

Catalytic activity of sulfated zirconia solid acid catalyst for esterification of myristic acid with methanol

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The catalytic activity and reusability of sulfated zirconia solid acid catalyst is evaluated for esterification of myristic acid with methanol. The catalyst exhibits excellent activity with 98% conversion of myristic acid and selective formation of methyl myristate in presence of a very small amount of catalyst, i.e., 0.5 wt% (to acid) at 60 °C after 5 h. The re-used catalyst also shows good catalytic performance without significant difference in activity up till five reaction cycles. Characterization of the used catalyst revealed no significant change in structural and textural properties, however a slight decrease in surface acidity was observed due to deposition of carbonaceous matter on the surface acid sites.

Keywords: Catalysts, Sulfated zirconia, Zirconia, Solid catalysts, Esterification, Myristic acid

Sulfated zirconia (SZ) is a potential heterogeneous acid catalyst for developing environmentally benign and friendly processes for alkane isomerization at mild temperature¹ and many other organic transformations due to its strong acidic properties.^{2,3} Among various heterogeneous acid catalysts such as zeolites, ion exchange resins and metal oxides, SZ has been screened as a potential heterogeneous acid catalyst for esterification of fatty acids as well as transesterification of triglycerides to synthesize fatty acid alkyl esters (FAAE).⁴ Industrially, FAAE have been prepared by the homogeneous base catalyzed transesterification of oils and fats or esterification of fatty acid with an alcohol in presence of conventional homogeneous acid catalyst such as sulfuric, *p*-toluene sulfonic or phosphoric acid. However, the use of heterogeneous acid catalysts is a sustainable alternate to conventional homogeneous liquid acids with respect to safe handling, ease of separation and re-use of the catalyst. A number of studies have reported significant activity of SZ catalyst for both esterification and transesterification reactions.⁴⁻¹¹ However, the reports show varied activity of fresh and re-used SZ catalyst, for example, Kiss *et al.*⁴ found complete regeneration of activity of used SZ catalyst for esterification of lauric acid after re-calcination. Similar observations were reported by Peters *et al.*¹²

for esterification of acetic acid with *n*-butanol, whereas Ni & Meunier¹³ observed that SZ catalyst was fully deactivated after the esterification of palmitic acid and could not be re-used. The leaching of active SO₄²⁻ groups from the surface of SZ catalyst and the formation of H₂SO₄/HSO₄⁻/SO₄²⁻ ions was also observed in presence of alcohol^{8,9} and water¹⁴ resulting in the deactivation of SZ catalyst.

In fact, the catalytic behavior of SZ catalyst depends upon its structural, textural and acidic features, which in turn is significantly influenced by the method of its preparation. The preparation methods have several varying factors starting from the metal precursor to drying and calcination temperatures.^{3,15,16} The amount of sulfur content and number, strength and nature of the surface sulfate species also have a strong impact on the surface acidity of SZ catalyst.³ Moreover, tetragonal crystalline phase of zirconia has been found to be more catalytic active than monoclinic phase of zirconia.¹⁷

In the present work, we have studied the structural, textural and acidic properties of SZ catalyst. The catalytic activity of fresh and re-used SZ catalysts was evaluated for esterification of a saturated fatty acid, myristic acid (*n*-tetradecanoic acid, C₁₄H₂₈O₂, found in palm kernel oil, coconut oil, butter and animal fats)

with methanol. The present study provides a novel insight into the key role of the acidic features of SZ catalyst that are mainly responsible for the catalytic performance of fresh and re-used catalyst as compared to structural and textural properties of the catalyst.

Materials and Methods

Catalyst synthesis

SZ catalyst was prepared by conventional precipitation method. In a typical experiment, aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ precursor (SD Fine Chem) was hydrolyzed by aqueous ammonia (25%; Rankem, India) under continuous stirring until the pH became 10. The precipitate was filtered, washed with distilled water until free from chloride ions (checked by AgNO_3 solution). The catalyst was dried in an oven at a temperature of 110 °C for 12 h and treated with H_2SO_4 (1 N, 15 mL/g) for 30 min followed by calcination at 600 °C for 4 h. The sample was designated as SZ-PP-f, where PP and f represent precipitated and fresh catalyst, respectively.

