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Preparation and characterization of zirconia–phosphate aerogels

Raymond A. Boyse and Edmond I. Ko [1]

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

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Zirconia–phosphate aerogels were prepared by two methods: a one-step sol–gel synthesis followed by supercritical drying and an incipient wetness impregnation synthesis of a calcined zirconia aerogel. These samples were characterized by nitrogen adsorption, X-ray diffraction, infrared spectroscopy, and 1-butene isomerization. We identified both the conditions when zirconia–phosphate aerogels possess Brønsted acid sites, and the phosphate species responsible for their generation.

Keywords: zirconia; phosphate; solid acid; aerogel; butene

1. Introduction

Solid acid catalysts have been studied for many reactions in the chemical and petroleum industry, including cracking, isomerization, and alkylation. They have the potential to lower reaction temperatures as well as reduce many problems associated with liquid acid catalysts, such as storage and handling. One category of solid acid materials is that of mixed oxides, which can be generally defined as two oxides mixed on a molecular level. An associated class of solid acid materials consists of one material promoted on top of an oxide, prepared by techniques such as incipient wetness impregnation or immersion. Most generally, these solid acids include those oxides that support another oxide, for example tungsten oxide [1], and in the case of this work, an oxide that supports oxoanions, for example sulfates [2]. In these catalytic materials, the incorporation of anions with the oxide is known to enhance or even generate acid sites on the surface of the oxide.

One particularly well studied catalytic material is sulfated zirconia [2,3]. This material has been noted for its strong Brønsted acid sites capable of the skeletal isomerization of *n*-butane. Using standard preparation techniques, such as incipient wetness impregnation, to promote sulfate anions onto the surface of zirconia, the acidic properties of zirconia–sulfate have been known to depend closely on the anion loading and material activation temperature. Careful variation of these two parameters is believed to enable S=O double bonds to generate strong Brønsted acid sites on the surface. Our one-step synthesis of zirconia–sulfate aerogels has identified other important relationships for the material, like that between the location of the dopant anions and the resulting strength and type of acid site generated [2]. This synthesis gives us excellent control over the interaction between the anion and the support by allowing us to vary the location of the anion in the oxide. Comparing the insight provided by this one-step synthesis to that obtained from other preparation techniques further allows us to speculate on the nature of the species affecting the catalytic and acidic properties of the oxide support.

We have extended our one-step synthesis to examine other oxide supports and other anions, for example zirconia–tungstate and niobia–phosphate [4]. This work specifically deals with the effect of phosphate anions on zirconia. Previous work has been done on zirconium phosphate as a layered acid catalyst in reactions like oxidation of ethylene and dehydration of cyclohexanol [5]. Zirconium phosphate is known to possess weak Brønsted acid sites, but work has focused on the physical control of the layered structure of the material in order to extend the uses of layered catalysts. In this paper, we are examining the effect of phosphate promotion onto a zirconia support. Our results demonstrate the relative effects of anions on the surface of an oxide, and in this case allow us to see the difference in the way that a group VI sulfate species and a group V phosphate species affect the acidity of a surface. Finally, we wish to establish this strategy, of using different preparative methods to study catalytic materials, as a valuable research tool.

2. Experimental

Zirconia–phosphate aerogels were prepared by two methods. The first was a one-step synthesis in which the phosphates were introduced directly in the sol–gel preparation. We define the aerogel formed by this synthesis as a co-gel. The details of the starting synthetic formulation of a zirconia aerogel, upon which the co-gel synthesis is based, can be found elsewhere [6,7]. The co-gel synthesis involved reducing the standard amount of nitric acid used in the zirconia aerogel formulation, and adding phosphoric acid as the source of phosphate.

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[1] To whom correspondence should be addressed.

Briefly, we added 16.2 ml of zirconium *n*-propoxide precursor (70 wt% in propanol, Alfa) to a solution of 15 ml *n*-propanol solvent and 1.767 ml nitric acid (70% w/w, Fisher). A second solution was prepared containing 1.31 ml distilled water (2.0 mol H_2O/mol Zr^{4+}) in 15 ml *n*-propanol (Fisher). 10 mol% PO_4^{3-} was incorporated by adding 266 μl of phosphoric acid (85% w/w, Fisher) to the zirconium *n*-propoxide precursor. The alcohol/water solution was then added to the solution containing the precursor, and was stirred with a magnetic stir bar until gelation occurred. The gelation point was recognized after about 35 s with the disappearance of the vortex caused by stirring. The alcohol trapped in the gel network was extracted, using an autoclave (Autoclave Engineers, model 08U-06-60FS), by flowing supercritical carbon dioxide downward through the gel for about 2 h with operating conditions of about 343 K, (20–25) × 10^3 kPa and a flowrate of 85 ℓ/h at ambient conditions. The product material was ground into a powder of < 100 mesh. The subsequent drying treatments consisted of vacuum drying at 383 K for 3 h to remove water, again at 523 K to remove residual organics, and calcination in 27 ℓ/h of flowing oxygen for 2 h at an activation temperature that ranged from 773 to 1373 K. We use the terms Co-773 and Co-1173 when referring to the co-gel that has been activated at 773 and 1173 K, respectively.

