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MIXED METAL PHOSPHO-SULFATES FOR ACID CATALYSIS

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ABSTRACT

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Mixed Metal Phospho-Sulfates have been prepared and evaluated for use as acid catalysts via 2-methyl-2-pentene isomerization and o-xylene isomerization. Particular members of this class of materials exhibit greater levels of activity than sulfated zirconia as well as lower rates and magnitudes of deactivation. ^{31}P MAS NMR has been used to examine the role of phosphorous in contributing to the activity and deactivation behavior of these materials, while powder x-ray diffraction, BET surface area, IR, and elemental analysis were used to characterize the bulk catalysts.

INTRODUCTION

The use of metal phosphates and sulfated metal oxides as solid acid catalysts has been the subject of much study, and the chemical mechanism responsible for acid properties in solids the subject of much debate. Historically, Lewis acidity in metal phosphates has been attributed to dehydroxylated surface metal sites, and Bronsted acidity to hydrated Lewis acid sites where the inductive effect of neighboring non-hydrated Lewis acid sites increases the lability of protons in the adsorbed water molecule¹. Surface P-OH groups were found to be the source of Lewis and Bronsted acid sites by others^{2,3}. Segawa, et. al.^{4,5,6} suggested that it is the electron withdrawing capability of bulk phosphate groups that enhance the acid strength of surface P-OH groups, with the electrons being withdrawn into the bulk via P-O-P bonds.

Ward & Ko^{7,8} described a similar mechanism to account for Bronsted acidity in sulfated zirconia. They suggest that the inductive power of a sulfate group, due to the strong electronegativity of the S=O bonds, promotes the lability of protons on an adjacent hydrated surface metal site. More recently, Farcasiu, et. al.⁹ and Ghenciu, et. al.¹⁰ have suggested that the activity typically attributed to Bronsted acidity in sulfated metal oxides is due to a reduction-oxidation mechanism. They showed that sulfate groups act as a one-electron oxidizing agent, which in conjunction with neighboring hydroxyl groups, initiate and propagate chemical reactions. This concept has been further supported by Xu and Sachtler¹¹ who correlated the activity associated with Bronsted acidity on sulfated zirconia with the oxidation state of the sulfur atom.

In this study a series of metal and mixed-metal phospho-sulfates have been prepared which contain greater amounts of bulk and surface sulfate groups than is typically found in solid acid catalysts. These materials have reasonably high surface areas and a minimum of 10 wt% sulfur which is completely stable in oxidizing environments to 450 °C. The structure of these materials is explored using ^{31}P Magic-Angle Spinning Nuclear Magnetic Resonance (MAS NMR), X-ray powder diffraction (XRD), and Fourier Transform Infra-Red spectroscopy (FTIR). An attempt is made to correlate structure with catalytic activity observed by 2-methyl-2-pentene and o-xylene isomerizations.

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EXPERIMENTAL

Synthesis & Characterization

Catalysts were synthesized by reacting mixed-metal solutions with stoichiometric amounts of phosphoric acid and water, and an excess of sulfuric acid. The resultant precipitates were calcined under flowing air at 300 °C at a ramp rate of 0.1 °C /minute and held at temperature for 72 hours. The calcined materials were ground with a mortar and pestle after which they were granulated by alternating 2000 PSI hydraulic loading, grinding, and sieving resulting in sample particles of 100-200 μm .

Powder X-ray diffraction data were collected at room temperature on a Siemens Model D500 diffractometer, with Θ -2 Θ sample geometry and Cu K α radiation, between 2 Θ = 5 and 60°. BET measurements were performed on a Quantachrome Autosorb automated gas sorption system, with adsorbed and desorbed volumes of nitrogen in the relative pressure range of 0.05-1.0. Chemical analysis was performed via DCP using an ARL SS-7 DCP, with the exception of sulfur analysis which was performed by Galbraith Laboratories. ^{31}P MAS NMR data were collected on a 9.4T system at 400 MHz for protons and 162 MHz for phosphorous, with a 90° pulse and spinning speeds between 6-7 KHz. The chemical shifts are relative to phosphoric acid as an external standard. De-convolution of spectra was performed using Peakfit 4.0 software (Jandel).

The FTIR spectra of the samples was obtained using both transmission and diffuse reflectance infrared methods. The transmission infrared spectroscopy was obtained with a Mattson Research Series 1 FTIR spectrometer equipped with an air-cooled source and a mercury-cadmium-telluride detector. The spectra were obtained at a resolution of 4 cm^{-1} after 100-200 scans. The diffuse reflectance spectra was obtained using a Nicolet 20SXB FTIR spectrometer equipped with a water-cooled source and a mercury-cadmium-telluride detector. The spectra were obtained at a resolution of 4 cm^{-1} after 250 scans. The IR cell was a Spectratech diffuse reflectance assembly. All spectra were taken at ambient temperature and in the N_2 purge of the IR chamber. The samples were diluted to a 5% sample in KBr mixture.

