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Active, Selective, and Recyclable $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/Activated$ Carbon Solid Acid Catalysts for Esterification of Malic Acid to Dimethyl Malate

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Received: 6 March 2020; Accepted: 25 March 2020; Published: 1 April 2020



Abstract: The esterification of malic acid using traditional homogenous catalysts suffers from the difficulty in reuse of the catalyst and undesirable side reactions. In this work, $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/activated carbon (AC)$ as solid acid catalysts were prepared for malic acid esterification with methanol. The conversion of malic acid over these two catalysts is comparable to that over H_2SO_4 and unsupported $Zr(SO_4)_2$ ·4H₂O catalysts; however; a 99% selectivity of dimethyl malate can be realized on these two supported catalysts, which is much higher than that of conventional H_2SO_4 (75%) and unsupported $Zr(SO_4)_2$ ·4H₂O (80%) catalysts, highlighting the critical role of AC and SiO₂ supports in tuning the selectivity. We suggest that the surface hydroxyls of AC or lattice O^{2-} ions from SiO₂ donate electrons to Zr^{4+} in $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts, which results in the increase in electron density on Zr^{4+} . The enhanced electron density on Zr^{4+} reduces the degree of H delocalization from crystal water and then decreases the Brønsted acid strength. Consequently, the reduced Brønsted acid strength of $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts can be easily separated from the reaction system by simple filtration with almost no loss of activity.

Keywords: malic acid; catalytic esterification; solid acid catalyst; $Zr(SO_4)_2$; intermolecular dehydration

1. Introduction

Production of chemicals from biomass resources is a promising strategy for solving the problem of the depletion of fossil fuels. Malic acid as a biomass-derived molecule can be produced via the bio-fermentation of biomass. Converting renewable biomass-derived malic acid to various malic acid esters has attracted considerable attention because they are widely used in the production of spices, mosquito-repellent incenses, and intermediates of medicines [1–3]. Generally, the esterification of malic acid uses a traditional homogenous acid catalyst (such as sulfuric acid, para-toluene sulfonic acid, and phosphoric acid) to promote the reaction rate in industry. Although homogenous (liquid) acids show excellent catalytic activity for malic acid esterification, unfortunately, they present two main drawbacks: (1) These liquid catalysts are difficult to separate from the reaction mediums, and inevitably suffer from the problem of non-recyclability and environmental unfriendliness; (2) excess high-acid strength will cause undesirable side reactions, among which mainly include intramolecular dehydration and intermolecular dehydration of alcohols. In comparison, heterogeneous (solid) acid catalysts can overcome the un-recyclability of liquid acid and are, accordingly, strongly recommended

as the candidates. Besides, some other general green methodologies such as catalyst-free esterification have attracted the attention of increasingly more people [4,5].

To date, various solid acid catalysts comprising metallic oxides (e.g., TiO_2 , MoO_3 , ZrO_2-SiO_2) [6–9], sulfated metallic oxides, mesoporous carbons (e.g., SO_4^{2-}/ZrO_2 , SO_4^{2-}/SnO_2 , $SO_4^{2-}/La_2O_3/HZSM-5$, SO_4^{2-}/C) [10–16], inorganic salts (e.g., $Zr(SO_4)_2 \cdot 4H_2O$, $Ce(SO_4)_2 \cdot 4H_2O$) [17,18], acidic resins (e.g., Amberlyst-15) [19–21], and molecular sieves {e.g., HZSM-5, SnTUD-1, -SO₃H-functionalized Cr(III)-MOF (Metal-Organic Frameworks)} [22–26] have been utilized for the catalytic esterification of fatty acids. In particular, the $Zr(SO_4)_2 \cdot 4H_2O$ catalyst has been evidenced to have extraordinarily catalytic activity for esterification [27,28].