The second preparative technique of phosphate incorporation was by incipient wetness impregnation. A zirconia aerogel was prepared by a standard recipe, with the same molar ratio of water to Zr^{4+} [6]. After the standard vacuum drying at 383 and 523 K, for 3 h at each temperature, the aerogel was calcined at 773 K in flowing oxygen before being impregnated. Nominally 10 mol% PO_4^{3-} was added using the required amount of ammonium dihydrogen phosphate (Fisher) dissolved in distilled water. This impregnated sample was vacuum dried at 383 K for 3 h, and subsequently calcined as before at a selected activation temperature. We define the calcined zirconia–phosphate sample synthesized by the incipient wetness preparation as an impregnated-gel and refer to the impregnated-gel activated at 773 K as IWP-773.

Textural characterization was performed on an Autosorb-1 gas sorption system (Quantachrome Corp.). Samples were first outgassed at 383 K, under vacuum, for 3 h. Forty point desorption isotherms were obtained, from which the BET surface area (taken at $P/P_0 \approx 0.3$), total pore volume (at P/P_0 close to unity), and the pore size distribution (BJH method) were calculated. Crystal structures were determined by X-ray diffraction using a Rigaku D/Max diffractometer with Cu K_α radiation.

The activities of the zirconia–phosphate aerogels in 1-butene isomerization were determined using a differential, downward flow, tubular fixed bed reactor of 1.27 cm internal diameter. Approximately 200 mg of sample was pretreated in the reactor at 473 K for 1 h under about 3.2 ℓ/h (53 sccm) flowing helium (Matheson HP). It was then cooled to 423 K and exposed to a feed stream of 0.3 ℓ/h (5.0 sccm) 1-butene (Matheson, research grade) in 5.7 ℓ/h (95.0 sccm) helium. The composition of the product stream was determined using a Gow-Mac 550P gas chromatograph with a thermal conductivity detector (Column: Supelco 23% SP1700 on 80/20 Chromosorb, 1/8″ × 13′). Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed on a Mattson Galaxy 5020 FTIR with a Harrick diffuse reflectance attachment (DRA-2). In addition, a Harrick reaction chamber (HVC-DR2) enabled us to perform in situ DRIFT spectroscopy of adsorbed pyridine. In these in situ experiments, the samples were given the same helium exposure, reaction pretreatment and temperature as those used in the catalytic reactor. The samples were dosed by diverting the helium flow through a pyridine saturator, allowing the spectra of the adsorbed pyridine to determine the ratio of Brønsted to Lewis acid sites by the method of Basila and Kantner [8]. All spectra were collected at a resolution of 2 cm^{-1} over a range of 400–4000 cm^{-1}.

3. Results and discussion

3.1. Physical characteristics of zirconia–phosphate

Table 1 shows the physical characteristics of both the co-gel and the impregnated gel as determined by nitrogen adsorption and X-ray diffraction. The surface area of the Co-773 is 141 m^2/g, which is about 20% more than that for a pure zirconia aerogel activated at the same temperature of 773 K [6]. This increase in the surface area of a pure oxide support after addition of a dopant anion is expected and has been seen in other systems such as zirconia–sulfate and niobia–phosphate. We explain this feature in terms of the inhibition of the typical sintering process by a dopant. Fig. 1 shows the effect that sintering has on the surface area and pore volume of the co-gel, a common trend for aerogels.

