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Levulinic acid esterification on SO_3H-modified mesoporous silicas

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Ordered mesoporous SBA-15 silica and a nanosized KIL-2 material with textural mesoporosity were synthesised and modified with sulphonic groups. Functionalisation with SO_3H groups was performed by a two-step procedure, in which mercapto-modified mesoporous silicas were obtained first in reaction with mercaptosilane followed by treatment in H_2O_2 to result SO_3H-modified mesoporous silicas. Initial and SO_3H-containing mesoporous materials were characterised by X-ray diffraction (XRD), N_2 physisorption, TG analysis, and TPD of ammonia. The catalytic performance of the SO_3H/SBA-15 and SO_3H/KIL-2 catalysts was studied in levulinic acid esterification with ethanol. A sulphonic-functionalised SBA-15 mesoporous material showed a higher conversion of levulinic acid to ethyl levulinate.

Key words: levulinic acid esterification, mesoporous silicas, KIL-2, SBA-15, biomass valorisation.

INTRODUCTION

The growing energy crisis and environmental concerns have prompted the utilisation of readily available lignocellulosic biomass materials as an alternative to the limited fossil resources [1,2]. Levulinic acid and its esters are promising platform chemicals for the production of a wide range of sources for biofuel, polymer, and fine chemicals industry [3−7]. Levulinic acid (LA) is generally produced by acid-catalysed hydrolysis of cellulose, and can be converted into levulinate esters, g-valerolactone, 1,4-pentanediol, and 5-nonanone (*via* pentanoic acid) as well as diphenolic acid as an intermediate for the synthesis of epoxy resins and polycarbonates [8−12]. Levulinate esters are also valuable compounds that can be used as fuel additives, solvents, and plasticisers. In particular, up to 5 wt.% ethyl levulinate can directly be used as a diesel miscible biofuel in regular diesel engines without modification because of its physicochemical properties similar to those of biodiesel, i.e., fatty acid methyl esters (FAME) [8]. Therefore, it has the potential to decrease the consumption of petroleum-derived fossil fuels. Generally, levulinate esters are produced by esterification of LA with several alcohols using mineral acids like HCl, H_2SO_4, and H_3PO_4 as catalysts, to give a high yield of corresponding products within a short reaction time. However, such homogenous acid catalysts cannot be recycled and always lead to technological problems (e.g., use of a large volume of base for neutralisation and corrosion of equipment). Their replacement with heterogeneous analogues, which are easily separable and reusable, is thus highly desirable. Various solid acids have been used for the esterification of levulinic acid with alcohols, e.g., zeolites and sulphated mixed oxides (sulphated zirconia (SO_4^{2-}/ZrO_2), niobia (SO_4^{2-}/Nb_2O_5), titania (SO_4^{2-}/TiO_2), and stannia (SO_4^{2-}/SnO_2) [8−12]. The number and the strength of acid sites and the applied preparation conditions are the key parameters for catalyst activity. One possible strategy to increase catalyst activity is to use a neutral, high surface area support, e.g., mesoporous silica materials, in order to ensure fine dispersion of the supported active phase. This approach may enhance the catalytic activity of the obtained catalysts in liquid-phase reactions by accelerating mass transport of reactant and product molecules as well.

In the present study mesoporous SBA-15 and KIL-2 materials were prepared and modified with SO_3H groups and studied in liquid phase esterification of levulinic acid with ethanol. The effect of the structural, textural, and acid properties of the obtained materials on their catalytic activity and stability was discussed.

EXPERIMENTAL

Synthesis of mesoporous KIL-2 silica

In the first step, the silica source (tetraethyl orthosilicate, 98% TEOS, Acros) as well as the templates (triethanolamine (99% TEA, Fluka) and tetra-

