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Solvent effects in esterification of phthalic anhydride on sulfated titania-based solid acid

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Esterification of phthalic anhydride with 2-octanol has been studied in the presence of sulfated titania. This study shows that sulfated titania has strong catalytic effects on esterification reactions. The catalyst was characterized with x-ray diffraction, FT-IR, Brunauer Emmett Teller, SEM and thermogravimetric methods. The effect of the type and volume of solvent has been investigated. Three solvents were used in this work: acetonitrile, dimethyl sulfoxide (DMSO) and an ionic liquid, 2-hydroxy ethylammonium formate. The results show that addition of various solvents has significant effects on the reaction rate of phthalic anhydride. DMSO and 2-hydroxy ethylammonium formate enhance the reaction rate but acetonitrile reduces it.



Keywords: solvent effects; esterification; sulfated titania; phthalic anhydride; 2-octanol

1. Introduction

Selective esterification of bifunctional carboxylic acids with alcohols is a useful organic synthesis reaction. The esters thus obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, plasticizers, pharmaceuticals, solvents, perfumes and cosmetics (1-3). Generally, octyl esters of phthalic anhydride are prepared under liquid-phase conditions by refluxing the reactants (carboxylic acid and alcohol) in the presence of small amounts of concentrated H₂SO₄, HCl, POCl₃ or sulfonic acids as a catalyst. Although many effective and reliable methods for the preparation of aromatic esters exist, there is still a need for research toward

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finding eco-friendly and economically viable processes. The use of the above-mentioned catalysts is undesirable from the environmental point of view as these chemicals are corrosive and generally encounter the problems of handling and transportation. Moreover, reusability of the catalysts cannot be expected. Hence, there are numerous global efforts to replace these environmentally harmful chemicals with more eco-friendly and less expensive catalysts. The use of heterogeneous catalysts for liquid-phase synthesis has a lot of benefits such as easy separation of product from the catalyst with simple filtration, easy recovery and reuse of the catalyst and avoidance of corrosion.

Solid acids such as zeolites, oxides, aluminophosphates and their modified forms such as sulfated oxides have been extensively studied as possible alternatives to conventional Lewis/Bronsted acid catalysts (4-9). Acidity of oxides are found to increase on sulfate ion treatment (10) and that of zeolites by protonation (11). The increase in acidity is due to an increase in the number and strengths of acid sites. In several reactions, it is observed that the yield and selectivity of a product depend not only on the concentration but also on the strength of the acid sites.

It has been observed that the solid acids such as modified zeolites and oxides catalyze very efficiently esterification and alkylation reactions (12–17). Solid super acids such as SO_4^{2-}/TiO_2 (H₀ < -11.93), which can be easily prepared, is sufficiently stable at the elevated reaction temperatures and regenerated conveniently. Different kinds of solid super acids and the field in which they are used have been developed. They have been used in isomerization, alkylation, acylation polymerization, oligomerization esterification and oxidation processes. (18–21). SO_4^{2-}/M_xO_y (M = Ti, Zr, Fe) is a useful catalyst for the esterification of the reaction of sebacic acid with ethanol and phthalic anhydride with 2-octanol. Dioctyl phthalate, the octyl ester of phthalic anhydride and diethyl sebacate are important chemicals which are used in polymer industries as a plasticizer and in detergent industries, respectively.

Room-temperature ionic liquids (RTILs) have recently gained increasing attention as environmentally benign alternatives to conventional organic solvents in a variety of synthetic (22, 23), catalytic (24) and electrochemical applications (25, 26), which is a result of their unique physical and chemical properties and the relative ease with which these properties can be fine-tuned by altering the cationic or anionic moieties comprising the RTILs (27, 28). They continue to excite interest for a number of reasons: the first arises from the claim that ionic liquids are environmentally benign solvents, particularly because they have very low vapor pressures under ambient conditions (29, 30). Second, that they might provide improved reactivities in a number of chemical processes (31, 32). Third, the fact that a wide range of cations and anions can be employed giving chemists the potential to design the solvent with specific properties that make the description of ionic liquids as "designer solvents" very appropriate (33, 34). Furthermore, they readily dissolve many organic, inorganic and organometallic compounds. ILs thus have the potential to act as high-performance green solvents for organic synthesis. Products are mostly separated from the reaction mixture via extraction with a solvent or via distillation.

The present investigation is aimed to find out the catalytic activity and the effect of sulfate ion treatment of titania in reactions between phthalic anhydride and 2-octanol. The results obtained are very encouraging in the sense that solid acids show not only high selectivity but also show high activity toward the formation of desired products (*35*).

