

Effect of Preparation Methods and Pluronic Template on the Catalytic Activity of Ca/SBA-15

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ABSTRACT: Two approaches for metal ion incorporation were employed to introduce Ca^{2+} into SBA-15; Direct Synthesis (DS) and Wet Impregnation (WI). The non-ionic template was removed by two different methods; calcination and solvent extraction. The obtained catalysts were characterized by means of X-Ray Powder Diffraction (XRD), Energy Dispersive X-ray (EDX), and FT-IR spectroscopy. The basicity was determined by using Hammett indicators and benzoic acid titration. The effects of synthesis methods and organic template on basicity and catalytic performance were studied in the transesterification of Canola oil with methanol. ^1H NMR was used to analyze the products. The best results were obtained using catalysts which prepared by wet impregnation method. Furthermore calcination is a better method of template removal. So calcined Ca/SBA-15 prepared by impregnation showed particularly the highest activity (conversion 84.2 %). Although this catalyst has a limited reusability in transesterification reaction.

KEYWORDS: Ca/SBA-15; Pluronic P123; Biodiesel; Impregnation; Direct Synthesis.

INTRODUCTION

Biodiesel is an excellent diesel fuel substitute with the advantage that it generates fewer emissions upon combustion. Biodiesel consists of methyl or ethyl esters derived from vegetable oil, animal fat, waste oil, and microalgae oil through the process of transesterification. The reaction can be catalyzed by either base or acid. The transesterification catalyzed by bases is much faster, and it is commercially chosen since they proceed under moderate operating conditions [1,2]. The problem occurs when the conventional alkaline catalyst is used for biodiesel production because the free fatty acids react with the alkaline catalyst to produce unwanted soap [3].

Calcium oxide (CaO) is one of the most commonly used base catalysts for the transesterification of vegetable oil.

Producing biodiesel using CaO as a solid base catalyst has many advantages, such as higher activity, mild reaction conditions, reusable, low cost and so on, but the leaching of CaO catalyst is the main drawback of it [4-6]. Therefore, supporting CaO onto carriers was proposed to improve the CaO catalysts [7,8].

Recently, mesoporous molecular sieves (like MCM-41, MCM-48, and SBA-15), have attracted much interest in catalysis, due to the high surface area, well-defined pore shape, narrow pore size distribution, and good thermal stability. These supports are particularly attractive applied in heterogeneous reactions involving large organic molecules where microporous zeolites cannot be used. Among different supports with an ordered mesopore structure,

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SBA-15 seem to be more suited to react in transesterification because SBA-15 has larger pore sizes (4.6–30 nm), thicker pore walls (3.1–6.4 nm) and better hydrothermal stability in comparison to the conventional MCM-41 support. Furthermore, SBA-15 with microporous walls is promising in a sense that while mesopores act as channels for the reactant transport with little diffusion limitation, micropores in the wall act as active sites for reactions or storage of the molecules.

There are a few reports on calcium-containing SBA-15 [9-12], and all of them employed the hydrothermal treatment for SBA-15 synthesis and calcination has been the only method for template removal. After Kubota's discovery on the basic properties of as-synthesized MCM-41 and SBA-15 [13], other groups have focused their attention on hybrid inorganic-organic molecular sieves. In the present work, the effect of template and calcium incorporation method has investigated in order to find the optimum condition for transesterification of canola oil with methanol.

EXPERIMENTAL SECTION

All reagents were purchased from Merck or Fluka and used as received. XRD measurements were performed on a Philips-PW 17C diffractometer with $\text{Cu K}\alpha$ radiation over the 2θ range $1\text{--}10^\circ$. The elemental chemical compositions of the samples were determined by EDX (VEGA\TESCAN-LMU, Czech Republic) under vacuum mode for precise measurement of both light and heavy elements. FTIR spectra were recorded on a Shimadzu FTIR-8300 instrument using KBr pressed powder discs.

Catalyst preparation

Direct Synthesis Method (DS)

In a typical non-hydrothermal synthesis [14], 0.98 g of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (P123) was first dissolved in an aqueous solution of 2 mol/L HCl (pH = 1) and maintained under stirring at 40°C for 2 h., then a calculated amount (0.57 g) of $\text{Ca}(\text{CH}_3\text{COO})_2$ was added under stirring for 0.5 h. Thereafter, 2.23 mL of tetraethyl orthosilicate (TEOS) was added dropwise to the solution and the latter stirred vigorously for 4 h at the same temperature. After this time, the reaction mixture was aged for 20 h at 40°C without stirring. Subsequently, the temperature was raised to 80°C and maintained at this value for 48 h. The solids

were filtered, washed with de-ionized water, dried at 60°C for 12 h. In some preparations, the neutral surfactant was removed either by hot solvent extraction or by calcination in air at 550°C for 6 h. The solvent extraction was performed by stirring 1 g of the air-dried product with a 1 mol/L HCl solution in ethanol (liquid: solid 300 mL/g) at 343 K for 24 h.

In order to compare the effect of the template, a series of as-synthesized molecular sieves, containing their organic template, were also tested for transesterification reaction without further modifying.

