Catalysis Today 148 (2009) 169–173

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Esterification over rare earth oxide and alumina promoted SO_4^{2-}/ZrO_2

G.X. Yu [a,b], X.L. Zhou [b,*], C.L. Li [b], L.F. Chen [c], J.A. Wang [c]

[a] School of Chemistry and Environmental Engineering, Jianghan University, Wuhan 430056, China
[b] School of Chemical Engineering, East China University of Science & Technology, Shanghai 200237, China
[c] ESIQIE, Instituto Politécnico Nacional, Av. Politécnico S/N, Col. Zacatenco, 07738 México D.F., Mexico

ARTICLE INFO

Article history:
Available online 15 April 2009

Keywords:
Sulfated zirconia
Rare earth oxide
Alumina promotion
Ethanol
Acetic acid
Esterification
Deactivation

ABSTRACT

Solid superacid catalysts including SO_4^{2-}/ZrO_2 (SZ), rare earth (RE) oxide-promoted SZ and RE oxides together with alumina-promoted SZ were prepared. Their catalytic performances in the esterification reaction of ethanol and acetic acid were investigated. The textural property, crystalline phase and surface acidity of the prepared catalysts were characterized by using nitrogen adsorption–desorption isotherms, X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy of pyridine adsorption techniques, respectively. Effects of the reaction time and catalyst reuse cycle as well as catalyst regeneration on the catalytic behaviors were studied. Experimental results showed that Yb_2O_3–Al_2O_3 promoted SZ (designated as SZAY) catalyst exhibited an optimal esterification performance; the Lewis acid sites with moderate and super strong strength could mainly be responsible for the esterification reaction; and doping both Yb_2O_3 and Al_2O_3 on SZ not only boosted the esterification activity but also alleviated catalyst deactivation resulted from the surface sulfur loss by solvation.

1. Introduction

Ethyl acetate is a useful solvent for the production of lacquers, enamels, inks, adhesives and pharmaceuticals. Recently, ethyl acetate has been used to replace aromatics as solvents in many chemical industrial processes due to its low toxicity. In the conventional approach for ethyl acetate production, sulfuric acid [1–4] was always used as catalyst, resulting in serious environment pollution and equipment corrosion problems besides the low product yield. In order to reduce environmental load, it is necessary to develop new and environmentally benign catalysts for the production of ethyl acetate.

Some of the solid acid catalysts have been investigated as potential replacements for mineral acids in the reactions of esterification and transesterification, these include: tungsten oxides [5–8], sulfated zirconia (SZ) [6,9–13] and organosulfonic functionalized mesoporous silicas [14–17]. In 1979, Hino et al. [18] reported that ferric oxide, prepared by calcination of iron sulfate to 700 °C, exhibited very high activity for chlorobenzene condensation polymerization, because of the residual sulfate ions on the ferric oxide surface. Later, they paid close attention to the roles of these ions and led to successful development of SO_4^{2-}-promoted solid superacids (SO_4^{2-}/M_xO_y) [19]. These catalysts showed high activity and selectivity in many acid catalytic reactions, including light alkanes isomerization [20,21], alkylation [22,23] and esterification [24,25]. It was also reported that sulfate zirconia showed the highest acid strength and excellent thermal stability among the catalysts aforementioned [26,27]. In addition, as a solid superacid, sulfate zirconia may alleviate corrosion of apparatus and thus reduce environmental pollution. Therefore, it was used as new catalytic material used in a variety of acid catalytic reactions. However, less attention has been paid to the promotion effects of different RE oxides and RE oxide–alumina on SZ in the esterification reaction. Particularly, up to now, the effect of the catalyst reuse cycle in the batch esterification reaction on the catalytic activity of the RE oxide–alumina doubly promoted SZ catalysts has not been reported in the literature, which is particular interesting in the evaluation of a catalyst lifetime.

In this paper, a series of solid superacid catalysts, including SO_4^{2-}/ZrO_2 (SZ), rare earth (RE) oxide-promoted SZ and RE oxide together with alumina-promoted SZ, were prepared. The textual properties and crystalline phases and surface acidity of these catalysts were characterized by different techniques. Effects of the physico-chemical properties of the catalysts on the esterification behaviors were investigated. Moreover, effects of reaction time and reuse cycle of SZ and SZAY on the esterification activity were also studied. The regeneration of the spent SZAY catalyst was examined and the catalyst deactivation was explored by analyzing the sulfur content changes of the SZAY catalyst before and after reaction.