2. Result and discussion

2.1. X-ray diffraction study

The average crystallite size L of the particle was determined by a x-ray diffraction (XRD) line broadening technique using the Scherrer equation, $L = 0.94 \lambda/b \cdot \cos \theta$, in which λ is the wavelength of the X-ray and b is the relative peak broadening. b was calculated as $b^2 = b_{exp}^2 - b_{ref}^2$,

where b_{exp} and b_{ref} are half-widths observed on a given sample and on a reference material, respectively. For the sample calcined at 500 °C, the orthorhombic TiOSO₄ phase appears therewith the anatase phase in the XRD patterns of the catalysts. Using the Scherrer equation, one can see that the average crystallite size *L* of the particles for the anatase phase is approximately 93 nm, and for the orthorhombic TiOSO₄ phase, it is approximately 84 nm for the sample calcined at 500 °C. It is well known that the crystallinity is dependent on the calcination temperatures. The crystallite size increases when the calcination temperature increases.

A clear relationship between sulfate content and crystallite size cannot be obtained in this work. However, it has been reported that the crystallite size increases in the presence of the sulfate, phosphate and tungstenate ions, SO_4^{2-} , PO_4^{3-} and WO_3^{2-} . These ions could possibly interact with TiO₂ particles and cause the growth of the particle. Even a very small amount of these ions is responsible for this effect (*35–39*).

2.2. FT-IR spectra

In order to identify the sulfate S=O species anchored to TiO₂, the characteristic FT-IR transmittance band around 1380–1360 cm⁻¹ was followed. These transmittance bands are assigned to S=O and O=S=O stretching vibrations (40). The FT-IR spectra of sulfated titania calcined at 300 °C and exposed to ambient conditions for 24 h are shown in Figure 1. The evolution of the 1360 cm⁻¹ band is shown as a function of the temperature. This band corresponds to $(TiO)_3$ –S=O and to $(TiO)_2$ –SO₂ asymmetric vibrations (41–44). It can be seen that the S=O band appears around 1320 cm⁻¹ in the sample observed after ambient exposure. This band is shifted to 1369 cm⁻¹ when the temperature of the sample reaches 400 °C (45). In our case, because the sample was exposed to a wet atmosphere, the S=O species coordinates with water and hence the S=O band appears at lower frequency as an S–O vibration band (46, 47). When the temperature of the sample was raised, the adsorbed water was eliminated and the band is then shifted to a higher frequency.



Figure 1. FT-IR spectrum of sulfated titania.

2.3. SEM study

Figure 2 shows the SEM image of sulfated titania. One can see in this image that the TiO_2 particles are nearly spherical and almost all of them have diameter below 300 nm. This image shows that the addition of sulfate ion on the surface of titania does not agglomerate the nanoparticles.

2.4. Thermogravimetric study

Figure 3 shows the thermal gravimetric curves of the sulfated titania nanoparticles. In Figure 3a, one can see one broad peak at 50–200 °C and one major peak at 500–550 °C. The first peak (at 50–200 °C) depends on the water lost from the catalyst. Water can be adsorbed physically and chemically on the sulfated titania surface. The adsorption energy of physically adsorbed water is less than that of the chemically adsorbed water. Thus, we see a broad peak for water loss in a thermogravimetric curve. This curve indicates that physically adsorbed water begins to desorb at temperatures around 50–100 °C and immediately chemically adsorbed water begins to disorb at temperatures 100-200 °C.

A major peak at 500–550 °C is depending on the desorption of sulfate groups from the sulfated titania surface. The sulfate ion was adsorbed on TiO_2 with a strong chemical bond and thus was desorbed at high temperatures.

Figure 3b shows that approximately 2% of the weight of the catalyst was lost up to 400 °C, which shows the weight percent of the water. But, approximately 10% weight lost around 500–550 °C indicates that the weight percent of the sulfate ion on the TiO₂ surface is 10%.

2.5. Surface area measurement

The Brunauer Emmett Teller (BET)-specific surface area of the support titania and calcined samples at 500 $^\circ C$ was 5 m²/g.



Figure 2. SEM image of sulfated titania.



Figure 3. Thermal gravimetric curve of sulfated titania nanoparticles.

2.6. Solvent effects on reaction rate

Figure 4 shows the dependence of the pseudo-first-order reaction rate constants of the esterification reaction vs. the volume of acetonitrile. One can see in this figure that reaction rate constants decrease continuously with the increase in the solvent volume from 0 to 3 ml. The dipolarity/polarizibility parameter (π^*) of acetonitrile is 0.75, and the reactants (2-octanol and phthalic anhydride) were soluble in this solvent. Thus, the addition of acetonitrile removes reagents from the surface of the catalyst and reaction rate constants decrease with the increase in the solvent volume.



Figure 4. Solvent effects on pseudo-first-order rate constants of esterification of phthalic anhydride in acetonitrile in various solvent volumes.