Table 1 also shows the stabilizing effect that the presence of phosphates has on the crystal structure of the system. From previous work with pure zirconia aerogels [6,7], we know that zirconia transforms from a tetragonal phase with activation at 773 K to a monoclinic phase with activation at 1173 K. Co-773 possesses the tetragonal crystal structure associated with pure zirconia. Co-1173 mostly exists in the tetragonal phase, with only

Table 1
Physical properties of zirconia–phosphate materials

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Crystal structure (vol% tetragonal)
Co-773	141	0.41	100
Co-1173	67	0.35	99
IWP-773	108	0.31	100

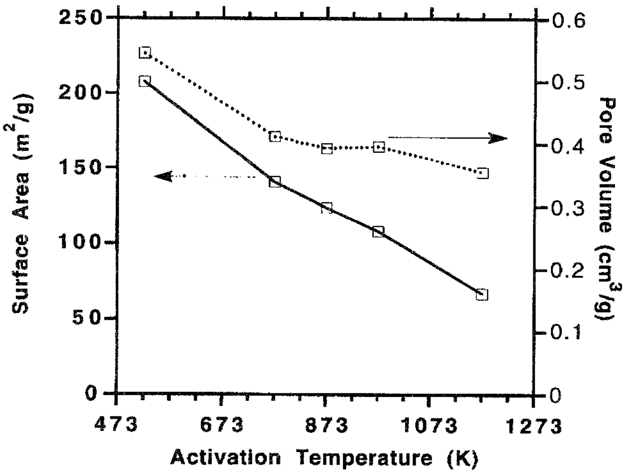

Fig. 1. BET surface areas and pore volumes of a zirconia–phosphate co-gel over a range of activation temperatures as determined by nitrogen adsorption.

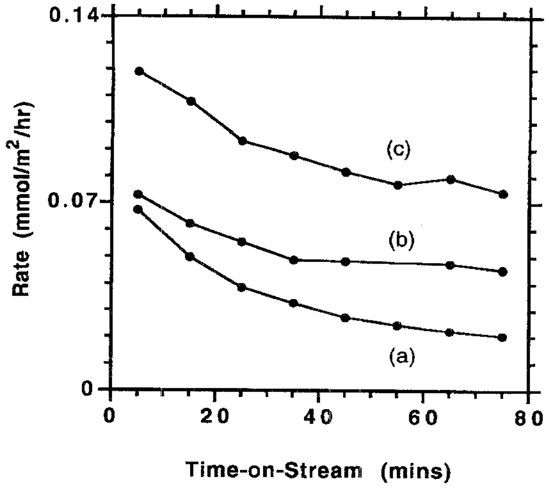

Fig. 2. 1-butene isomerization rates for catalysts. (a) 10 mol% PO_4 co-gel activated at 773 K (Co-773). (b) 10 mol% PO_4 co-gel activated at 1173 K (Co-1173). (c) 10 mol% PO_4 promoted aerogel prepared by incipient wetness impregnation activated at 773 K (IWP-773).

1 vol% being monoclinic, showing that the presence of phosphate inhibits the transformation of zirconia to the monoclinic phase even after activation at 1173 K. No other crystal phases existed, as determined by X-ray diffraction, between the activation temperatures of 773–1173 K. Therefore, the addition of phosphates to the system has retarded the crystal structure transformation, with the monoclinic phase emerging only after calcination at 1373 K.

Thermogravimetric analysis was used to confirm that there is no detectable decomposition of phosphate from the co-gel during a heating ramp of 10 K/min up to a temperature of 1273 K. Therefore, the physical features of the co-gel system can be described as follows. The one-step preparation has distributed phosphate throughout the zirconia. The oxide transforms into the tetragonal phase as expected with activation at 773 K, but the phosphates inhibit sintering thus reducing the loss of surface area associated with activation to higher temperatures. Phosphate species remain present in the system with activation up to 1173 K and prevent the structure transformation to the monoclinic phase.

3.2. *Acidic nature of zirconia–phosphate*

Fig. 2 shows the activity of representative samples, prepared by two different methods, in the isomerization of 1-butene which requires weak Brønsted acid sites. Curves (a) and (b) show the activities of Co-773 and Co-1173, while curve (c) is the activity of IWP-773. The samples deactivated with time-on-stream, with steady state activity reached after about 75 min. The lower activity of Co-773 when compared to IWP-773, which have equal nominal loadings, is a consequence of the one-step preparation which distributes the phosphate throughout the aerogel resulting in phosphate buried in the bulk having no effect on the acid site enhancement of the material's surface. Table 2 lists the ratio of cis-2-butene to trans-2-butene in the reaction products. These ratios are sufficiently close to one to conclude that the isomerization of 1-butene is taking place over Brønsted acid sites [9]. Thus, initial examination of the co-gel, using 1-butene isomerization as a probe reaction for Brønsted acid sites, demonstrates that the co-gel does possess Brønsted acid sites, and that a higher activation temperature tends to increase the steady state activity of the co-gel by moving the phosphate to the surface of the support.