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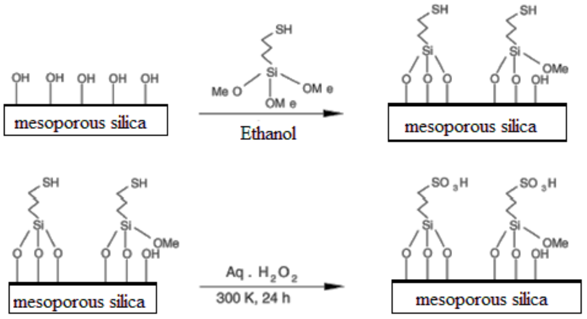
ethylammonium hydroxide (20% TEAOH, Acros)) were mixed with a molar composition of 1.0 TEOS : 0.5 TEA : 0.1 TEAOH : 11 H_2O to obtain a homogeneous gel. The gel was aged overnight at room temperature and then dried in an oven for 24 h at 323 K. In the second step, the gel was solvothermally treated in ethanol in Teflon-lined stainless steel autoclaves at 423 K for 48 h. Removal of the template was performed by calcination at 773 K for 10 h using a ramp rate of 1 K/min in air flow.

Synthesis of mesoporous SBA-15 silica

In principle, Pluronic P123 (12.0 g) were dissolved in a solution containing 365.8 g distilled H_2O and 37.1 g 37% HCl under vigorous stirring at 308 K. After the surfactant was completely dissolved, 24.0 g TEOS were added and agitation continued for 24 hours. The obtained gel was placed into an autoclave and kept at 373 K for another 24 hours followed by filtration, washing with distilled water, and drying at room temperature. For template removal, the obtained powder sample was calcined at a temperature ramp of 1 K/min up to 823 K and dwelling times of 2 hours at 563 K and 6 hours at 823 K.



Scheme 1. Functionalisation of mesoporous silicas by SO_3H groups.

Functionalisation of KIL-2 and SBA-15 by SO_3H groups

The initial SBA-15 and KIL-2 materials were functionalised with 3-mercaptopropyl trimethoxysilane by dispersing in toluene at refluxed condition for 6 h and then filtered, washed, and dried in oven at 328 K for 3 h. Further, the obtained mercapto-modified mesoporous silicas were dispersed in H_2O_2 and stirred for 24 h at room temperature. The oxidised materials were filtered and dried in a vacuum oven at 323 K for 8 h and denoted as SO_3H/SBA-15 and SO_3H/KIL-2, respectively.

Methods of characterization

X-ray powder diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO (HTK) high-resolution diffractometer using Cu Ka1 radiation (1.5406 E) in the 2 q range from 5 to 80 (100 s per step 0.016) for the samples and from 10 to 80 (100 s per step 0.016) for the sample holder using a fully opened X'Celerator detector.

Nitrogen physisorption measurements were carried out at 77 K using a Tristar 3000 Micromeritics volumetric adsorption analyser. Before adsorption analysis, the samples were outgassed under vacuum for 2 h at 473 K in the port of the adsorption analyser. BET specific surface areas were calculated from adsorption data in the relative pressure range from 0.05 to 0.21 [13]. The total pore volume was estimated based on the amount adsorbed at a relative pressure of 0.96 [14]. Mesopore and micropore volumes were determined using the t-plot method [15]. Pore size distributions (PSDs) were calculated from nitrogen adsorption data using an algorithm based on the ideas of Barrett, Joyner, and Halenda (BJH) [16]. The mesopore diameters were determined as the maxima on the PSD for the given samples.

Thermogravimetric analysis (TGA) was performed by a DTA-TG SETSYS2400, SETARAM analyser under the following conditions: temperature range 293−1273 K, static air atmosphere, heating rate of 5 K/min.

Ammonia temperature-programmed desorption (NH_3-TPD) was carried out using a Micromeritics 2920 Autochem II chemisorption analyser. In the NH_3-TPD experiments, the catalyst was pretreated at 773 K under a stream of helium for 60 min. After that, the temperature was decreased to 353 K. A mixture of 9.8% NH_3 in He as passed over the catalyst at a flow rate of 25 ml/min for 60 min. Excess ammonia was removed by purging with helium for 25 min. The temperature was then raised gradually to 1173 K by ramping at 10 K/min under helium flow and desorption data were collected. The TCD signals were calibrated using various gas concentrations of ammonia ranging within 0−10% in He. The quantity of desorbed ammonia was calculated from a detailed deconvolution of NH_3-TPD profile. In the TPD profile of the prepared catalysts, weak acidic sites were observed at 372–673 K as well as moderate acidic sites at 673–873 K and strong acidic sites above 873 K.