---

* Corresponding author. Tel: +86 21 64252041; fax: +86 21 64253049.
E-mail address: xiaolong@ecust.edu.cn (X.L. Zhou).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.03.006

2. Experimental

2.1. Catalyst preparation

$Zr(NO_3)_4{\cdot}5H_2O$ was dissolved in de-ionized water to prepare a 0.4 mol l^{-1} zirconium ion-containing solution. Concentrated NH_4OH was added to it to adjust the pH value between 9 and 10. The precipitate was aged for 24 h followed by filteration, washing and then it was dried at 110 °C for 12 h to form $Zr(OH)_4$. The latter was impregnated in a 0.5 mol l^{-1} of H_2SO_4 solution for 12 h. The H_2SO_4 treated solid was dried at 110 °C for 12 h and then was calcined in a muffle furnace at 600 °C for 4 h and finally SO_4^{2-}/ZrO_2 (SZ) was obtained.

For the preparation of RE oxides doped SZ catalysts, a given amount of $Zr(OH)_4$ sample was impregnated with a $RE(NO_3)_3$ solution to obtain solid with 3.0 wt.% rare earth oxide (La_2O_3, CeO_2 or Yb_2O_3). After dried at 110 °C for 12 h, it was impregnated with a 0.5 mol l^{-1} of H_2 SO_4 solution for 12 h. The treated solid was dried at 110 °C for 12 h and then sent to a muffle furnace for calcination at 600 °C for 4 h and thus the rare earth oxide-promoted SZ catalysts, including SO_4^{2-}/ZrO_2-La_2O_3 (designated as SZL), SO_4^{2-}/ZrO_2-Ce_2O_3 (designated as SZC) or SO_4^{2-}/ZrO_2-Yb_2O_3 (designated as SZY), were prepared.

For the preparation of RE oxide–Al_2O_3 doubly promoted catalysts, $Zr(OH)_4$, prepared as described above, was mixed with pseudo-boehmite (aluminum content was noted as weight percentage of alumina, 76.2 wt.%; pore volume, 0.342 ml/g; surface area, 273 m^2/g) and kneaded. The mixture was dried at 110 °C for 12 h and pulverized to 40–60 meshes for further use. Afterwards, it was impregnated with a given amount of $RE(NO_3)_3$ solution to prepare a sample with 3.0 wt.% rare earth oxides (La_2O_3, Ce_2O_3 or Yb_2O_3) and 3.0 wt.% alumina in the oxide mixture. After dried at 110 °C for 12 h, it was impregnated in a 0.5 mol l^{-1} of H_2 SO_4 solution for 12 h. The impregnated solid was dried at 110 °C for 12 h and then calcined in a muffle furnace at 600 °C for 4 h, and finally the RE oxide together with Al_2O_3-promoted SZ catalysts, including SO_4^{2-}/ZrO_2-La_2O_3-Al_2O_3 (designated as SZAL), SO_4^{2-}/ZrO_2-Ce_2O_3-Al_2O_3 (designated as SZAC) or SO_4^{2-}/ZrO_2-Yb_2O_3-Al_2O_3 (designated as SZAY), were obtained.

2.2. Catalyst characterization

The surface area and pore diameter of the catalysts were measured by N_2 adsorption–desorption isotherms method at −196 °C with a Mircomeritics ASAP 2010 instrument. Prior to analysis, each sample was degassed at 200 °C for 6 h under 10^{-3} Torr. The surface area was calculated by BET method and the pore size distribution patterns were obtained from the analysis of the desorption portion of the isotherms using the BJH method.

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/Max 2550 X using Cu Kα (λ = 0.154 nm) radiation in an operating mode of 40 kV and 30 mA. Data was collected from 2θ between 20° and 75° in a step of 0.02°/s.