We used DRIFT spectroscopy to further characterize our co-gels. Fig. 3 shows an in situ DRIFT spectrum of Co-773, under conditions simulating the 1-butene isomerization. By comparing the spectrum of Co-773 to that of a pure zirconia aerogel, we assigned the peak centered at 1075 cm^{-1}, over the range 900–1200 cm^{-1}, to the phosphate present in the co-gel [10–12]. Those peaks in the range of 1300–1700 cm^{-1} also exist for the zirconia aerogel and are associated with those residual organic groups not removed during heat treatments, so no assignments could be made to phosphate signatures

Table 2
Chemical properties of zirconia–phosphate materials

Sample	1-butene isomerization activity (mmol/(h m^2))		cis-/trans-2-butene ratio	Brønsted/total acid site ratio [d]
	initial [a]	final [b]		
Co-773 [c]	0.0671	0.0205	1.66 ± 0.02	0.00
Co-1173 [c]	0.0728	0.0452	2.05 ± 0.05	0.24
IWP-773	0.1189	0.0740	2.01 ± 0.04	0.23

[a] After 5 min time-on-stream.
[b] After 75 min time-on-stream.
[c] Different batch to that used in the physical characterization.
[d] Brønsted acid sites that adsorbed pyridine irreversibly at 423 K.

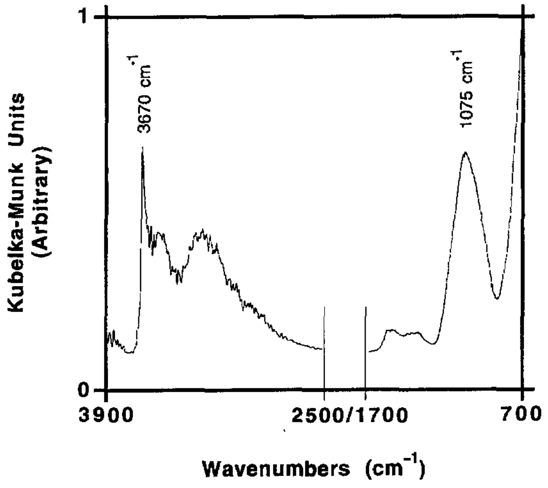

Fig. 3. In situ DRIFT spectrum of a zirconia–phosphate co-gel activated at 773 K. In situ conditions simulate 1-butene isomerization conditions: helium atmosphere at 423 K after 1 h pretreatment at 473 K.

that may have been superimposed on this region. The zirconia–phosphate co-gel also possessed a peak at 3670 cm^{-1} which is associated with isolated OH groups bonding to the surface through (i) more than one Zr cation [13], or (ii) a single P cation [14]. This peak at 3670 cm^{-1} is less defined on a zirconia aerogel, but its existence on a zirconia aerogel supports the assumption that this OH group is bonding through Zr cations. Qualitatively similar DRIFT spectra were obtained for Co-1173 and IWP-773.

Table 2 compares the properties of the co-gel, as already described using 1-butene isomerization, with those properties determined by DRIFT spectroscopy of adsorbed pyridine. Both Co-773 and Co-1173 were active in the isomerization of 1-butene at 423 K. The addition of phosphate in the sol–gel step followed by activation at both 773 and 1173 K has resulted in the generation of surface sites on the material capable of isomerizing 1-butene. However, diffuse reflectance spectra of the two samples showed that they were very different. Co-773 did not possess any Brønsted acid sites as determined by the adsorption of pyridine, whereas Co-1173 did exhibit Brønsted acidity, with about 24% of the acid sites being Brønsted in nature, and the remainder Lewis. Recall that the in situ DRIFT experiments were done at 423 K in order to simulate the condition for 1-butene isomerization. Apparently at this temperature, Co-773 could not adsorb pyridine irreversibly, and hence no pyridinium ion was detected by infrared measurements, whereas Co-1173 could. In other words, even though both samples are active in isomerizing 1-butene, Co-1173 contains *stronger* Brønsted acid sites as a result of its higher activation temperature.