Catalytic experiments

Prior to catalytic measurements, the materials were pretreated *ex-situ* for 1 h at 413 K under static conditions in ambient air. A batch reactor with magnetic stirrer was used to perform the esterification reaction. In a typical experiment, the reactor was charged with 2 g LA and 0.050 g powder catalyst (2.5 wt.% catalyst/LA), the LA/ethanol weight ratio being 1:5. The reactor was heated to the desired reaction temperature (343 K) for 1 h. Analysis of the reaction products was performed using HP-GC with FID and a WCOT fused silica 25 m 0.25 mm coating CP-SIL 43CB column. Mass balance was made based on carbon-containing products.

RESULTS AND DISCUSSION

Physicochemical properties

Low-angle powder XRD patterns of KIL-2 and SBA-15 indicate that KIL-2 had a disordered mesoporous structure, whereas SBA-15 demonstrated an ordered 2D hexagonal (p6mm) pore arrangement (not shown). A somewhat decreased intensity and some broadened reflections were observed for the SO_3H-modified silicas indicating a certain structural disorder. To gain information about textural characteristics of the studied materials nitrogen physicsorption measurements were carried out (Table 1).

The isotherms of the SBA-15 samples were of type IV with a H1 type hysteresis loop between 0.6 and 0.7 (Fig. 1) relative pressures, typical of SBA-15 structure.

The KIL-2 samples exhibited adsorption isotherms of IV type with a relatively narrow hysteresis loop at a higher relative pressure, which is due to textural mesoporosity. A significant decrease of the textural parameters, such as surface area and total pore volume of the SO_3H-mesoporous samples was registered. The surface area of SO_3H/KIL-2 was diminished from 668 to 465 m^2/g, whereas more significant surface area reduction from 878 to 463 m^2/g was observed for SO_3H/SBA-15 catalyst (Table 1). These data indicate that a substantial part of propyl sulphonic groups was located inside the channels of mesoporous supports.

TG plots of sulphonic functionalised SBA-15 and KIL-2 samples are presented in Fig. 2. The TG profiles show that the weight losses over 723 K were 7.6 and 8.6 wt.% for the SO_3H/SBA-15 and SO_3H/KIL-2 samples, respectively (Table 1), which was due to decomposition of SO_3H groups. A TG peak for SO_3H/SBA-15 was shifted to a higher temperature in comparison with that for SO_3H/KIL-2. Despite the differences in pore structure, the amount of the formed propyl sulphonic groups was similar.

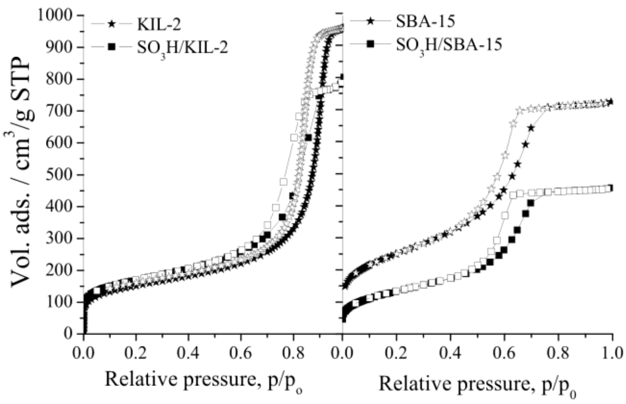


Fig. 1. Nitrogen adsorption/desorption isotherms of SBA-15 and KIL-2 silicas and their sulphonic analogues.

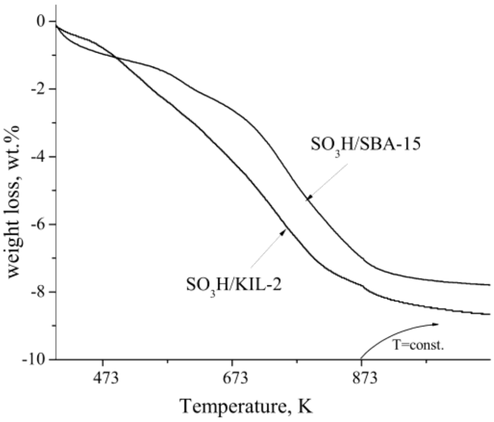


Fig. 2. TGA of SO_3H/SBA-15 and SO_3H/KIL-2 samples.

