

Article ID: 1001-3555(2019)02-0149-10

Water-tolerant Co-functionalized Mesostructure SBA-15 as Efficient Catalysts for Glycerol-acetic acid Esterification

LI Rui-yun^{1, 2}, SONG He-yuan^{1, 2}, JIN Fu-xiang¹, CHEN Jing^{1*}

(1. State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;
2. University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract: A series of water-tolerant propylsulfonic acid and *n*-octyl group co-functionalized mesostructure SBA-15 were prepared by post-modification. Physico-chemical properties of synthesized catalysts were examined by N₂ adsorption-desorption (BET), XRD, FT-IR, TG, TEM and acid-base titration. Catalytic performance was evaluated in the glycerol-acetic acid esterification reaction and effect of reaction temperature, reaction time, catalyst loading, and molar ratio of reactants on conversion and selectivity were investigated. Octyl-PrSO₃H-SBA-15 used as catalyst could obtain 100% glycerol conversion and 89.9% diacetin and triacetin selectivity for high acid content and hydrophobicity. Water tolerance of the catalysts were examined by the addition of the increasing amount of water, and Octyl-PrSO₃H-SBA-15 exhibited better water tolerance compared to less hydrophobic PrSO₃H-SBA-15. Co-functionalized mesoporous catalysts are reusable, with no obvious loss in catalytic activity after nine cycles.

Key words: mesoporous silica; propylsulfonic acid; *n*-octyl group; co-functionalization; water tolerance

CLC number: O643.32

Document code: A

Biodiesel represents an alternative to oil-based diesel. It is a renewable, high quality fuel with excellent lubricating characteristics, synthesized in the transesterification of lipids (mostly vegetable origin) and low-molecular alcohols^[1-4]. According to OECD 2015 market report^[5], global biodiesel production may rapidly increase to 39 billion liters in 2024. Glycerol is the by-product of biodiesel production and the global glycerol market is rising rapidly. Due to oversupply, the glycerol price is dropping significantly and, at the same time, the sustainability issues occur^[6].

Moreover, the glycerol co-produced in the biodiesel production is usually “crude glycerol” containing water, methanol and other impurities^[7]. The conversion of crude glycerol into the chemicals with added value can expand the glycerol market and increase the efficiency of biodiesel industry. As shown in Scheme 1,

glycerol can be converted into many valuable chemicals through esterification, acetalization, dehydration, and hydrogenolysis^[8-13]. One well-commercialized process is esterification of glycerol with various amount of acetic acid to produce monoacetin, diacetin and triacetin (MA, DA and TA). DA and TA used as transport fuel additives can improve low-temperature and viscosity properties, making them the common components of bio-additives^[14].

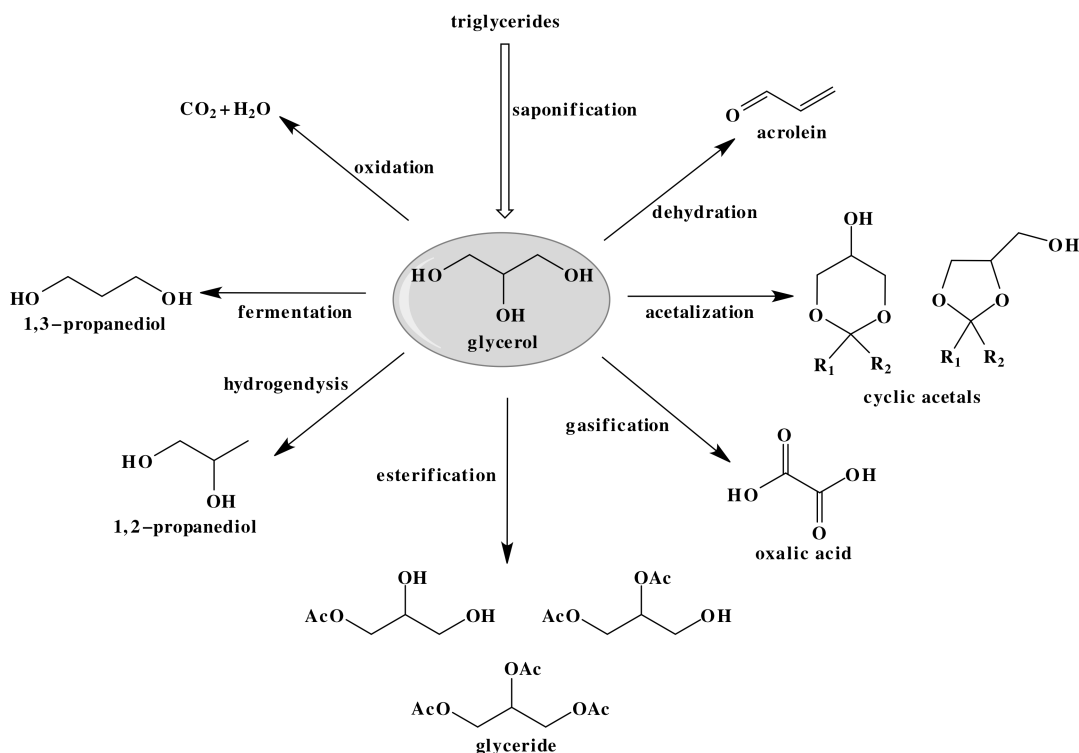
Traditionally, the esterification reaction was conducted in the homogeneous system using strong acids (H₂SO₄, HCl, HI and PTSA)^[15]. However, environmental problems such as waste management, corrosion of equipment and toxicity caused by these catalysts are incompatible with the tight environmental legislation. Thus, the replacement of homogeneous catalysts by the heterogeneous, renewable solid acids became an

Received date: 2019-03-18; **Revised date:** 2019-03-30.