Wet Impregnation Method (WI)

In addition to the direct synthesis, Ca/SBA-15 was also prepared by wet impregnation. A predetermined weight (0.57 g) of $\text{Ca}(\text{CH}_3\text{COO})_2$ and 1 g of ethanol-extracted or calcined SBA-15 were stirred in an aqueous solution for 3 h. After stirring, the aqueous solutions were evaporated in air at 120°C for 2 h.

To investigate the effect of the template, Calcium acetate was also added to the as-synthesized SBA-15 before template removal (Ion Exchange method; IE).

The basic strength of catalysts

Hammett indicator method was used to determine the basic strength of the catalyst [15]. The following Hammett indicators were used: bromothymol blue ($H=7.2$), phenolphthalein ($H=9.3$) and alizarine yellow ($H=11.0$). Basicity was measured by the method of Hammett indicator-benzene carboxylic acid (0.01 mol/L anhydrous methanol solution) titration [16].

Transesterification reaction

The catalytic activity of the prepared catalysts was tested through transesterification of canola oil. The canola oil had the following characteristics: acid value 0.4 mg KOH/g, saponification value 191 mg KOH/g, specific gravity 0.92. The molecular weight can be calculated from its saponification value and it was 876 g/mol. Transesterification reaction of canola oil with methanol was performed in a batch reactor, consisting of a 250 mL three-necked glass flask immersed in an oil bath equipped with a water-cooled condenser, a temperature-controlled magnetic stirrer [17]. No inert atmosphere was used and all reactions occurred in contact with air and at ambient pressure. The reactor was initially filled

with the desired amount of canola oil (0.5 mL), placed on the magnetic stirrer (600 rpm), and preheated to 80 °C. Then, the reaction was timed as soon as the mixture of methanol (0.3 mol) and catalyst (100 mg) was added to the reactor. The mixture was refluxed for 6 h under stirring at 500 rpm.

The progress of the reaction was monitored using TLC to check the conversion of the free fatty acids to methyl esters using hexane-ethyl acetate (95 : 10, v/v) as developing solvent. After the reaction finished, the catalyst was separated from the reaction product by centrifugation. The methanol was then removed from both methyl ester and glycerol layer by heating at 70 °C for 30 min. The crude ester phase separated from the bottom glycerol phase after centrifuging washed by warm deionized water, several times until the washed water became clear. Eventually, the washed ester phase was dried with anhydrous MgSO₄ [18]. The final product submitted to NMR analysis in CDCl₃ using TMS as an internal standard.

The conversion yield of the oil to the corresponding methyl ester was calculated using Eq. (1):

$$Y = 100 \times (2AME / 3ACH_2) \quad (1)$$

Where *Y* is the methyl ester yield, and *AME* and *ACH₂* are the areas of the methoxy and methylene protons, respectively [19].

The obtained FAME had following properties: acid value 0.13 mg KOH/g, saponification value 190 mg KOH/g and specific gravity 0.88.

RESULTS AND DISCUSSION

Characterization

As previously indicated, the absence of the hydrothermal step in the synthesis modifies the structural and textural characteristics of the SBA-15 support [20]. For the samples studied, the specific surface area and the mesopore wall thickness decreased with increasing time and temperature of the hydrothermal treatment. In our work, all the SBA-15 samples were prepared via the non-hydrothermal procedure.

The low angle XRD patterns of SBA-15 exhibit three well-resolved peaks with a very intense diffraction peak at $2\theta \approx 1$ and two peaks with lower intensity at the higher degree ($2-3^\circ$) which were indexed to the 100, 110, and 200 planes characteristic for textural uniformity of the hexagonal P6mm structure [21, 22]. All Ca/SBA-15

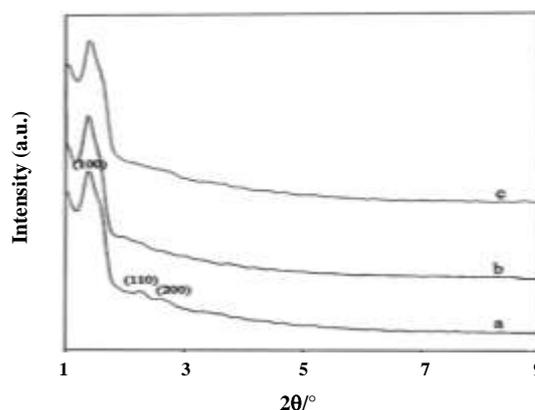


Fig. 1: XRD Patterns of a) SBA-15 , b) Ca/SBA-15 (DS) and c) Ca/SBA-15 (WI).

mesoporous structure of parent SBA-15 was preserved after the introduction of calcium species (Fig. 1). However, two low intensity peaks for (110) and (200) reflections centered at $\sim 2.3^\circ$ and $\sim 2.6^\circ$, respectively, were observed only for SBA-15 and implied the loss of some degree of ordered structure. This can be attributed to modification of the pore wall with calcium, which reduces the scattering contrast between the pores and the walls of the SBA-15.