Catalyst characterization

Structural and textural properties

The crystallinity and the crystalline phase of sulfated zirconia catalyst calcined at 600 °C was determined by X-ray powder diffractometer (Philips X'pert, The Netherlands) using Cu-K α radiation ($\lambda = 1.54059 \text{ \AA}$). The crystallite size of the catalysts was determined from the characteristic peak of tetragonal phase of zirconia ($2\theta = 30.22^\circ$) using Scherrer formula.¹⁸ FT-IR spectra of the catalysts were recorded on a Perkin Elmer FT-IR spectrophotometer, Spectrum GX (USA) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellets. TGA and DTA were carried out on a thermal analyzer (Mettler Toledo Star System, Switzerland) in the temperature range of 50–850 °C at intervals of 10 °C min^{-1} under N_2 flow. The bulk sulfur (wt%) retained in the sulfated zirconia samples after calcination at 600 °C was analyzed by elemental analyzer (Perkin Elmer 2400, USA). The XPS spectra were recorded on a X-ray photoelectron spectrometer (PHI 5000) using Mg-K α X-ray source (1253.6 eV) with a resolution of 0.05 eV/step and pass energy at 72 eV under a working pressure of 1.7×10^{-8} Torr for fresh (SZ-PP-f) catalyst and 3.1×10^{-8} Torr for re-used (SZ-PP-r) catalyst.

Specific surface area, pore volume and pore size distribution of the catalysts were determined from N_2 sorption isotherms at $-196 \text{ }^\circ\text{C}$ (ASAP 2010, Micromeritics, USA). Surface area and pore size were calculated by BET (Brunauer-Emmett-Teller) and BJH (Barrett-Joyner-Halenda) methods, respectively. The samples were degassed under vacuum (1×10^{-3} mm Hg) at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture.

The microscopic studies were carried out with a scanning electron microscope (SEM) (Leo series VP1430, Germany) having a silicon detector under a pressure of $>1.34 \times 10^{-2}$ Pa. The samples were dispersed in ethanol by sonication and coated with gold using a Polaron Sputter Coater. TEM micrographs were obtained with a transmission electron microscope (Jeol JEM 2100) by dispersing the catalyst sample in ethanol by sonication and deposited on a Cu grid coated with carbon film.

Acidic properties

The total surface acidity of the catalysts was measured by temperature programmed desorption (TPD) of NH_3 (Micromeritics Pulse Chemisorb 2720). In a typical procedure, a mixture of 10% NH_3 and He gas was passed for 30 min at 40 °C over the sample (*in situ* activated at 120 °C for 2 h). The excess physisorbed NH_3 was flushed out for 10 min with pure He gas flow. The sample was then heated at a rate of 10 °C min^{-1} , up to 900 °C, and volume of desorbed NH_3 was measured.

Brönsted and Lewis acid sites were differentiated using pyridine as a probe with a FT-IR spectrophotometer equipped with diffuse reflectance FT-IR (DRIFT) accessory (Graseby Specac, P/N 19900). The heating was done by an automatic temperature controller (Graseby Specac, P/N 20130). The sample was exposed to pyridine vapors under vacuum for 1 h followed by evacuation of excess physisorbed pyridine for 10 min. The spectra were recorded at room temperature ($\sim 27 \text{ }^\circ\text{C}$) and in the temperature range of 150–450 °C after holding at each temperature for 10 min, thus allowing sufficient time for pyridine desorption at that temperature.

Esterification of myristic acid with methanol

In a typical reaction procedure,¹⁹ optimized amount of myristic acid (99%, Spectrochem Pvt. Ltd., India), anhydrous methanol (Qualigens, India) (acid:alcohol molar ratio = 1:10) and catalyst

(0.5 wt% to acid) were taken in a round bottom flask and the reactant mixture was magnetically stirred (600 rpm) in an oil bath maintained at a constant temperature of 60 ± 1 °C for 5 h. The reaction mixture was analyzed using a gas chromatograph (HP 6890) having a DB-225 capillary column (20 m length, 100 μm dia. and 0.10 μm film thickness) and FID detector. The conversion of myristic acid and selectivity for methyl myristate was calculated by GC.