Foundation: This project was supported by the National Natural Science Foundation of China (Grant No. 21673259) and the Natural Science Foundation of Jiangsu Province of China (No. BK20171241) (国家自然科学基金 (21673259); 江苏省自然科学基金 (No. BK20171241)).

First author: Ruiyun Li (1990-), female, master, E-mail: liruiyun@licp.cas.cn (李瑞云 (1990-), 女, 博士研究生. E-mail: liruiyun@licp.cas.cn).

Corresponding author: Tel: 0931-4968068; E-mail: chenjl@licp.cas.cn.



Scheme 1 Glycerol conversion to monoglycerides, diglycerides and triglycerides

important task. Some heterogeneous catalysts used in esterification reaction including zeolites (HUSY, HZSM-5, SBA-15), ion exchangers (Amberlyst-15, Amberlyst-16), metal oxides and heteropolyacids et al^[16–20].

InbaeKim^[21] tested the various solid acids as esterification catalysts and obtained the following order of efficiency: PrSO₃H-SBA-15 > Amberlyst-15 > HPMo/Nb₂O₅ > HPMo/SBA-15 > HUSY > SCZ > SiO₂-Al₂O₃. Hu et al^[22] used metal oxides of bismuth, antimony, tin, and niobium as efficient catalysts in the same esterification reaction, reaching 96.8% of glycerol conversion and 54.2% selectivity toward diacetin. Manayil^[23] investigated the reaction between acetic acid and aromatic alcohols, catalyzed by propylsulfonic acid functionalized silica PrSO₃H-SBA-15. It was confirmed that the mesoporous PrSO₃H-SBA-15 showed better catalytic performance than microporous zeolites in esterification with benzyl-alcohol^[24–25].

Mesoporous silica materials possess hexagonal array and uniform channel distribution^[26]. Functionalized mesoporous silica is a highly attractive material for het-

erogeneous catalysis and widely used as heterogeneous catalysts. To increase the acidity of mesoporous silica, the mesostructured SBA-15 was functionalized with propyl, arene, and perfluoro sulfonic acids by post-grafting^[27].

Water as by-product of esterification reaction may reduce the performance of heterogeneous catalyst greatly. Modification of mesoporous materials with hydrophobic groups and the formation of hydrophobic environment into the catalyst's pores is one of the methods for increasing the efficiency of esterification reaction^[28–29].

In this study, an array of co-functionalized SBA-15 with excellent hydrophobic properties and acid content were synthesized and their performance was evaluated using glycerol-acetic acid esterification as a model reaction. The effect of reaction conditions on the selective formation of diacetin and triacetin was also investigated. The water-tolerability was studied by adding excess amounts of water. The application of sulfonated mesoporous SBA-15 as heterogeneous catalysts for glycerol-acetic acid esterification is described in this manuscript for the first time.

1 Experimental

1.1 Materials

The mesoporous silica material was synthesized following the previously described procedure^[30–32]. 3-mercaptopropyltrimethoxysilane (MPTMS, 95%) was obtained from Aldrich Chemicals. Methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES), *n*-propyltriethoxysilane and *n*-decyltriethoxysilane were purchased from Alfa Aesar. N-Octyltrimethoxysilane (OTMS) and perfluorooctyltrimethoxysilane (PFOTS) were purchased from Acros organics. Toluene, anhydrous methanol and ethanol were obtained from Rianlon Chemical Co., Ltd. Other reagents were analytical grade, and used without additional purification.

1.2 Synthesis of catalysts

1.2.1 Synthesis of PrSH-SBA-15 Mercaptopropyl grafted mesoporous SBA-15 was synthesized using previously described post-grafting method. The 1 g of SBA-15 was dispersed into 30 mL deionized water, various amounts of MPTMS were added and the mixture was heated at 100 °C for 24 h under reflux. The products were washed with MeOH and vacuum-dried for 12 h and obtained products were denoted as PrSH-SBA-15.

1.2.2 Synthesis of co-functionalized catalysts (Octyl/Propyl/Decyl-PrSO₃H-SBA-15-SH, PrSO₃H-PFO-SBA-15, PrSO₃H-Ph-SBA-15, PrSO₃H-Me-SBA-15)

Several PrSO₃H-functionalized SBA-15 and its co-derivatized catalysts were prepared by previously described method. 3 g of PrSH-SBA-15 was dispersed in 30 mL toluene, followed by the addition of 4 mmol of OTMS (PFOTS or PTES or MTES). The mixture was heated at 130 °C for 24 h (under reflux). The resulting materials were filtered, washed with MeOH and vacuum-dried for 12 h.

1.2.3 Oxidation of -PrSH to -PrSO₃H Complete oxidation of -Octyl/Decyl/Propyl/PFO/Ph/Megrafted-

PrSH to -PrSO₃H were conducted with hydrogen peroxide. 1 g of the synthesized thiol-propyl functionalized materials was added to 30 mL of 30% aqueous H₂O₂ and the mixture was stirred at room temperature for 24 h. Afterward, the products were filtered, and washed with MeOH and vacuum-dried for 24 h, and isolated as white powders.

1.3 Material Characterization

The pore size, pore volume and the surface area of derivatized mesoporous silica were determined by N₂ adsorption-desorption on a TristarII 3020 instrument (Micromeritics, USA). Before adsorption, the samples were degassed at 423 K for 4 h. The powder X-ray diffraction data were acquired on a PANalytical Empyrean apparatus (Netherlands) with 0.02° step in the small-angle. Fourier transform infrared (FT-IR) spectra were recorded at room temperature in the 4000~400 cm⁻¹ on a Nexus 870 spectrometer (Nicolet Instruments Co., USA). Simultaneous thermal analyzer Netzsch Model STA 449 F3 (Netzsch, Germany) was utilized for recording thermogravimetry/differential scanning calorimetry (TG/DSC) profiles of all samples under N₂ atmosphere.