Isomerization

The materials were tested for activity toward 2-methyl-2-pentene isomerization and o-xylene isomerization using a packed bed flow reactor. Approximately 50 mg of granulated sample was placed in a 6 mm O.D., 40 cm long fritted glass tube and held in place with glass wool. The samples were pretreated at elevated temperatures in ultra-high purity helium (99.999% Matheson) flowing at 40-60 cc/min. All pre-treatments and reactions were at atmospheric pressure.

After pretreatment, the catalyst sample was cooled and the reaction was run isothermally at 150 °C. Flowing He was used to carry the 2-methyl-2-pentene and o-xylene from the 0 °C saturator to the reactor bed, at 10 cc/min and 1.5-2.0 cc/min, respectively. The products and reactants flowed through heated lines to a HP 5890 series II gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC was equipped with an automatic sampling valve that injected 1 cc of reactor effluent into a Supelco SPB-1 column for ptenenes or a Supelco Alphasex column for xylenes, connected to the FID.

RESULTS & DISCUSSION

Characterization Results

Table 1 lists the results of BET surface area and XRD analysis for the samples used for catalytic testing. In general, the metal to phosphorous ratio was fixed at 1.3:1.0 and in the mixed metal systems the ratio of metal1:metal2 was 1.0:1.6. (Zr/Ti/P/S has a molar Zr:Ti:P ratio of 1.0:1.6:2.0, etc). The samples that contained sulfur were 10-15 wt% sulfur. XRD analysis showed that the samples which exhibited crystallinity were in the NASICON system with structures of the type $M1_xM2_{(2-x)}(PO_4)_2(SO_4)$. Based upon the synthesis method employed and the precursor stoichiometry, the tendency to crystallize in the NASICON system was not unexpected¹². However, the XRD peaks are very broad and set in the low humps generally associated with amorphous materials, suggesting that the material is not fully crystalline. The lack of complete crystallinity may be due to the lack of a balancing counter-ion or precursor non-stoichiometry with respect to $M_2(PO_4)_2(SO_4)$.

TABLE 1

Phospho-Sulfate Catalyst BET Surface Area and XRD Results

Sample	(M ² /g)	XRD
Zr/P/S	4	NASICON/amorphous
Zr/Ti/P	434	amorphous
Zr/Ti/P/S	35	NASICON/amorphous
Zr/Al/P/S	47	NASICON/amorphous
Zr/Ta/P/S	41	NASICON/amorphous
Ta/P/S	60	amorphous

Calculations were performed using a formal charge model that assumes the most stable configuration for a material is when the net charge on the greatest number of oxygen atoms is minimized. This model has been used to predict the structure and relative acidity in mixed-metal oxides¹³ but was extended here to include metal phosphates and sulfates. Test calculations were performed on naturally occurring metal phosphate and metal sulfate minerals as a means to validate the incorporation of these additional elements. The stoichiometry of the catalysts as determined by elemental analysis were used as the basis of calculation in the formal charge model. The most stable configuration was determined to be the $M_2(PO_4)_2(SO_4)$ NASICON structure. Two other equally favorable configurations have increased numbers of M-O-S bonds at the expense of M-O-P bonds *which correspondingly increased the numbers of non-bonding oxygen atoms (NBO's) in the form of hydroxyl groups*. The increase in NBO's creates a situation where the material can exist with a consistent stoichiometric yet non-systematic structure (i.e. amorphous). We therefore suggest that the structure of the catalysts are comprised of a continuum of these NASICON and amorphous structural elements. The local interaction between sulfate groups and the metals determines the relative amounts of NASICON type crystal structure or an equally stable amorphous phase.

³¹P MAS NMR Results

³¹P MAS NMR of the six phospho-sulfate catalysts yielded a set of three different spectra. Each of these had two samples associated with it and are labeled groups 1-3, the similarity of the samples within each group being based upon similar chemical shifts. The result of de-convolution of these spectra are given in Table 2 and the peak assignments associated with the de-convolution in Table 3.

