, as measured using cal-ad,[5−8] and the solid acid's reactivity in acid-catalyzed reactions can be an important tool in solid acid catalyst design and selection.

Experimental Section

Catalyst Preparation. Several steps are employed for the preparation of silica-supported WO_3. First, the silica gel is conditioned by washing the silica gel (Davison 80−200 mesh) with 1 M HCl, followed by deionized water, then 30% H_2O_2, and again deionized water. The washed silica is dried at 100 °C overnight under vacuum and is then allowed to stand exposed to the atmosphere for 1 day. TGA shows that a properly conditioned silica gel evolves 4.1% by weight water, whereas an unconditioned Davison silica gel evolves 8.6% by weight water.

The conditioned silica is refluxed for 2 h in CCl_4 or CH_2Cl_2 solvent, to which 5×10^{-4} mol of tungsten(VI) chloride/g of silica is added. The temperature is adjusted to 70 °C, and this mixture is allowed to stir for 1 day. Color changes are quickly apparent from blue to red to yellow. These color changes are characteristic of the hydrolysis of tungsten hexachloride to the oxychloride and then to hydrated tungsten oxide. After 1 day, the mixture is filtered and the solid is washed with 1 M HNO_3 followed by DI water, yielding a yellow solid. The yellow solid catalyst is dried at 100 °C overnight and activated before use at 200 °C in flowing air for 2 h. This material is referred to as SG-W.

Silica-supported tungsten oxide is also prepared from thermal decomposition of ammonium tungstate on silica. A solution of

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* Corresponding author. Tel: (352) 392-5263. Fax: (352) 392-4658.

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ammonium tungstate corresponding to 10 wt % WO_3/g of silica is prepared in water. Silica gel is added to the solution, and the water is evaporated. The resulting solid is calcined at 500 °C in air to decompose the ammonium tungstate, and a green solid results. This material is referred to as SG-WO_3.

Catalytic Reaction. The alkylation of phenol with methanol was performed using 1 g of catalyst at 200 °C, a 1:3 mole ratio of phenol to methanol fed by syringe pump at 1 mL/h, and a N_2 carrier gas flow rate of 5 mL/min. The catalyst bed volume was 2 cm^3. Products were analyzed using gas chromatography and calibrated with known standards. Isomerization of pentane was performed using a flow reactor, 1 g of catalyst, 200−300 °C reaction temperatures, 5 mL/min flow rate of N_2 carrier gas, and a feed of pentane vapor from a saturator at room temperature. Dehydration of 1-propanol was performed using a flow reactor, 0.5 g of catalyst, a 170 °C reaction temperature, and 1-propanol saturated in N_2 carrier gas (saturator at 60 °C) at a flow rate of 20 mL/min.

Surface Characterization. Raman spectroscopy was performed using a Dilor OMARS 89 spectrophotometer with an optical multichannel analyzer. Infrared studies were done by pressing KBr pellets and analyzed on a Nicolet model 5PC FTIR. Powder X-ray diffraction (XRD) studies were done using a Phillips X-ray diffractometer, and a 2θ range of 5−70° was obtained. X-ray photoelectric spectra (XPS) were obtained on a Kratos XSAM 800 spectrophotometer. Samples were mounted onto the adhesive side of aluminum tape and scanned at 90° using Al Kα radiation. Scanning electron microscopy (SEM) analysis was done using a JEOL 35C electron microscope with an acceleration voltage of 25 kV using several magnifications.

Cal-Ad Analysis of Solids. Calorimetric titrations were carried out as described previously.[5−8] One gram of catalyst was slurried in cyclohexane solution and titrated calorimetrically with pyridine under stirring conditions. The cyclohexane and pyridine reagents were distilled from P_2O_5 prior to use. The heat evolved was measured after each injection of known amounts of pyridine solution into the calorimeter. In the cal-ad process, an adsorption isotherm is measured over the range of base additions used in the calorimetric titrations. The combined data from calorimetric titration and adsorption measurements are analyzed to determine accurate equilibrium constants, K_i, moles of site, n_i, and enthalpies, ΔH_i. Errors were acquired by a nonlinear regression analysis using a least-squares algorithm.

