Surface Acidity and Catalytic Activity of Tungstophosphoric Acid Supported Mesoporous Zirconia Catalyst

Awad I. Ahmed, A.A. El-Khouly and Y. S. Samy*

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

* Author to whom correspondence should be addressed; E-Mail: yostinasamir89@hotmail.com;

Article history: Received 3 September 2013, Received in revised form 29 September 2013, Accepted 3 October 2013, Published 8 October 2013.

Abstract: Mesostructure zirconium oxide (ZrO₂) was synthesized using a cationic surfactant (cetyltrimethyl-ammonium bromide, CTAB) as the organic supramolecular template. After calcination at 550°C, mesoporous ZrO₂ was modified with different loading of tungstophosphoric acid TPA and calcined at 400 °C. The 25 wt% TPA/ZrO₂ samples were calcined at 400, 500 and 600 °C to study the effect of calcination temperature on the chemical and physical properties of catalysts. The surface acidity was measured with nonaqueous titration of n-butyl amine in acetonitrile. FT-IR spectrum of pyridine adsorbed on the catalysts showed the presence of both Brønsted and Lewis acid sites that increased with increasing TPA content. The catalytic activity was tested by the Pechmann reaction of TPA/ZrO₂. The catalytic activity well associated with Brønsted acid sites of these catalysts. The catalyst was reused for three times with excellent yield from 7-hydroxy-4-methyl coumarin.

Keywords: zirconium oxide, TPA, coumarin, CTAB.

1. Introduction

Mesoporous materials have attracted much interest due to their large surface area and narrow pore size distribution, which make them ideal candidates for catalysts, molecular sieves, and electrodes in solid-state ionic devices [1,2]. The mesoporous materials were also important because the regular pore
structure can serve as a support for conductive and magnetic materials, leading to quantum wires for smart electronic devices [3,4]. Solid acids have emerged as potential alternate catalysts to homogeneous liquid acids [5,6] due to their non-hazardous nature, requirements in catalytic amounts, enhanced selectivity and easier post-reaction work-up. The ease of separation without resulting into problem of waste disposal. Heteropolyacids (HPA) has got extensive studies as an efficient solid acid catalyst due to its unique advantages, such as strong Brönsted acidity, structure alterability and environmental friendliness [7,8]. Nowadays, most studies focus on the catalytic behaviors of the Keggin structured TPA [9], among which 12-tungstophosphoric acid with the formula of H₃PW₁₂O₄₀ is known to be a highly active catalyst for a variety of acid-catalyzed reactions [10,11]. Supported heteropolyacids are important for many applications, because bulk HPAs have low specific surface area (1–10m²/g). In the case of unsupported heteropolyacids, when the reactants have a polar character, the catalytic reactions occur not only at the surface but also in the bulk of the solid heteropolyacids [12]. This is the reason why in spite of their low surface areas, they demonstrate quite high catalytic activity. When non-polar reactants are used, it is important to increase the surface area or even better to increase the number of accessible acid sites of the HPA. This can be achieved by dispersing the heteropolyacids on solid supports with high surface areas [13,14]. Coumarin and its derivatives have been attracting great interest because they occupy a special place in the realm of natural products and synthetic organic chemistry. Among the various coumarin derivatives, 7-substituted coumarin are consisting an important group of coumarin derivatives showing various bioactivities and also other applications [15]. For example, 7-hydroxy-4-methyl coumarin (β-ethylumbelliferone) is used as fluorescent brightener, efficient laser dye, standard for fluorometric determination of enzymatic activity, as a starting material for the preparation of insecticide and furano coumarin [16-18]. For the synthesis of 7-hydroxy-4-methyl coumarin only few studies are reported [19] using solid catalysts. Here, we will use ZrO₂ as a catalyst support for different amounts of tungstophosphoric acid (TPA) and study the effect of TPA content and calcination temperature on the acidic properties and formation of 7-hydroxy-4-methyl coumarin via the Pechmann reaction of resorciol and ethyl acetoacetate of pure ZrO₂ catalysts.