TABLE 2

³¹P NMR Results

Notation = chemical shift (% total area)

Group 1		Group 2		Group 3	
Zr/Ti/P	Zr/Ti/P/S	Zr/P/S	Zr/Al/P/S	Zr/Ta/P/S	Ta/P/S
	-52.3 (3%)	-47.2 (67%)	-49.2 (84%)	-47.3 (9%)	-46.0 (1%)
-36.1 (21%)					
-31.3 (20%)	-31.5 (26%)	-34.3 (28%)	-35.3 (13%)	-31.1 (71%)	-31.4 (34%)
-17.1 (46%)	-19.6 (44%)	-23.6 (5%)	-23.1 (3%)	-15.9 (10%)	-21.6 (43%)
-5.7 (4%)	-11.0 (15%)			-11.1 (9%)	-11.6 (22%)
-0.9 (4%)	-0.4 (12%)				
+2.4 (4%)				+2.2 (1%)	

TABLE 3

³¹P NMR Peak Assignments

NBO = non-bridging oxygen atom, BO = bridging oxygen atom

Chemical shift	Assignment	Reference
> -5 ppm	PO ₄ with 3 NBO, 1 BO	14
-5 to -25 ppm	PO ₄ with 2 NBO, 2 BO, with the range in shift due to varying levels of hydration, P=O vs P-OH, and P-O-M to different metals.	4, 5
-30 to -40 ppm	PO ₄ with 0 NBO, 4 BO	15, 16
< -45 ppm	PO ₄ with 1 NBO, 3 BO	14, 17

The high degree of peak overlap characteristic of the Group 1 samples (Table 2) made accurate de-convolution difficult, however, the general trend shows the tendency of sulfur to inhibit metal -phosphate group condensation, demonstrated by the overall increase in phosphorous with NBO's in the Zr/Ti/P/S versus the Zr/Ti/P.

The Group 2 samples have a denser structure (with respect to phosphorous) than Group 1 samples, in which the vast majority of phosphate groups have at least three BO's. The fact that the aluminum containing sample is structurally similar to the pure zirconium sample suggests that the presence of aluminum allowed for formation of a more condensed structure. If the Zr/Al/P/S is denser than the Zr/Ti/P/S of group 1, the number of P-O-M bonds has increased at the expense of phosphorous NBO's.

Group 3 contains both of the tantalum containing samples. The Zr/Ta/P/S has by far the greatest amount of fully coordinated phosphate groups than any of the six samples

examined. The fact that the Zr/Ta/P/S has a significant -50ppm shift as compared with the Ta/P/S suggests that this shift may be attributed to zirconium-phosphate coordination. Also, since the NASICON structure implies octahedral coordination of metals and the Ta/P/S has a dissimilar spectra to Zr/P/S we conclude that tantalum is not coordinating octahedrally. This is supported by XRD results which show that decreasing the Zr:Ta molar ratio gradually decreases the crystalline peak intensities until there is no crystalline phase present at all, (as is the case with the Ta/P/S). Furthermore, NASICON materials of the type $Ta_xM_{(2-x)}(PO_4)_3$ ($M = Zr$ or Ti) are known to exist but none of the type $Ta_xM_{(2-x)}(PO_4)_2(SO_4)$.¹²

2-methyl-2-pentene Isomerization Results

2-methyl-2-pentene isomerization is an acid catalyzed reaction in which distribution of the three major products yields information about the relative strength of acid sites on the catalyst^{18,19,20}. The rearrangement of 2-methyl-2-pentene (2M2P) progresses by formal protonation of the olefin followed by isomerization and deprotonation of reaction intermediates¹⁸. *Weak* acid sites produce a double bond migration yielding 4-methyl-2-pentene (4M2P), *medium* strength acid sites produce a methyl shift yielding 3-methyl-2-pentene (3M2P), and *strong* acid sites produce an extensive rearrangement to 2,3 dimethylbutene (2,3DMB)²⁰. The weak and medium sites have acid strengths that are typically attributed to Lewis acidity and the strong sites to Bronsted acidity.

FIGURE 1

Rate of 2M2P Isomerization (to 3M2P) versus Time

The production rate versus time of 3M2P is presented in Figure 1. Data for the strong and weak sites display the same relative position of samples to one another and similar rate versus time curve shape. Detailed 2-methyl-2-pentene isomerization reaction data for these samples, presented elsewhere²¹, has shown that catalytic deactivation under 450 °C was caused solely by carbon build-up, and the activity could be fully regenerated by subsequent treatment with oxygen. In general, the tantalum containing materials maintained a greater amount of their activity (over any time span). This resistance to deactivation was attributed to the ability of tantalum to transport oxygen from its matrix, preventing the deposition of carbon and hence, deactivation. Over 450 °C, deactivation is accompanied by sulfur loss. There is still carbon build-up but the activity is no longer fully regenerable²².

2-methyl-2-pentene isomerization results shows that materials which are structurally similar (as monitored by ^{31}P MAS NMR) can have drastically different activities. For instance, the tantalum containing materials and the Zr/Al/P/S show significantly higher isomerization rates over the other samples, yet they have distinctly different NMR spectra. Furthermore, the Zr/Al/P/S and Zr/P/S have nearly identical NMR spectra, yet Zr/Al/P/S is one of the most active samples and Zr/P/S is the least active. Thus, the state of phosphorous is not solely responsible for the observed activity.