The amount of the acidic sites in catalysts was quantified via acid-base titration. The sample was dispersed in 50 mL of 2 mol/L NaCl (50 mL), left for 24 h, and titrated with 0.01 mol/L solution of NaOH.

1.4 Glycerol-acetic acid reaction

Typically, the reaction mixture consisting of 2 g of glycerol, a corresponding amount of acetic acid and catalysts were added into the round-bottom flask. The qualitative and quantitative analysis of the resulting solution was performed on an Agilent 7890/5975A GC-MS and Agilent 7890A gas chromatograph with HP-5 column (0.32 mm×30 m×0.32 μm).

The conversion percentage of glycerol and selectivity for glycerol-acetic acid esterification products were calculated as:

$$\text{Conversion of glycerol (mol\%)} = \frac{\text{Initial glycerol (mol\%)} - \text{Final glycerol (mol\%)}}{\text{Initial glycerol (mol\%)}} \times 100\%$$

$$\text{Selectivity for esterification products (mol\%)} = \frac{\text{Desired product (mol\%)}}{\text{Total obtained products (mol\%)}} \times 100\%$$

2 Results and discussion

2.1 Catalysts Characterization

The structural properties of modified and non-modified mesoporous SBA-15 were initially assessed by powder XRD (Fig.1). All functionalized materials exhibited three diffraction peaks characteristic for parent SBA-15, confirming the maintenance of a hexagonal, mesoporous structure in catalysts. The same conclusion can be derived from TEM images of corresponding samples (Fig.2).

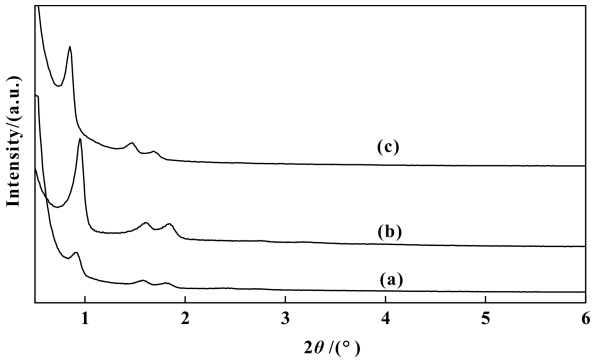


Fig.1 Small-angle XRD patterns of (a) SBA-15; (b) PrSO₃H-SBA-15; (c) Octyl-PrSO₃H-SBA-15

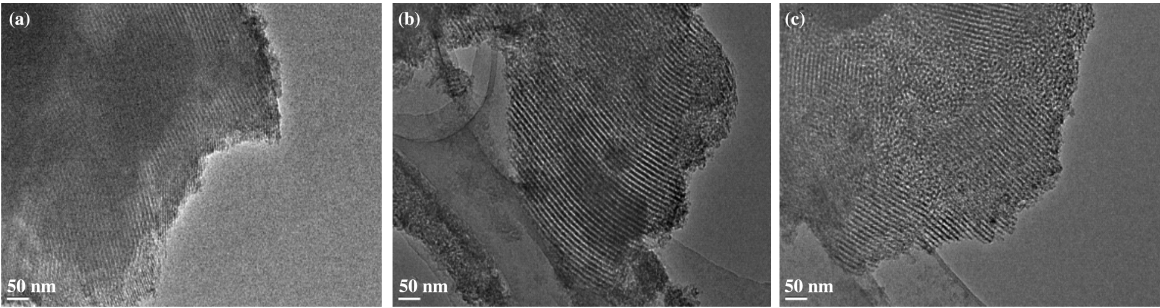


Fig.2 TEM images of (a) SBA-15; (b) Octyl-PrSO₃H-SBA-15; (c) PrSO₃H-SBA-15

Physico-chemical properties of parent and modified materials are listed in the Table 1. The surface area and the pore diameter of parent material SBA-15 were 542 m² g⁻¹ and 9.7 nm, respectively. The corresponding values for functionalized Octyl-PrSO₃H-SBA-

15 were 387.4 m² g⁻¹ and 8.8 nm, respectively. Functionalization with MPTMS and *n*-octyl groups apparently reduces the surface area, pore diameter and pore volume. The incorporation of functional groups occupies the inner surface of mesoporous silica pores.

Table 1 Structure parameter of the catalytic materials in present work

composition	Surfacearea ^a /(m ² · g ⁻¹)	Average pore diameter ^b /nm	Total BJH porevolume	Acidcapacity ^c /(mmol · g ⁻¹)
SBA-15	542	9.7	1.30	—
Octyl-PrSO ₃ H-SBA-15	386	8.8	0.85	1.30
Octyl-PrSH-SBA-15	162	7.7	0.31	—
PrSO ₃ H-SBA-15	343	9.8	0.84	1.03
Propyl-PrSO ₃ H-SBA-15	304	9.0	0.68	1.14
Decyl-PrSO ₃ H-SBA-15	368	9.0	0.83	1.20
PrSO ₃ H-Me-SBA-15	371	8.7	0.81	1.28
PrSO ₃ H-Ph-SBA-15	387	8.8	0.85	1.13
PrSO ₃ H-PFO-SBA-15	378	8.7	0.82	1.17

a. From BET equation; b. Analyzed from the desorption branch; c. Total acidity based on base-acid titration.