Measurement of the pyridine in solution in equilibrium with the solid after each injection was determined using a Perkin-Elmer Lambda 6 UV−vis spectrophotometer as described previously.[5−8] Suprasil quartz cells were employed in the adsorption studies.

Results and Discussion

Characterization of Tungsten Oxide Acids. Most supported tungsten oxide catalysts are made by using ammonium tungstate or other water-soluble tungsten salts as the tungsten oxide precursor.[9] Thermogravometric analysis of a sample of ammonium tungstate shows that a high temperature (∼500 °C) is necessary to completely convert the ammonium salt to tungsten oxide. At these elevated temperatures, dehydration of hydrated tungsten oxide and of the support (silica in this case) will occur, reducing the number of Bronsted acid sites and causing aggregation.

The preparation using WCl_6, described in this report, provides a low-temperature route to hydrated tungsten oxide on silica. The reaction of tungsten hexachloride with the hydroxyl functionality of the silica support provides good dispersion, and the subsequent low-temperature hydrolysis of the remaining chlorides results in a catalyst which retains more silica and tungsten hydroxyl functionality ($WO_3 \cdot H_2O$ species) than those from thermal decomposition preparations. The silica hydroxyl functionality is an anchoring site forming Si−O−W species.

Upon addition of WCl_6 to a silica−CCl_4 slurry, the color changes from blue (WCl_6) to red (tungsten oxyhalide) as evidence of the reaction of WCl_6 with surface silanols. The reaction liberates HCl gas. Proper silica conditioning and the use of a dry inert solvent are needed to prevent water from competing with the surface hydroxyl groups in the hydrolysis of WCl_6. When preconditioned silica is reacted with WCl_6, collection and back-titration of the HCl evolved show that four of the six chlorides have reacted with surface hydroxyls, corresponding to a surface reaction described by eq 1 (where

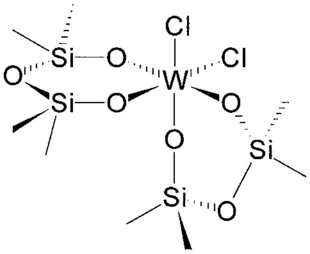

Figure 1. Anchoring species from reaction of SG with WCl_6.

$$WCl_6 + 4SG\text{-}OH \rightarrow W(OSG)_4Cl_2 + 4HCl \qquad (1)$$

SG is silica gel). The catalyst has also been prepared by a solid state reaction between the tungsten hexachloride and silica, showing that the CCl_4 is not participating in the reaction.

On average, the anchoring species is $W(OSG)_4Cl_2$, and a probable structure is given in Figure 1. A 1 M HNO_3 wash hydrolyzes the remaining chlorides, catalyzes the conversion of W−O−Si linkages to W−OH and Si−OH, and changes the color to yellow ($WO_3 \cdot H_2O$). No residual chlorine is observed in ESCA, and nitrogen analysis indicates that no nitrate remains on the catalyst. A crystalline, silica-supported, hydrated tungsten oxide results upon drying at 200 °C. The tungsten species is complicated because water can be eliminated to form WO_3 aggregates with hydroxyl functionality. Characterization (vide infra) suggests that the anchoring unit is $(SGO)_{4-n}$−$W(OH)(O-)_{1+n}$, which is attached to octahedral $WO_3 \cdot H_2O$ aggregates. The material resulting from the WCl_6 anchoring followed by the nitric acid wash will be referred to as SG-W.

Conditioned silica gel was also reacted with $WOCl_4$ in the same manner as done with WCl_6. Collection and back-titration of the evolved HCl show that four chlorines have reacted. After acid wash, the infrared spectrum and the calorimetric titration are identical to those of the material obtained from the WCl_6 preparation.

BET analysis of the silica gel used in the preparation has a surface area of 265 m^2/g, and a pore volume of 1.1 cm^3/g. SG-W showed only a minimal drop in surface area to 242 m^2/g and a pore volume of 0.96 cm^3/g, indicating that the silica gel lattice is intact after the preparation. SEM was used to investigate the tungsten oxide morphology and dispersion over the silica surface as shown in Figure 2. The catalyst as prepared consists of uniform, small clusters of tungsten oxide approximately 600 nm × 700 nm. Both the SEM and BET analyses show a good dispersion of tungsten oxide on SG-W.