FTIR spectrum of adsorbed pyridine was recorded on a Bruker IES-88 spectrometer. The sample was pressed to a 15 mm plate and put in a wafer. It was degassed in vacuum of 10^{-4} Torr at 450 °C for 2 h and lowered the IR cell temperature to 200 °C. Pyridine was adsorbed for 10 min and 30 min for equilibrium. Then it was scanned under the same condition for 40 min. Afterwards, the temperature was raised to 300 °C and the IR spectrum was recorded after 10 min for equilibrium. The same procedures were carried out at 400 °C and 450 °C. The number of Brönsted and Lewis acid sites was calculated according to the integral area of the bands at approximately 1540 $cm^{-1}$and 1450 cm^{-1}, respectively.

Sulfur content of the sample was measured by CSLS-2 type coulomb-meter. The sample was decomposed by combustion and all the sulfur species were converted into SO_3 which was absorbed by calcium iodide solution and the sulfure amount was determined by titration.

2.3. Catalytic activity test

46 g of ethanol and 30 g of glacial acetic acid in a molar ratio of 2 were placed in a three-necked flask with a thermometer reflux condenser and magnetic stirrer. 1.92 g of catalysts (2 wt.% of catalysts) mixed with the reactants were added to the reactor. The stirrer was switched on and the oil bath was heated to remain the flask at a constant temperature of 87 °C. The reaction was carried out at a fixed reaction time and then the temperature was cooled down after the reaction was finished. The liquid product was obtained by separating the catalyst from the reaction mixture. It was analyzed with a GC-14C with a HP-5 column (30 m × 0.320 mm × 0.25 μm). The chromatographically pure ethyl acetate was used to calibrate the gas chromatography. Ethyl acetate yield = N_1/N_0 (N_1 is denoted as the amount of ethyl acetate in the products, N_0 is denoted as the amount of ethyl acetate when glacial acetic acid in the reaction mixture is completely consumed). Catalytic activity of a tested catalyst was expressed by ethyl acetate yield.

In the present work, in order to test a catalyst lifetime, the SZ and ZSAY catalysts are repeatedly used for the batch reaction process under the same reaction conditions described above. Each catalytic evaluation lasts for 150 min and then the catalyst was separated from the products and was reused for the next evaluation. One reuse cycle of a catalyst is defined as the catalyst undergoing the batch reaction once. Therefore, ethyl acetate yield changes as times of reuse cycle will give the information of the catalyst life.

3. Results and discussion

3.1. Catalyst activity over the samples

Ethyl acetate yields in the esterification reaction of acetic acid and ethanol over the seven solid super-acid catalysts were shown in Fig. 1, which showed the product yields increased in an order of: SZY < SZL < SZC < SZAC < SZAL < SZ < SZAY. It was indicated that the activity of each RE oxide-promoted SZ catalyst was lower than that of undoped SZ or RE oxide–alumina doubly promoted SZ

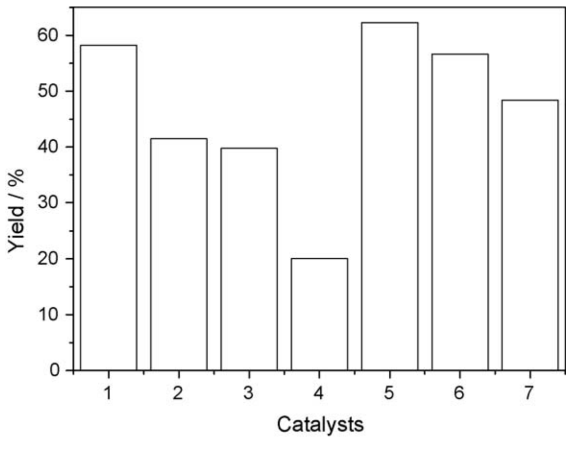


Fig. 1. Yield of ethyl acetate from acetic acid and ethanol esterification for a reaction time of 1 h over catalysts, including: (1) SZ, (2) SZC, (3) SZL, (4) SZY, (5) SZAY, (6) bSZAL, (7) SZAC. Reaction condition: Ethanol/ acetic acid, 2:1 (molar ratio); reaction temperature, 87 °C; reaction time, 1 h; catalyst amount /reactant amount, 2.0 wt.%.