In spite of $Zr(SO_4)_2$ ·4H₂O exhibiting excellent catalytic performance for the esterification of fatty acid, unfortunately, it partially solutes in water, which comes from the product of esterification leading to inferior reusability [29]. Currently, an effective strategy for overcoming the leaching of $Zr(SO_4)_2$ is to immobilize $Zr(SO_4)_2 \cdot 4H_2O$ on various porous materials. Juan et al. synthesized the supported Zr(SO₄)₂·4H₂O/HMS catalyst and applied it to the catalytic esterification of oleic acids, and the supported catalyst could be reused in four consecutive cycles with almost no loss of activity, which is dramatically superior to the unsupported Zr(SO₄)₂·4H₂O [28]. Furthermore, not only the improvement in the reusability but also an obvious enhancement in the catalytic performance of the supported $Zr(SO_4)_2 \cdot 4H_2O$ catalysts compared to unsupported $Zr(SO_4)_2 \cdot 4H_2O$ could be observed [30]. Sohn et al. found that the catalytic activity of $Zr(SO_4)_2/\gamma$ -Al₂O₃ was higher than that of bulk $Zr(SO_4)_2$ ·4H₂O for 2-propanol dehydration and cumene dealkylation, and they suggested that the higher acid strength of $Zr(SO_4)_2/\gamma$ -Al₂O₃ than unsupported $Zr(SO_4)_2$ ·4H₂O may be responsible for enhancing the activity [31]. Lavrenov and coworkers have reported that the selectivity of alkylation over a $Zr(SO_4)_2$ /silica gel catalyst appeared to be better than that of the unsupported catalyst for the alkylation of isobutane with butene, and the intrinsic investigation revealed that the more uniform distribution of strong acid centers on the supported catalysts ensured highly selective alkylation [32]. In general, the interaction between $Zr(SO_4)_2 \cdot 4H_2O$ and the support can modify the acid properties of the catalyst, which may bring about a positive effect on the activity and selectivity.

Herein, the present work is devoted to synthesizing recyclable solid acid catalysts $(Zr(SO_4)_2/activated carbon (AC) and Zr(SO_4)_2/SiO_2)$ for the esterification of malic acid to dimethyl malate with high selectivity. The catalytic performance of these two catalysts was examined and compared to that of traditional H₂SO₄ and unsupported Zr(SO₄)₂·4H₂O catalysts. Furthermore, X-ray diffraction (XRD), N₂ physical adsorption, X-ray photoelectron spectra (XPS), and pyridine adsorption infrared (IR) techniques were executed on Zr(SO₄)₂·4H₂O, Zr(SO₄)₂/AC, and Zr(SO₄)₂/SiO₂ catalysts to determine the structure and acid properties of these catalysts. The crucial function of the AC and SiO₂ support tuning the selectivity was extensively and thoroughly investigated. In addition, the influence of different experimental parameters on the catalytic behavior was evaluated in order to find the most suitable conditions for dimethyl malate production. In addition, the reusability of Zr(SO₄)₂/AC and Zr(SO₄)₂/SiO₂ catalysts was examined.

2. Results and Discussion

The crystalline structures of various $Zr(SO_4)_2$ catalysts are shown in Figure 1, where pattern (1) is the typical XRD pattern of an orthorhombic phase of $Zr(SO_4)_2 \cdot 4H_2O$ (PDF#08-0495), and all of the diffraction peaks can be assigned to an orthorhombic phase of $Zr(SO_4)_2 \cdot 4H_2O$. For $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts, only weaker diffraction peaks around $2\theta = 20.5^\circ$, 25.7° , and 30.0° assigned to the $Zr(SO_4)_2 \cdot 4H_2O$ phase were detected. The attendance of diffraction peaks attributed to the $Zr(SO_4)_2 \cdot 4H_2O$ phase in $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ samples suggests that $Zr(SO_4)_2 \cdot 4H_2O$ was successfully supported on SiO₂ and AC. Furthermore, diffraction peaks attributed to $Zr(SO_4)_2 \cdot 4H_2O$ of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ samples are weaker than those of the unsupported sample, manifesting that $Zr(SO_4)_2 \cdot 4H_2O$ was well dispersed on AC and SiO₂.



