SELECTIVE CONVERSION OF FRUCTOSE TO METHYL LEVULINATE USING SULPHATED ZIRCONIA-ALUMINA BINARY OXIDES

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ABSTRACT

Biomass constitutes a huge reservoir of renewable organic carbon that can be used for sustainable production of value-added chemicals and polymeric materials. Levulinate esters are biomass derived platform chemicals with potential applications as fuel additives, fragrances, and plasticizers. Moreover, they can be derivatized to produce herbicides, cancer therapeutics and surfactants. In this study, sulphated ZrO_2-Al_2O_3 binary oxides were synthesized by a modified co-precipitation method and found to be highly active and selective for direct conversion of fructose to methyl levulinate. The samples were characterized using powder x-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The synthesized sulphated binary oxides were amorphous with large mesopores (≥ 3.4 nm) and high pore volumes (0.121-0.315 cm^3g^{-1}). The synthesized materials were used for conversion of fructose to methyl levulinate, with methanol as a solvent, in a continuously stirred pressurized reactor. The most active catalyst (ZA20), containing 20% alumina, selectively converted fructose to methyl levulinate with a high yield of 65% after 1 h at 200°C. The optimal catalyst loading, reaction time, and temperature were 40 mg, 30 min and 200°C, respectively. The catalysts were gradually deactivated with successive reuse due to surface deposition of humins but were easily regenerated by calcination in static air at 500°C for 3 h. However, activity was not fully recovered after regeneration, presumably due to leaching of sulphate species in the polar solvent media. The formation of ethers during conversion was negligible suggesting that methanol can be recycled after distillation.

Keywords: Sulphated binary oxides, mixed-metal oxides, solid superacids, biochemicals, biomass conversion, levulinate esters

INTRODUCTION

The bulk of global chemicals and fuels demands are currently being met with non-renewable fossil fuels. However, diminishing fossil fuel resources as demand increases, uncertainties of future supplies due to geopolitical factors, and adverse environmental effects due to emission of CO_2 into the atmosphere call for urgent development of alternative technologies for sustainable production of fuels and chemicals (Serrano-Ruiz *et al*., 2010). Lignocellulosic biomass (e.g. agricultural and forest residues, cellulosic municipal and industrial wastes, and energy crops) constitutes a huge reservoir of renewable organic carbon that can be used for sustainable production of biofuels, chemicals, and resins with minimal environmental effects (Chheda *et al*., 2007). Lignocellulosic biomass can be converted to several platform chemicals that can be derivatized further to produce high-value bio-based specialty chemicals and polymeric materials (Werpy and Petersen, 2004).

Levulinate esters are among biomass-derived platform chemicals that are increasingly being explored for use as specialty chemicals, green solvents, and oxygenated fuel additives (Christensen *et al*., 2011; Démolis *et al*., 2014). Levulinate esters can also be derivatized to

produce herbicides, cancer therapeutics (Brunner *et al*., 2003, Dabrowski *et al*., 2003), surfactants, lubricants, and polymeric materials (Selifonov *et al*., 2014).

Several studies have reported the synthesis of levulinate esters from biomass resources through acid-catalyzed alcoholysis of sugars, esterification of levulinic acid, and conversion of furfural and its derivatives (Démolis *et al*., 2014). Homogeneous acids have high catalytic activities but have several disadvantages including excessive generation of liquid wastes, corrosion of equipment, and difficulties of product purification and catalyst recyclability (Rackemann and Doherty, 2011). Solid acids can overcome these challenges but their usage is limited by their low activity and selectivity due to diffusional limitations and the difficulties of optimizing the acidity required for a specific product (Peng *et al*., 2011; Saravanamurugan and Riisager, 2012; Rinaldi and Schüth, 2009; Tong *et al*., 2010; Qi *et al*., 2009). There is therefore a need to develop solid superacids with high activity and selectivity to enable commercial conversion of biomass to levulinate esters.

Mesoporous metal oxides are well suited for conversion of monosaccharides to biochemicals

because the mesopores allows for unhindered access of catalytic sites in their pore system (Rinaldi and Schüth, 2009). The acidity of metal oxides can be enhanced by chemical combination of dissimilar oxides to form homogeneous binary oxides (Miller and Ko, 1997). The acidity can be increased further through incorporation of sulphate species (Yang *et al*., 2003; Matsuhashi *et al*., 1999; Brei, 2005).