The tungsten XPS spectrum of SG-W, shown in Figure 3, is characteristic of WO_3 supported on silica.[11ab] The broad feature of the spectrum is attributed to tungsten existing in nonequivalent sites on the surface.[11] The charge-corrected tungsten $4f_{7/2}$ peak is located at 35.4 eV with a fwhm of 2.2 eV. Line splitting, due to spin−orbit coupling, gives rise to a tungsten $4f_{5/2}$ peak at 33.2 eV with a fwhm of 2.1 eV. The peak positions and

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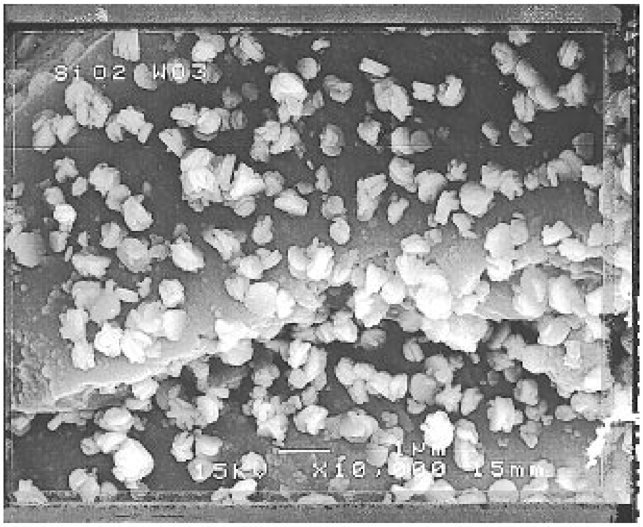

Figure 2. SEM 10 000× magnification of SG-W. (This figure has been reproduced at 68% of the original.)

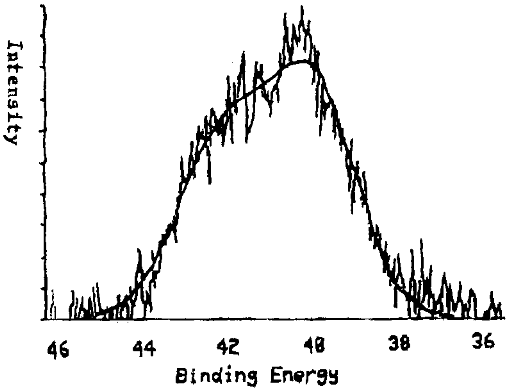

Figure 3. Tungsten 4f XPS spectrum for SG-W (not charge corrected).

fwhm are consistent with those for supported WO_3.[11b] XPS intensity ratios can provide information regarding overlayer-support dispersion[11c] using the following equation:

$$(I_p/I_s)_{expt} = (p/s)_b(\sigma_p/\sigma_s) \qquad (2)$$

where I_p is the intensity of the electrons from the promoter, I_s is the intensity of electrons from the support, $(p/s)_b$ is the bulk atomic ratio of the promoter and the support, and σ_p and σ_s are the Scofield cross sections.[11d] The model is used to predict XPS intensity ratios based on the bulk ratio of the overlayer and support. From this, a theoretical value of 100% dispersion can be calculated. XPS analysis of the intensity ratios of $W4f_{7/2}$ and Si 2p show the presence of 9.6 wt % tungsten oxide on the surface (97% disperse) of SG-W, which compares favorably to the theoretical surface dispersion of 10.5 wt %. The slightly lower amount of tungsten oxide observed on the surface by XPS is due to the presence of tungsten oxide clusters as shown in SEM. Using the Si 2p peak to correct the tungsten XPS spectrum for charging, only tungsten(VI) is observed by XPS on the surface of the catalyst, as evidenced by the $W4f_{7/2}$ peak at 35.4 eV. No peak is observed corresponding to the $W4f_{7/2}$ tungsten(IV) peak at 32.4 eV.