Figure 1. XRD patterns of (1) $Zr(SO_4)_2 \cdot 4H_2O_2$, (2) $Zr(SO_4)_2/SiO_2$, and (3) $Zr(SO_4)_2/activated$ carbon (AC).

 $Zr(SO_4)_2$ loading and textural properties of SiO₂, $Zr(SO_4)_2/SiO_2$, AC, and $Zr(SO_4)_2/AC$ samples are summarized in Table 1. The Zr amounts in $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts were detected by inductive coupled plasma optical emission spectroscopy (ICP-OES) analysis, and the active species Zr(SO₄)₂ loadings on these two catalysts were then calculated according to the Zr amounts. The actual $Zr(SO_4)_2$ loadings on $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts were ca. 30% (Table 1). The Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size were determined according to N_2 physical adsorption isotherms (Figure S1). The surface areas of $Zr(SO_4)_2/SiO_2$ (139 m²/g) and $Zr(SO_4)_2/AC$ (468 m²/g) catalysts are drastically smaller than those of SiO₂ (214 m²/g) and AC (1053 m^2/g) supports, respectively, but which are still higher than that of bulk $Zr(SO_4)_2 \cdot 4H_2O(5-11 m^2/g)$ [28]. Higher surface area is favorable for dispersing active sites and tends to give higher catalytic activity. On the other hand, the mesopore volume and size of $Zr(SO_4)_2/SiO_2$ are obviously lower than those of the SiO₂ support, which indicates that $Zr(SO_4)_2 \cdot 4H_2O$ deposits on the mesopores of SiO₂. For the $Zr(SO_4)_2/AC$ catalyst, the micropore volume and size of $Zr(SO_4)_2/AC$ are slightly lower than those of AC; however, the mesopore volume and size of $Zr(SO_4)_2/AC$ are obviously lower than those of AC. These results manifest that $Zr(SO_4)_2.4H_2O$ prefers to deposit on the mesopores than the micropores of AC. As we know, the presence of mesopores in a catalyst is significantly important for the liquid phase catalytic reaction, because mesopores facilitate the mass transfer in the liquid phase, which is beneficial to the contact between the catalyst and reactant.

Sample	Zr(SO ₄) ₂ Loading (wt.%)	BET Surface Area (m²/g)	Pore Volume (mL/g)		Average Pore Size (nm)	
			V _{micro}	V _{meso}	D _{micro}	D _{meso}
SiO ₂	-	214	-	1.40	-	26.8
Zr(SO ₄) ₂ /SiO ₂	28.5	139	-	0.95	-	22.5
AC	-	1053	0.34	0.21	1.39	14.8
Zr(SO ₄) ₂ /AC	27.9	468	0.33	0.11	1.19	7.8

Table 1. $Zr(SO_4)_2$ loadings and textural properties of SiO₂, $Zr(SO_4)_2/SiO_2$, AC, and $Zr(SO_4)_2/AC$ samples.

Figure 2 shows the catalytic performance of H_2SO_4 , $Zr(SO_4)_2 \cdot 4H_2O$, $Zr(SO_4)_2/SiO_2$, and $Zr(SO_4)_2/AC$ catalysts for conversion of malic acid. The conversion of malic acid over $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ solid acid catalysts is comparable to that over H_2SO_4 and unsupported $Zr(SO_4)_2 \cdot 4H_2O$ catalysts (Figure 2a) from 20 to 120 min; however, the selectivities of dimethyl malate (DM) over $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts are both 99% at 120 min, which are 0.24 and 0.19 times higher than those of the conventional H_2SO_4 (75%) catalyst and unsupported $Zr(SO_4)_2 \cdot 4H_2O$ (80%) catalyst, respectively, highlighting the critical role of AC and SiO_2 supports in tuning the selectivity. Besides, the yield of DM over $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts is obviously higher than those over

 H_2SO_4 and $Zr(SO_4)_2 \cdot 4H_2O$ catalysts (Figure 2c). Consequently, pyridine adsorption IR and XPS were carried out on the supported and unsupported $Zr(SO_4)_2 \cdot 4H_2O$ catalysts to investigate the function of AC and SiO₂ support.