The difference between these two samples also manifests itself in the hydroxyl region of the infrared spectra. The disappearance of the peak at 3670 cm^{-1} with the emergence of peaks associated with the pyridinium ion on Co-1173 indicated that these OH groups were the source of Brønsted acid sites [15], while the disappearance of the peak at 3670 cm^{-1} without the signature of the pyridinium ion on Co-773 suggested hydrogen bonding between adsorbed pyridine and surface OH [15]. Therefore, the co-gel required activation at 1173 K to generate acid sites that could irreversibly adsorb pyridine at 423 K, thus confirming them as stronger Brønsted acid sites than those on Co-773.

A close examination of IWP-773 allows us to fully understand the activation behavior of the co-gel samples. IWP-773 possessed phosphate species only on the surface of the zirconia support by nature of the incipient wetness preparation. Table 2 shows a remarkable similarity in the chemical nature of IWP-773 and Co-1173, both possessed Brønsted acid sites that irreversibly adsorbed pyridine at 423 K. The only difference was the activity in 1-butene isomerization; the lower activity of Co-1173 could be explained by having some phosphate trapped in the bulk that did not contribute to surface acid site enhancement. The similarity between these two samples attested that the location of the phosphate species was crucial in the type and strength of acid site generated.

3.3. Location and nature of the phosphate species

Our acidic and catalytic data led to two observations about zirconia–phosphate aerogels. First, the co-gels activated at 773 and 1173 K were different from each other. The Co-1173 sample had more and stronger Brønsted acid sites than the Co-773 sample. Second, the impregnated aerogel (IWP-773) was very similar to the co-gel activated at 1173 K (Co-1173). In our work with zirconia–sulfate aerogels prepared by the same one-step synthesis, we observed the following behavior. As the activation temperature is increased, the effect of sintering is more prominent in that sulfate is expelled onto the surface and transformed into an active surface species which causes the generation of strong Brønsted acid sites. Associated with the sintering of the sample is a decrease in surface area and crystal structure transformations. In other words, the changing behavior of the co-gel is explained in terms of the location of the sulfate species, or in this case the phosphate species. IWP-773 has had phosphate species promoted only onto the surface of the material. The surface phosphate enhanced Brønsted acid sites on the surface capable of both isomerizing 1-butene and adsorbing the pyridinium ion irreversibly at 423 K. Co-1173 also possessed Brønsted acid sites similar to those of IWP-773, and hence contained phosphate on the surface of the support. On the other hand, our results demonstrate that Co-773 did not possess surface phosphate groups that were responsible for stronger Brønsted acid sites on Co-1173.

The co-gel also provided materials with the potential for identifying the signature of the phosphate species as well as the nature of the phosphate species themselves that generate the Brønsted acid sites capable of adsorbing pyridine irreversibly at 423 K. Fig. 4 shows DRIFT spectra for the samples IWP-773, Co-1173 and Co-773 in the range 800–1300 cm^{-1}. We have already established the presence of an active phosphate species present on Co-1173 and IWP-773 but not on Co-773. Examination of these spectra showed a reproducible shoulder at 1200 cm^{-1} for those samples with Brønsted acid sites capable of adsorbing pyridine irreversibly at 423 K. This shoulder is caused by the presence of the active phosphate species mounted on the surface of the co-gel.

Referring to literature on the infrared signatures of phosphate groups, we examined the peak in the region from 800 to 1200 cm^{-1} caused by the P–O vibrations of the PO_4^{3-} species [10–12]. The broadness of the peaks is a result of the varying ionic character of the PO_4^{3-} group throughout the material. The emergence of the shoulder at 1200 cm^{-1} is caused by a species whose infrared signature is shifting to higher wavenumbers, indicating the changing of a species with predominantly P–O single bonds to one with bonds better resembling P=O double bonds. Therefore, our results are consistent with a PO_4^{3-} species changing into a PO_2^- species [11].

We summarize our results with the model in fig. 5. The top panel of fig. 5 represents a co-gel activated at 773 K, which we have referred to as Co-773. By nature of the one-step preparation, phosphate groups have been dispersed throughout the bulk of the co-gel. The lack of a shoulder at 1200 cm^{-1} in the DRIFT spectrum indicates *no* PO_2^- species is present on the surface of the material, and therefore no Brønsted acid sites capable of adsorbing pyridine irreversibly at 423 K. However, the phosphate in the bulk does stabilize weak Brønsted acid sites causing activity in 1-butene isomerization. With activation at a higher temperature of 1173 K, sintering causes PO_4^{3-} to be promoted onto the surface with a PO_2^- species extending out of the surface which is identifiable by DRIFT spectroscopy. We believe the site generation mechanism involves the PO_2^- species, with near double bond character, that creates a region of low electron density inducing a nearby hydroxyl group to behave as a Brønsted acid site.