The XPS spectrum of a sample of SG-WO_3 prepared from thermal decomposition of ammonium tungstate is similar to that shown in Figure 2 for the SG-W. However, the XPS intensity ratio of $W4f_{7/2}$ and Si 2p on SG-WO_3 reveals only a 67% dispersion. The high-temperature thermal decomposition of ammonium tungstate leads to aggregation of the surface species. A previous report of grafting $MoCl_5$ onto silica shows that a better dispersion is achieved using controlled hydrolysis compared to thermal decomposition.[12a]

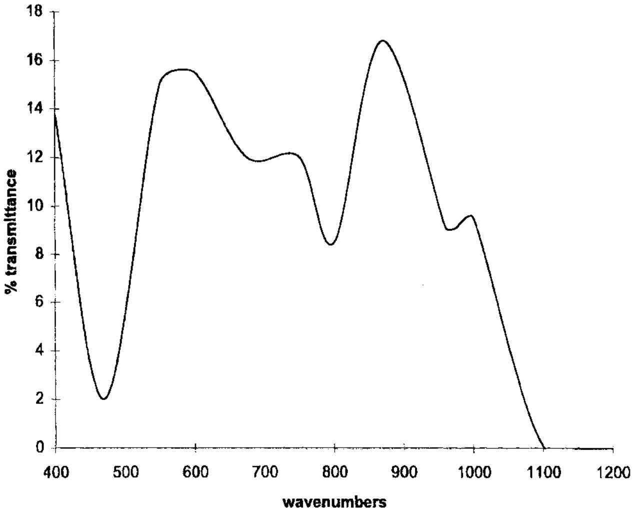

Figure 4. Infrared spectrum of SG-W.

Debate exists as to whether octahedral or tetrahedral tungsten is present on tungsten oxide supported catalysts.[12b] Crystalline WO_3 is octahedral with a distorted ReO_3 structure. There are a great number of possible arrangements of these octahedra giving rise to both monoclinic and hexagonal forms of WO_3. Distortions of the ideal structure occur with introduction of waters of hydration, and a large number of hydration levels are possible. Tungsten exists in a tetrahedral arrangement in Na_2WO_4. Preparation techniques or calcination is reported to cause supported tungsten oxide to adopt a tetrahedral geometry[13] which can be distorted.

Raman and infrared analysis[12−14] can been used to determine the structure of tungsten oxide. The infrared spectra of our silica-supported tungsten oxide catalyst has a band around 940 cm^{-1}, which overlaps those from silica gel (Figure 4), that is assigned to the W=O stretch. Clusters containing hydrated six-coordinate tungsten oxide give rise to a band around 672 cm^{-1}. This band, attributed to a W−O−W stretch, is observed for tungstic acid but not for anhydrous WO_3. Figure 4 contains an intense band at this frequency indicating supported, hydrated tungsten oxide species in our preparation. This result confirms the aggregation found with SEM.

The species 12-silicomolybdic acid, $H_4 SiMo_{12}O_{40}$, is reported to form when $MoCl_5$ grafted on silica is washed with nitric acid.[10] Temperature-programmed reduction of supported tungsten oxide on silica gel is interpreted as having peaks characteristic of $H_4SiW_{12}O_{40}$ sites.[12] The absence of a band at 892 cm^{-1} in our material indicates that the Keggin structure was not formed.

When the tungsten oxide loading is increased, the aggregate band at 672 cm^{-1} increases in intensity. The most active loading of tungsten oxide on a high-surface-area support (300 m^2/g) is reported to be[9] approximately 10%. Other tungsten oxide bands are obscured by those from silica.

Raman spectroscopy shows characteristic features that can be used to determine tetrahedral and octahedral coordination of tungsten. Peaks centered at 680 and 250 cm^{-1} are attributed to a distorted octahedral coordination of hydrated tungsten