2. Experimental

2.1. Synthesis of Catalysts

The synthesis method was based on the use of cationic surfactant (CTAB), as structure directing agent, and the simple chemical materials [ZrOCl₂·8H₂O and NH₄OH], as inorganic precursor and counterions respectively. Reaction was performed at room temperature. The synthetic procedure (ZrO₂) was as follows: 3g CTAB were mixed with 25mL distilled water with stirring until a homogenous solution was obtained, 2mL NH₄OH was then added into the CTAB solution with stirring, when the
mixing solution became homogenous, a Zr$^{4+}$ solution of 13g ZrOCl$_2$.8H$_2$O diluted with 25mL distilled deionized water was introduced producing a white slurry. After stirring 3h the resulting product was filtered washed with distilled water to remove the chloride ions, dried at 120 °C overnight in an oven. The dried samples were calcined at 550°C for 6 hrs to get pure mesoporous zirconium oxide. The ZrO$_2$ were impregnated with the appropriate amount of TPA solution to obtain, 5, 10, 15, 25, 35 and 50 wt% TPA. These samples were dried at 120°C for 24 hrs, followed by calcination at 400, 500, and 600°C for 2hrs in a muffle furance. In the designation of these samples, the roman numbers I, II and III refers to the calcination temperatures. The designation 25TPA-Zr-III indicates the sample containing 25 wt% TPA and calcined at 600°C.

2.2. Surface Acidity Measurements

2.2.1. Non aqueous potentiometric titration

The total acidity of all catalysts was determined by means of the n-butylamine titration method [20-22], using an orion 420 digital A model using a double junction electrode. In this method 0.1 gm catalyst was heated under vacuum, then 10 mL of acetonitrile was added, and after agitation for 2 hours the suspension was titrated by 0.01 N n-butylamine in acetonitrile.

2.2.2. Pyridine adsorption

The nature of acid sites and the Lewis and Bronsted acid sites ratio were determined by pyridine adsorption at room temperature. 0.1g of each sample was degassed at 250°C for 2h to reduce the amount of adsorbed molecular water. Following, the evacuation the samples were maintained in contact with pyridine vapour at room temperature, for 1 month. The FT-IR spectra of the samples were conducted using Mattsoh 5000 FT-IR spectrophotometer; by mixing 0.01g of the sample with 0.1g KBr in 30 mm diameter self supporting discs were used.

2.3. Catalytic Activity

A mixture of resorcinol (1.1 g,10 mmol) and ethyl acetoacetate (2.5 mL , 20 mmol) was added in a 50 mL round flask. The flask containing the reaction mixture was placed in oil bath and refluxed for 2h at 120°C, in the presence of (0.1 g) of activated catalyst . The reaction mixture was filtered by pouring into 50mL beaker containing crushed ice. The product was characterized by melting point and FT-IR spectroscopy. The yield of coumarin derivative was obtained as follows:

\[
\text{Yield(wt\%)} = \frac{\text{obtained weight of product}}{\text{Theoretical weight of product}} \times 100
\]
3. Results and Discussion

3.1. Surface Acidity

3.1.1. The results from non-aqueous titration

The acidity measurements of the catalysts by means of potentiometric titration with n-butyl amine [23, 24] were used to estimate the number of acid sites and their relative acid strength according to the values of the initial electrode potential (E_i). On the other hand, the acid strength of these sites may be classified according to the following scale [25]: E_i > 100 mV (very strong sites), 0 < E_i < 100 mV (strong sites), -100 < E_i < 0 mV (weak sites) and E_i < -100 mV (very weak sites). The potentiometric titration curves obtained for the prepared catalysts are shown in Fig.1. Moreover, the computed number of the acid sites as well as the values of the initial electrode potential (E_i) are listed in table 1.

