PHOSPHORUS PROMOTED SO₄²/TiO₂ SOLID ACID CATALYST FOR ACETALIZATION REACTION

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ABSTRACT

A novel phosphorus modified SO_4^{2-}/TiO_2 catalyst was synthesized by a facile coprecipitation method, followed by calcination. The catalytic performance of this novel solid acid was evaluated by acetalization. The results showed that the phosphorus was very efficient to enhance the catalytic activity of SO_4^{2-}/TiO_2 . The solid acid owned high activity for the acetalization with the yields over 90%. Moreover, the solid acid could be reused for six times without loss of initial catalytic activities.

Keywords: solid acid, TiO₂, acetalization, coprecipitation, phosphorus.

INTRODUCTION

Acid catalyzed reactions played an important role in chemical industry to produce various chemicals.^{1,2} Over 15 million tons of homogeneous acid (sulfuric acid, phosphorus acid, etc) is annually consumed as an unrecyclable catalyst, which requires costly and inefficient separation of the catalyst from homogeneous reaction mixture. Thus, heterogeneous catalyst has received tremendous interest because catalyst reuse and recycling can further improve the overall productivity and cost-effectiveness, thereby minimizing the waste generation and catalyst contamination, leading to a greener and more sustainable chemical transformation process.³⁻⁵ Solid acid could be easily separated from the reaction mixture by simple filtration or centrifugation and do not require the neutralization procedure. During the past decades, many solid acids have been developed for the replacement of homogeneous acid catalyst.^{6,7} However, till now, preparation of a solid acid as active, stable and inexpensive as sulfuric acid is still great challenging for the researchers.

TiO₂ based solid acid are quite promising because they are environmentally benign, easy to prepare, low cost, excellent thermal stability and strong surface acidity.^{8,9} As mixed oxides usually show better physicochemical and acidic properties than individual component oxides, TiO₂ mixed oxides were synthesized to further increase the catalytic performance of TiO₂.^{10,11} Herein, phosphorus was firstly incorporated into the TiO₂ particles and its catalytic performance was evaluated by the acetalization reaction (Schemce 1).



Scheme 1. Scheme representation of acetalization reaction

EXPERIMENTAL

Materials

All organic reagents were commercial products of the highest purity available (>98%) and were used for the reactions without further purification. TiO_2 (anatase) particles was purchased from Shanghai Reagent Plant.

Catalyst preparation

The phosphorus modified SO₄²/TiO₂ (SO₄²/TiO₂-P) was prepared as follows: 2 g titanium butoxide was dissolved in 10 ml anhydrous ethanol and 2 g H₃PO₄ was added to the titanium butoxide/ethanol solution. A white precipitate was produced and the suspension was stirred at room temperature for another 3 hrs. The prepared phosphorus modified TiO₂ was separated by centrifugation and then treated at 500 °C (TiO₂-P) in air for 5 hrs.

Sulfated TiO₂-P (SO₄²⁻/TiO₂-P) was prepared as follows: 2 g TiO₂-P powder was added into 10 mL of H₂SO₄ aqueous solution (0.5M) and stirred magnetically for 2 hrs. The SO₄²⁻/TiO₂-P catalyst was separated by centrifugation and then treated at calcined at 200 °C in air for 2 h before catalysis use.

Sulfated TiO, was also prepared for comparison and the sulfation process

of TiO₂ particles was the same as that of TiO₂-P. General procedure for acetalization reaction

Aldehyde or ketone (20 mmol), diol (24 mmol), 5 mL cyclohexane, and the catalyst (20 mg) were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and a thermometer, and a Dean-Stark apparatus which was constituted with manifold and condenser to remove the water continuously from the reaction mixture. The reaction was refluxed for 2 h to complete the reaction.