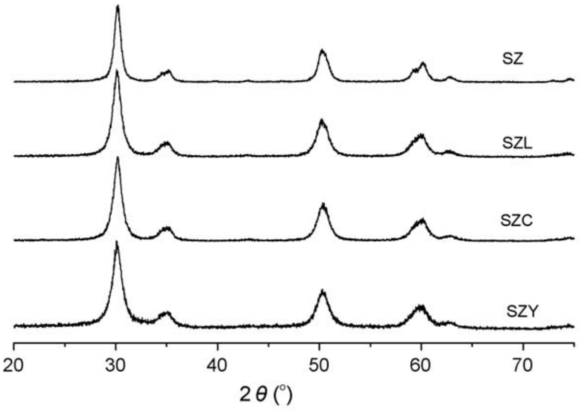
catalysts. In addition, in the series of rare earth oxide–alumina doubly promoted catalysts, the Yb_2O_3–Al_2O_3 promoted SZ (SZAY) exhibited the highest esterification activity; the Yb_2O_3-promoted SZ (SZY) gave the lowest catalytic activity among the catalysts.

3.2. *Textural properties and crystalline structure of the catalysts*

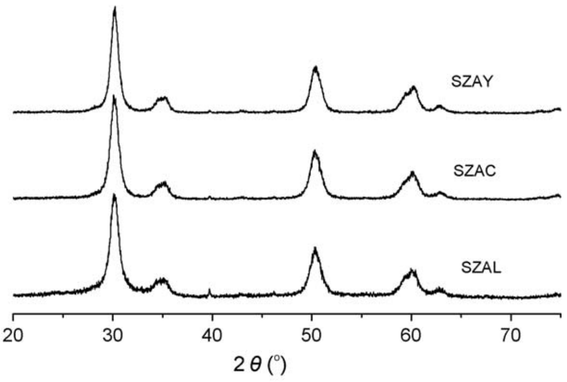
Textural data of the various solid catalysts were reported in Table 1. The SZ sample had a surface area of 92 m^2/g with a relatively low pore volume, 0.085 cm^3/g. After promoted with rare earth oxide or/and alumina, both surface area and pore diameter were significantly enhanced. The surface area of the RE oxide-promoted catalyst samples was increased by approximately 10–20% compared with that of SZ sample. Similar increment was observed for the RE oxide–alumina promoted SZ samples. Among these catalysts, SZAY had the maximum surface area, pore volume and pore diameter.

XRD patterns of the RE oxide-promoted SZ catalysts were shown in Fig. 2(a). An intense and well-defined peak, exhibiting high crystallinity, appeared at 2θ of 30° and a moderate one at proximately 50°, together with some small peaks at 35°, 60° and 63°, was observed. These peaks were all assigned to ZrO_2 tetragonal crystal phase, which is known to facilitate the catalytic activity [26,28]. The diameter of the ZrO_2 crystalline particles is relatively small as indicated by its wide diffraction peak. No rare earth oxide characteristic peaks in the XRD patterns were observed in these samples, it probably resulted from the solid state reaction between RE oxide and ZrO_2 to form a solid fused compound because the rare earth oxides are easy to form solid solution with ZrO_2 due to their similar atomic radium. Fig. 2 (b) showed the XRD patterns of the RE oxide–alumina- promoted SZ samples. Similar to the RE oxide promoted SZ samples, only tetragonal ZrO_2 phase was formed, no alumina or rare earth oxide phases could be detected.

According to the data reported in Fig. 1, Fig. 2 and Table 1, no strict correlation between the textural properties and the esterification performance could be established; however, it was no doubt that the increment of surface area and pore parameter in the SZAY catalyst may be beneficial to the catalytic activity.



(a). SZ and Re-oxide-promoted SZ



(b). RE-oxide together with alumina-promoted SZ

Fig. 2. XRD patterns of the related catalyst samples.

3.3. *Surface acidity of the samples*

In order to form a catalytically active form, it is usually necessary to anchor the sulfate groups with ZrO_2 tetragonal crystal phase [29,30]. Surface acidity is the most important function of sulfated zirconia and its analogues, and it is unambiguously connected to the presence of SO_4^{2-} groups because zirconium oxide exhibits low acidic properties [31]. However, the acid strength of sulfated zirconia is still open to debate. On one hand, it has been claimed that sulfated zirconia has super strong acid sites [32–37]; on the other hand, some authors have reported that its acidity is similar to that of HY but less than that of HZSM-5 [38–40]. It is well known that the IR spectrum of adsorbed pyridine is one of the most suitable analytical tools to distinguish, at the surface of oxides, the Brönsted acidity and s-coordinative Lewis acidity [41,42]. Surface acidity of SZ and promoted SZ catalysts measured by FTIR characterization using pyridine as a probe base was shown in Table 2, where three kinds of acid sites with varying strength were separated. The acid sites measured at 200 °C were assigned to weak acid sites, those at 300 °C were assigned to moderately strong acid sites, and those at 400 °C and 450 °C were assigned to superacid sites.