O-xylene Isomerization Results

The products from catalytic transformation of o-xylene are indicative of the catalytic mechanism. Three mechanisms have been identified as active in this reaction: 1) acid mechanism which yields isomerization products p- and m- xylene as well as disproportionation products toluene and benzene; 2) hydrogenation mechanism which yields dimethylcyclohexanes; 3) bifunctional mechanism (combined acid and hydrogenation) which yields trimethylcyclopentanes. Some isomerization and disproportionation products are produced from bifunctional catalysis but the amount is considered to be negligible¹⁶.

O-xylene isomerization was performed over zeolite ZSM-5, sulfated zirconia, zirconium pyrophosphate, as well as the six phosphates and phospho-sulfates under consideration here. In general, ZSM-5 showed excellent conversion at lower temperatures and good selectivity toward p-xylene. Sulfated zirconia showed good conversion at higher temperatures but with less conversion to p-xylene. The zirconium pyrophosphate, mixed-metal phosphates, and phospho-sulfates on the other hand, showed no o-xylene isomerization activity.

Discussion

Since the 2M2P isomerization rate versus time plot for each sample is virtually the same in each of the three acid site strength categories, and the relative magnitudes of sample 2M2P isomerization rates remains constant in each of the acid site strength categories, the same catalytic mechanism is probably responsible for each isomerization product. This behavior, (combined with the relationship between regenerable activity and sulfur loss found with the phospho-sulfates) suggests that a mechanism consistent with that proposed by Farcasiu¹⁰ is responsible for the activity rather than a purely acid type mechanism.

Differences between the activity of the phospho-sulfates and sulfated zirconia may be attributed to two sources, the different state of the sulfate groups and different type hydroxyl sites. Bonding in sulfated metal oxides between an adsorbed sulfate and the surface is less covalent in nature than the structurally incorporated sulfate groups. The decreased covalent character of the metal-sulfate bonds would thus tend to increase their oxidizing strength versus the structurally incorporated sulfate groups of the phospho-sulfate materials. Only the adsorbed sulfate can isomerize xylene, which has a higher activation energy toward isomerization than does 2M2P. Differences in activity between these two materials may also be due to the nature of the hydroxyl group. Sulfated zirconia has exclusively Zr-OH hydroxyls (bridging or coordinative), whereas IR analysis of the phospho-sulfates shows that at temperatures greater than 200 °C the metal sites were largely dehydroxylated and that only P-OH groups were still present at reaction temperatures.

The enhanced rate of 2M2P isomerization, as well as diminished deactivation behavior of the phospho-sulfates versus sulfated zirconia may be attributed to the greater sulfate content of the phospho-sulfates. Beyond the possibility of increased number of surface sulfate sites, structurally incorporated sulfate is stabilized against reduction to inactive sulfite by the covalency of the sulfate-metal bonding, and can continue to act as an oxidant by electron withdrawal from the surface to bulk sulfate groups. Deactivation occurs when carbon adsorbs on surface hydroxyl sites effectively blocking hydride transfer.

The reason why some metals show greater activity in mixed metal systems and others show greater activity in a single metal environment in the phospho-sulfate catalysts is still unclear. Physical differences in metal-sulfate interaction may play a role, such as bridging versus chelating bidentate sulfate bonding. It is also conceivable that changes in metal coordination or extent of metal polyhedra distortion can effect the strength of sulfate group oxidizing ability, although it is doubtful that this phenomena is independent of other factors. Catalytic activity has been shown to scale with metal valency, mixed-metal coordination¹², as well as metal electronegativity²³. These results suggest that a relationship exists between the fundamental electro-chemical properties of the metal and catalytic activity. If the observed activity in phosphate, phospho-sulfate, and sulfated-metal oxide catalysts is due to an electron withdrawing mechanism, it should be possible to find an (at least partial) explanation in molecular orbital theory.

CONCLUSION

The catalytic activity in metal phospho-sulfates is largely a function of the electronic properties of the metals and the type and extent of interaction between the metal and the sulfate groups. Phosphate groups contribute to the activity by providing surface hydroxyls and stabilizing the metal-sulfate structure. This was monitored by ³¹P MAS NMR, XRD, FTIR, and elemental chemical analysis.

Work currently in progress will hopefully further our understanding between the fundamental electrochemical properties of metals, their interaction with sulfate groups, and the effect on catalytic activity. We believe that by gaining a better understanding of these issues that we will be able to design and synthesize more versatile and selective catalysts. Furthermore, we are attempting to synthesize metal phospho-sulfates via templating, to yield catalysts with enhanced surface area and controlled pore properties.

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