The used SZ catalyst was recovered from the reaction mixture by centrifugation, washed with methanol 3-4 times (15-20 mL) to remove the reactant and product molecules from the surface, dried at 120 °C for 12 h and activated at 450 °C for 2 h before re-use for further reaction cycles. The sample was designated SZ-PP-r, where 'r' represents re-used catalyst.

Results and Discussion

Characterization of fresh SZ catalyst

X-ray diffraction patterns of SZ-PP-f catalyst showed tetragonal crystalline phase (2θ (°) = 30.3, 35.4, 50.2, 60.3, 62.7) after calcination at 600 °C (Supplementary Data, Fig. S1). The sample was found to have a nano-crystallite size of 11 nm (Table 1) with good crystallinity.

FT-IR-spectrum of SZ-PP-f (Supplementary Data, Fig. S2) exhibited the presence of sulfate bands at 1235, 1141, 1043 and 994 cm^{-1} , characteristic of inorganic chelating bidentate sulfate assigned to asymmetric and symmetric stretching frequencies of $\text{S}=\text{O}$ and $\text{S}-\text{O}$ bonds with C_{2v} symmetry and ν_3 and ν_1 stretching mode of SO_4^{2-} groups.²⁰ The absence of covalent $\text{S}=\text{O}$ band at ~ 1400 cm^{-1} suggests the partial ionic nature and hydrated state of sulfate groups at the

surface of zirconia. A broad peak at ~ 3400 cm^{-1} attributed to the $\nu_{\text{O-H}}$ stretching mode of water with hydrogen bonding and a peak at ~ 1630 cm^{-1} attributed to $\delta_{\text{O-H}}$ bending mode of water molecules associated with the sulfate group and zirconia surface was observed. The bulk sulfur present in sulfated zirconia sample was 1.14 wt% (Table 1). Thermal analysis of catalyst showed the total weight loss in the range of 26 wt% while the DTA curves showed the presence of two peaks, one at ~ 100 °C due to desorption of physisorbed water molecules and other at 650-700 °C due to dehydroxylation and removal of sulfate species (Supplementary Data, Fig. S3).

N_2 sorption isotherm of SZ-PP-f showed a well-defined isotherm of mesoporous materials (Fig. 1a) with type IV isotherm.²¹ The H2 hysteresis loop at P/P_0 partial pressures from 0.4 to 0.8 indicated the filling of the ink bottle-type mesopores having

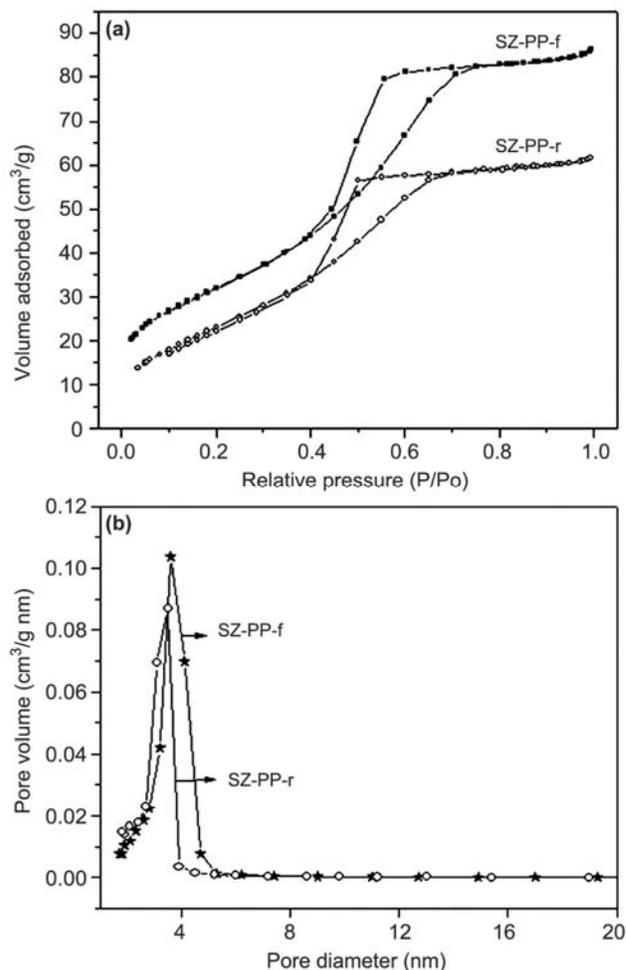


Fig. 1—(a) N_2 -adsorption-desorption isotherm, and, (b) Pore size distribution of fresh and re-used sulfated zirconia catalysts.