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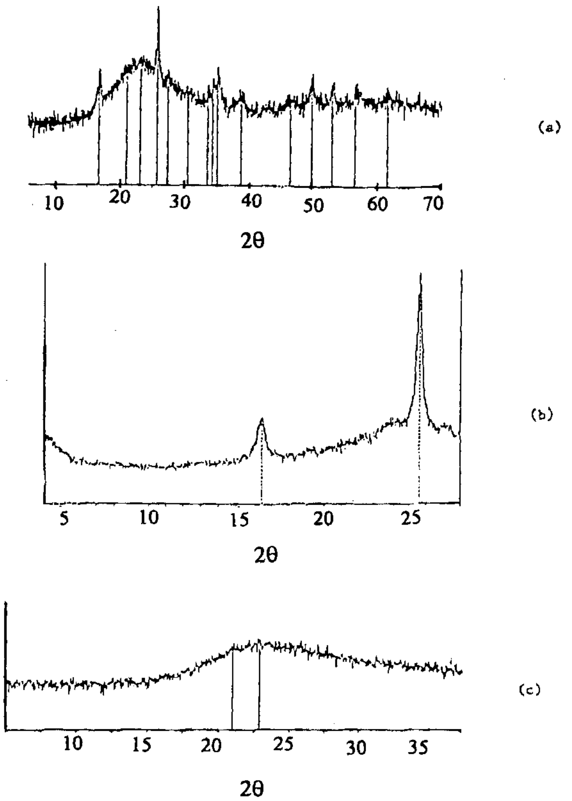

Figure 5. Powder XRD of (a) SG-W, (b) solid prepared by thermal decomposition of ammonium tungstate on silica, and (c) SG-W with no 1 M HNO_3 wash in preparation.

oxide.[15] The spectrum for SG-W compares well with the reported Raman spectra for $WO_3{\cdot}H_2O$.[13,15] On the basis of Raman spectrum peak intensities and the absence of the intense tetrahedral band at 930 cm^{-1}, it is concluded the coordination of tungsten is octahedral on the SG-W catalyst.

Powder XRD analysis of SG-W and SG-WO_3, shown in Figure 5a,b, are characteristic of tungsten oxide and their associated hydrates.[16] Crystallinity of some of the supported tungsten oxide of SG-W is observed even though, in most cases, high-temperature calcination is usually required to impart crystallinity. To confirm that the nitric acid wash was indeed causing cyrstallinity, a powder XRD pattern of a sample prepared by hydrolysis of WCl_6 without a HNO_3 wash was obtained. As shown in Figure 5c, this sample of supported tungsten hydroxide is amorphous.

Solid Acidity Measurements. Cal-ad analysis was carried out on the SG-W catalyst, SG-WO_3, and silica gel,[5] and the results are shown in Table 1. The number of acid sites, n_i, equilibrium constants, K_i, and strengths (ΔH_i,) for the i-different acid sites on the solids, are determined by simultaneously analyzing data from calorimetric titrations and adsorption experiments[5−8] for reaction with pyridine. The subscripts (i) label the different sites involved, with $i = 1$ describing the site with the largest K, $i = 2$ the next largest K, and so on. The cal-ad measurements are carried out in a hydrocarbon solvent close in molecular mass to those of the donor to cancel the contribution from a dispersion component to the measured enthalpy of the reaction.[5] Thus, the cal-ad procedure produces thermodynamic data and number of sites for the specific donor−acceptor reaction. The results show that 6.5×10^{-5} mol of a strong acid site per gram is present on SG-W, while only 1.6×10^{-5} mol of strong site per gram is present on SG-WO_3 prepared from decomposition of ammonium tungstate. Also, the total number of acid sites $n_1 + n_2$ is 4.8×10^{-4} mol/g on SG-W and is 2.7×10^{-4} mol/g on the SG-WO_3. The XPS results show that SG-W has better dispersion and hence more acid sites than SG-WO_3. Of the total of 5.0×10^{-4} mol of tungsten chloride/g of silica used in the preparation of SG-W, acid sites 1 and 2 (0.48 mmol) correspond to 96% of the tungsten added. The XPS data showed that the tungsten oxide is 97% disperse. The agreement of the cal-ad and XPS results provides additional confirmation of the validity[5,6,8] of cal-ad as a procedure for determining solid acid strength.

The combination of results from the above characterization studies suggests that SG-W is a Bronsted acid with $(SiO)_nWOH$ acceptor sites. Coordinated SiO− groups enhance the acidity over that of tungstic acid, and aggregates lead to partial crystallinity. Hydrolysis of the chloro complex illustrated in Figure 1 leads to oxygen bridges to attached octahedral, hydrated WO_3 units. The weaker acid sites are attributed to hydroxyl functionality on the WO_3 aggregates. If the strong acid groups are attributed to hydroxyls on tungsten bound to silica in the anchoring unit, the moles of strong acid groups (6×10^{-5}) compared to the moles of tungsten supported indicate that the average anchoring site in SG-W has 5.5 octahedral $WO_3{\cdot}xH_2O$ units attached. The correspondence between the total acid sites and the amount of tungsten added suggests that both sites n_1 and n_2 arise from tungsten species. The idealized representation of the surface species is $(SiO)_{4-n}W(OH)(O-)_{1+n}(WO_3{\cdot}xH_2O)_{5.5}$.

