



Effect of Preparation Method in Activating Active Sites and Catalytic Activity of $\text{SO}_4^{2-}/\text{ZrO}_2$ in Biodiesel Production

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Abstract. The effect of precursor type and concentration in activating different sulfated zirconia catalysts and their activities for transesterification was investigated. Double sulfation ensured sulfate incorporation while subsequent drying and calcination at 600°C for 5 h stabilized the surface structure of the catalysts. XRD and BET analyses elucidated the structural and textural properties of the catalysts. Higher concentration of combined precursors and concentration of sulfuric acid in SZ increases the surface area of the materials. The results showed that minor amounts of precursor enhanced catalytic activity of the materials while sulfate content determines the amounts of Brønsted and Lewis acidities. The synergetic effect from a combination of precursors gave more 95% conversion from the simultaneous esterification of free fatty acids (FFA) and transesterification of triglycerides (TG).

Keywords: Preparation; bi-functional catalyst; acid activation; solid acid catalyst; biodiesel.

1 Introduction

The potency of public concern in the 21st century forces decision makers to enact policies not primarily based on science and technology. Consequently, it is necessary to devise catalytic processes with ca. 100% yields. The high activity of sulfated zirconia (SZ) attracted substantial attention for converting triglycerides (TGs) into biodiesel at moderate to high temperatures. It is instructive to highlight that high activity of SZ is a function of their strong acidity. However, despite numerous encouraging results, some aspects of SZ catalytic reactivity and physicochemical properties remain debatable. This is plausible because of the sensitivity of the material to the activation conditions and preparation method [1]. Moreover, the scarcity of licensed processes is an indication that solid acid catalysis needs extensive experimentation. These will help in establishing the numerous potentials of these catalysts as well as ensuring biodiesel prominence. Despite these challenges, last century witnessed catalysis as the major backbone for most industrial processes such as petrochemistry (especially, petroleum catalytic refining) and bulk chemistry. However, recent environmental and socioeconomical challenges have brought about new demands which require novel catalytic solutions [2]. Inherent with these new challenges are the potentials for greater efficiency and sustainability of such systems [3]. Moreover, the searches for newer solutions have led experts to explore in details, the attributes of different materials, systems and devices [4]. One key task is in achieving phase-homogeneous solids with uniform morphological and chemical properties. This challenge is a fundamental prerequisite to any rational catalyst design. This study therefore, aims at exploring the effect of slight changes to preparatory method in developing SZ catalysts. It highlights how preparation method affects catalytic performance of the catalyst within prevailing reaction conditions.

2 Research Methodology

Sigma-Aldrich supplied all the reagents for this study except where stated otherwise. Required amount of $ZrOCl_2 \cdot 8H_2O$ was dissolved in distilled water and stirred for 5 min to 0.34M concentration. Adding urea in drop-wise manner to a pH of 2 precipitated the active species from the solution. Adding 0.5M $(NH_4)_2SO_4$ produced a gel-like acidic solution. This was aged for 1 to 14 days in closed polyethylene (PE) bottles at 90°C. After cooling to room temperature, the solution was filtered. The filtrate was washed with excess distilled water (6 times with 100 ml each time). Drying of the solid was for 20 h in open air inside a fume cupboard and at 90°C for 4 h before calcining in air at 550°C for 5 h. This sample was labeled 007(F1). To obtain strong acid sites, resulfation step was performed on the remaining samples. The solid was kneaded into powder and mixed with 0.5M H_2SO_4 for 2 h. The solution was filtered through fritted glass, dried at 130°C for 16 h and calcined at 600°C for 5 h

The above procedure was repeated for Sample 008(F₂) except that required amount of $ZrOCl_2 \cdot 8H_2O$ was dissolved in distilled before adding urea to pH value of 2 and mixing with required amount of $ZrCl_4$. Similarly, the procedure was repeated for sample 009(F₃) except that required amount of $ZrO(NO_3) \cdot xH_2O$ was dissolved in 400 ml distilled water before adding urea to pH value of 1.25 and mixing with required amount of ZrO_2 and $Al(NO_3)_3 \cdot 9H_2O$. The solution was stirred at 210 rpm under heating at 50°C for 2 h. Ammonia solution was added and stirred for 40 min before aging at room temperature for 10 days. The solid was filtered and dried in fume cupboard before drying at 90°C for 24h and calcined at 550°C for 4 h. The transesterification reaction was conducted in a 1 L high temperature-high pressure stainless steel Lab-Autoclave batch reactor (AMAR Equipment, India.). Commercial palm oil was obtained from commercial outlet in Kuala Lumpur. Preliminary experiments were done to ascertain the influence of reaction temperature, methanol/oil molar ratio and reaction time on TG conversion (data not shown). Methanol-to-oil mole ratio of 5 and 2 wt% catalyst were employed for 1 to 2 h reaction time at 180 to 220 °C.