Table 1 — Structural, textural and acidic properties of fresh and re-used sulfated zirconia catalysts

Sample code	SZ-PP-f	SZ-PP-r
Crystallite size (nm) ^a	11	20
Lattice strain (%) ^a	1.034	0.869
BET surface area (m^2/g)	116	88
Total pore volume (cm^3/g)	0.13	0.094
BJH pore diameter (Å)	36	32
S (wt%) ^b	1.14	0.82
Total acid sites (mmol/g)	1.16	0.692
B/L ratio ^c	1.29	1.15

^acalculated by PXRD; ^bby elemental analyser; ^cB and L = Brönsted and Lewis acid sites at 150 °C.

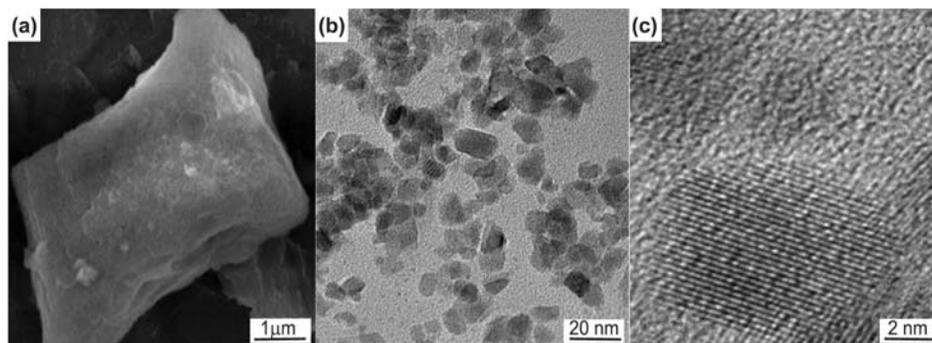


Fig. 2—(a) SEM, (b) TEM, and, (c) HR-TEM images of SZ-PP-f catalyst.

uniform pore size distribution (Fig. 1b). BET surface area, total pore volume and BJH pore size of SZ-PP-f were found to be $116 \text{ m}^2/\text{g}$, $0.13 \text{ cm}^3/\text{g}$ and 36 \AA , respectively (Table 1).

The surface morphology of SZ-PP-f sample examined by SEM was found to have irregular rectangular shaped particles (Fig. 2a). TEM micrograph (Fig. 2b) showed the aggregate of particles with average crystallite size of 9 nm , which is in agreement with crystallite size calculated by PXRD. The high-resolution TEM (HR-TEM) image (Fig. 2c) exhibited the lattice fringes; the width between two fringes (2.90 \AA) agreed with the d -spacing (2.94 \AA) of characteristic peak of tetragonal (111) zirconia ($2\theta = 30.22^\circ$) shown by PXRD.

Acidic properties

NH_3 -TPD showed three different types of desorption peaks, namely weak (98°C), moderate to strong (531°C) and very strong acid sites (815°C). The total surface acidity of SZ-PP-f catalysts was observed as 1.16 mmol/g (Table 1).

The DRIFT spectra of pyridine adsorbed SZ-PP-f catalyst exhibited the characteristic peaks for pyridinium ion (Brönsted acid sites) at 1540 cm^{-1} and covalently bonded pyridine (Lewis acid sites) at 1440 cm^{-1} along with peak at 1487 cm^{-1} representing the combined Brönsted and Lewis acid sites. Both acid sites were observed to be strong enough as they were present even after heating at 450°C , though the intensity of the peaks was decreased after successive heating (Fig. 3). The quantification of Brönsted (B) and Lewis (L) acid site concentration showed the B/L ratio to be 1.29 (calculated from the peak area of 1540 and 1440 cm^{-1} at 150°C) (Table 1).