Within experimental error, the strongest sites of both SG-W and SG-WO_3 have comparable sterngth (ΔH). Calorimetric titration of WO_3 (from Aldrich) and H_2WO_4 (from Aldrich) with pyridine was carried out without the adsorption analysis to obtain a rough estimate of the acid strength of these solids. Calorimetry alone, using small additions of pyridine,[5−8] can provide[7] estimates (±2 kcal/mol) of the strongest site when $K_1 \gg K_2$ as is the case for SG-W and SG-WO_3. The enthalpy of reaction with pyridine for strongest site on WO_3 is −10 kcal/mol, and that for H_2WO_4 is −17 kcal/mol. The strongest sites of both SG-W and SG-WO_3 are stronger acids than these tungsten compounds, indicating that the Si−O−W bonds attaching the tungsten to the surface increase the acidity of the silica-bound W−OH groups. The weaker sites are comparable in acidity to H_2WO_4.

It is informative to compare SG-W with other solid acids that have been investigated using the cal-ad method. SG-$OAlCl_2$, the strongest solid acid known, has a $-\Delta H_1$ of 51 kcal/mol, the zeolite HZSM-5 has a strong acid site $-\Delta H_1$ of 41 kcal/mol,[7] HY has a $-\Delta H_1$ of 34 kcal/mol, sulfated zirconia has a $-\Delta H_1$ of 31 kcal/mol,[6] and silica gel has a $-\Delta H$ of 13 kcal/mol. Cal-ad characterizes the acidity of the stronger SG-W site as moderate strength, comparable to that of sulfated zirconia and slightly weaker than that of HY.

Catalytic Reactions. The effectiveness of an acid catalyst will depend upon the number of acid sites per gram as well as the strength of the acid−substrate interaction. At present, a pyridine one-parameter, enthalpy-based scale is offered to measure strength. The most straightforward correlation of these enthalpies to catalytic effectiveness involves the concept of acid strength threshold, i.e., the minimum acidity needed for a reaction to occur in a reasonable time (hours vs days). A second straightforward correlation involves competing substrate reactions where the relative rates influence the relative amounts of products which depend upon relative acidities. The most complex correlations, which will not be addressed in this study, are reactivity comparisons of different catalysts that are based

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Table 1. CAL-AD Analysis of Solid Acids

catalyst	$-\Delta H_1$ (kcal/mol)	K_1 (L/mol)	n_1 (mol/g)	$-\Delta H_2$ (kcal/mol)	K_2 (L/mol)	n_2 (mol/g)
silica gel	12.6	1.7×10^4	8.6×10^{-4}	5.3	3.2×10^2	8.6×10^{-4}
SG-W	31.7 (±1.9)	6.8×10^8 $(\pm 1.5 \times 10^{8)}$	6.5×10^{-5} $(\pm 4.2 \times 10^{-6)}$	16.2 (±1.0)	7.1×10^2 (±359)	4.1×10^{-4} $(\pm 2.0 \times 10^{-4)}$
SG-WO$_3$[a]	27.4 (±2.4)	1.2×10^9 $(\pm 8.9 \times 10^{8)}$	1.6×10^{-5} $(\pm 1.9 \times 10^{-6)}$	17.8 (±2.5)	5.8×10^3 $(\pm 1.9 \times 10^{3)}$	2.4×10^{-4} $(\pm 1.0 \text{x} 10^{-4)}$

[a] Prepared by calcination of $(NH_4)_2WO_3$.