Table 1. Physicochemical properties of the studied samples.

Sample	S_{BET} m^2/g	Pore volume cm^3/g	Pore diameter[a] nm	SO_3H amount[b], wt.%	SO_3H amount[c], wt.%	Desorbed NH_3[d], mmol/g
SBA-15	878	1.14	5.5	-	-	-
KIL-2	668	1.45	15.2	-	-	-
SO_3H/SBA-15	463	1.00	5.1	7.6	7.3	0.60
SO_3H/KIL-2	465	1.10	14.4	8.6	8.2	0.45

[a] Pore diameter was calculated by the BJH method (desorption branch) for SBA-15 samples and by NLDFT method for KIL-2 samples (adsorption branch); [b] determined by TG analysis of fresh catalyst; [c] determined by TG analysis of spent catalyst; [d] calculated by TPD of ammonia.

Characterisation of the acidic properties by TPD of adsorbed ammonia.

TPD of ammonia was performed to determine the amount and strength of acid sites (Fig. 3). The quantity of desorbed ammonia was calculated from a detailed deconvolution of the NH_3-TPD profile (Table 1). The most intensive peak over 773 K in the TPD curves could probably be associated with strong Brönsted acidity of the samples and with partial decomposition of SO_3H groups. The TPD peak for the SO_3H/SBA-15 sample was more intensive then that for SO_3H/KIL-2.

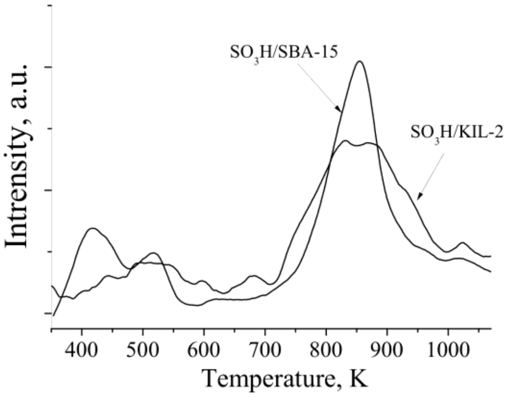


Fig. 3. TPD-NH3 of SO_3H/SBA-15 and SO_3H/KIL-2 samples.

It can be concluded that the acid sites formed on the two supports possess the same strength regardless of silica. Silica texture influences mainly the amount of acid sites formed.

Catalytic activity for LA esterification with ethanol

Samples were investigated in the esterification of levulinic acid with ethanol. The only registered products were ethyl levulinate and water. (Fig. 4). After 6 hours of reaction time over both samples, a conversion of about 22−30% was attained and in the next 2 hours, the catalysts kept the same catalytic activity.

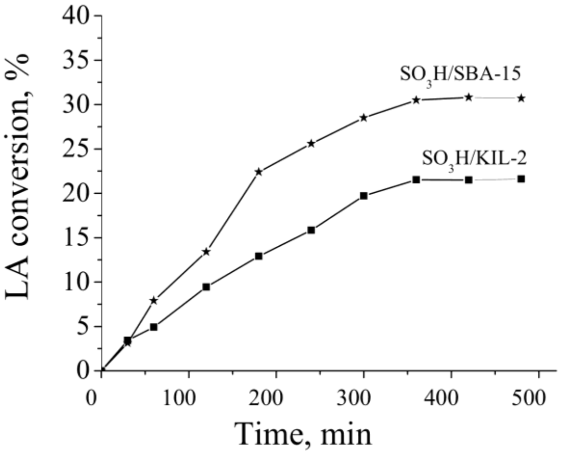


Fig. 4. Catalytic activity of SO_3H/SBA-15 and SO_3H/KIL-2 samples in levulinic acid esterification with ethanol at 343 K.