It was seen that the total amount of each kind of the acid sites on the RE oxide-promoted SZ catalysts was all less than that of respective acidity of the pure SZ sample, showing that the promotion of rare oxide on the SZ sample leads to the amount of acid sites diminishing. When the SZ catalyst was doubly promoted with rare earth oxide and alumina, the total amount of the acid sites varied differently, depending upon rare earth oxides.

Table 1
Textural structure of solid superacid catalysts.

Catalyst	BET surface area (m^2/g)	Total pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
SZ	92	0.085	3.95
SZL	114	0.130	4.50
SZC	122	0.112	4.35
SZY	123	0.158	4.77
SZAL	113	0.117	5.33
SZAC	109	0.114	5.36
SZAY	131	0.171	5.49

Table 2
Surface acid properties of varying catalyst samples.

Desorption temperature	Acid	SZ	SZL	SZC	SZY	SZAL	SZAC	SZAY
200 °C ($\mu mol\ g^{-1}$)	B Acid	33	29	30	38	36	28	31
	L Acid	178	124	141	67	181	175	225
	Total	211	153	171	105	217	203	256
300 °C ($\mu mol\ g^{-1}$)	B Acid	22	19	22	25	26	14	23
	L Acid	124	83	97	36	117	113	158
	Total	146	102	119	61	143	127	181
400 °C ($\mu mol\ g^{-1}$)	B Acid	12	11	11	12	12	8	13
	L Acid	80	48	55	16	78	62	93
	Total	92	59	66	28	80	70	106
450 °C ($\mu mol\ g^{-1}$)	B Acid	9	9	9	9	8	6	9
	L Acid	54	34	38	11	52	44	70
	Total	63	43	47	20	60	50	79

Table 3
Surface moderate and super acid sites of unit BET area of varying catalyst samples.

Desorption temperature	Acid	SZ	SZL	SZC	SZY	SZAL	SZAC	SZAY
400 °C (μmol m^{-2})	B Acid	0.130	0.096	0.090	0.098	0.106	0.073	0.099
	L Acid	0.870	0.421	0.451	0.130	0.690	0.569	0.710
	Total	1.000	0.517	0.541	0.228	0.696	0.642	0.809
450 °C (μmol m^{-2})	B Acid	0.098	0.079	0.074	0.073	0.071	0.055	0.069
	L Acid	0.587	0.298	0.311	0.089	0.460	0.404	0.534
	Total	0.685	0.377	0.385	0.162	0.531	0.459	0.603

For the SO_4^{2-}/SZ–Ce–Al–O (SZAC) and SO_4^{2-}/SZ–La–Al–O (SZAL) samples, the moderately strong and superacid sites were slightly lowered, whilst the amount of these acid sites in SO_4^{2-}/SZ–Yb–Al–O (SZAY) sample was significantly increased in comparison with that in pure SZ sample.

Variations of the amount of moderately strong and super strong acid sites were similar, either total acid sites or Lewis acid sites, followed an order of: SZY < SZL < SZC < SZAC < SZAL < SZ < S-SZAY. If compared it with the order of the esterification activity given in Fig. 1, one may find that the variation of the catalytic activity and amount of moderately strong and super strong acid sites followed the same trend. Therefore, the catalytic activity may be correlated with moderately strong and super strong Lewis acids, demonstrating that the enhancement of the moderate and super Lewis acids of the catalysts would benefit the esterification activity.