Sulphated metal oxides are usually synthesized through incipient wetness impregnation of metal hydroxides with H_2SO_4 or $(NH_4)_2SO_4$ solutions (Fa *et al*., 1997). However, materials synthesized using the afore-mentioned method under similar preparation conditions often have different sulphur loadings and catalytic activity (Fa *et al*., 1997). In this study, sulphated metal oxides were synthesized using a modified co-precipitation method that led to direct incorporation of sulphate ions in the amorphous hydroxides. The synthesized materials were highly active and selective for conversion of fructose to methyl levulinate.

MATERIALS AND METHODS
Preparation of Sulphated ZrO_2-Al_2O_3 catalysts
Sulphated ZrO_2-Al_2O_3 catalysts were prepared by a modified co-precipitation method. 3 mL of concentrated sulphuric acid (H_2SO_4, J.T Baker) was dissolved in 50 mL of distilled deionized water (DDW). Then, 5.781 g (0.0250 moles) of zirconyl nitrate ($ZrO(NO_3)_2$. xH_2O, 99.9%, Alfa Aesar) was added and the solution vigorously stirred. In another beaker, the desired amount of aluminium nitrate ($Al(NO)_3$. $9H_2O$, >98%, Sigma-Aldrich) was dissolved in 50 mL of DDW. The two solutions were mixed and vigorously stirred to form a homogeneous solution.

Ammonium hydroxide (28.0-30.0%, Mallinckrodt Baker) was added dropwise, with continuous vigorous stirring, until the pH of solution was between 9 and 10. The resultant precipitate was aged for 24 h at room temperature in the mother liquor with stirring. The precipitate was then filtered, washed with DDW, oven dried at 110^oC overnight, and crushed into powder. The powdered samples were then calcined in air at 500^oC for 3 h. The sulphated ZrO_2-Al_2O_3 samples were designated ZA10-ZA90 with numerals indicating the percent of alumina in each bimetallic oxide. Sulphated ZrO_2 and sulphated Al_2O_3 were prepared using the same method without the addition of aluminium nitrate and zirconyl nitrate, respectively.

Characterization of Catalysts
The structural properties of the samples were studied by powder x-ray diffraction (XRD). The XRD patterns were obtained using a Scintag Model PDS-2000 x-ray powder diffractometer. The wavelength of Cu-Kα x-ray radiation used was 1.5418 Å while the beam voltage and current were 45 kV and 40 mA, respectively. Scans were done in continuous mode at a rate of 2° per minute in the 2θ range of $0-90^o$.

The textural properties of the samples were studied through nitrogen sorption measurements using Quantachrome Autosorb-1-C high performance surface area and pore size analyser (Quantachrome Instruments, FL, USA). The adsorption and desorption experiments were done at 77 K after initial pre-treatment of the samples by degassing at 300^oC for 12 h. Surface areas and pore size distributions were determined by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively.

Conversion of Fructose to Methyl Levulinate
The conversion of fructose to methyl levulinate was performed in a continuously stirred pressurized reactor (Parr Instrument Company, USA). In a typical reaction, 90 mg of fructose, 50 mg of the catalyst, and 10 mL of absolute methanol (J.T Baker) were loaded into the reactor. The reactor was tightly sealed, purged and then pressurized to 20 bars with nitrogen gas. The temperature of the reactor was then raised to 200^oC and held for 1 h. The reactor was then submerged in ice-cold water to quench the reaction. The reactor contents were collected, centrifuged, and the supernatant filtered with a 0.45 μm filter. Stability studies were performed by catalyst recovery and reuse under the same reaction conditions without any pre-treatment. The catalyst was regenerated after the 5th reuse by calcination in static air at 500^oC for 3 h and then reused under the same reaction conditions.

Qualitative and Quantitative Analysis of Products
The qualitative identification of the products was done using a HP 5890 Series II gas chromatograph equipped with a BD-17MS capillary column (20.0 m x 180 μm x 0.18 μm) coupled with an HP 5971 mass selective detector. Quantitative analysis of the methyl levulinate was done using a HP 5890 series II GC system equipped with a MTX®-biodiesel TG w/Integra-Gap™ capillary column (14.0 m x 530 μm x 0.16 μm) and a flame ionization detector. The calibration curve was obtained using commercial methyl levulinate (Sigma-Aldrich) and 1-Octanol (Sigma-Aldrich) as an internal standard.