The highest catalytic activity was observed for the sulphonic-modified SBA-15 samples resulting in a conversion of 31% after 6 h. This effect could be attributed to the presence of SO_3H groups on the surface of the catalyst, which leads to an increase in Brönsted acidity. Formation of a higher amount of acid sites can be due to the presence of a higher amount of accessible silanol groups in SBA-15 during the functionalisation process in comparison with KIL-2, where the grafting silane can be easily blocked in the nanoparticles aggregates of SO_3H/KIL-2. Ziarani *et al.* [17] also found that SO_3H/SBA-15 was a highly active green recyclable catalyst in various acid reactions. A stable activity for LA esterification in three reaction cycles was determined for the SO_3H/SBA-15 catalyst (Fig. 5).

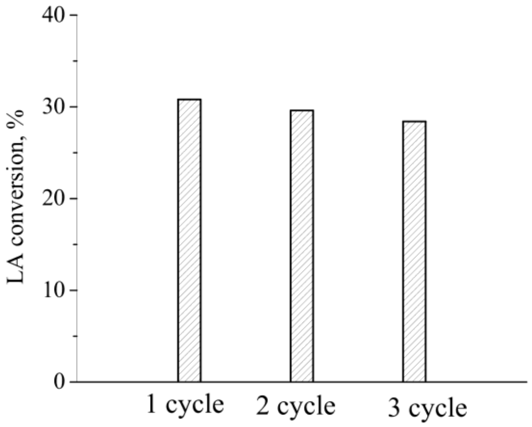


Fig. 5. Catalytic activity of SO_3H/SBA-15 sample.

The stable catalytic activity of the SO_3H/SBA-15 samples can be explained by easier accessibility of the reactants to the strong Brönsted acid sites in straight 2D channels of SBA-15 structure. The SO_3H/SBA-15 sample showed (Fig. 5) a LA conversion of 28.4% after three reaction cycles, whereas it was 30.8% in the first cycle. Catalyst reusability and stability are of key importance for practical applications as the catalyst lifetime predetermines the cost of the overall process. No leaching of sulphonic groups was registered on the SO_3H/SBA-15 samples after the third reaction cycle (Table 1) which could be a possible reason for excellent reusability with only a slight loss in catalytic activity.

Acquired catalytic data on activity and stability of the sulphonic-modified mesoporous SBA-15 silica material indicate that this catalyst is efficient, reusable, and stable solid acid for levulinic acid esterification.

CONCLUSIONS

Sulphonic-modified mesoporous SBA-15 and KIL-2 silicas were prepared by post synthesis method and investigated in levulinic acid esterification with ethanol. The obtained materials exhibited a high catalytic activity due to the formation of strong Brönsted acid sites. SO_3H/SBA-15 type mesoporous silica with its straight, easily accessible channels and affordable amount of silanol groups for post synthesis modification is a better choice as a catalyst for the studied reaction compared with SO_3H/KIL-2 structure possessing textural mesoporosity. A good catalytic stability and resistance of the SO_3H/SBA-15 catalyst toward sulphonic groups leaching were also demonstrated.

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ЕСТЕРИФИКАЦИЯ НА ЛЕВУЛИНОВА КИСЕЛИНА ВЪРХУ SO_3H-МОДИФИЦИРАНИ МЕЗОПОРЕСТИ СИЛИКАТИ

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(Резюме)

Мезопорести SBA-15 и KIL-2 материали бяха синтезирани и модифицирани със сулфонови функционали групи, с цел получаване на хетерогенни кисели катализатори. Функционализирането със SO_3H групи се извършваше чрез двустепенна процедура, при която първоначално се получава меркапто-модифицирани мезопорести силикати и в последваща обработка в H_2O_2 се получава модифицирани със SO_3H групи мезопорести силикати. Получените материали бяха охарактеризирани с рентгенова дифракция (XRD), N_2 физисорбция и температурнопрограмирана десорбция на амоняк. Каталитичното поведение на SO_3H/SBA-15 и $S0_3H$/KIL-2 е изследвано в реакцията на естерификация на левулинова киселина с етанол. Функционализираният със SO_3H групи SBA-15 мезопорест катализатор показа по-висока каталитична активност в тази реакция до етиллевулинат.