3 Main Results

3.1 Catalyst Characterization

Analyzing isolated samples of catalyst precursors or intermediates facilitates circumventing the high complexities of catalytic systems. It provide important information regarding the reaction mechanism and structure/activity relationships of the catalyst. This *ex situ* approach also enables the researcher to work with simplified systems under pre-defined conditions such as with simplified systems or polished crystals under ultra-high vacuum.

3.1.1 X-ray Diffraction Analysis

XRD analysis was performed with PAN analytical X'pert Empyrean X-ray diffractometer with $CuK\alpha$ radiation at 40 kV and 40 mA performed the XRD analysis. The XRD diffractograms of synthesized SZ catalysts revealed a tetragonal–monoclinic phase transition (Figure 1). The XRD patterns also show the significant impact of calcination temperature and precursor concentration on the crystal phase and crystallite size. It is also

evident the characteristic peak areas of tetragonal is more prominent than that of the monoclinic phases. In addition, the intensity of the peaks reflects both adsorption and amount of phase in the synthesized materials.

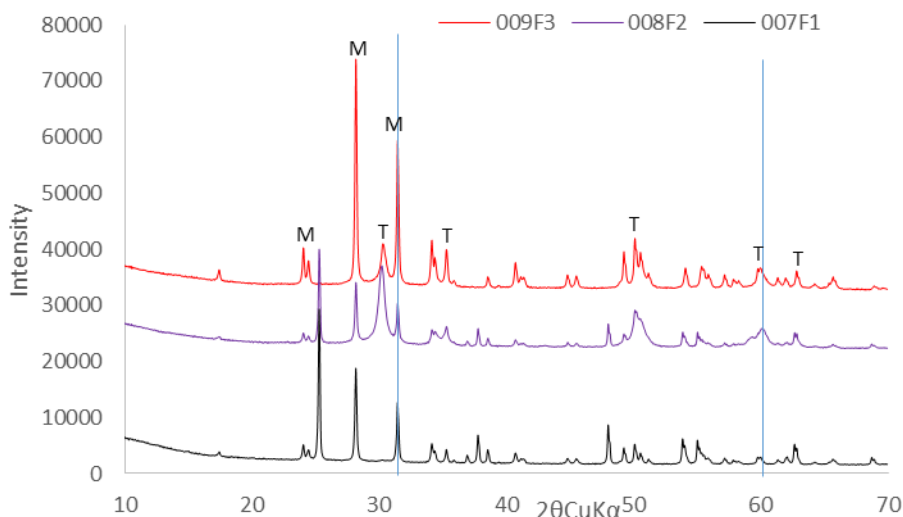


Figure 1 X-ray diffraction patterns for 007F₁, 008F₂ and 009F₃.

3.1.2 BET analysis

Brunauer–Emmett–Teller (BET) analysis was conducted with Quantachrome Nova 1200. Table 1 presents the textural and percentage conversions obtained from the three mesoporous SZ catalysts. The difference in chemical composition of the catalytic materials plausibly explains the significant variations in textural and catalytic activities. Thus, for instance, the S_{BET} of 009F₃ was 15.0543 m²/g (95.83% conversion) while 007F₁ had 7.6917 S_{BET} value and a lower conversion of 51.57%. However, the pore size distribution ($2 < dp < 50$ nm) of all the synthesized catalysts confirms mesoporous structure which permits the TG molecule access to the active sites within the materials.

Table 1 Textural surface area of synthesized sulfated zirconia

Sample	SSA ^a (cm ² /g)	Ext. SA ^b (cm ² /g)	Pore vol. (cm ³ /g)	Pore size ^a (nm)	Conv ⁿ (%)
007F ₁	7.6917	6.6926	0.033578	21.4448	51.57
008F ₂	41.2160	39.8731	0.070824	6.8324	73.45
009F ₃	15.0543	14.3529	0.038344	9.6520	95.83

^a BET specific surface area and pore size

^b t-plot external surface area

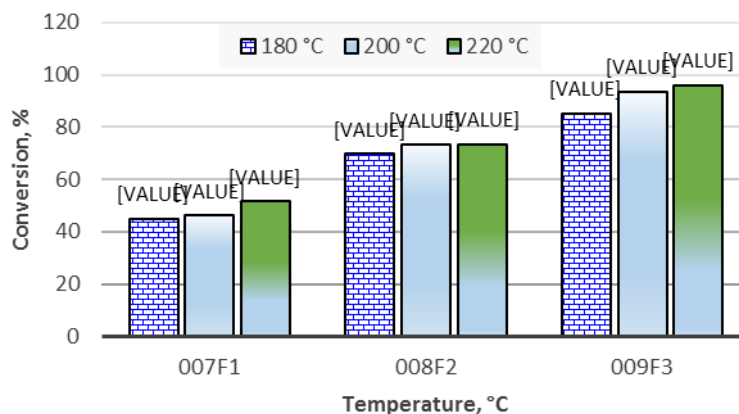


Figure 2 Some selected conversions obtained from (a) 007F₁, (b) 008F₂ and (c) 009F₃