RESULTS
Structural Analysis
Figure 1 shows the XRD patterns of sulphated ZrO_2, ZrO_2-Al_2O_3 binary oxides and Al_2O_3 samples. Sulphated ZrO_2 was highly crystalline with diffraction peaks corresponding to the monoclinic phase of

zirconia. Sulphated Al_2O_3 was poorly crystalline with broad diffraction peaks corresponding to α-alumina.

The synthesized sulphated ZrO_2-Al_2O_3 binary oxides were essentially amorphous.
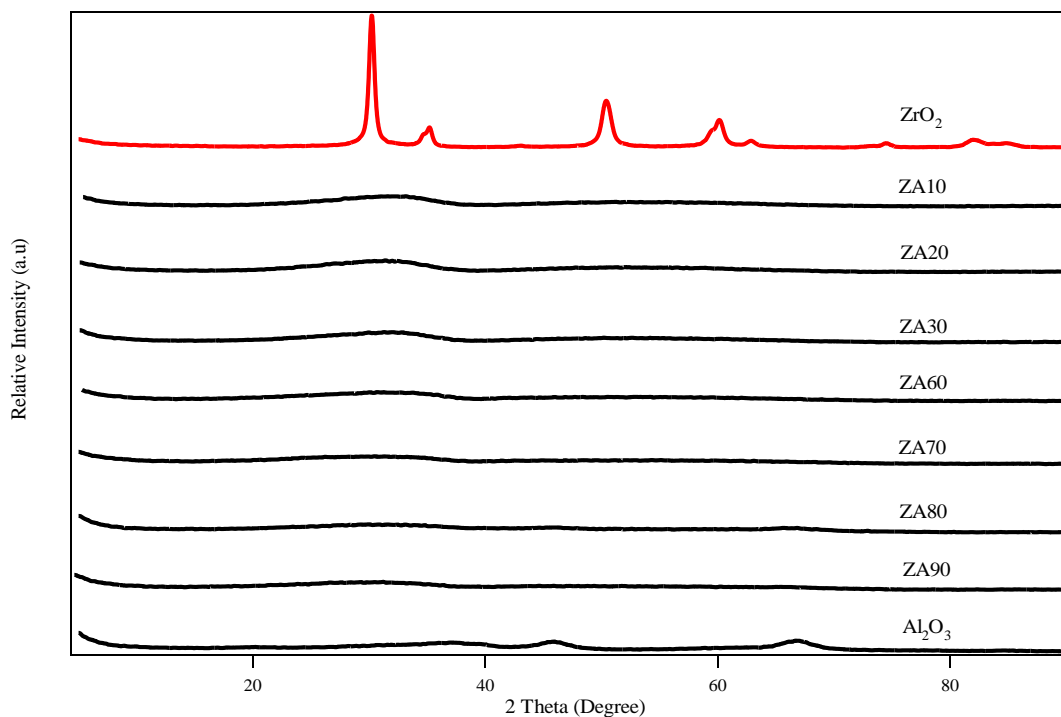

Figure 1. The XRD patterns of the synthesized materials

Textural Analysis

The textural properties of the synthesized samples are summarized in Table 1. Generally, incorporation of alumina into zirconia caused a gradual increase in the surface areas of the resultant binary oxides. Sulphated ZrO_2 and samples with low (≤40%) alumina loading had low surface areas compared to samples with high (>40%) alumina content. Sulphated Al_2O_3 had the highest surface area. The synthesized materials were porous with pore diameters in the mesoporous range. The size of the pores in the ZA60 sample were significantly larger compared to the rest of the synthesized materials. The pore volumes ranged from 0.121 to 0.315 cm^3g^{-1} for ZA80 and Al_2O_3 samples, respectively.

Conversion of Fructose to Methyl Levulinate

The yields of methyl levulinate obtained from fructose using the synthesized materials are tabulated in Table 2. These materials selectively converted fructose to methyl levulinate with no other by-products, except insoluble humins. Intermediate products (e.g. 5-hdroxymethylfurfural) were not obtained. Sulphated ZrO_2 gave a yield of 44.1%. The highest yield (65%) was obtained using sulphated ZrO_2-Al_2O_3 sample with a 20% alumina (ZA20). The other binary oxides gave lower yields than sulphated ZrO_2. No methyl levulinate was obtained using sulphated Al_2O_3. On the basis of its high conversion of fructose to methyl levulinate, the ZA20 sample was chosen for further catalytic tests.