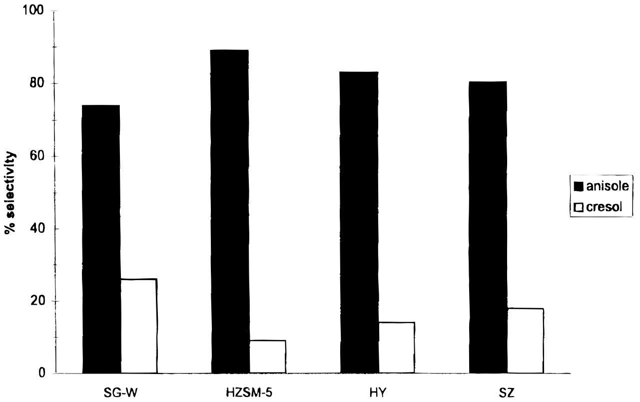

Figure 6. Alkylation of phenol product selectivities using various solid acid catalysts.

on conversions. For these comparisons, the reaction order in acid and the number of Bronsted sites on the solid acid are considerations to normalize reactivity to a per mole of acid basis. Needless to say, the reaction should be acid and not redox catalyzed.

The alkylation of phenol with methanol has been used as a model test reaction for evaluating the acidity of solid acids.[17] The alkylation reaction gives anisole and cresols as the primary reaction products.[18] The product distribution is dependent on the acidity of the catalyst.[18] Very strong acid catalysts are reported to favor O-alkylation giving anisole, while moderate strength acids favor ring alkylation producing cresols (ortho and para).[18] Product dependence on acidity was demonstrated by comparing the selectivities of phenol alkylation with methanol using HZSM-5 and Na-ZSM-5.[19] This reaction was studied with various solid acids (including SG-W), and the results are shown in Figure 6. Higher selectivity to anisole is seen for stronger acids, and, consistent with the cal-ad analysis, SG-W is a weaker acid than HZSM-5.

The SG-W catalyst and a solid prepared from thermal decomposition of ammonium tungstate on silica were tested in the isomerization of pentane. The isomerization of light paraffins requires a very strong acid catalyst,[20] and no isomerization or cracking activity was observed for SG-W or SG-WO$_3$ under the conditions tested. This indicates that, in order to isomerize pentane or lighter paraffins, a cal-ad acid strength greater than −32 kcal/mol (using pyridine as the probe in cyclohexane) is necessary. HZSM-5, which has a strong site acidity of −41 kcal/mol, isomerizes light paraffins.

The dehydration of alcohols can be catalyzed by acids of moderate strength. The SG-W-catalyzed dehydration of 1-propanol to propene gives 20% conversion at 170 °C. These preliminary results suggest that thresholds for acid-catalyzed reactions can be correlated with cal-ad acidities to provide a practical application of the acid strength measurements on new solid acid catalysts.

Conclusion

A new tungsten oxide−silica-supported solid acid has been prepared and characterized. Its properties are different from those of a material prepared by thermal decomposition of ammonium tungstate on silica. Cal-ad analysis reveals that the strong-acid site of the SG-W catalyst is a moderate-strength solid acid, whose acidity is less than that of HZSM-5, but enhanced as compared to that of silica or tungsten oxide alone. Cal-ad shows two acid sites and also provides the number of each of these acid sites per gram of solid, *n*. The agreement between the moles of tungsten added and the sum of the stronger and weaker acid sites from cal-ad indicates that both sites arise from tungsten species. The stronger acid site has an idealized structure illustrated by replacing Cl by OH in Figure 1 and forming $WO_3 \cdot H_2O$ with the strong-acid site $(SiO)_{4-n}W(OH)(O-)_{1+n}$ also functioning as the anchoring site. The weaker site is from the tungstic acid like portion. XPS and SEM results indicate a good dispersion of tungsten, and the former provide independent support for the *n* values obtained with the cal-ad analyses of these solid acids.

A series of solid acids characterized by cal-ad were studied in model acid-catalyzed reactions to illustrate the protocol for comparison of reactivity with acidity. The concept of acid strength threshold for acid-catalyzed reactions is introduced. SG-W was unable to catalyze light paraffin isomerization establishing a cal-ad acid strength threshold above 32 kcal/mol for this reaction. SG-W is a fair catalyst for 1-propanol dehydration, suggesting that it is close to the threshold acidity for this reaction and that stronger acids are desired. Product selectivities for competing reactions in acid-catalyzed phenol alkylation correlate to the cal-ad measure of acid strength for the series of acids studied and correlate to SG-W being a weaker acid than HZSM-5.

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