In order to further expound the effect of surface acid properties of the samples on the catalytic activity, the amounts of the surface superacid per unit BET area in the catalysts are shown in Table 3. Maximum amount of surface super Lewis acid sites of unit BET area was found in SZ catalyst rather than SZAY. Similarly, the SZ catalyst contains maximum amount of the total surface super acid sites per unit BET area. If compared it with the esterification activity data given in Fig. 1, no strict relationship between the surface superacid amount per unit BET area and the catalytic performance could be established. It may suggest that the number and strength of these acid sites vary with factors such as sulfur concentration, activation temperature, and crystalline structure of the samples rather than BET area.

3.4. Effect of reaction time

It was elucidated in the above sections that SZAY exhibited the optimal activity and therefore it was selected to examine the effect of reaction time on ethyl acetate yields. As shown in Fig. 3, the ethyl acetate yield was rapidly raised up from 26.50% to 63.50% as the reaction time increased from 30 min to 60 min, and then it reached a maximum 86.60% after 150 min of reaction, afterwards it remained almost unchanged in longer duration of reaction.

3.5. Effect of SZAY catalyst reuse cycle

After the reaction was finished, the spent catalyst was separated from the liquid products and then mixed with the fresh starting material in a flask for reaction. The important impact of the catalyst reuse cycle on the catalytic activity, expressed by the variation of the product yields, was tested in our work.

As exemplified by esterification on SZ and SZAY catalysts, it was seen from Fig. 4 that the yield of ethyl acetate over SZ catalyst markedly diminished as increasing the catalyst reuse number. After the fifth time for the catalyst reuse cycle, the ethyl acetate yield reduced to 36.59%, which is approximately half of the yield (72.60%) achieved on the fresh catalyst. As for SZAY, the ethyl acetate yield shows only a mild change after four times in the catalyst reuse cycle, it diminished from only from 86.60% to 80.00%. Since the fifth of the catalyst reuse, the ethyl acetate yield was rapidly decreased and it reached 37.00% at the eighth of reuse. These results indicated that the catalytic activity got decayed after several times of catalysts reuse. However, the double promotion of SZ by Al_2O_3 and Yb_2O_3 may effectively alleviate the catalyst deactivation rate.

3.6. Catalyst deactivation

It was observed from above experiments that the catalytic activities of SZAY and SZ catalysts gradually diminished as increasing the number of the catalyst reuse cycle. To examine the regeneration behaviors of deactivated catalysts, after the reuse cycle, the deactivated SZAY catalyst was regenerated by calcination it in air stream in a muffle furnace at 500 °C for 3 h. The regenerated SZAY catalyst was again used for catalyzing the esterification reaction of ethanol and glacial acetic acid in another batch under the same reaction condition as described above (mixture with a mole ratio of ethanol and acetic acid: 2:1; reaction temperature of 87 °C and reaction time of 2.5 h, the amount of SZAY catalyst in the feed solution was also adjusted to 2.0 wt.%). Ethyl acetate yield over SZAY catalyst and its sulfur content of the catalyst were given in Table 4. The yield of ethyl acetate was raised from 37.00% achieved on the deactivated catalyst (after reuse cycle of eight times) to 58.40% obtained on the regenerated SZAY catalyst, which showed that an approximately 20% increment was achieved. However, after regeneration, the catalytic activity of the catalysts had not be completely regenerated, it reached only 67% of that achieved on the fresh catalysts, indicating that part of its catalytic activity was lost.

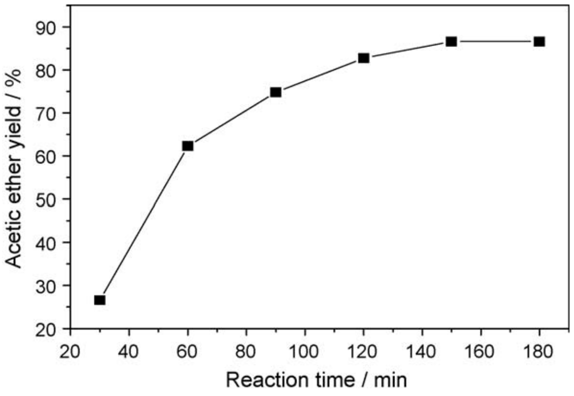


Fig. 3. Effect of reaction time on ethyl acetate yields for the SZAY catalyst.

