Sol-gel synthesis of ternary phosphate–ZrO₂–SiO₂ catalysts for alcohol dehydration

Quan Zhuang and Jack M. Miller

Abstract: Phosphate– ZrO_2 – Si_2O catalysts were synthesized by sol-gel method using tributyl phosphite, zirconium propoxide, and tetraethyl orthosilicate as precursors. They were characterized by N₂ adsorption, ³¹P CP MAS NMR, and DRIFTS. At lower P content, monomeric phosphates were formed on the surface of the catalysts, which were mainly responsible for the isopropanol dehydration activity. At higher P content, polyphosphates were formed, and thus, the dehydration activity decreased. An optimum P content for dehydration activity was found to be at 10 mol%.

Key words: sol-gel synthesis, ternary oxides, phosphate, acid catalyst, alcohol dehydration, 31 P CP MAS NMR, N₂ adsorption, DRIFTS.

Résumé : On a synthétisé des catalyseurs phosphate– ZrO_2 – SiO_2 par la méthode sol-gel utilisant du phosphite de triéthyle, du propylate de zirconium et de l'orthosilicate de tétraéthyle comme précurseurs. On les a caractérisés par adsorption de N₂, RMN CP MAS du ³¹P et DRIFTS. À des teneurs faibles en P, il se forme des phosphates monomères à la surface des catalyseurs qui se sont avérés responsables pour activité de déshydratation de l'isopropanol. À des teneurs en P plus élevées, il se forme des polyphosphates et il en résulte une diminution de l'activité de déshydratation. On a déterminé que la teneur optimale en P pour l'activité de déshydratation est de 10 mol%.

Mots clés : synthèse sol-gel, oxydes ternaires, phosphate, catalyseur acide, déshydratation des alcools, RMN CP MAS du 31 P, adsorption du N₂, DRIFTS.

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Introduction

Recently, phosphorus-containing oxides have been synthesized by various methods to obtain inorganic materials with new porous structures and (or) new properties. Among them, SAPO and AIPO types have been reported as having uniform porous structure, showing molecular sieve function, as well as catalytic activity, for some reactions due to the surface acidity (1, 2). Meanwhile, supported phosphoric acid catalysts prepared by impregnation have been widely used as catalysts for catalyzing olefin hydration (3), alkylation (4), dehydration (5–7), and dimerization (4).

On the other hand, there have been extensive studies on sol-gel synthesis of oxides, because it may provide specific properties to the oxide that cannot be obtained by the conventional coprecipitation preparation (8). Under appropriate synthesis conditions, such as metal alkoxide concentration, pH, the type of complexing agent, the amount of hydrolyzing water, drying technique, the textural properties of the oxide can be controlled. Since the advent of this method, it has stimulated more and more interest in its application in the field of catalytic materials research. The sol-gel synthesis

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method can be used to prepare both catalyst and catalyst support (9).

In this paper, we report our attempt to prepare the ternary phosphate–zirconia–silica catalysts by the sol-gel synthesis method using tributyl phosphite, zirconium(IV) propoxide, and tetraethyl orthosilicate as precursors. Its catalytic performance was evaluated for isopropanol dehydration, and N₂ adsorption, DRIFTS, and ³¹P CP MAS NMR were employed to characterize the catalysts.

Experimental

Sol-gel synthesis of the catalysts

n-Butanol was obtained from Caledon Laboratories, all other chemicals were obtained from Aldrich and used as received.

A series of P–ZrO₂–SiO₂ (Zr:Si molar ratio was fixed at 75:25) catalysts with P contents of up to 25 mol% were synthesized by the sol-gel method. Briefly, tributyl phosphite (density 0.925 g mL⁻¹), zirconium propoxide (70%, density 1.044 g mL⁻¹), and tetraethyl orthosilicate (98%, density 0.93 g mL⁻¹) were used as the precursors and 2,4-pentanedione (H-acac) as the complexing agent (8).² The appropriate amounts of zirconium propoxide and tetraethyl orthosilicate were desolved in the solvent, *n*-butanol (density 0.81 g mL⁻¹). The solution was heated to 60°C under stirring to mix the components thoroughly, then it was cooled down to room temperature. Tributyl phosphite and H-acac were added and the solution were hydrolyzed over night by adding water. A yellowish transparent gel was obtained, which

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Reagent	P mol%					
	0	5	10	15	20	25
Tributyl phosphite	0.00	3.00	6.00	9.00	12.00	15.00
Zirconium propoxide	84.14	79.94	75.73	71.52	67.31	63.11
Teraethyl orthosilicate	12.74	12.10	11.47	10.83	10.19	9.56
<i>n</i> -Butanol	166.63	167.82	169.04	170.60	171.43	172.61
2,4-Pentanedione	12.00	12.00	12.00	12.00	12.00	12.00
H ₂ O	47.50	47.50	47.50	47.50	47.50	47.50