![Fig. 1: Potentiometric titration curves of n-butylamine in acetonitrile for (a) Zr-550°C, (b) 5 TPA-Zr-I, (c) 10 TPA-Zr-I, (d) 15 TPA-Zr-I, (e) 25 TPA-Zr-I, (f) 35 TPA-Zr-I and (g) 50 TPA-Zr-I samples.](image)

As shown in table 1, it seems that zirconium oxide presented weak acid sites (E_i = +86.3 mV), addition of TPA was accompanied by a gradual increase in both surface acidity and acid strength to 25wt% TPA (E_i = +568.0 mV). These results indicate that 25 TPA/ZrO_2 contains the strongest and the highest number of acid sites, this may be due to the high dispersion of acidic protons of TPA on the
surface of ZrO$_2$ [26], which leads to the strong interaction of TPA with the support and the generation of acid sites [27]. The total number of acid sites/g = (equiv./g) x N/1000, where N is Avogadro’s number. The value of meq amine /g solid. Where the plateau is reached, indicates the total number of acid sites that presented in Fig. 1. The total acidity and acid strength of the catalysts calcined at 400, 500 and 600$^\circ$C are decreased with increasing the calcination temperature. This is possibly due to multilayer formation, bulk properties of TPA will be more predominant, causing destruction of TPA to yield WO$_3$ crystallites. The initial electrode potential ($E_i$) indicates the maximum acid strength of the sites.

### Table 1: Total number of acid sites for TPA-Zr catalysts with different calcination temperatures.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>No. of acid sites/g x10$^{-19}$</th>
<th>$E_i$(mV)</th>
<th>B/L</th>
<th>Yield% of coumarin</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>6.5</td>
<td>74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 TPA/ZrO$_2$-I</td>
<td>6.98</td>
<td>184.6</td>
<td>3.01</td>
<td>36.6</td>
</tr>
<tr>
<td>10 TPA/ZrO$_2$-I</td>
<td>8.13</td>
<td>267.1</td>
<td>5.67</td>
<td>51.4</td>
</tr>
<tr>
<td>15 TPA/ZrO$_2$-I</td>
<td>10.72</td>
<td>448.1</td>
<td>5.92</td>
<td>62.9</td>
</tr>
<tr>
<td>25 TPA/ZrO$_2$-I</td>
<td>12.47</td>
<td>568.0</td>
<td>6.09</td>
<td>97.1</td>
</tr>
<tr>
<td>35 TPA/ZrO$_2$-I</td>
<td>9.09</td>
<td>364.7</td>
<td>1.41</td>
<td>85.7</td>
</tr>
<tr>
<td>50 TPA/ZrO$_2$-I</td>
<td>6.87</td>
<td>138.4</td>
<td>1.18</td>
<td>47.4</td>
</tr>
<tr>
<td>25 TPA/ZrO$_2$-II</td>
<td>7.89</td>
<td>246.7</td>
<td>0.96</td>
<td>45.1</td>
</tr>
<tr>
<td>25 TPA/ZrO$_2$-III</td>
<td>6.74</td>
<td>104.6</td>
<td>0.54</td>
<td>28.6</td>
</tr>
</tbody>
</table>

#### 3.1.2. Pyridine adsorption

The types and strengths of acid sites on solid catalysts can be measured simultaneously by using pyridine adsorption in conjunction with FTIR spectroscopy; however, the accuracy of each measurement may be comprised to the non-selective adsorption of pyridine. The FTIR spectra of pyridine adsorbed on the acid sites of the catalysts exhibited bands characteristic for Lewis acid sites as well as Brønsted acid sites. The percentage of Lewis-Brønsted acid sites can be calculated by using the integrated areas or the relative intensity of the characteristic bands of pyridine adsorbed on Lewis and/or Brønsted acid
sites. In this study the ratio of Brønsted to Lewis acid sites was calculated by using the integrated areas [28, 29].