Figure 5 shows the dependence of pseudo-first-order reaction rate constants vs. the addition of dimethyl sulfoxide (DMSO). In this figure, one sees the opposite behavior. The rate constants increase with the increase in the solvent volume. The dipolarity/polarizibility parameter (π^*) of DMSO is 1, and this solvent is more polar than acetonitrile. In this case, increasing the volume of the polar solvent decreases the solubility of reactants in the solvent, and the tendency of reactants to adhere to the surface of the catalyst was increased. This increases the coverage of the catalyst surface with reactants and thus the reaction rate was increased.

Figure 6 shows the dependence of the reaction rate constants on the volume of the ionic liquid (2-hydroxyethylammonium formate). The behavior of the system is close to that of the DMSO solvent. The dipolarity/polarizibility parameter (π^*) of the ionic liquid is greater than DMSO and is 1.15; thus, as one can expect, the increase in the solvent decreases the solubility of reactants.



Figure 5. Solvent effects on pseudo-first-order rate constants of esterification of phthalic anhydride in DMSO in various solvent volumes.



Figure 6. Solvent effects on pseudo-first-order rate constants of esterification of phthalic anhydride in ionic liquid in various solvent volumes.

Thus, the reactant concentrations increase on the surface of the catalyst and then the reaction rate was increased.

2.7. Catalyst recycling

Figure 7 shows the effect of the times of catalyst recycling on the reaction yield in 15 min. This figure clearly shows that five times recycling and the reuse of the catalyst do not have negative effects on the reaction yield. This behavior indicates that the sulfate group leaching from the catalyst surface and other physical and chemical damages were negligible in this catalyst at least for five times recycling.

2.8. Catalyst efficiency

Table 1 shows the effect of catalyst on the reaction rate of the esterification reaction. One can see in Table 1 that in the case of acetonitrile, sulfated titania has a weaker catalytic effect in comparison with the conventional inorganic acid catalyst (sulfuric acid), but in DMSO and 2-hydroxyethylammonium formate, sulfated titania has a strong catalytic effect than sulfuric acid. As mentioned in Section 2.6, the solubility of reactants in acetonitrile is better than that in DMSO and ionic liquid. Thus, in acetonitrile, a homogeneous catalyst (sulfuric acid) was better



Figure 7. Effects of catalyst recycling of reaction yield in 15 min.

Table 1. Catalyst effects on the reaction rate of esterification of phthalic anhydride and 2-octanol in various solvents.

Solvent	Catalyst	Pseudo-first-order reaction rate constant (s^{-1} g^{-1})
Acetonitrile	No catalyst	0.00310
Acetonitrile	Sulfuric acid	0.01367
Acetonitrile	Sulfated titania	0.00247
DMSO	No catalyst	0.00514
DMSO	Sulfuric acid	0.01911
DMSO	Sulfated titania	0.03468
Ionic liquid	No catalyst	0.01043
Ionic liquid	Sulfuric acid	0.03178
Ionic liquid	Sulfated titania	0.04214

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than a heterogeneous catalyst; in contrast, in DMSO and ionic liquid, the solubility of reactants is weak, and thus the tendency of reactants to adhere to the surface of the heterogeneous catalyst is more than acetonitrile. As a result, in these solvents, the heterogeneous catalyst works better than the conventional homogeneous acid catalyst.

3. Conclusions

The pseudo-first-order reaction rate constants of the esterification of phthalic anhydride with 2-octanol were obtained at the reflux condition in three solvents (acetonitrile, DMSO and 2-hydroxyethylammonium formate). The results show that with increasing dipolarity/polarizibility parameters (π^*) of the solvents, one can see the increase in reaction rate constants. As an explanation, we think that the increase in solvent polarity can decrease the solubility of the reactants in the solvent, and thus, the concentration of the reactants on the catalyst surface was increased. The increase in the reactants on the catalyst surface results in the increase in the reaction rate.

4. Experimental

Phthalic anhydride, titania and sulfuric acid were purchased from Merck. 2-Octanol was purchased from RIEDEL-DE HAEN and used without further purification. The reactor consisted of a 50 ml two-necked Pyrex flask fitted with a reflux condenser and a stopper. The temperature was controlled with a glycerin bath. In a typical kinetic run, 0.5 g of acid was mixed with 4.5 ml of alcohol, 0.02 g of catalyst and sufficient amount of solvent (in each run varies between 0.5 and 3 ml) in a 50 ml flask and heated to the boiling point of the mixture. SO_4^{2-}/TiO_2 was prepared by immersing TiO₂ in 1 N H₂SO₄ solution for 30 min and then decanted and dried from 80 °C to 150 °C. The resultant solid was calcinated at 500 °C and powdered. The catalyst was characterized with XRD, FT-IR and BET methods. The reaction mixture was analyzed by the titration method. The unconverted acid was determined by standardized 0.1 N NaOH.

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