Catalytic activity and re-usability of SZ catalyst

The esterification of myristic acid with methanol carried out in presence of SZ-PP-f catalyst showed

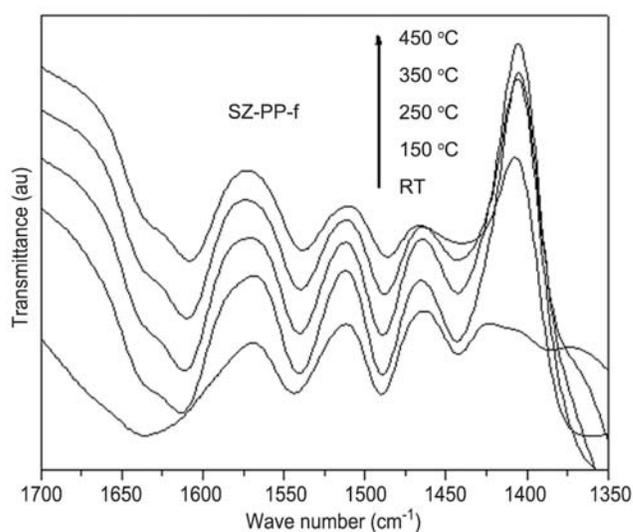


Fig. 3—DRIFT spectra of pyridine adsorbed sulfated zirconia catalysts at room temperature and after pyridine desorption at varying temperatures.

increase in conversion with time and exhibited maximum 98% conversion of myristic acid at 60°C after 5 h (Fig. 4). The selective formation of methyl myristate was confirmed by GC-MS. The re-used SZ-PP-r catalyst also showed good performance without significant decrease in activity until five reaction cycles (Fig. 5).

Characterization of re-used SZ catalyst

The re-used SZ-PP-r catalyst was characterized after the 5th reaction cycle to study the change, if any, in the catalyst structural, textural and acidic properties. The PXRD patterns of the fresh and re-used catalysts were found to be similar, indicating that the crystalline phase and nature remained intact (Supplementary Data, Fig. S1), however, the crystallite size of re-used catalyst (SZ-PP-r) increased from 11 to 20 nm (Table 1), which may be due to increase in the surface roughness leading to decrease

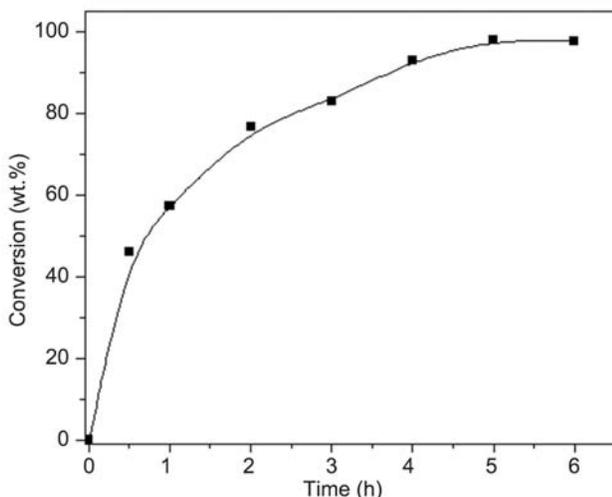


Fig. 4—Esterification of myristic acid with methanol over sulfated zirconia catalyst. [React. cond.: acid-to-methanol ratio = 1:10; SZ = 0.5 wt%; temp. = 60 °C].

in lattice strain and thus increasing the crystallite size. FT-IR spectrum of re-used catalyst was found to be similar to the fresh one (Supplementary Data, Fig. S2), indicating no significant loss or change in sulfate species and the absence of any adsorbed organic species on the surface of the re-used catalyst. However, the sulfur content of the SZ-PP-r catalyst was found to decrease from 1.14 wt% to 0.82 wt% after five reaction cycles (Table 1). The carbon content of both fresh and re-used catalysts were in the similar range (0.04-0.06 wt%). Among the textural properties, BET surface area of the re-used catalyst was slightly decreased with no significant change in pore volume and diameter (Table 1). N_2 -sorption isotherms (Fig. 1a) and pore size distribution (Fig. 1b) of re-used SG-PP-r catalyst was also similar to those of the fresh catalyst.