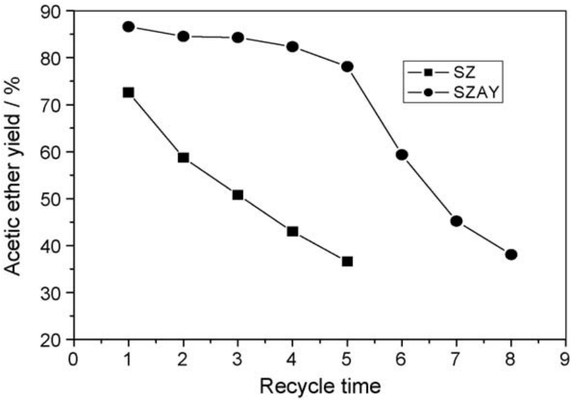


Fig. 4. Ethyl acetate yield as a function of time of the catalyst reuse cycle.

Table 4
Ethyl acetate yield over the fresh, used and regenerated SZAY catalysts and their sulfur content.

Item	Fresh SZAY	Used SZAY (after 8th recycling)	Regenerated SZAY
Ethyl acetate yield (%)	86.60	37.00	58.40
Sulfur content (wt.%)	2.15	1.08	1.08

It is well known that the sulfur content of the catalysts is an essential factor for remaining the acidity of the catalysts, which may greatly influence the catalytic activity [19,26,28]. During the esterification reaction, the sulfur content in the catalyst may be reduced due to some causes, for example, sulfur solvation. In order to verify the possible loss of the sulfur in the catalyst, the sulfur contents of the fresh, used and regenerated SZAY catalyst samples were measured, as shown in Table 4. It was found that when the number of the catalyst reuse cycle increased to the eighth time, the sulfur content decreased from 2.13 wt.% in the fresh catalyst to 1.08 wt.% in the used catalyst. Previous investigations confirmed that deactivation of SO_4^{2-}-promoted zirconia catalysts usually resulted from the several factors, for example, loss in sulfate ions by solvation in the solution and coking on the catalyst surface [26,28]. In our catalyst reuse cycle experiment, after several times of the reuse cycle, the color of the catalyst surface became dark grey, indicating that surface coking took place during the reaction. On the other hand, because the ethyl acetate synthesis reaction was carried out at low temperatures, water produced by esterification should remain in the reactor, which may lead to the loss of sulfate ions by solvation, decreasing the catalyst acidity. This factor would probably play a predominant role for our catalyst deactivation.

4. Conclusions

After promoted with rare earth oxide or/and alumina, both surface area and pore diameter of the SZ catalysts were significantly enhanced. Only tetragonal ZrO_2 crystal phase was formed for all the samples. In the synthesis of ethyl acetate by the esterification of ethanol and acetic acid, the catalytic activity of the SZ catalyst could not be promoted by only doping with rare earth oxides, including La_2O_3, Ce_2O_3 and Yb_2O_3. However, double promotion with Yb_2O_3 and Al_2O_3 could greatly enhance the catalytic activity and stability of the SZ catalysts. The SZAY catalyst exhibited the optimal catalytic activity, reaching 86.60% at ethanol and acetic acid molar ratio of 2:1 and 2.0 wt.%. of the catalyst, for a reaction time of 150 min under temperature of 87 °C. Our work showed that changes in catalyst activity were in close correlation with variations of the amount of moderately strong and super strong Lewis acidity. The loss of sulfur species by solvation and coking during the reaction led to the catalyst deactivation.

Acknowledgment

We would like to thank the financial support from the key international cooperative research projects by the National Ministry of Science and Technology, P.R. China (No. 2004CB720603).