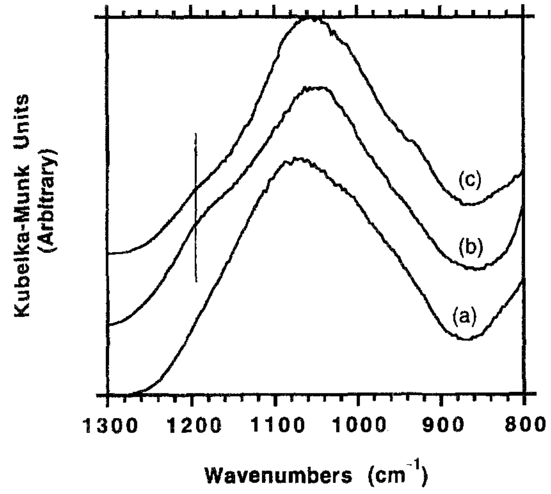

Fig. 4. In situ DRIFT spectra of zirconia–phosphate materials. (a) Co-773, (b) Co-1173, (c) IWP-773.

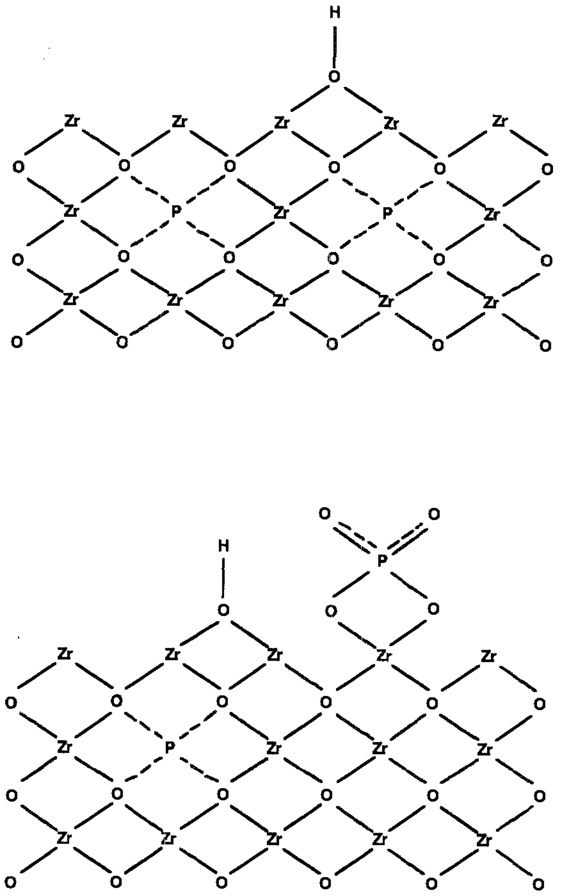

Fig. 5. Schematic model of a zirconia–phosphate co-gel. Top panel: Co-773, bottom panel: Co-1173.

This model is similar to that used to successfully understand the behavior of the zirconia–sulfate system [2]. Together our results establish a link between phosphate promotion and sulfate promotion in generating Brønsted acid sites on a zirconia support. The role of the anion in acid site generation appears to be the same for both materials. The difference between the systems is that surface promoted phosphate generates weaker Brønsted acid sites than surface promoted sulfate, demonstrated by the ability of zirconia–sulfate to isomerize *n*-butane, whereas zirconia–phosphate does not. The differences in anion stability on the support, and effectiveness in Brønsted site generation appear inherent to the phosphorus and sulfur atoms. This observation highlights the benefit of examining different anions in order to relate catalytic properties to preparation methods, an approach that might be particularly useful in studying multicomponent systems.

4. Conclusions

We have demonstrated a one-step synthesis for the promotion of phosphate onto a zirconia support. The presence of phosphate stabilizes the crystal structure of the support and inhibits the loss of surface area that occurs at higher activation temperature due to sintering. The importance of preparation and activation temperature is shown to be crucial in the type of surface site generated. The contribution of this work is the demonstration of using two preparation methods to effectively understand the acidic behavior of the materials. Specifically, by comparing a one-step synthesis with the conventional preparation technique of incipient wetness impregnation, we identified (i) the active species in the generation of Brønsted acid sites capable of 1-butene isomerization and pyridine adsorption, and (ii) the role of the location of the phosphate groups and consequently the importance of the preparation.

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