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Zirconium-Titanium Phosphate Acid Catalysts Synthesized by Sol Gel Techniques

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ABSTRACT

Recently a large effort has been put into identifying solid acid materials, particularly sulfated zirconia and other sulfated metal oxides, that can be used to replace environmentally hazardous liquid acids in industrial processes. We are studying a group of mixed metal phosphates, some of which have also been sulfated, for their catalytic and morphological characteristics. Zirconium and titanium are the metals used in this study and the catalysts are synthesized from alkoxide starting materials with H_3PO_4 , H_2O , and sometimes H_2SO_4 as gelling agents. The measurement of acidity was achieved by using the isomerization of an olefin as a model reaction. The phosphate stabilized the mixed metal sulfates, preventing them from calcining to oxides boosting their initial catalytic activity. The addition of sulfate prevented the formation of the catalytically inactive mixed metal pyrophosphates when calcined at high temperatures ($>773\text{ K}$).

1. INTRODUCTION

The desire to replace mineral acids in industrial processes has lead to a significant amount of work on solid acid catalysts. Recent work has focused on sulfated zirconia and other sulfated metal oxide catalysts. These sulfated metal oxides have proved disappointing (particularly those without a platinum promoter) because of their rapid deactivation and because of the suspicion that the sulfate acts as an oxidizing material rather than a superacid, making the sulfate a stoichiometric reagent rather than a true catalyst.¹

Metal phosphates have also been investigated as potential as acid catalysts. For zirconium phosphate, the most extensively investigated crystalline form is the α -layered salt, zirconium bis(monohydrogen orthophosphate), $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$.²³ Surface P-OH groups in metal phosphates have been identified as the source of Lewis and Bronsted acid sites.⁴⁵ Based on the study of zirconium phosphate others have suggested, that it is the electron withdrawing capability of the bulk phosphate groups that enhance the acid strength of surface P-OH groups, the electrons being withdrawn into the bulk via P-O-P bonds.³ The work that we report on in this article look at metal phosphate materials synthesized using sol gel techniques which give a different than metal phosphates that have been previously studied for their catalytic activity.

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The activity of sulfated zirconia (SZ) is particularly sensitive to the synthesis process. As a consequence, the synthesis of sulfated zirconia has been well studied.⁶⁻¹¹ When SZ is synthesized from the precipitation of inorganic salts (ZrCl_4 or $\text{ZrO}(\text{NO}_3)_2$), the sulfate is added to the amorphous $\text{Zr}(\text{OH})_4$ prior to calcination in the form of H_2SO_4 . The zirconia-sulfate mix is calcined and a tetragonal ZrO_2 is formed which gives a catalytically active SZ. If the $\text{Zr}(\text{OH})_4$ is calcined without sulfating first, the monoclinic form of ZrO_2 forms and later sulfating with H_2SO_4 does not produce an effective catalyst. When SZ is made using sol gel methods, starting with zirconium isopropoxide or some other zirconium alkoxide, the point of addition of H_2SO_4 is less significant. It can be added both with the gelling water or the zirconia can be sulfated after drying and before calcination. Although some authors report there is a difference in textural characteristics depending upon when the sulfate is added, the conclusion of its effects on reactivity are varied.^{9 10} When water and sulfuric acid are added to a zirconium alkoxide/alcohol solution, zirconium sulfate may initially form, however, calcination causes the oxide to be the dominant phase.

Acidity was measured using the isomerization of 2-methyl-2-pentene.¹²⁻¹⁴ as a test reaction. This acid catalyzed reaction can lead to 17 different hexene isomers; however, only three major products emerge. The total activity of the catalyst is thought to be indicative of the ability of the catalyst to protonate the olefinic reactant.

2. EXPERIMENTAL

The mixed metal phosphates were made using sol gel techniques by mixing two miscible alkoxides together: in this case primarily titanium isopropoxide (TIPT) and zirconia n-propoxide in isopropanol. Next, a 5% H_3PO_4 solution in H_2O was added as a gelling agent. The phosphate is then dried and calcined.

The sulfated metal phosphates were made using two different methods. The first method added sulfate following calcination: 1) Two miscible alkoxides are mixed together in isopropanol. A 5% H_3PO_4 solution in H_2O is added as a gelling agent. The phosphate is dried and calcined. It is re-dissolved in concentrated H_2SO_4 , dried and re-calcined. The second method added sulfate during the gelling process: 2) Two miscible alkoxides are mixed together in isopropanol. Along with the 5% H_3PO_4 solution in H_2O that is added as a gelling agent, H_2SO_4 is also added. The precipitated material, which is extremely hygroscopic at this point, is dried (523 K for 3-4 days) and calcined. The sulfated zirconia was supplied by Magnesium Electron, Inc. (MEI).