References

[1] Y. Izumi, R. Hasebe, K. Urabe, J. Catal. 84 (1983) 402.
[2] Y. Izumi, K. Urabe, Chem. Lett. 10 (1981) 663.
[3] I. Mochida, Y. Anju, A. Kato, T. Seiyama, J. Catal. 21 (1971) 263.
[4] A. Corma, H. Garcia, S. Iborra, J. Primo, J. Catal. 120 (1989) 78.
[5] S. Furuta, H. Matsuhashi, K. Arata, Catal. Commun. 5 (2004) 721.
[6] D.E. López, J.G. Goodwin Jr., D.A. Bruce, E. Lotero, Appl. Catal. A: Gen. 295 (2005) 97.
[7] D.E. López, K. Suwannakarn, J.G. Goodwin Jr., D.A. Bruce, J. Catal. 247 (2007) 43.
[8] K.N. Rao, A. Sridhar, A.F. Lee, S.J. Tavener, N.A. Young, K. Wilson, Green Chem. 8 (2006) 790.
[9] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Chem. Eng. J. 116 (2006) 61.
[10] A.A. Kiss, A.C. Dimian, G. Rothenberg, Adv. Synth. Catal. 348 (2005) 75.
[11] A.A. Kiss, F. Omota, A.C. Dimian, G. Rothenberg, Topics Catal. 40 (2006) 141.
[12] A.H. West, D. Posarac, N. Ellis, Int. J. Chem. React. Eng. 5 (2007).
[13] J. Ni, F.C. Meunier, Appl. Catal. A: Gen. 333 (2007) 122.
[14] I.K. Mbaraka, D.R. Radu, V.S.Y. Lin, B.H. Shanks, J. Catal. 219 (2003) 329.
[15] I.K. Mbaraka, B.H. Shanks, J. Am. Oil Chem. Soc. 83 (2006) 79.
[16] I.K. Mbaraka, K.J. McGuire, B.H. Shanks, Ind. Eng. Chem. Res. 45 (2006) 3022.
[17] M.A. Jackson, I.K. Mbaraka, B.H. Shanks, Appl. Catal. A: Gen. 310 (2006) 48.
[18] M. Hino, S. Kobayashi, K.J.A.M. Arata, Chem. Soc. 101 (1979) 6439.
[19] M. Hino, K.J.C.S. Arata, Chem. Comm. 2 (1980) 851.
[20] K. Takao, Catal. Today 81 (2003) 57.
[21] T. Løften, E.A. Blekkan, Appl. Catal. A: Gen. 299 (2006) 250.
[22] G. Busca, Chem. Rev. 107 (2007) 5366.
[23] J. Zhao, Y.H. Yue, W.M. Hua, H.Y. He, Z. Gao, Appl. Catal. A: Gen. 336 (2008) 133.
[24] S.B. Wang, J.A. Guin, Fuel Proc. Technol. 84 (2003) 135.
[25] S. Furuta, H. Matsuhashi, K. Arata, Appl. Catal. A: Gen. 269 (2004) 187.
[26] X.M. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 320.
[27] G.D. Yadav, J.J. Nair, Microporous Mesoporous Mater. 33 (1999) 1.
[28] A. Corma, Chem. Rev. 95 (1995) 559.
[29] D. Spielbauer, G.A.H. Mekhemer, M.I. Zaki, H. Knözinger, Catal. Lett. 40 (1996) 71.
[30] C.R. Vera, C.L. Pieck, K. Shimizu, J.M. Parera, Appl. Catal. A 230 (2002) 279.
[31] K. Tanabe, M. Misono, Y. Ono, Stud. Surf. Sci. Catal. 51 (1989) (1909).
[32] T. Riemer, D. Spielbauer, M. Hunger, G.A.H. Mekhemer, H. Knozinger, Chem. Commun. (1994) 1181.
[33] A. Corma, V. Fornes, M.I. Juanrajadell, J.M.L. Nieto, Appl. Catal. A 116 (1994) 151.
[34] C. Morterra, G. Verrato, F. Pinna, M. Signoretto, G. Strukul, J. Catal. 149 (1994) 181.
[35] G. Yaluris, R.B. Larson, J.M. Kobe, M.R. Gonzalez, K.B. Fogash, J.A. Dumesic, J. Catal. 158 (1996) 336.
[36] D. Fraenkel, Chem. Lett. (1999) 917.
[37] H. Matsuhashi, K. Arata, Chem. Commun. (2000) 387.
[38] L.M. Kustov, V.B. Kazansky, F. Figueras, D. Tichit, J. Catal. 150 (1994) 143.
[39] V. Adeeva, J.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, J. Catal. 151 (1995) 364.
[40] R.S. Drago, N. Kob, J. Phys. Chem. B 101 (1997) 3360.
[41] E.P. Parry, J. Catal. 2 (1963) 371.
[42] C. Morterra, G. Cerrato, M. Visca, D.M. Lenti, Chem. Mater. 3 (1991) 132.