Table 1. Textural properties of the synthesized sulphated samples

Samples	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)[a]
ZrO_2	58	3.4	0.182
ZA20	34	3.4	0.174
ZA40	76	3.8	0.242
ZA60	111	12.4	0.233
ZA80	175	3.4	0.121
Al_2O_3	268	4.3	0.315

[a]BJH desorption cumulative pore volume

Table 2. Yield of methyl levulinate from fructose using the synthesized materials

Sample	Yield (%)	Sample	Yield (%)
ZrO_2	44.1	ZA60	19.4
ZA10	40.8	ZA70	31.8
ZA20	65.1	ZA80	22.4
ZA30	31.5	ZA90	9.3
ZA40	31.0	Al_2O_3	0
ZA50	23.2		

Conversion conditions: 50 mg catalyst, 90 mg fructose, 10 mL methanol, $200^{o}C$, 1 h.

Effects of Reaction Time

Figure 2 shows the effect of reaction time on the conversion of fructose to methyl levulinate using the ZA20 sample. The reactor was heated from room temperature to $200^{o}C$, held for different times, and then quenched with ice-cold water. The zero time (0 h) was defined as the time required to raise the reactor temperature to $200^{o}C$. The yield of methyl levulinate obtained at 0 h was 55%. The yield increased to ca. 64% when the reactor temperature was held constant for 30 min. There was no further significant increase in yield when the reactor temperature was held at $200^{o}C$ for more than 30 min.

Effects of Reaction Temperature

Figure 3 shows the effect of reaction temperature on the yield of methyl levulinate from fructose. Conversion of fructose to methyl levulinate was not observed at $100^{o}C$. Methyl levulinate yields of ca. 15, 54, and 68% were obtained at 150, 180 and $200^{o}C$, respectively.

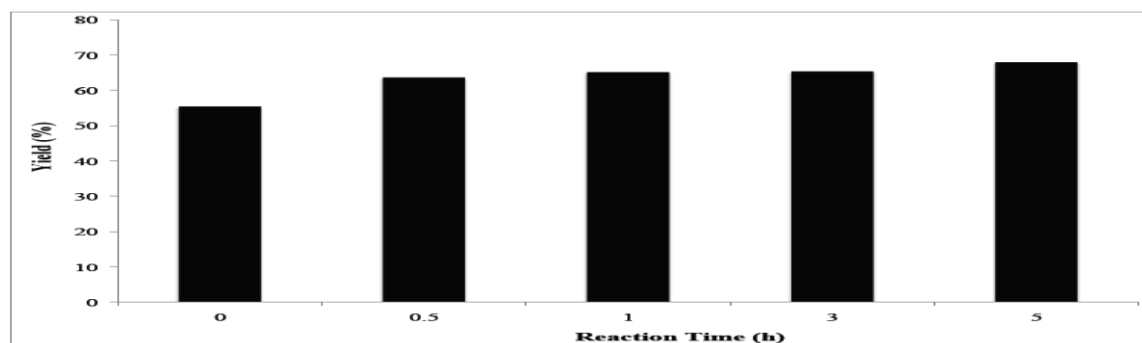**Figure 2. Effect of reaction time on the yield of methyl levulinate from fructose (50 mg catalyst, 90 mg fructose, 10 mL methanol, $200^{o}C$).**
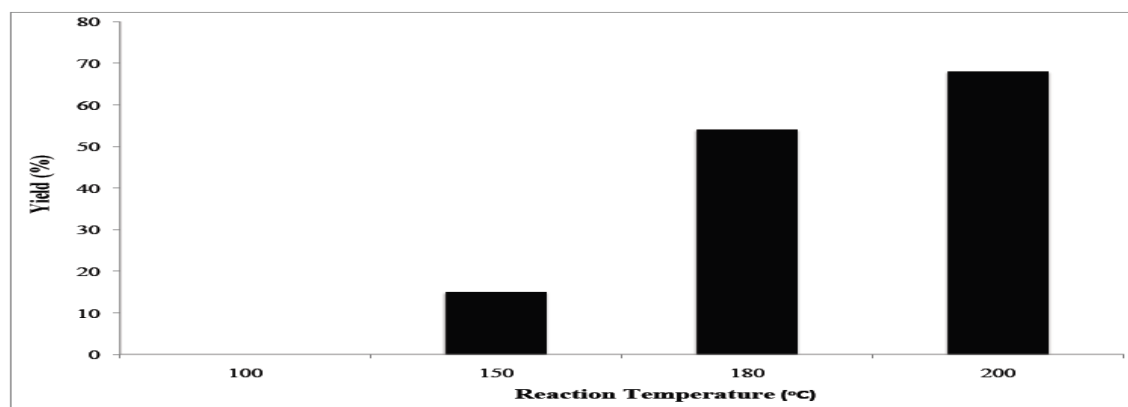