Figure 2. Dependence of (**a**) conversion of malic acid, (**b**) selectivity of dimethyl malate (DM) and 2-methoxy dimethyl succinate (DS) and (**c**) yield of dimethyl malate (DM) on reaction time over H_2SO_4 , $Zr(SO_4)_2$ ·4 H_2O , $Zr(SO_4)_2$ /SiO₂, and $Zr(SO_4)_2$ /AC catalysts. Reaction conditions: Methanol (5 mL), malic acid (1 g), catalyst amount (0.1 g), reaction time (2 h), reflux temperature, stirring speed (600 rpm).

The main side product was 2-methoxy dimethyl succinate (DS) whose structure is graphed in Equation (2) over the $Zr(SO_4)_2 \cdot 4H_2O$ catalyst by the GC-MS (gas chromatography with mass spectrometry) result. We speculate that DS may have come from the intermolecular dehydration of malic acid with methanol. Thus, the esterification main reaction (Equation (1)) competed with the intermolecular dehydration side reaction (Equation (2)) over the $Zr(SO_4)_2 \cdot 4H_2O$ catalyst. As we know, esterification and intermolecular dehydration reaction rates both strongly rely on the properties of acid catalysts. The mechanism for the esterification of acid with alcohol over an acid catalyst is as follows: A proton bonds with O from carbonyl to enhance the electron-deficiency of C from carbonyl, which is beneficial to the nucleophilic attack of alcohol [33]. The mechanism for the intermolecular dehydration of alcohol over the acid catalyst is that the proton bonds with the O from hydroxyl to facilitate dehydration [34,35].

$$COOHCH(OH)CH_2COOH + 2CH_3OH \rightarrow COOCH_3CH(OH)CH_2COOCH_3 + 2H_2O$$
(1)

$$COOHCH(OH)CH_2COOH + 3CH_3OH \rightarrow COOCH_3CH(OCH_3)CH_2COOCH_3 + 3H_2O$$
(2)

The acidity of $Zr(SO_4)_2.4H_2O$, $Zr(SO_4)_2/SiO_2$, and $Zr(SO_4)_2/AC$ catalysts was examined by pyridine adsorption IR, as shown in Figure 3. The band at 1539 cm⁻¹ is the characteristic peak of pyridinium ions, which are adsorbed on the Brønsted (B) acid sites, while the characteristic peak at 1445 cm⁻¹ is assigned to pyridine coordinately bonded to Lewis (L) acid sites [36]. As shown in Figure 3, L and B acid sites both exist on the surface of $Zr(SO_4)_2.4H_2O$, $Zr(SO_4)_2/SiO_2$, and $Zr(SO_4)_2/AC$. According to the previous research, L acid sites of $Zr(SO_4)_2.4H_2O$ come from the electron-deficiency of Zr^{4+} . B acid sites of $Zr(SO_4)_2.4H_2O$ originate from the interaction of crystal water with Zr^{4+} , and the increase in electron-deficiency of Zr^{4+} enhances the degree of H delocalization from crystal water and then increases the B acid strength [30,31,37]. The concentrations of B and L acid sites can be obtained by Equations (3) and (4) based on the integrated absorbance of B and L bands [36]. The concentrations of L and B acid sites of $Zr(SO_4)_2.4H_2O$, $Zr(SO_4)_2/SiO_2$, and $Zr(SO_4)_2/AC$ are listed in Table 2. For all of these three catalysts, the concentrations of B acid sites on these three catalysts are significantly higher than those of L acid sites. As we know, the esterification and intermolecular dehydration reactions occurring at lower temperature were catalyzed by the B acid rather than L acid.



Figure 3. Pyridine-adsorbed IR spectra of (1) $Zr(SO_4)_2 \cdot 4H_2O$, (2) $Zr(SO_4)_2/SiO_2$, and (3) $Zr(SO_4)_2/AC$ catalysts.