Characterization

The acidity was determined according to the literature.¹² The quantitative analysis was performed on a Shimadzu (GC-14B) gas chromatograph. The morphologies of electrospun fiber mats were recorded with a scanning electron microscope (SEM) (Jeol, jsm-6360lv, Japan). Samples for SEM were coated with a 2-3 nm layer of Au to make them conductive. The elemental analysis was taken on the EuroEA 3000 from Leeman, USA. FT-IR/ATR spectra were recorded on a FT-IR spectrometer (Nicolet, Nexus-470, USA) with the accessories of attenuated total reflection. Phase composition of samples was determined by means of X-ray powder diffraction (XRD) (Rigaku D, max-3BX, Japan). Surface area was measured by TriStar II 3020 from Micromeritics, USA.

RESULTS AND DISCUSSION

Characterization of the catalyst

The surface morphologies of SO₄²/TiO₂-P and TiO₂ powder were shown in Figure 1. It can be found that the SO₄²/TiO₂ catalyst was spherical particle with diameters about 1 μ m, while the SO₄²/TiO₂-P powder was irregular. The BET measurements also showed that the surface specific area of SO₄²/TiO₂ catalyst (134 m²/g) was a little larger than that of SO₄²/TiO₂-P (125 m²/g).



Figure 1. SEM images of SO_4^2/TiO_2 -P (a) and SO_4^2/TiO_2 (b).

The FT-IR spectra of TiO_2 -P before and after thermal treatment were shown in Figure 2. After thermal treatment, the intensities of absorption at 3300 cm⁻¹ and 1626 cm⁻¹ assigned to –OH group were significantly decreased. The strong absorbance band at 1015 cm⁻¹ was attributed to the P-O group. It can be concluded that the phosphorus has been successfully incorporated into the TiO₂ structure.



Figure 2. FT-IR spectra of TiO₂, TiO₂-P befor and after calcination.

The crystal phases of the two catalysts were analyzed by the XRD pattern. The diffraction peaks at 25° was the characteristic peaks of the (101) planes of anatase phase of TiO₂, which is known for its high catalytic activities. The treatment of sulfuric acid had no influence on the crystal phase of TiO₂.



Figure 3. XRD patterns of TiO₂, SO₄²/TiO₂ and SO₄²/TiO₂-P catalysts.

The elemental analysis catalyst showed that the sulfur contents in $SO_4^{2/}$ TiO₂ and $SO_4^{2/}$ TiO₂-P catalysts were 6.51% and 6.72%, respectively. This result demonstrated that the amounts of absorbed H₂SO₄ in the two catalysts were comparable. The acidity measurement showed that the acidities of SO₄^{2/} TiO₂ and SO₄^{2/}/TiO₂-P were 1.95 mmol/g and 2.67 mmol/g, respectively, which indicated the phosphorus could increased the acid centre in the surface of SO₄^{2/} TiO₂ catalyst.

The catalytic activities for the acetalization

A comparative study on the catalytic activities of the $SO_4^{2/}$ /TiO₂-P with heterogeneous and homogeneous acid catalyst was carried out (Table 1). It is interesting to found that the phosphorus species could significantly increase the catalytic activity of $SO_4^{2/}$ /TiO₂ catalyst (Entry 1-3 in Table 1). Yang *et al* have reported that the sulfate species and silica species could work together to increase the acidity and catalytic activity of $SO_4^{2/}$ /TiO₂ catalyst.¹³ Thus, it can be concluded that the sulfate species and phosphorus species may also have the similar synergetic effects, which is responsible for the high catalytic activity of $SO_4^{2/}$ /TiO₂-P catalyst. Due to the disfavored kinetics of the biphasic catalytic system, the heterogeneous catalyst usually was not as active as the homogeneous catalyst. Although the catalytic activity of $SO_4^{2/}$ /TiO₂ catalyst could be obviously enhanced by incorporation of phosphors, it is still slightly lower than that of homogeneous H₂SO₄ catalyst.

Table 1. The cat	alytic activity	comparison of	different catalysts.
	2		2

Entry	Catalyst	Conversion (%)	Yield (%)
1	SO4 ²⁻ /TiO2	87	86
2	SO4 ²⁻ /TiO2 ^b	85	82
3	SO42-/TiO2-P	99	97
4	H_2SO_4	100	99

^{a:} Catalytic condition: 20 mmol cyclohexanone; 24 mmol 1,2-ethenediol; 10 mg catalyst in 5 mL cyclohexane under reflux for 2 h; with Dean-Stark apparatus.