NH_3 -TPD results showed decrease in total surface acidity of re-used catalyst after five reaction cycles. Similarly, B/L ratio was also decreased (Table 1).

XPS studies of fresh and re-used SZ catalysts

The above results revealed the consistency in structural and textural characterization of fresh and re-used SZ-PP catalyst. However, surface acidity in terms of total number of acid sites and B/L ratio was decreased, which affected the activity of the catalyst slightly. The decrease in acidity may be either due to decrease in oxidation state of sulfur (from S^{VI}) due to the formation of organo-sulfur complexes or blockage of active sites by organic compounds formed during the reaction. Therefore, XPS studies of SZ-PP-f and

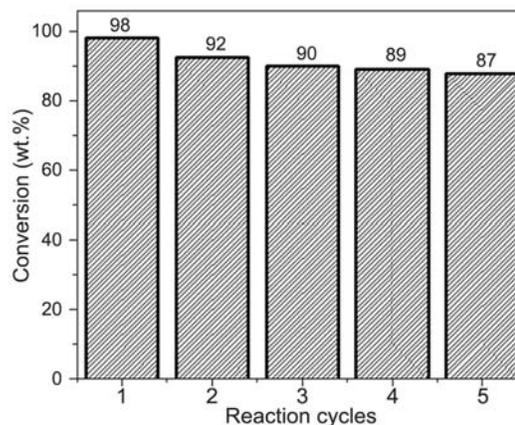


Fig. 5—Re-cycling of sulfated zirconia catalyst for esterification of myristic acid with methanol. [React. cond.: acid-to-methanol ratio = 1:10; SZ = 0.5 wt%; temp. = 60 °C; time = 5 h].

SZ-PP-r catalyst were carried out to understand the reason of decrease in surface acidity.

XPS spectra of SZ-PP-f and SZ-PP-r catalyst (Fig. 6) showed the peaks for Zr 3d, O 1s, C 1s and S 2p in both fresh and re-used catalysts. The Zr 3d consists of two peaks; one intense peak at 184.5 eV and the other small peak at 186.6 eV for Zr^{4+} indicating Zr 3d_{5/2} and Zr 3d_{3/2} lines, respectively.²² In addition, a small satellite peak of Zr 3d was observed at 175.7 eV.²³ The peaks were observed at slightly higher binding energy relative to that reported for Zr 3d (~182-185 eV) in SZ samples,²²⁻²⁵ which may be due to the presence of the strong electron-withdrawing effect of sulfate species bonded to the zirconia surface indicating higher acidic character of zirconium species.¹⁷ The intensity of both peaks was reduced in the re-used catalyst.

The O 1s peak at 533.4 eV in fresh SZ-PP-f catalyst has become broad and is shifted to lower binding energy in the re-used SZ-PP-r catalyst. The broadness of O 1s peak in the re-used catalyst shows the presence of two components, one at 532 eV and the other, a shoulder at ~530 eV. The O 1s peak at higher binding energy (>530 eV) is for oxygen associated with sulfate and hydroxyl groups while the peak at lower binding energy (~530 eV) is indicative of oxygen of the zirconia framework.²⁶ The presence of O 1s peak at higher binding energy in both fresh (at 533.4 eV) and re-used (at 532 eV) catalysts indicates the presence of sulfate species with hydroxyl groups of zirconia surface. Both O 1s and Zr 3d XPS spectra of the re-used catalyst indicate the variation in the ZrO_2 chemical environment.