Figure 3. Effects of reaction temperature on conversion of fructose to methyl levulinate (50 mg catalyst, 90 mg fructose, 10 mL methanol, 1 h)

Effects of Catalyst Loading

Figure 4 shows the effects of catalyst loading on the yield of methyl levulinate from fructose. The yield of methyl levulinate obtained using 10 mg of the catalyst was ca. 10%. The yield increased to ca. 65% with 40 mg of catalyst. There was no significant difference in the yield obtained with a catalyst loading of 40 mg and 50 mg.
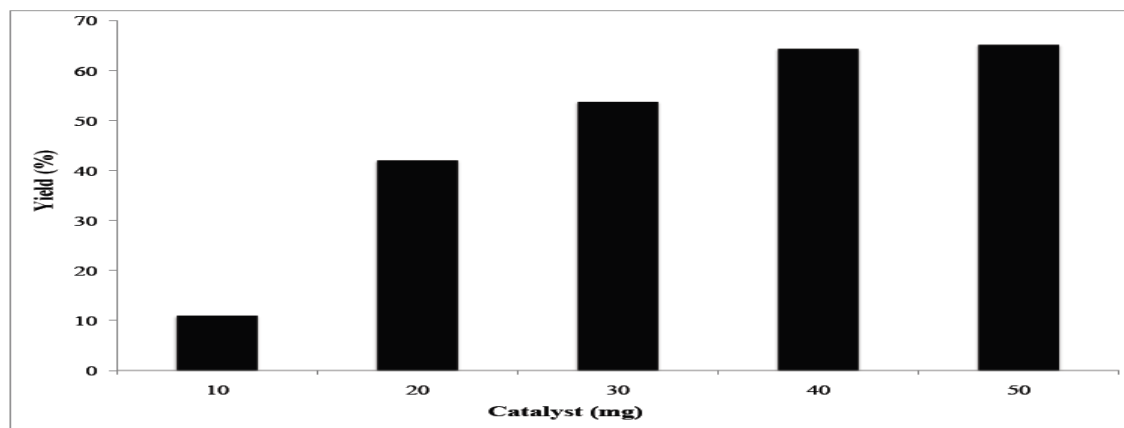
Reusability of the Catalyst

Figure 5 shows the yield of methyl levulinate from fructose after successive reuse of the ZA20 sample. The yield of methyl levulinate decreased gradually with successive reuse with the catalyst being completely deactivated after the 4th reuse. The deactivated catalyst was regenerated by calcination in static air for 3 h. The yield of methyl levulinate with the regenerated catalyst was ca. 40%.
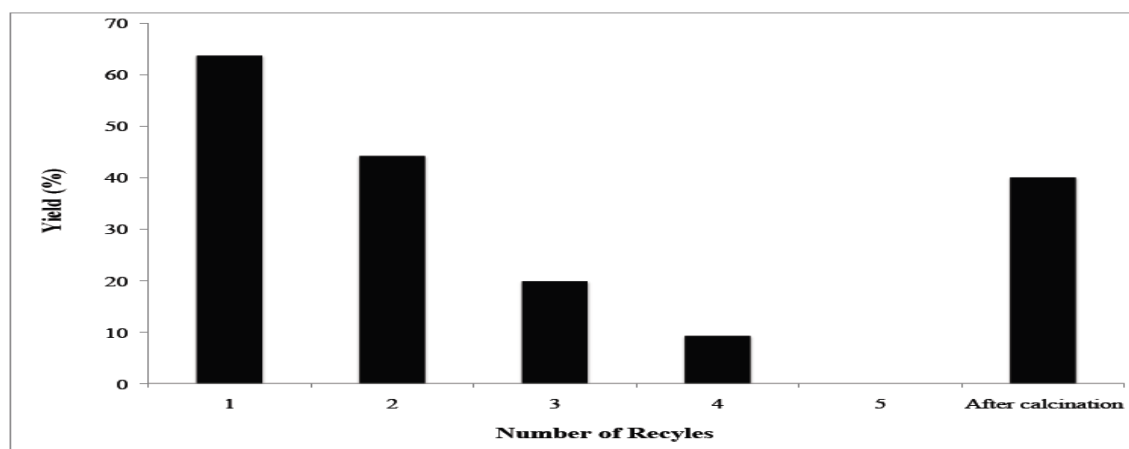