To certify the successful incorporation of the organic functional groups on the mesostructured SBA-15, FT-IR spectra of catalysts used in the experiment were recorded (Fig.3). The signals at 3480 cm^{-1} are associated with O - H and Si - O of silica. Comparing with the

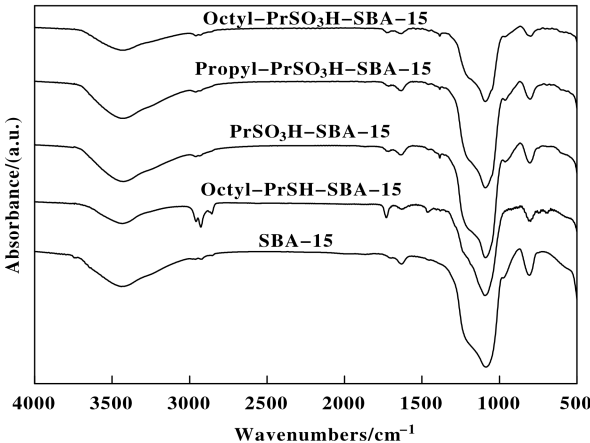


Fig.3 Fourier transform infrared spectra of the samples

parent SBA-15, the characteristic bands around 1244 cm^{-1} and 1100 cm^{-1} were attributed to the asymmetric vibration of S = O and asymmetric stretching vibration of SO_3H group, confirming the complete sulfonation and oxidation of the materials^[33]. The strong C-H vibration of the alkyl groups in *n*-octyl were observed at 2938 cm^{-1} indicating the successful incorporating of alkyl groups. All these results reveal that the $-\text{SO}_3\text{H}$ group and alkyl groups were successfully attached to the walls of SBA-15 molecular sieve.

The thermal stability of mesoporous materials were measured via TG, and the weight losses were illustrated in Fig.4. TG analysis of catalysts shows two weight

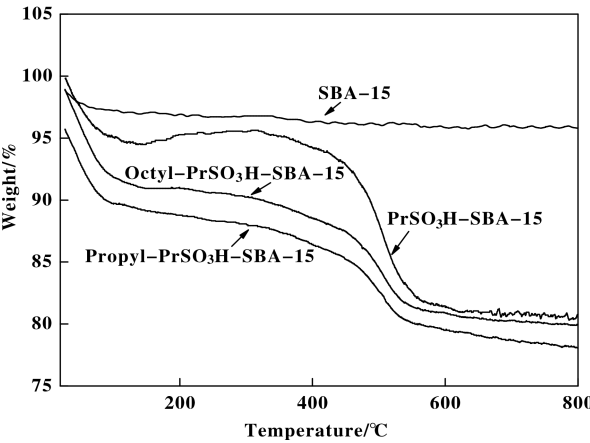


Fig.4 TG curves of the synthesized catalysts

losses. The first weight loss occurs below $100\text{ }^\circ\text{C}$ as a result of water desorption and the second loss peak at $500\text{ }^\circ\text{C}$ is corresponding to the cleavage of chemically bound organic groups. These results suggested the excellent thermal stability of the series of catalysts.

2.2 Comparative analysis of solid catalysts

The progress of glycerol-acetic acid reaction can be divided into three consecutive stages. First, equal amounts of glycerol and acetic acid react to form monoacetin (MA). In the second step, MA reacts with an equal amount of acetic acid to obtain diacetin (DA) followed by the formation of triacetin (TA) in the third step. In the manufacturing process, MA is considered as the undesired reaction product. The acid-catalyzed three-step mechanism can be simplified by the following scheme:



In our experimental setup, the glycerol-acetic acid esterification was performed at $110\text{ }^\circ\text{C}$, with 1 : 9 molar ratio of glycerol to acetic acid. Initially, the commercial, tridimensional zeolites (HY and HZSM-5) and ion-exchange resin Amberlyst-15 were used as catalysts, and the results are shown in Fig.5. Within the first 4 h of reaction, catalyst Octyl- $\text{PrSO}_3\text{H-SBA-15}$ showed superior properties compared to Amberlyst-15, HY, HZSM-5 and $\text{PrSO}_3\text{H-SBA-15}$. It indicated that the co-functionalized Octyl- $\text{PrSO}_3\text{H-SBA-15}$ has a superior conversion rate and selectivity towards DA and TA.

Furthermore, catalysts with various organo-functional groups were evaluated and the results shown in Fig.6. It can be obviously seen that all the catalysts obtained high glycerol conversion. The diacetin and triacetin selectivity of Propyl- $\text{PrSO}_3\text{H-SBA-15}$, Decyl- $\text{PrSO}_3\text{H-SBA-15}$, $\text{PrSO}_3\text{H-PFO/PH/Me-SBA-15}$ is lower than Octyl- $\text{PrSO}_3\text{H-SBA-15}$ apparently. Alkyl groups with different chain length were incorporated on the propylsulfonic acid functionalized SBA-15 and *n*-octyl is the best choice. Octyl- $\text{PrSO}_3\text{H-SBA-15}$ obtained 100% glycerol conversion and 89.9% diacetin and triacetin selectivity.

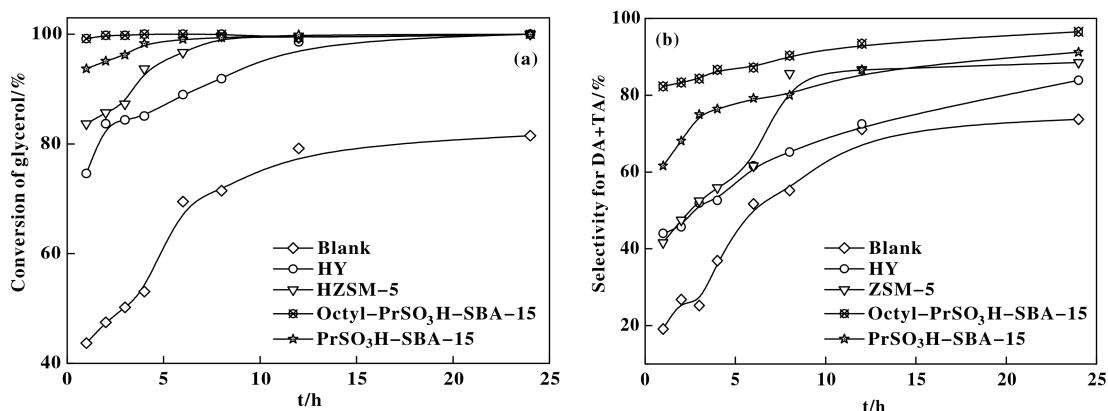


Fig.5 Glycerol-acetic acid esterification over different catalysts

Reaction conditions: 1.09% (Weight percentage) of Octyl-PrSO₃H-SBA-15, glycerol : acetic acid = 1 : 9 (molar ratio), 110 °C, 4 h