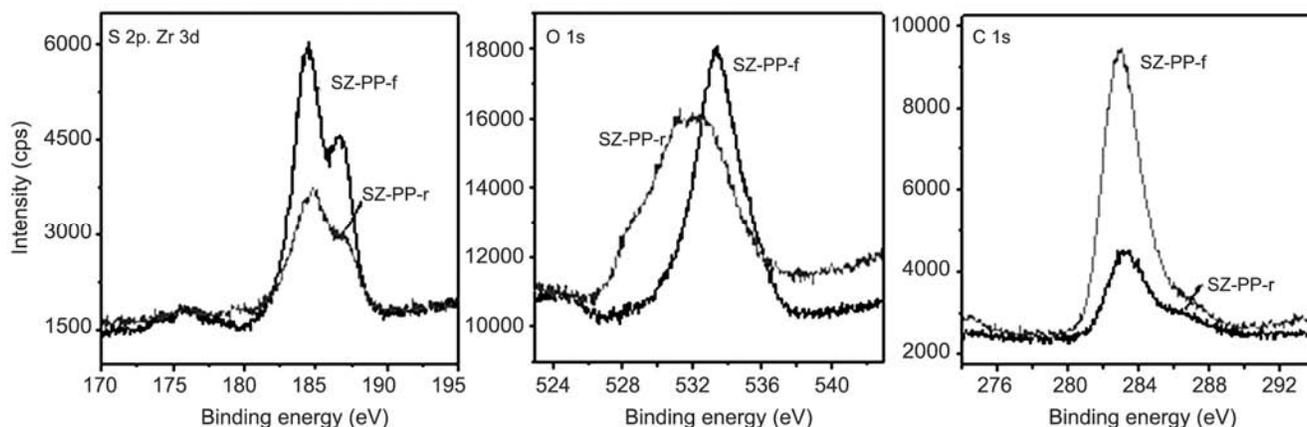


Fig. 6—XPS of fresh (SZ-PP-f) and re-used (SZ-PP-r) catalysts.

The S 2*p* spectrum was not very clear, probably due to the low intrinsic sensitivity factor of sulfur.²⁵ A very weak peak at ~170 eV is in agreement with S^{VI} in sulfates and SZ samples and corresponded to protonated sulfate species.¹⁷ No appreciable presence of sulfur species of lower valence state was observed in the re-used catalyst.

The presence of C 1*s* peak at 283 eV in fresh SZ-PP-f catalyst indicates the presence of carbon impurities (C-C/C-H species) (0.04 wt% by elemental analysis). The intensity of C 1*s* peak was significantly enhanced in re-used catalyst, which may be due to the deposition of carbonaceous material (0.06 wt% by elemental analysis). The organic species, i.e., reactants/products/organo-sulfur complexes, which could not be completely removed during normal washing of the re-used catalyst, is deposited as a coke on the surface acid sites of the catalyst during thermal activation of the catalyst, resulting in decrease in acid sites, and thus, slightly affecting the activity of the catalyst.

To study the effect of activation on the activity, the re-used SZ-PP-r catalyst was activated at varied temperatures (450, 500, 600 °C), time (2-4 h) and atmosphere (in muffle furnace with static air and in tubular furnace with air flow). The re-used catalyst activated at 450 or 500 °C under air flow for 4 h showed slightly higher activity (~2%) than the re-used catalyst, activated under static air for 2 h, due to the removal of carbonaceous matter with air flow.

Recently we have studied the esterification of myristic acid with short chain alcohols over SZ catalyst prepared by sol gel method,¹⁹ which

also exhibited >98% conversion at 60 °C after 5 h. Thus, both conventional precipitation and sol-gel methods have been found suitable for developing an efficient nano-crystalline sulfated zirconia catalyst having comparable acidity and activity for the studied reaction under the present reaction protocol.

Conclusions

Sulfated zirconia catalyst is a highly efficient catalyst for esterification of myristic acid with methanol. The re-used catalyst also showed good performance without significant decrease in activity. The characterization of spent catalyst revealed no significant change in structural and textural properties, although slight decrease in surface acidity was observed due to deposition of carbonaceous matter on the surface acid sites. Attempts for complete removal of carbonaceous species from used catalyst are under progress.

Supplementary Data

Supplementary data associated with this article, i.e., Figs S1-S3 including the PXRD pattern, FT-IR spectra and TG/DTA of the SZ catalyst are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_53A\(07\)799-805_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_53A(07)799-805_SupplData.pdf).

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