Table 2. Concentrations of B and L acid sites on prepared catalysts.

Catalyst	B Acid Sites (mmol/g)	L Acid Sites (mmol/g)
Zr(SO ₄) ₂ ·4H ₂ O	0.2011	0.0251
Zr(SO ₄) ₂ /SiO ₂	0.4182	0.0103
Zr(SO ₄) ₂ /AC	0.3057	0.0012

Because $Zr(SO_4)_2 \cdot 4H_2O$ reacts with NH₃ at higher temperature, NH₃-temperature programmed desorption (NH₃-TPD) is not suitable for the determination of acid strength of the catalyst. As in previous discussion, the B acid strength intensely depends on the electron-deficiency of Zr^{4+} in $Zr(SO_4)_2 \cdot 4H_2O$; therefore, we applied the XPS technique to characterize the electron density on Zr^{4+} , and to then determine the B acid strength of supported and unsupported $Zr(SO_4)_2 \cdot 4H_2O$. As shown in Figure 4a, the binding energy peaks at ca. 186 and 184 eV in $Zr(SO_4)_2 \cdot 4H_2O$, $Zr(SO_4)_2/SiO_2$, and $Zr(SO_4)_2/AC$ samples are ascribed to Zr^{4+} $3d_{3/2}$ and Zr^{4+} $3d_{5/2}$, respectively [28]. As shown in Figure 4b,c, the binding energy peak at 532.5 eV in AC is attributed to surface hydroxyls [38]; the binding energy peak at 532.5 eV in SiO₂ is assigned to O^{2-} ions [39,40].



Figure 4. (a) XPS spectra at Zr3d binding energy region, and (**b**,**c**) XPS spectra at O1s binding energy region.

Binding energies of the Zr_{3d} and O_{1s} regions of various samples are listed in Table 3. Zr $3d_{5/2}$ and Zr $3d_{3/2}$ binding energies of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ are 0.4 eV lower than those of $Zr(SO_4)_2 \cdot 4H_2O$, suggesting that the electron density on Zr^{4+} of supported $Zr(SO_4)_2 \cdot 4H_2O$ is higher than that of unsupported $Zr(SO_4)_2 \cdot 4H_2O$. The O_{1s} binding energy of $Zr(SO_4)_2/AC$ (533.1 eV) is higher than those of pure AC (532.5 eV) and bulk $Zr(SO_4)_2 \cdot 4H_2O$ (532.6 eV); similarly, the O_{1s} binding energy of $Zr(SO_4)_2/SiO_2$ (532.9 eV) is also higher than that of pure SiO₂ (533.8 eV) and bulk $Zr(SO_4)_2 \cdot 4H_2O$ (532.6 eV). These results illustrate that surface hydroxyls of AC or O^{2-} ions from SiO₂ donate electrons to Zr^{4+} in $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts, resulting in the decrease in electron density on oxygen and the increase in electron density on Zr^{4+} , which reduces the degree of H delocalization from crystal water and then decreases the B acid strength. The reduced B acid strength of $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts suppresses the intermolecular dehydration side reaction, thereby greatly enhancing the selectivity of dimethyl malate.

Table 3. Binding energies of the Zr3d and O1s regions of various samples.

Sample	BE _{Zr3d3/2} (eV)	BE _{Zr3d5/2} (eV)	BE _{O1s} (eV)
Zr(SO ₄) ₂ ·4H ₂ O	186.9	184.5	532.6
Zr(SO ₄) ₂ /SiO ₂	186.6	184.2	532.9
$Zr(SO_4)_2/AC$	186.6	184.2	533.1
SiO ₂	-	-	532.5
AC	-	-	532.5