Crystal phase was identified using powder x-ray diffraction at room temperature on a Siemens Model D500 diffractometer, with θ -2 θ sample geometry and Cu K- α radiation, between $2\theta=5$ and 60° . BET measurements were performed on a Quantachrome Autosorb automated gas sorption system. Chemical analysis was performed via DCP

using an ARL SS-7 DCP, with the exception of sulfur analysis which was performed by Galbraith Laboratories.

A flow-through microreactor system was used for the isomerization reaction. Approximately 50 mg of sample was positioned vertically on a glass frit and topped with glass wool as a fixed bed in a 6 mm O.D., 40 cm long Pyrex tube. The samples were pretreated at elevated temperatures in either ultra-high purity helium (99.999%) or flowing hydrocarbon-free air flowing at 40-60 cc/min. All pretreatments and reactions were at atmospheric pressure.

A 10 cc/min He flow was used to carry the 2-methyl-2-pentene from the 273 K saturator to the reactor bed which was held constant at 423 K. The products flowed through heated lines to a HP 5890 series II gas chromatograph equipped with an FID and an automatic sampling valve.

3. RESULTS

To study the effect of calcination temperature and sulfating on catalyst activity, an active zirconium-titanium phosphate mixture was chosen and systematically studied as shown in Figure 1. The morphology, surface area, and catalytic activity for the catalysts in Figure 1 are reported in Table 1. The catalytic activity for materials whose final calcination temperature is 773 K is the lowest. As pyrophosphates, these inactive catalyst also have a morphology different from the other catalysts. The condensation of the phosphates to pyrophosphates significantly decreases the activity of the catalyst, which indicates the importance of the P-OH bonds for acidic catalytic activity. Although P-O bonds are still present in pyrophosphates, the number of P-OH bonds have significantly diminished.

Figure 1. The synthesis scheme for zirconium/titanium phosphate and sulfated zirconium/ titanium sulfate.

The number of P-O-P bonds and P-O-M bonds increase as the material condenses to the pyrophosphate. Although the sulfated catalysts are much more active than the "non-sulfated" phosphates, the deactivation rate is much slower for the phosphate catalysts. Figure 2 compares the activity versus time of C with SB. In addition, the isomerization activity of sulfated zirconia was measured and is recorded on the same plot for reference. The sulfated form of the phosphate initially gives a very active catalyst for this acid catalyzed reaction on a surface area basis. Since the sulfate clearly contributes a hefty portion of the acidity to the catalyst, we attempted to prepare a Ti-only catalyst like A, except sulfuric acid was used, along with H₂O, as the gelling agent in place of phosphoric acid. This synthesis is similar to what is reported in References 8,9, and 10 for sulfated zirconia using sol gel techniques. In calcining up to 773 K, the crystal structure was amorphous. Above 773 K the sulfated titanium material crystallized into the anatase form and at 973 K it started forming the rutile phase. When zirconia is prepared this way, calcination also produces the oxide phase. Like the sulfated titanium, there is enough sulfate left behind on the zirconium material to dramatically effect the catalyst activity. If the Ti-only catalyst is synthesized with using both sulfuric and phosphoric acid with the water as a gelling agent (synthesis 2 described above except with only one metal alkoxide, titanium tetra-isopropoxide), then the catalyst remains amorphous even after calcination at 973 K. The synthesis and morphologies are summarized in Table 2. Figure 1. Synthesis scheme for zirconium/titanium phosphate (B-D) and sulfated zirconium/ titanium phosphate (SB-SD) catalysts.

Table 1

Initial isomerization rate of 2-methyl-2-pentene, morphology and surface area for the zirconium/titanium phosphate catalysts and their sulfated analogs.