Table 1. Reagent amounts (g) used in the catalyst P–ZrO₂–SiO₂ preparation.





was dried at 100°C to remove the solvent and then calcined at 500°C for 3 h to remove the organics. The total concentration of the alkoxides in *n*-butanol solution was 0.8 M. The molar ratio of the complexing agent to the alkoxides was 1:2. The molar ratio of hydrolyzing water to alkoxide was 11:1. Table 1 shows the reagent amounts used in the catalyst preparation.³

Characterization of the catalysts

 N_2 adsorption analysis was measured by using a Coulter SA 3100 instrument at -196°C. Samples were degassed under vacuum at 200°C for 1 h immediately prior to N_2 adsorption analysis. From the isotherm, the Brunauer–Emmett–Tellar (BET) surface area, pore volume, and pore size distribution were calculated by using the Barret, Joyner, and Halenda (BJH) method (10).

CP MAS NMR experiments were carried out on a Bruker Avance DPX 300 multinuclear FT NMR instrument. A standard bore Bruker MAS/CP MAS probe with 4 mm zirconia rotors was used. ³¹P NMR spectra were obtained at 121.50 MHz using cross polarization with proton decoupling during acquisition and referenced to $(NH_4)_3PO_4$ (chemical shift = 0 ppm). Samples were spun at 8 kHz. A 1 ms crosspolarization contact time was used with a 4 s recycle delay between the pulses. 124 FIDs were accumulated with a spectral window of 36 kHz. Prior to recording the spectra, the samples were degassed at 100°C for 30 min in a flow of helium and immediately transferred into the zirconia rotors for the NMR measurements.

DRIFTS spectra were acquired using a Spectra Tech DRIFTS accessory (The Collector) in an ATI Mattson RS-1 FT-IR spectrometer equipped with a Michelson interferometer, a helium-neon laser, a KBr beam splitter, a DTGS (deuterated triglycerol sulfate) detector with a spectra range of 4000–400 cm⁻¹, and a standard high-intensity source. The diffuse-reflectance FT-IR were recorded at 100°C under vacuum after evacuating the samples at 100°C for 30 min. The sample chamber was designed to be used in situ on the collector DRIFTS accessory.

Isopropanol dehydration evaluation

The catalytic activity evaluation of the catalysts for isopropanol dehydration was performed using a continuous flow fixed-bed micro reactor made of Pyrex glass.² The inner diameter of the reactor was 6 mm, its length was 25 cm. With each reaction, 200 mg of fresh catalyst was put into the middle of the reactor. A thermocouple was placed just below the catalyst bed to monitor the reaction temperature, which was manipulated by a temperature controller. Before each reaction, the catalyst was heated to the reaction temperature under a flow of N2. The reactions were performed at the temperature range of 150-230°C at 1 atm (1 atm = 101.325 kPa). The reactant, isopropanol, was introduced into the reactor by a N₂ bubbler, which was kept at 23°C (11).² The flow rate of N₂ was 100 mL min⁻¹, giving a weight hour space velocity (WHSV) of the reactant as 1.8 h⁻¹. The products were analyzed by an on-line PerkinElmer Sigma 3B gas chromatograph, employing a Porapaq R column, 800/100 mesh, 6 ft \times 0.125 in, with a thermal conductivity detector (TCD). To analyze all of the products in the exit stream from the reactor, the GC column was heated by programming from 150 to 220°C for 15 min.² The activities were stablized in ca. 20 min. After that time, two consecutive analyses were carried out, which were within 5%. An average is reported throughout the Discussion section. The main product was propylene, with trace amounts of diisopropyl ether as byproduct, with selectivity close to 100%.

Results and discussion

Figure 1 shows the N_2 adsorption isotherms of the catalysts. The catalysts display type IV isotherms (10). By add-

³The mol% of phosphorous quoted throughout is based on the synthesis concentrations, not analysis of the calcined catalysts.



Fig. 3. ³¹P CP MAS NMR spectra of the catalyst, P 10 mol%, after treating at 100, 233, 366, and 500°C, respectively (downward).



ing phosphorus in the form of tributyl phosphite into the sol-gel synthesis solutions, the N₂ adsorption of the resultant catalysts increases, especially at the intermediate and high relative pressure range. The pore size distributions of the catalysts are displayed in Fig. 2. It can be seen that the textural structure of the catalysts are mesoporous. As the amount of P is increased in the synthesis solution, the pore size distribution broadens to the larger pore diameter side, and the total pore volume of the catalysts increases. From P 0.0 to 25 mol%, the surface area increases from 180 to 250 m² g⁻¹ and the pore volume from 0.10 to 0.14 cm³ g⁻¹.

To evaluate the evolution process of the ternary $P-ZrO_2-SiO_2$ catalysts, ³¹P CP MAS NMR spectra of the catalyst with P 10 mol% calcined at different temperatures were acquired and the results are shown in Table 2 and Fig. 3. As

Table 2. ³¹P CP MAS data of the catalyst P–ZrO₂–SiO₂ (P 10 mol%) after calcining at different temperatures.