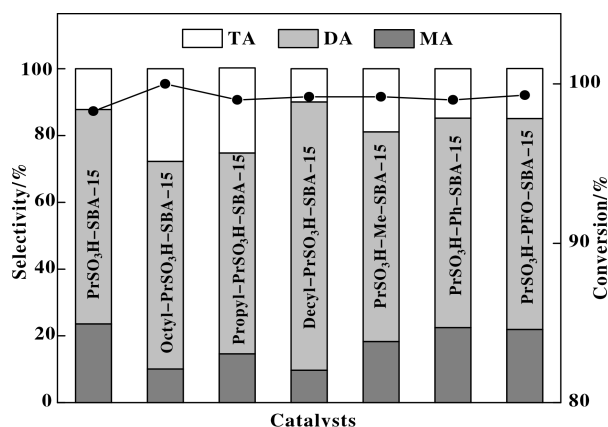


Fig.6 Catalytic activity and selectivity of catalysts with various organo-functional groups in the glycerol-acetic acid esterification reaction

Reaction conditions: glycerol : acetic acid = 1 : 9 (molar ratio), catalyst amount 1.09% (Weight percentage), 110 °C, 4 h

The acid content of the functionalized mesostructured catalysts were quantified using acid-base titration. The acidity of sulfonic acid mesoporous silica functionalized with electron-withdrawing groups like phenyl (in Sample PrSO₃H-Ph-SBA-15) or fluorinated groups (in Sample PrSO₃H-PFO-SBA-15) is close to the material containing only sulfonic acid groups (Table 1). The catalyst Octyl-PrSO₃H-SBA-15 had the highest content of acidic groups (1.30 mmol/g), which is consistent with its superior catalytic performance.

2.3 Effect of reaction conditions

The effect of reaction conditions (reaction temperature, reaction time, the amount of catalyst and the molar ratio of reactants) on glycerol conversion and se-

lectivity towards DA and TA were investigated using Octyl-PrSO₃H-SBA-15 as catalysts. As shown in Fig.7, reaction temperature, reaction time, the amount of catalyst and the molar ratio of reactants exhibited varying degrees of effect on catalytic performance. Among all reaction parameters investigated, the temperature had the highest influence on the efficiency and selectivity of this reaction.

2.4 Water tolerance

Esterification is an equilibrium reaction and the reaction rate depends on the local H₂O concentration near the acid site which may reversely hydrolysis reaction. Water tolerance of Octyl-PrSO₃H-SBA-15 and PrSO₃H-SBA-15 were synthesized and tested in this study by adding the increasing amount of water (5% (Weight percentage), 10% (Weight percentage), 15% (Weight percentage) and 20% (Weight percentage)) into the reaction mixture keeping all other reaction parameters constant (Fig.8). For both catalysts, the addition of 20% (Weight percentage) water significantly reduces the glycerol conversion, compared to 15% water-doped system. The Octyl-PrSO₃H-SBA-15 catalyst reaches 99.5% conversion and 74.8% selectivity toward DA and TA at 20% (Weight percentage) of water, while PrSO₃H-SBA-15 has 94.6% conversion and 61.2% selectivity under the same experimental conditions.

The competitive adsorption of water and alcohol at the acid site may leads to the loss of catalytic activity. Octyl-PrSO₃H-SBA-15 has better water tolerance compared to PrSO₃H-SBA-15, which can be rationalized

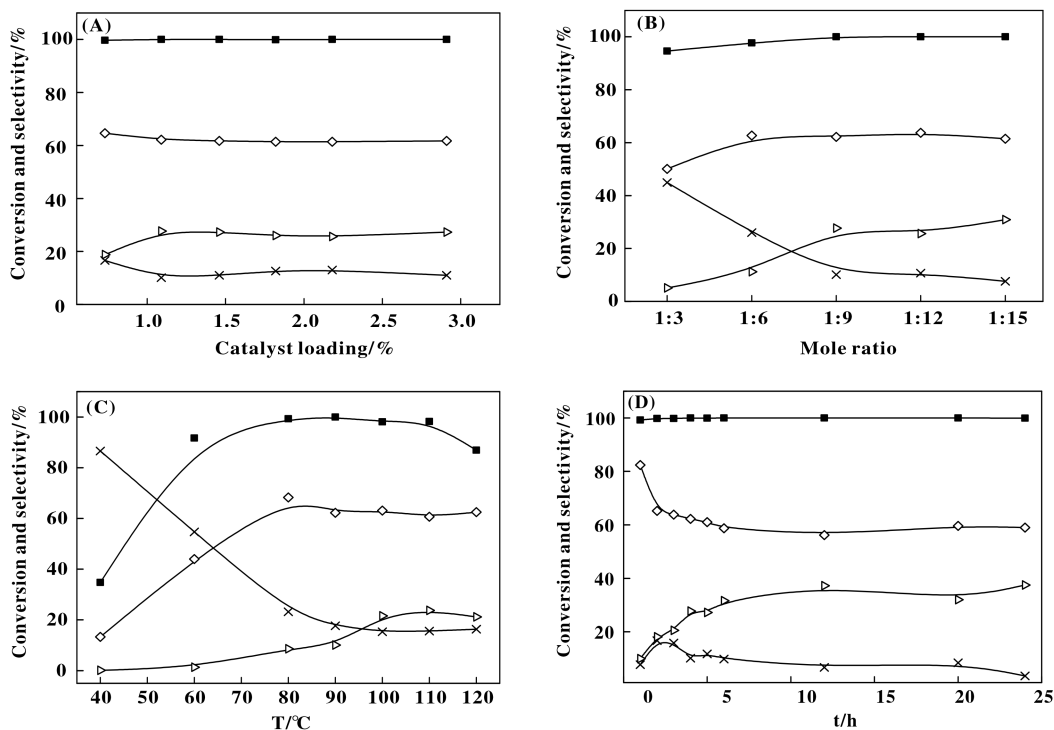


Fig.7 Effect of reaction conditions in the glycerol-acetic acid esterification reaction