Figure 4. Effects of catalyst loading on conversion of fructose to methyl levulinate (ZA20 catalyst, 90 mg fructose, 10 mL methanol, 200°C, 1 h)

Figure 5. Yield of methyl levulinate from fructose after successive reuse of catalyst (50 mg ZA20 catalyst, 90 mg fructose, 10 mL methanol, 200°C, 1 h)

DISCUSSION

Sulphated ZrO_2-Al_2O_3 binary oxides were synthesized using a modified co-precipitation method that led to direct incorporation of sulphate species in the precipitated hydroxides. The precipitates were then aged in the mother liquor with continuous stirring to allow for homogeneous incorporation of sulphate ions in the resultant hydroxides. The synthesized binary oxides are therefore expected to have high acidities due to the presence of sulphate species and the creation of

new acidic sites through generation of excess charge (Brei, 2005, Miller and Ko, 1997).

Sulphated ZrO_2 was highly crystalline with diffraction peaks corresponding to the monoclinic phase of zirconia. However, incorporation of alumina inhibited the crystallization of zirconia producing amorphous binary oxides. The surface areas of the synthesized samples increased gradually with addition of alumina to zirconia, which has been attributed to the

corresponding change in structural properties from crystalline to amorphous (Reddy and Khan, 2005). However, the yields of methyl levulinate obtained from fructose suggest that activities of the synthesized materials are independent of surface area.

The synthesized materials have large ($\geq$3.4 nm) mesopores and significant pore volumes ($\geq$0.121cm^3/g) allowing reactants to access sites in the pores, and unhindered diffusion of methyl levulinate out of the pores before taking part in secondary reactions (Zeng *et al.,* 2010). Sulphated ZrO_2-Al_2O_3 oxides of different compositions gave different yield of methyl levulinate presumably due to differences in the densities of acid sites. However, intermediate hydrolysis products were not obtained suggesting that these materials have the high acidity required for conversion of fructose to methyl levulinate. The high selectivity of these materials can therefore be attributed to the presence of strong acid sites and large mesopores (Lourvanij *et al.*, 1993; Zeng *et al.*, 2010).

The rate of conversion of fructose to methyl levulinate increased with temperature. However, the colour of the products and spent catalysts increasingly turned dark brown with increase in reaction temperature. This suggests that the formation and deposition of insoluble humins on the surface of the catalysts increased with increase in reaction temperature. The formation of insoluble humins also increased as the loading of the catalysts increased. Consequently, high reaction temperatures and catalyst loadings did not increase the yields of methyl levulinate but led to conversion of fructose to humins, due to higher rates of polymerization (Antal *et al.*, 1990; Peng *et al.*, 2011).

The gradual decrease in conversion of fructose to methyl levulinate on successive reuse of the catalyst is attributed to the blockage of the active sites due to deposition of solid humins on the surface of the catalyst (Peng *et al.*, 2011). Calcination in static air regenerated deactivated catalysts by removal of humins through combustion. However, the activity was not fully recovered presumably due to reduction of acidity through leaching of sulphate species in the polar solvent (Suwannakarn *et al.*, 2008).

CONCLUSION
Sulphated ZrO_2-Al_2O_3 binary oxides were successfully synthesized using a facile co-precipitation method. The binary oxide with alumina loading of 20% was highly active and selective for conversion of fructose to methyl levulinate. The high activity is attributed to the high density of acidic sites in the binary oxide. The high selectivity is attributed to the presence of high strength acidic sites and large mesopores in the synthesized materials. The catalysts were easily separated from the reaction mixture and reused after thermal treatment. Formation of dimethyl ether was negligible suggesting that the solvent can be distilled and recycled.

RECOMMENDATION
Sulphated ZrO_2-Al_2O_3 binary oxides are promising materials for conversion of fructose to methyl levulinate. Further studies should be undertaken to quantify and optimize the acidities, the chemical stability and the catalytic performance of these materials for conversion of lignocellulosic biomass.

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