The optimization of reaction parameters is very important for commercial feasibility. Figure 5 shows the influence of the catalyst amount of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts on the conversion of malic acid. Catalyst amount is defined as the weight ratio of a supported catalyst system to reactant malic acid. The esterification of malic acid was executed at different catalyst amounts while other parameters were kept constant. The conversion of malic acid by $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts increased along with the enhancing of the catalyst amount from 2 wt.% to 10 wt.%; however,

by further increasing the catalyst amount, the conversion of malic acid remains unchanged. This result indicates that the increase in catalyst amount from 2 wt.% to 10 wt.% enhanced the contact chance between the reactant and catalyst, which brings about the enhancement of conversion. By further increasing the catalyst amount, the conversion of malic acid is governed by other reaction conditions such as the mole ratio of methanol to malic acid, which is controlled by chemical reaction equilibrium. It is very interesting for the similar behavior observed for these two tested heterogeneous catalysts on Figure 5. For these two heterogeneous catalysts, the active species $Zr(SO_4)_2$ loadings are very similar (~30%), as shown in Table 1. In addition, AC or SiO₂ may only act as the role of structural promoter to disperse the active center. Thus, $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts show similar catalytic behavior when the active species $Zr(SO_4)_2$ loadings on these two heterogeneous catalysts are similar.



Figure 5. Effect of catalyst amount of (**a**) $Zr(SO_4)_2/SiO_2$ and (**b**) $Zr(SO_4)_2/AC$ catalysts on the conversion of malic acid. Reaction conditions: Methanol amount (5 mL), malic acid amount (1 g), reaction time (2 h), reflux temperature, stirring speed (600 rpm).

As we know, the esterification reaction is reversible and excess alcohol shifts the equilibrium to the right side of the reaction (Le Chatelier's Principle) in order to obtain a high yield of the ester product [41]. The molar ratio of methanol to malic acid was varied from 7:1 to 20:1 when the other parameters were kept constant. As shown in Figure 6, excess methanol significantly enhances the final conversion of malic acid. The conversion of malic acid over $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts reaches the maximum (~97%) at a 16:1 molar ratio of methanol to malic acid is no longer enhanced.

Figure 7 shows the reusability of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts. These two supported catalysts can be easily separated from the reaction system by simple filtration. The recyclability of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts were examined in a new reaction cycle without any treatment, such as calcination or washing. These two catalysts were reused in five consecutive cycles with very little loss of activity, further enhancing the feasibility of these catalysts in the esterification of malic acid. We have also checked the concentration of Zr ions in the solution and the $Zr(SO_4)_2$ loadings in the $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts after the reaction by using ICP-OES. There were negligible Zr elements detected in the solution after the first, second, third, fourth, and fifth cycles (Table S1), and

the $Zr(SO_4)_2$ amounts in the $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts before and after five cycles of reaction were almost not changed (Table S2), which indicates that the leaching of $Zr(SO_4)_2$ did not occur.



Figure 6. Effect of molar ratio of methanol to malic acid on the conversion of malic acid over (a) $Zr(SO_4)_2/SiO_2$ and (b) $Zr(SO_4)_2/AC$ catalysts. Reaction conditions: Malic acid amount (1 g), catalyst amount (0.1 g), reaction time (2 h), reflux temperature, stirring speed (600 rpm).



Figure 7. Recyclability of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts. Reaction conditions: Methanol (5 mL), malic acid (1 g), catalyst amount (0.1 g), reaction time (2 h), reflux temperature, stirring speed (600 rpm).

In order to enhance the feasibility of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts in the esterification of malic acid, we carried out the scale-up and esterification of malic acid with other alcohols (ethanol) experiments. The results and reaction conditions of scale-up and ethanol experiments are shown in Table S3 and Table S4, respectively. The conversion of malic acid achieved ca. 98% and the selectivity of DM reached 99% over the $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts, when the malic acid amount expanded 10 times (10 g). Besides, the malic acid conversion was 97% and diethyl malate selectivity was 99% with the application of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts for malic acid esterification by ethanol, which indicates that the applicability of $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ catalysts is extended to esterification by other alcohols.