Sample	Calcination K	Initial Rate Mol/min/m ² x 10 ⁻⁷	XRD Results	BET Surface Area m ² /g
A	368	2.1	amorphous	510
B	573	5.5	amorphous	434
C	673	3.2	Ti _x Zr _{2-x} (PO ₄) ₃	400
D	773	0.3	Ti _x Zr _{1-x} P ₂ O ₇	367
SB	573	23.9	Ti _x Zr _{2-x} (PO ₄) ₃ (SO) ₄ (NASICON type)/ amorphous	51
SC	673	39.0	Ti _x Zr _{2-x} (PO ₄) ₃ (SO) ₄ (NASICON type)/ amorphous	40
SD	773	1.5	Ti _x Zr _{2-x} (PO ₄) ₃ (SO) ₄	47

Table 2

The effect of calcination on the morphology of a sulfated and sulfated plus phosphated titanium catalyst.

Catalyst	Titanium, sulfate catalyst Ti:S = 2:3 ($\text{Ti}_2(\text{SO}_4)_3$)		Titanium, sulfate, phosphate Ti:S = 2:3 ($\text{Ti}_2(\text{SO}_4)_3$)	
Reagents	TIPT/ H_2SO_4		TIPT/ H_2SO_4 / H_3PO_4	
	Calcination K	Crystal phase	Calcination K	Crystal phase
	773	Amorphous, $\text{Ti}_2(\text{SO}_4)_3$	773	Amorphous, $\text{Ti}_2(\text{SO}_4)_3$
	883	Anatase	883	Amorphous
	993	Anatase/rutile	993	Amorphous
	1073	Rutile		

The sulfur content of the sulfated-phosphorous catalysts is significantly greater than the sulfated metal oxides. The sulfated metal phosphates made in our laboratory by the method described above consistently had a sulfur content of 10-15 weight percent sulfur¹⁵ compared to the 1-3 wt% sulfur found on sulfated zirconia. The amorphous nature of the catalyst and the large weight percent of sulfur present indicates the sulfur has been incorporated into the bulk catalyst.

Figure 2. Rate of isomerization of 2-methyl-2-pentene for Zr/Ti phosphate and sulfated Zr/Ti phosphate. These are compared to sulfated zirconia.

4. DISCUSSION

The mixed metal phosphate catalysts made in this study were a very different species than the catalytic phosphates previously studied. This is most likely from the significantly different synthesis route which we took that was based on sol gel techniques. Exposure to high calcination temperatures (> 773 K) decreased the catalytic activity of the metal phosphates and caused the transformation of metal phosphate into metal pyrophosphate.

This transformation condenses the phosphate, which has many P-OH bonds available for catalyzing a reaction, to the $M_2P_2O_7$ form which does not have as many hydroxyl groups as the phosphate. In addition, the $M_2P_2O_7$ is a very stable structure that does not lend itself well to catalytic activity.

Although the amorphous phosphates (B and C) are low in relative activity based on surface area, these are very high surface area materials and on a per gram basis are quite active. Their slow deactivation compared to the sulfated zirconia and other sulfated catalysts is a beneficial characteristic. Unfortunately, the transformation to pyrophosphate at higher temperatures is an unavoidable characteristic for these phosphates. However, as can be seen in Table 1, the addition of sulfate, prevents the formation of the pyrophosphates at higher temperatures. In fact, XRD analysis of the sulfated metal phosphates showed a crystallinity that was from the NASICON system which have structures of the type $M1_xM2_{(2-x)}(PO_4)_2(SO_4)$. The x-ray diffraction peaks for the SB and SC are very broad and set in the low humps generally associated with amorphous materials, suggesting that the material is not fully crystalline.¹⁵

5. CONCLUSIONS

Sulfating a metal such as titanium or zirconium may produce a sulfate initially, but upon calcining the oxide will form. Addition of phosphoric acid disrupts the formation of the oxide and stabilizes the sulfate into the structure. It allows crystallization of sulfate as opposed to the oxide. Ti-O-P bonds appear to be preferred over Ti-O-Ti bonds and Ti-O-S bonds. This same chemistry appears to take place with zirconium as well as titanium. Preventing the formation of the oxide allows more sulfate to remain in the bulk of the catalyst, effecting its catalytic properties at higher temperatures.

Also, the addition of sulfate to the titanium-zirconium phosphate appears to prevent the formation of pyrophosphate at higher temperatures and actually causes a more crystalline material to form at lower temperatures than what would form without the sulfate. (See Table 1.) This results in the catalyst being active at higher temperature. This correlates with other observations made that associate the acidity of metal phosphates with the surface P-OH groups.^{4,5} Additionally, since the electron withdrawing capability of the bulk phosphate groups enhances the acid strength of surface P-OH groups³, it is not surprising to find the phosphate catalysts more acidic than the condensed pyrophosphates.

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