The infrared spectra in the spectral region 1700-1400 cm\(^{-1}\) of adsorbed pyridine on the different samples of mesoporous ZrO\(_2\) calcined at 550°C and 5-50 wt.% TPA/ZrO\(_2\) calcined at 400°C are shown in Fig. 2. The samples show typical bands of adsorbed pyridine at around 1484 cm\(^{-1}\) on Lewis acid sites and 1533 cm\(^{-1}\), 1632 cm\(^{-1}\) on Brønsted acid sites, in addition, the band at 1502 cm\(^{-1}\) indicates the formation of the adjacent Lewis and Brønsted acid sites together [30]. The bands located at around 1533 cm\(^{-1}\) and 1632 cm\(^{-1}\) are due to pyridinium ion (PyH\(^+\)) reflecting its interaction with Brønsted acid sites, and bands at 1484 cm\(^{-1}\) are characteristic for coordinatively bonded pyridine on electron acceptor sites (Lewis center). The ratio of Brønsted to Lewis acid sites is presented in table 1. From table 1 and Fig. 3, it can be seen that, the ratio of Brønsted to Lewis acid sites increases gradually with increasing the TPA loading to reach a maximum at 25wt% TPA/ZrO\(_2\) loading, then decreases. The increase in the ratio of Brønsted to Lewis acid sites with an increase in TPA loading may be due to weak interaction of TPA with precalcined ZrO\(_2\) at 550°C, giving rise to excess free acidic protons of TPA on the surface of ZrO\(_2\) [31]. The decrease in surface acidity with an increase in TPA loading above 25 wt. % may be due to the aggregation of TPA on ZrO\(_2\) surface that will lead to a decrease in the surface acidity.

![Fig. 2: FT-IR spectra of pyridine adsorbed on (a) ZrO\(_2\) (550°C), (b) 5%, (c) 10%, (d) 15%, (e) 25%, (f) 35% and (g) 50% TPA/ZrO\(_2\) calcined at 400°C.](image-url)
Fig. 3: Effect of TPA content on Brønsted to Lewis acid sites ratio of TPA/ZrO$_2$ samples.

The effect of calcinations temperature on the infrared spectra of the adsorbed pyridine for the sample 25% TPA/ZrO$_2$ is shown in Fig. 4. From table 1 and Fig. 5, the ratio of Brønsted to Lewis acid sites decreases gradually with increasing the calcination temperature. This may be due to increase of the W atoms density on ZrO$_2$ surface with increase calcination temperature due to destruction of TPA to yield WO$_3$.

Fig. 4: FT-IR spectra of pyridine adsorbed on 25% TPA/ZrO$_2$ sample calcined at (a) 400$^\circ$, (b) 500$^\circ$ and (c) 600$^\circ$C.
3.2. Catalytic Activity for Synthesis of 7-hydroxy-4-methyl Coumarin

The synthesis of 7-hydroxy-4-methyl coumarin was carried out by using 1.1 g resorcinol and 2.5 mL ethylacetoacetate with 0.1 g of the activated catalyst. The reaction was carried out in oil bath at 120°C under stirring for 2 h. After the reaction, the product was separated by transferring the hot reaction mixture in ice bath and stirring for around 15 min, then filtration. The product was characterized by melting point (m.p = 185 °C) [32].

3.2.1. Effect of molar ratio

The effect of molar ratio on the formation of 7-hydroxy-4-methyl coumarin in presence of 25 wt% TPA/ZrO₂ is presented in Fig. 6. It can be observed that the percentage yield of 7-hydroxy-4-methyl coumarin increases from 44.6% to 97.1% with the increase in the molar ratio of resorcinol: ethylacetoacetate from 1:1 to 1:2. A further increase of this molar ratio to 1:3 was accompanied by a remarkable decrease in the percentage yield of 7-hydroxy-4-methyl coumarin to 74.3%. The decrease in catalytic activity may be explained on the basis of the fact that the increase in the ethylacetoacetate concentration hinders the reaction by blocking the active sites on the catalyst surface [33].

3.2.2. Effect of weight percentage on TPA on the catalytic activity

Fig. 7 and table 1 show that the yield of 7-hydroxy-4-methyl coumarin increases gradually with increasing the amount of TPA loaded on ZrO₂ till reaches a maximum (97.1%) over the 25 wt% TPA/ZrO₂ catalyst, then decreases. It can be also noticed that the 7-hydroxy-4-methyl coumarin yield
similarly changes as the ratio of Brønsted to Lewis acid sites. Therefore, the reaction yield increases with the increase in Brønsted to Lewis acid sites ratio. This results shows that the catalytic activity and Brønsted to Lewis acid sites ratio increases with increase in TPA loading up to 25wt% TPA/ZrO₂, then decrease with further increase in TPA content.