3. Materials and Methods

3.1. Materials

 $Zr(SO_4)_2$ ·4H₂O, SiO₂ (Aerogel) of 99% purity, and dimethyl malate of 98% purity were purchased from Aladdin, Shanghai, CN. Malic acid of 98% purity was obtained from Macklin Shanghai, CN. H₂SO₄ (98%), HNO₃ (65–68%), and CH₃OH (99.5%) were purchased from Sinopharm Chemical Reagent, Shanghai, CN. AC was supplied by Changzhou University, Changzhou, Jiangsu, CN.

3.2. Catalyst Preparation

AC needed to be pretreated before use as a support. Typically, AC (10 g) was immersed in the 3 M HNO₃ under vigorous stirring at 70 °C for 4 h and was then washed with deionized water until neutral pH. Subsequently, the treated AC was dried at 110 °C in air overnight. The acid treatment can modify the surface properties of AC in favor of active component loading. Acid treatment for AC will introduce hydroxyl groups onto the AC surface, which can strengthen the interaction between the active species and AC support, thus enhancing the active species amount.

 $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts were prepared by an impregnation method with $Zr(SO_4)_2$ as the precursor, which were dried at 110 °C overnight and calcinated at 250 °C for 4 h; ultimately, $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts were obtained. The theoretical $Zr(SO_4)_2$ loading on AC or SiO_2 was 30 wt.%.

3.3. Catalytic Reaction

Catalytic esterification of malic acid with methanol was performed in a 50 mL three-necked flask. Certain amounts of malic acid (7.5 mmol, 1 g) and methanol (123.6 mmol, 5 mL) were added in the vessel. The typical reaction was carried out at reflux temperature with a 0.1 g catalyst under magnetic stirring of 600 rpm. Then, the post-reaction solution was analyzed by high-performance liquid chromatography (HPLC, Agilent, Santa Clara, CA, USA) and gas chromatography with mass spectrometry (GC-MS, Agilent, Santa Clara, CA, USA). The HPLC was equipped with a column (Aminex HPX-87H Ion Exclusion column 300 mm × 7.8 mm) and an ultraviolet detector. GC-MS was equipped with a flame ionization detector (FID) and HP-5MS column (30 m × 0.25 mm, 0.25 μ m). As the decomposition temperature of malic acid is 140 °C, which is much lower than the injection temperature (280 °C) of GC, GC-MS was not suitable for determining the conversion of malic acid. Therefore, the conversion of malic acid was determined by HPLC through the external standard method; the selectivity of dimethyl malate and side products was determined by GC-MS with n-pentane as the internal standard.

3.4. Catalyst Characterization

The Zr amounts in the catalysts and the concentration of Zr ions in the solution after the reaction were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer ICP-OES 7300DV, PerkinElmer, Waltham, MA, USA) measurements.

The structural information of the catalysts was determined by X-ray diffraction (XRD, Brucker D8 Advance, Madison, WI, USA), using Cu K_{α} radiation ($\lambda = 1.5405$ Å) under 40 kV and 40 mA at room temperature.

The N₂ physical adsorption/desorption isotherms of samples were obtained by a Micromeritics ASAP 2020 M+C apparatus (Norcross, GA, USA). Pretreatment of samples was conducted in vacuum for 4 h at 200 °C. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, the mesopore volume and mean mesopore size were determined by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherms, and the micropore volume and average micropore size were calculated by the t-plot method.

The acidity of the sample was determined by pyridine adsorption infrared (IR) on a Thermo Fisher Nicolet 6700 spectrometer (Thermo Fisher Nicolet, Waltham, MA, USA). Each finely ground

sample (ca. 30 mg) was pressed into a thin wafer with a diameter of 1.3 cm, and the thin wafer was then placed into a quartz cell equipped with CaF_2 windows. Before pyridine adsorption, the sample was evacuated at 200 °C for 4 h and cooled to room temperature. Then, pyridine as a molecular probe was exposed to the disk at room temperature for 1 h, and the sample was then evacuated at 150 °C for 1 h to remove the physical adsorption species on the surface; ultimately, the infrared spectrum was recorded. The concentrations of Brønsted (B) and Lewis (L) acid sites can be obtained by Equations (3) and (4) based on the integrated absorbance of B and L bands [36].