^{b:} The synthesis and sulfation processes of TiO₂ were the same with that of $SO_4^{2/7}$ TiO₂-P but with H₂O as the replacement of H₂PO₄.

Effect of catalyst amount on the acetalization

Table 2 summarizes the dependence of the acetalization with the catalyst loading. It can be found that the yields for the acetalization of cyclohexanone with 1,2-ethenediol gradually increased with the increment of $SO_4^{2/}/IO_2P$ catalyst. Excellent conversion and yield could be obtained even by just using 10 mg catalyst. When the amount of $SO_4^{2/}IO_2P$ catalyst increased to 20 mg, the yield was up to 99% and the further addition of catalyst has no obvious effect on the yield of acetalization, indicating that 20 mg $SO_4^{2/}/IO_2P$ catalyst was enough for the acetalization.

Table 2. Effect of catalyst amount on the conversion and yield of acetalization of cyclohexanone with 1,2-ethenediol.^a

Amount of SO ₄ ²⁻ /TiO ₂ -P (mg)	10	20	30	40	50
Conversion (%)	98	99	99	99	99
Yield (%0	98	99	99	99	99

^aReaction condition: 20 mmol cyclohexanone; 24 mmol 1,2-ethenediol; 5 mL cyclohexane under reflux for 2 h.

Acetalization catalyzed by SO₄²⁻/TiO₅-P catalyst

A series of carbonyl compounds and diols were employed to examine the scope of $SO_4^{2/}TiO_2$ -P catalyst (Table 3). Examination of entry 1-8 in table 2 showed that the aliphatic aldehydes were more reactive than the aromatic aldehydes due to the electronic effect. Due to the steric hindrance, the cyclohexanone acted more effective than the 2-butanone (Entry 11, 12, 15, and 16 in Table 3). As the five- and six- membered ring were more stable than seven-membered ring, 1,2-ethanediol, 1,2-propylenediol and 2,2-dimethyl-1,3propanediol worked better with carbonyl compound than 1,4-butanediol.



Figure 4. The reuse of the SO_4^{2}/TiO_2 -P catalyst.

Entry	Carbonyl compound	Product	Conversion (%)	Yield (%)
1	СІ́СНО	CI	99	99
2		CI O	99	99
3		CI	99	98
4		CI	98	98
5	СНО	$\langle \! \rangle \! + \! \langle \! \rangle$	98	98
6			98	98
7			96	96
8			96	95
9	0		99	99
10			99	99
11			99	97
12			93	93
13	— 0		99	99
14			99	99
15			99	98
16			99	98

Table 3. The SO₄⁻²/TiO₂-P catalyst catalyzed acetalization.^a

^{ac} Catalytic condition: 20 mmol carbonyl compound; 24 mmol diol; 20 mg catalyst in 5 mL cyclohexane under reflux for 2 h; with Dean-Stark apparatus.

Reuse of SO₄²⁻/TiO₂-P catalyst

As the $SO_4^{2-/T}iO_2$ -P catalyst is immiscibility with organic compound and solvent, the catalyst could be recovered by centrifugation. The reusability of the $SO_4^{2-/T}iO_2$ -P catalyst was evaluated by the acetalization of cyclohexanone with 1,2-ethanediol. After the reactions, the $SO_4^{2-/T}iO_2$ -P catalyst was recovered by centrifugation and reused in the second run directly. Figure 4 clearly showed that the catalytic activity of the $SO_4^{2-/T}iO_2$ -P was unchanged even after six runs.

CONCLUSION

In summary, a novel phosphorus modified $SO_4^{2/}/TiO_2$ solid acid was prepared. The phosphorus species could increase the catalytic activity of

 $SO_4^{2/}$ /TiO₂ solid acid. The $SO_4^{2/}$ /TiO₂-P catalyst was very efficient for the acetalization. Moreover, the $SO_4^{2/}$ /TiO₂-P solid acid could be recovered conveniently and reused for six times without loss of its initial activity. This environmentally benign heterogeneous $SO_4^{2/}$ /TiO₂-P solid acid will have potential for large-scale industrial applications.

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