■ Conversion of glycerol × Selectivity for monoacetin ◇ Selectivity for diacetin ▴ Selectivity for triacetin

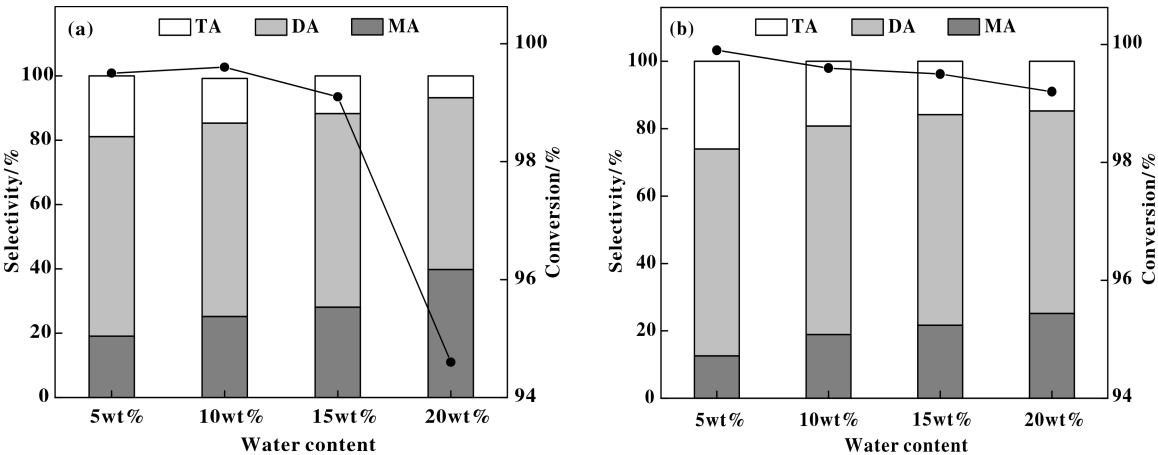


Fig.8 Comparison of water tolerance test: (a) PrSO₃H-SBA-15 and (b) Octyl-PrSO₃H-SBA-15

Reaction conditions: 1.09% (Weight percentage) of Octyl-PrSO₃H-SBA-15 catalyst, glycerol : acetic acid= 1 : 9 (molar ratio) , 110 °C , 4 h

by the presence of hydrophobic groups bounded to the surface of pores which impedes the entrance of water into the pores and interaction with acidic groups. Therefore, increasing the hydrophobicity of catalyst can reduce the adsorption of water on the acid site. Co-functionalized catalyst with octyl chains was used to tune the hydrophobicity of the catalyst and to drive reactively formed water away from the acid site.

2.5 Reusability

The stability and reusability of Octyl-PrSO₃ H-SBA-15 catalyst was also evaluated. After each glycerol-acetic acid reaction cycle, the solid catalysts were prepared for the next run by centrifugation and subsequent washing of solid residue with methanol. As shown in Fig.9, Octyl-PrSO₃ H-SBA-15 retained its catalytic activity for nine recycles, without significant decrease

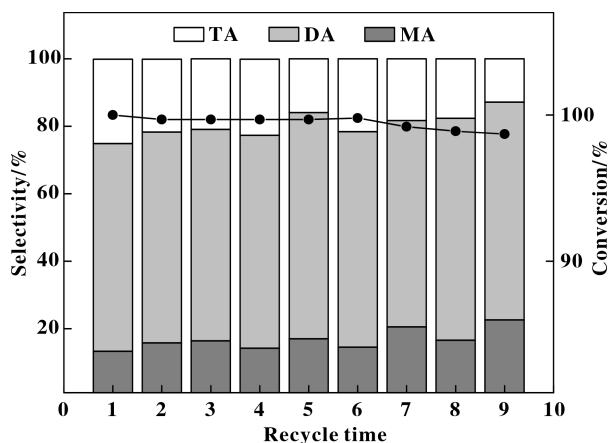


Fig.9 Reusability of Octyl-PrSO₃H-SBA-15 in esterification of glycerol with acetic acid

Reaction conditions: 1.09% (Weight percentage) of Octyl-PrSO₃H-SBA-15, glycerol : acetic acid = 1 : 9 (molar ratio) 110 °C , 4 h

in conversion of glycerol and selectivity toward DA and TA. After nine recycles, the conversion and selectivity were 95.9% and 69.6%, respectively.

3 Conclusion

The glycerol-acetic acid esterification reaction was used as a model system for studying the catalytic performance of water-tolerant co-functionalized SBA-15 catalysts. The structure of catalysts was investigated by BET, FT-IR, TG, TEM and acid-base titration. The effect of reaction parameters such as the reaction temperature, reaction time, the amount of catalyst, and the molar ratio of reactants were discussed. Octyl-PrSO₃H-SBA-15 showed 100% conversion and 89.9% selectivity toward diacetin and triacetin with the molar ratio of glycerol to acetic acid 1 : 9 at 110 °C for 4 h. Water tolerance of novel catalysts (Octyl-PrSO₃ H-SBA-15 and PrSO₃H-SBA-15) was thoroughly investigated. Octyl-PrSO₃H-SBA-15 showed superior performance and could be recycled for nine times without losing the conversion efficiency and selectivity toward DA+TA formation.