Fig. 6: Effect of molar ratio on the yield % 7-hydroxy-4-methylcoumarin over 25 wt.% TPA/ZrO₂ catalyst.

Fig. 7: Effect of TPA content on the % 7-hydroxy-4-methyl coumarin and B/L ratio for TPA/ZrO₂ catalysts calcined at 400°C.
3.2.3. Effect of calcination temperature on the catalytic activity

The effect of the calcination temperatures on the yield of 7-hydroxy-4-methyl coumarin over the 25wt% TPA/ZrO$_2$ catalyst is shown in Table 1 and Fig. 8. It can be seen that with increasing the calcination temperatures the yield of 7-hydroxy-4-methyl coumarin decreases. This may be due to the decrease in the catalyst acidity and number of Brønsted acid to Lewis acid ratio as result of the decomposition of TPA into its constituent oxides [9]. The sharp decrease in both of Brønsted to Lewis acid ratio and the catalytic activity with the increase in the calcination temperature up to 600°C indicates that the plausible mechanism for the formation of 7-hydroxy-4-methyl coumarin takes place through the chemisorptions of carbonyl group of ethyl acetoacetate on the Brønsted acid sites of the catalyst [34]. This is followed by a nucleophilic attack by resorcinol on it to give the intermediate which rapidly undergoes cyclization through intramolecular condensation yielding 7-hydroxy-4-methylcoumarin.

![Fig. 8: Effect of calcination temperature on the % 7-hydroxy-4-methyl coumarin and B/L ratio for 25% TPA/ZrO$_2$ catalysts.](image)

3.2.4. Reusability study

Reusability of the catalyst is an important aspect of any industrial process. For this purpose, reusability of the catalyst 25% TPA/ZrO$_2$ is tested by carrying out repeated runs of the reaction at 120°C, keeping the reactants molar ratio (resorcinol: ethyl acetoacetate) at 1:2. In order to regenerate the catalyst
after each 4hrs reaction, it was separated by filtration, washed with distilled water several times, dried and calcined at 400°C for 2 hrs. The reaction was again performed on the reactivated catalyst at 120°C.

Fig. 9 shows effect of recycle times on the amount of 7-hydroxy-4-methyl coumarin. It was observed with increasing number of cycles of the reaction, the catalytic activity of catalysts is slightly decreased (97.1%, 93.7% and 87.4%). Several studies have been carried out to study the effect of reusability times on the catalytic activity of catalysts. For example Ahmed et al. [35] found the yield percent of 7-hydroxy-4-methyl coumarin decreases with reuse times 95.8%, 88.6% and 78.2% in the fresh and used catalysts. Khder et al. [32] have reported the yield percentage of 7-hydroxy-4-methyl coumarin decreases to 96%, 95.4% and 93.8% indicates excellent reusability with activity loss from the first run (96%).

![Fig. 9: Effect of reuse of the 25wt%TPA/ZrO₂ catalyst on %Yield percentage of 7-hydroxy-4-methyl coumarin.](image)

### 4. Conclusion

The potentiometric titration with n-butylamine and FT-IR spectra can be used to perform the characterization of 12-tungstophosphoric acid impregnated on zirconium oxide prepared by impregnation of powdered ZrO₂ calcined at 550°C with TPA aqueous solution followed by calcination in air at 400°C. The acidity of catalysts increases in proportion to the TPA content up to 25% TPA-Zr-I. The correlation between catalytic activity and acidity holds for synthesis of 7-hydroxy-4-methyl...
coumarin. The optimum conditions have been found that, the molar ratio of resorcinol: ethylacetoacetate is 1:2 and reaction time is 2 hrs. Catalyst activity also indicates that the activity for synthesis of 7-hydroxy-4-methyl coumarin is related to the availability of Brønsted acid sites originated from the Keggin structure of TPA anions which in turn depends of the TPA content and calcination temperature.

References