4 Discussion of Results

Usually tetragonal phase transition occurs at above 1170 °C. However, according to [5] SZ precipitation preparation method produces monoclinic–tetragonal phase transformation of zirconia at lower temperature [6]. Therefore, the low temperature employed during double sulfation in this study facilitated the transition of monoclinic phase from the tetragonal phase which retards crystallization of zirconia support [7,8]. Furthermore, the lower surface energy of the tetragonal phase compared to monoclinic phase also ensures transforming of the metastable tetragonal phase into the monoclinic phase [6]. All the XRD patterns of 007F₁, 008F₂ and 009F₃ displayed presence of mixture of monoclinic and tetragonal phases (Figure 1). Sample 007F₁ displayed zirconia predominantly in monoclinic phase with little tetragonal phase with respect to intensity. The monoclinic phase with the highest intensity is at $2\theta = 28.16$ (61.21%) while that of the tetragonal is at $2\theta = 50.09$ (13.27%). In contrast, sample 008F₂ exhibits zirconia predominantly in tetragonal phase with little monoclinic phase with respect to intensity. The tetragonal phase with the highest intensity is at $2\theta = 30.19$ (81.74%) while that of the monoclinic is at $2\theta = 28.17$ (64.43%). The samples exhibited good performances when evaluated for transesterification of palm oil (Figure 2). Sample 008F₂ displayed higher activity compared to 007F₁. We ascribed this to the dominant presence of tetragonal phase as shown by the XRD patterns. This indicates that monoclinic phase does not favor transesterification of palm oil as much as tetragonal phase of the evaluated materials. This is in consonance with the report of Ramu et al [9].

It is evident from Figures 1 and 2 that slight modification in catalyst preparation condition changes the morphology of the material which yields different catalytic activity. This morphological change could be favorable or detrimental to the catalytic activity of the catalyst. The domain sizes and lattice strains (the contribution from crystalline sizes and strains) displayed by the peaks were affected due to such modifications. The peaks also reveal the active metal concentrations in the different modified catalysts. The intensity of monoclinic phase ZrO₂ (Baddeleyite) appeared in XRD patterns of 007F₁ and 008F₂ but became prominent in 009F₃ (Figure 1). Essential requirements for zirconia or ZrO₂ mixed oxides heterogeneous catalysis include good system of channeled pores for diffusion and enhanced textural properties. Interestingly,

the XRD shoulder with the maximum intensity is centered at 27.78. This is situated at the same peak position which graphically exhibits Bragg's diffraction angle. Further, the position matches what is expected for the strongest Bragg reflection of the crystalline monoclinic ZrO₂ phase (baddeleyite). Similarly, the XRD peak centered at 31.58 is in consonance with the expected position for the second strongest Bragg reflection of baddeleyite. These facts suggest that incipient ordered structure at 27.78 and the associated shoulder at 31.58 are responsible for activity and stability of the modified zirconia. It is also instructive to note the role that impregnating sulfate onto zirconium oxide produces acidic solid catalysts. This reflects the high conversions displayed by the synthesized materials. Interestingly also, despite the low S_{BET} values of the synthesized catalytic materials (Table 1), high conversions were obtained. This further affirms the presence of sulfate active sites of within the surface structure of the catalysts as reported by [10]. However, the conversion obtained from utilizing 007F₁ samples were low compared to that of 008F₂ and 009F₃ samples. Plausibly, the resulfation step and mixed oxide incorporated higher density of Brönsted and Lewis acid sites on the latter catalysts. Consequently, the authors are exploring ways of optimizing the process (SO₄/ZrO₂-550°C) with hope of achieving same conversion at lower temperature and shorter time.

5 Conclusion

This study demonstrated the effect that slight variation in preparation method has on the performance of SZ. Evidently slight modification in catalyst preparation condition yields different catalytic activity. The domain size and lattice strain (the contribution from crystalline size and strain) was affected due to such modifications. These observations highlights the possibility of improving on the reported formulations to facilitate higher intrinsic efficiency in biodiesel production. The study also shows how to achieve a flexibility of properties from unlimited number of possible manipulations from one catalyst precursor.

6 References

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