<i>T</i> (°C)	³¹ P chemical shift (ppm)			
100	-4.1			
233	-5.4			
366	-8.2			
500	-11.5			





Table 3. ³¹P CP MAS data of the catalysts P–ZrO₂–SiO₂ with different P content after calcining at 500°C.

P mol%	³¹ P chemical shift (ppm)			
5	-10.4			
10	-11.5			
15	-12.0			
20	-14.7			
25	-14.7			

Note: P concentrations are based on synthesis, not analysis.

the calcining temperature is increased, the chemical shift of ^{31}P NMR resonance shifts up field, from -4.1 ppm after being heat treated at 100°C to -11.5 ppm with the sample treated at 500°C. The intensities of the ^{31}P NMR peaks decrease when increasing the temperature of heat treatment. The ^{31}P NMR resonance peaks at the above chemical shift ranges are due to the monomeric phosphates (2, 12). It is well-known that P(III) can be easily oxidized to P(V) (13). Thus in our system, after heat treating the gel in air, the P(III) from tributyl phosphites is oxidized to P(V) in the form of phosphates.

Figure 4 and Table 3 show the ³¹P NMR spectra of the catalysts with different P contents after calcining at 500°C. It can be seen that when the P content in the catalyst is increased, the intensity of the ³¹P resonance increases, with an

Fig. 5. DRIFTS spectra of the catalyst after calcining at different temperatures (P 10 mol%).



upfield shift (from -10.4 ppm with P 5 mol% to -14.7 ppm with P 25 mol%). These changes are caused by partial formation of polyphosphates when the P contents in the catalysts are increased.

The DRIFT spectra of the catalyst with P 10 mol% after calcining at different temperatures were measured, and the results are shown in Fig. 5 together with the DRIFT spectra of ZrO₂:SiO₂ (75:25) calcined at 233 and 500°C, respectively. The absorption peaks at ~980 cm⁻¹ are assigned to Si—OH stretching and Zr-O-Si modes of ZrO₂–SiO₂ (14). Nogami (15) reported that the peaks at 500–600 cm^{-1} are due to the polyhedra ZrOx. It can be seen that in our catalysts these ZrOx polyhedra exist. The absorption at \sim 3730 cm⁻¹ is caused by the vibration of Si—OH. The peaks at ~3500 cm⁻¹ are ascribed to the hydrogen-bonded hydroxyl band (16, 17). As shown in the ³¹P CP MAS NMR results, after calcining, the phosphorus species in the gel gradually change to the phosphate, and hence, the new absorption peaks at ~3650 cm⁻¹ could be reasonably assigned to the OH groups affiliated to the phosphates, which are acidic. The peaks at 1540 and 1445 cm⁻¹ appear after increasing the calcining temperature to 233°C. On further increasing the calcining temperature, they disappear. Since we could not observe these peaks with pure ZrO₂-SiO₂ system, they must be related with some specific intermediate organic phosphorous species being formed, which then migrate to the surface and decompose during the evolution of the structure of the final catalysts on heat treatment at higher temperature (18). The phosphorus-containing gel is yellow, whereas ZrO₂-SiO₂ is nearly white and tributyl phosphite is colorless, indicating that at the gel stage the two materials have different structures. This can be seen from their DRIFTs spectra after calcining at 233°C. On heat treating at higher temperature (500°C) the frameworks of the two materials are similar, because they show similar DRIFTs spectra. The phosphates



Fig. 7. The activity (as conversion) of $P-ZrO_2-SiO_2$, P 0.0 and 10 mol% vs. reaction temperature.



may have only weak interaction with the framework of ZrO_2 -SiO₂.

Figure 6 shows the catalytic activities of the sol-gel synthesized catalysts with different P content for isopropanol dehydration. As the P content is increased, the activity increases first, then decreases, and then levels off, giving an optimum content of P at 10 mol%. It is clear that the dehydration activity of the catalysts are due to the acidity of the phosphates on the surface (3). As the P content in the catalysts is increased, some of the monomeric phosphates change to polyphosphates as evidenced by the results of ³¹P NMR characterization. This may explain the decline of the activity of the catalysts with higher P content.

Figure 7 shows the activities of the two catalysts without P and with 10 mol% of P, respectively, under different temperatures. Under the tested reaction temperature range, the activity of the P containing catalyst is higher than the catalyst without P.

Conclusions

By sol-gel method, phosphate– ZrO_2 – SiO_2 catalysts were synthesized. The ³¹P CP MAS NMR spectra revealed that at lower P content, monomeric phosphates were formed on the surface of the catalysts, which were mainly responsible for the isopropanol dehydration activity. When P content was increased, polyphosphates were formed, causing the decrease of the activity. The optimum P content was 10 mol%.

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