C (pyridine on B sites) = 1.88 IA (B)
$$R^2/W$$
, (3)
C (pyridine on L sites) = 1.42 IA (L) R^2/W . (4)
C = concentration (mmol/g catalyst)
IA (B, L) = integrated absorbance of B or L band
R = radius of catalyst disk (cm)
W = weight of disk (mg)

X-ray photoelectron spectra (XPS) were obtained with an ESCALAB 250 Xi (Thermal Fisher Scientific, Waltham, MA, USA) spectrometer equipped with a hemispherical electron analyzer and mono Al K_{α} 150 W X-ray source. The XPS spectra of AC and Zr(SO₄)₂/AC samples were calibrated by setting the sp² hybrid of the C 1s peak to 284.3 eV, and the XPS spectra of SiO₂, Zr(SO₄)₂·4H₂O, and Zr(SO₄)₂/SiO₂ samples were calibrated by setting the sp³ hybrid of the C 1s peak to 284.8 eV.

4. Conclusions

In summary, we applied $Zr(SO_4)_2/SiO_2$ and $Zr(SO_4)_2/AC$ as solid acid catalysts for malic acid esterification by methanol. These two solid acid catalysts exhibit outstanding catalytic activity, which is comparable to traditional H₂SO₄ and unsupported $Zr(SO_4)_2 \cdot 4H_2O$ catalysts. Moreover, a 99% selectivity of dimethyl malate can be realized on these two supported catalysts, which is much higher than that of the unsupported $Zr(SO_4)_2 \cdot 4H_2O$ (80%) catalyst, highlighting the critical role of AC and SiO₂ supports in tuning the selectivity. Pyridine-adsorbed IR combined with XPS reveals that surface hydroxyls of AC or O²⁻ ions from SiO₂ donate electrons to Zr^{4+} in $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts, resulting in the decrease in electron density on oxygen and the increase in electron density on Zr^{4+} , which reduces the degree of H delocalization from crystal water and then decreases B acid strength. The reduced B acid strength of $Zr(SO_4)_2/AC$ and $Zr(SO_4)_2/SiO_2$ catalysts suppresses the intermolecular dehydration side reaction, thereby greatly enhancing the selectivity of dimethyl malate. In addition, these two supported catalysts can be easily separated from the reaction system by simple filtration with almost no loss of activity.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/4/384/s1, Figure S1: N₂ physical adsorption isotherms of (a) SiO₂, (b) Zr(SO₄)₂/SiO₂, (c) AC, and (d) Zr(SO₄)₂/AC samples; Figure S2: GC-MS spectra of post-reaction solution over (1) Zr(SO₄)₂/SiO₂ and (2) Zr(SO₄)₂/AC catalysts. Table S1: The concentration of Zr ion in the solution after the reaction; Table S2: The Zr(SO₄)₂ loadings of Zr(SO₄)₂/SiO₂ and Zr(SO₄)₂/AC catalysts after the 5 cycles reaction; Table S3: Scale-up experimental results over Zr(SO₄)₂/SiO₂ and Zr(SO₄)₂/AC catalysts. Table S4: Catalytic performance of Zr(SO₄)₂/SiO₂ and Zr(SO₄)₂/AC catalysts for malic acid esterification by ethanol.

Author Contributions: Conceptualization, P.Y. and G.L.; methodology, P.Y. and Z.W.; software, P.Y.; validation, G.L. and Z.W.; formal analysis, P.Y. and C.C.; investigation, C.C.; resources, X.L.; data curation, G.L. and Z.W.; writing—original draft preparation, P.Y.; writing—review and editing, P.Y. and G.L.; visualization, P.Y.; supervision, X.L.; project administration, G.L. and X.L.; funding acquisition, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Strategic Priority Research Program of Chinese Academy of Sciences, grant number XDA 21000000.

Acknowledgments: The authors thank the financial support from the Strategic Priority Research Program of the Chinese Academy of Sciences and Changzhou University.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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