Acknowledgment: This work was supported by the National Natural Science Foundation of China (Grant No. 21673259) and the Natural Science Foundation of Jiangsu Province of China (No. BK2017 1241).

References:

- [1] Zhou C H, Beltramini J N, Fan Y X, *et al.* Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals [J]. *Chem Soc Rev*, 2008, **37**(3) : 527–549.
- [2] Margolese D, Melero J A, Christiansen S C, *et al.* Direct syntheses of ordered SBA-15 mesoporous silica containing sulfonic acid groups [J]. *Chem Mater*, 2000, **12** (8) : 2448–2459.
- [3] Climent M J, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels [J]. *Green Chem*, 2014, **16**(2) : 516–547.
- [4] Trejda M, Stawicka K, Ziolek M. New catalysts for biodiesel additives production [J]. *Appl Catal B: Environ*, 2011, **103**(3/4) : 404–412.
- [5] Gomes L, Simões S J C, Forti M C. OECD/Food and agriculture organization of the united nations [J]. *OECD-FAO Agricultural Outlook 2015*, *OECD Publishing*, Paris, 2015.
- [6] Anitha M, Kamarudin S K, Kofli N T. The potential of glycerol as a value-added commodity [J]. *Chem Engineer J*, 2016, **295**: 119–130.
- [7] Hu S, Luo X, Wan C, *et al.* Characterization of crude glycerol from biodiesel plants [J]. *J Agric Food Chem*, 2012, **60**(23) : 5915–5921.
- [8] Ma T, Ding J, Shao R, *et al.* Dehydration of glycerol to acrolein over Wells-Dawson and Keggin type phosphotungstic acids supported on MCM-41 catalysts [J]. *Chem Engineer J*, 2017, **316**: 797–806.
- [9] Liu Feng-guo (刘丰国), Zhao Li-zhi (赵立知), Hua Dong-long (花东龙), *et al.* The mini-review on novel catalytic conversion of glycerol to acrylic acid (催化转化丙三醇生产丙烯酸工艺研究简述) [J]. *Zhejiang Chem Indus* (浙江化工), 2015, **46**: 43–47.
- [10] Katryniok B, Paul S, Dumeignil F. Recent developments in the field of catalytic dehydration of glycerol to acrolein [J]. *ACS Catal*, 2013, **3**(8) : 1819–1834.
- [11] Nakagawa Y, Tomishige K. Heterogeneous catalysis of the glycerol hydrogenolysis [J]. *Catal Sci Technol*, 2011, **1**(2) : 179–190.
- [12] Wang Y, Zhou J, Guo X. Catalytic hydrogenolysis of glycerol to propanediols: a review [J]. *RSC Adv*, 2015, **5**(91) : 74611–74628.
- [13] Fang Wei-guo (方伟国), Yao Xiao-lan (姚小兰), Yang Ji-dong (杨继东), *et al.* Research progress of catalysts in hydrogenolysis of bioglycerol to 1, 3-propanediol

- (生物基氢解合成 1, 3-丙二醇催化剂的研究进展) [J]. *J Mol Catal (China)* (分子催化), 2018, **32**(6): 581–593.
- [14] Melero J A, Vicente G, Morales G, *et al.* Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters[J]. *Fuel*, 2010, **89**(8): 2011–2018.
- [15] Liu F, Wang L, Sun Q, *et al.* Transesterification catalyzed by ionic liquids on superhydrophobic mesoporous polymers: Heterogeneous catalysts that are faster than homogeneous catalysts[J]. *J Am Chem Soc*, 2012, **134**(41): 16948–16950.
- [16] Li R, Song H, Chen J. Propylsulfonic acid functionalized SBA-15 mesoporous silica as efficient catalysts for the acetalization of glycerol [J]. *Catal*, 2018, **8**: 297.
- [17] Reddy P S, Sudarsanam P, Raju G, *et al.* Synthesis of bio-additives: Acetylation of glycerol over zirconia-based solid acid catalysts[J]. *Catal Commun*, 2010, **11**(15): 1224–1228.
- [18] Trejda M, Stawicka K, Dubinska A, *et al.* Development of niobium containing acidic catalysts for glycerol esterification[J]. *Catal Today*, 2012, **187**(1): 129–134.
- [19] Wang Bao-jie (王宝杰), Zhao Hong-juan (赵红娟), Wang Jiu-jaing (王久江), *et al.* Comparative study of three zeolites with different topologies (SAPO-34, Al-ITQ and ZSM-5) in MTO reaction (三种不同拓扑结构的分子筛在甲醇制烯烃反应中的性能对比) [J]. *J Mol Catal (China)* (分子催化), 2018, **32**(6): 493–500.
- [20] Rastegari H, Ghaziaskar H S, Yalpani M. Valorization of biodiesel derived glycerol to acetins by continuous esterification in acetic acid: Focusing on high selectivity to diacetin and triacetin with no byproducts[J]. *Indus Engineer Chem Res*, 2015, **54**(13): 3279–3284.
- [21] Kim I, Kim J, Lee D. A comparative study on catalytic properties of solid acid catalysts for glycerol acetylation at low temperatures [J]. *Appl Catal B: Environ*, 2014, **148/149**: 295–303.
- [22] Hu W, Zhang Y, Huang Y, *et al.* Selective esterification of glycerol with acetic acid to diacetin using antimony pentoxide as reusable catalyst [J]. *J Energy Chem*, 2015, **24**(5): 632–636.
- [23] Manayil J C, Inocencio C V M, Lee A F, *et al.* Mesoporous sulfonic acid silicas for pyrolysis bio-oil upgrading via acetic acid esterification[J]. *Green Chem*, 2016, **18**(5): 1387–1394.
- [24] Konwar L J, Mäki Arvela P, Begum P, *et al.* Shape selectivity and acidity effects in glycerol acetylation with acetic anhydride: Selective synthesis of triacetin over Y-zeolite and sulfonated mesoporous carbons[J]. *J Catal*, 2015, **329**: 237–247.
- [25] Silva L N, Gonçalves V L C, Mota C J A. Catalytic acetylation of glycerol with acetic anhydride[J]. *Catal Commun*, 2010, **11**(12): 1036–1039.
- [26] Li Xiang-zhen (李祥珍), Wang Xiao-zhong (王晓钟), Liu Yu (刘瑜), *et al.* Research progress in the synthesis of mesoporous Al-SBA-15 material (介孔材料 Al-SBA-15 的合成研究进展) [J]. *Chem Indus Engineer Pro* (化工进展), 2013, **32**(7): 1555–1563.
- [27] Melero J A, Grieken R V, Morales G, *et al.* Acidic mesoporous silica for the acetylation of glycerol: synthesis of bioadditives to petrol fuel [J]. *Energy Fuel*, 2007, **21**(3): 1782–1791.
- [28] Karimi B, Mirzaei H M, Mobaraki A. Periodic mesoporous organosilica functionalized sulfonic acids as highly efficient and recyclable catalysts in biodiesel production [J]. *Catal Sci Technol*, 2012, **2**(4): 828–834.
- [29] Zhang W H, Lu X B, Xiu J H, *et al.* Synthesis and characterization of bifunctionalized ordered mesoporous materials[J]. *Adv Func Mater*, 2004, **14**(6): 544–552.
- [30] Pirez C, Caderon J M, Dacquin J P, *et al.* Tunable KIT-6 mesoporous sulfonic acid catalysts for fatty acid esterification[J]. *ACS Catal*, 2012, **2**(8): 1607–1614.
- [31] Das D, Lee J F, Cheng S. Selective synthesis of Bisphenol-A over mesoporous MCM silica catalysts functionalized with sulfonic acid groups[J]. *J Catal*, 2004, **223**(1): 152–160.
- [32] Rhijn W M V, Vos D E D, Sels B F, *et al.* Sulfonic acid functionalised ordered mesoporous materials as catalysts for condensation and esterification reactions [J]. *Chem Commun*, 1998, **3**: 317–318.
- [33] Pirez C, Wilson K, Lee A F. An energy-efficient route to the rapid synthesis of organically-modified SBA-15 via ultrasonic template removal [J]. *Green Chem*, 2014, **16**(1): 197–202.

耐水性共功能化介孔 SBA-15 的制备及其在甘油与乙酸酯化反应中的应用

李瑞云^{1,2}, 宋河远^{1,2}, 金福祥^{1,2}, 陈 静^{1*}

(1. 中国科学院兰州化学物理研究所 碳基合成与氧化国家重点实验室, 甘肃 兰州 730000;

2. 中国科学院大学, 北京 100049)

摘要: 通过后嫁接法合成了一系列耐水性的丙烷磺酸和正辛基共功能化的介孔 SBA-15 催化剂. 采用 BET、XRD、FT-IR、TG、TEM 及酸碱滴定的方法对催化剂进行了结构性能表征, 并将其应用在丙三醇和乙酸的酯化反应中. Octyl-PrSO₃H-SBA-15 由于较高的酸量以及极好的耐水性而在丙三醇和乙酸酯化反应中取得了 100% 的丙三醇转化率和 89.9% 的甘油二乙酸酯和三乙酸酯收率. 对影响丙三醇转化率和产物选择性的反应温度、反应时间、催化剂用量及反应物比例等进行了讨论. 通过向反应体系中加入一定量额外的水对功能化的催化剂的耐水性进行了考察. 催化剂 Octyl-PrSO₃H-SBA-15 具有比 PrSO₃H-SBA-15 更好的耐水性能, 并且对该催化剂 Octyl-PrSO₃H-SBA-15 在循环使用 9 次以后, 其催化活性基本保持不变.

关键词: 介孔材料; 丙烷磺酸; 正辛基基团; 共功能化; 耐水性

《分子催化》简介

《分子催化》是由中国科学院兰州化学物理研究所主办、中国科学院主管、科学出版社出版的向国内外公开发行的学术性刊物. 主要报道有关分子催化方面最新进展与研究成果. 辟有学术论文、研究简报、研究快报及综述等栏目. 内容侧重于配位催化、酶催化、光助催化、催化过程中的立体化学问题、催化反应机理与动力学、催化剂表面态的研究及量子化学在催化学科中的应用等. 工业催化过程中的均相催化剂、固载化学的均相催化剂、固载化的酶催化剂等活化、失活和再生; 用于新催化过程的催化剂的优选与表征等方面的内容, 本刊亦有报道. 读者对象主要是科研单位及工矿企业中从事催化工作的科技人员、研究生、高等院校化学系和化工系的师生.

《分子催化》已被美国化学文摘(CA)、俄罗斯化学文摘、中国科学引文数据库、中国化学文献数据库、中国学术期刊文摘、中国化工文摘等国内外文献数据库收录. 《分子催化》现为《中文核心期刊要目总览》的中国核心期刊和中国科技核心期刊. 曾荣获中科院和甘肃省科委“优秀期刊三等奖”和“优秀科技期刊”奖.

《分子催化》为双月刊, 每逢双月末出版, 大 16 开本, 约 16 万字, 每册定价 30.00 元. 中国标准刊号: ISSN 1001-3555/CN 62-1039/O6.

欢迎订阅, 欢迎来稿.