Influence of the calcium incorporation technique

Most attempts to introduce surface-bound active sites have centered on aqueous impregnation methods. Wet impregnation involves bringing the solution into the pore space of the support; by this technique, the volume of solution used is low and the whole precursor is expected to be retained on the support after drying. For comparison, Ca/SBA-15 was also synthesized by the direct synthesis method. During direct synthesis, a calcium precursor salt was present in the SBA-15 synthesis gel.

The elemental concentration distribution on the catalyst and catalysts basicity are reported in Table 1. EDX results showed that using WI method high metal loading can be attained, because there is no intermediate washing step involved in wet impregnation method, whilst in the direct synthesis method, the metal precursor is introduced directly into the synthesis mixture at the beginning of the preparation process. Carbon comes from the P123 used for SBA-15 synthesis that was absent in the calcined SBA-15. As extracted catalysts still contained low template amount, the EDX analysis of extracted

Table 1: Elemental compositions, basic strength, and basicity of Ca/SBA-15 catalysts.

Catalysts	C* (wt. %)	Ca* (wt. %)	Basic Strength (H)	Basicity (mmol/g)
[P123]Ca/SBA-15 (DS)	17.70	0.29	7.2 < H_ < 9.8	0.80
Extracted Ca/SBA-15 (DS)	7.81	0.11	7.2 < H_ < 9.8	0.48
Calcined Ca/SBA-15 (DS)	0.00	0.22	7.2 < H_ < 9.8	0.97
Extracted Ca/SBA-15 (WI)	8.11	8.98	7.2 < H_ < 9.8	2.22
Calcined Ca/SBA-15 (WI)	0.00	10.58	7.2 < H_ < 9.8	2.82
[P123]Ca/SBA-15 (IE)	18.36	0.22	7.2 < H_ < 9.8	0.48

*determined by EDX analysis

catalysts also showed a low carbon content. Furthermore, the solvent extraction method decreases metal loading because, during this process, the calcium ions leach out of the support prepared by direct synthesis.

The basicities obtained by Hammett titration, are in good agreement with the EDX analysis. As expected, the catalyst prepared by the impregnation method, which had the highest calcium as mentioned above showed the highest basicity. Although the calcium content in calcined Ca/SBA-15 (DS) is equal to [P123]Ca/SBA-15 prepared by ion exchange, template-containing Ca/SBA-15 showed lower basicity. It can be concluded that the presence of P123 decreases the basicity of SBA-15. Furthermore, a large number of surface hydroxyl groups are lost during the calcination process to remove the organic template so calcined mesoporous silica had higher base strength. Basicity in calcined catalysts is due to $\text{Ca}^{2+}\text{O}^{2-}$ ion pairs; actually, calcium oxide is more basic than calcium.

Influence of the template

The pluronic triblock copolymer is most commonly used as template in SBA-15 synthesis. It is necessary to remove the occluded organic molecules to prepare the sieves porous for adsorption and catalysis. In general, the template molecules are burned off by calcination at 500-600°C in air or oxygen. An alternative method for template removal is extraction with a hot conventional solvent. In this work, the organic template molecule was removed from the silicate lattice by both of these two techniques. A series of as-synthesized molecular sieves was also utilized for calcium incorporation. Solvent extraction possesses the outstanding advantages of template recovery and environmental friendliness. Compared with solvent extraction, traditional calcination

method has the disadvantage of high temperature that may cause framework collapse and then affect the application performance.

The removal of the template from as-synthesized SBA-15 was confirmed by Infrared spectroscopy. The nearly complete removal of the surfactant could be confirmed with the absence of peaks around 2970 and 2927 cm^{-1} , corresponding to the pluronic template. Fig. 2 shows the FTIR spectra of template-containing Ca/SBA-15, solvent extracted and calcined Ca/SBA-15 materials. The broad transmission band at approximately 3400 cm^{-1} could be attributed to surface silanols and adsorbed water molecules. The asymmetric Si–O–Si stretching vibration modes, appear at 953 and 1085 cm^{-1} . The symmetric stretching mode occurs at 800 cm^{-1} , while the band at 457 cm^{-1} is assigned to the Si–O–Si bending mode. The [P123]Ca/SBA-15 samples (a,b) exhibit absorption bands around 2970 and 2927 cm^{-1} , corresponding to C-H stretch vibrations of the propyl chains of the surfactant molecules. Two weak peaks in this region also were observed in the spectra of solvent extracted Ca/SBA-15 samples. This was probably caused by the incomplete extraction of the template. So the traditional calcination method fully eliminates the template, however, with the other method used, there are always some traces of surfactant left. These results were also confirmed by EDX analysis (Table 1).

In Pluronic triblock copolymer, polyethylene oxide (PEO) blocks are hydrophilic, while polypropylene oxide (PPO) blocks are hydrophobic and the oxygen atom of polyethylene oxide can coordinate with metal ions. Moreover, the hydroxy groups of P123 can act as anchor points [23]. So we expected this template has a positive influence on calcium distribution inside the mesoporous silica. The EDX data in Table 1 indicates that calcium

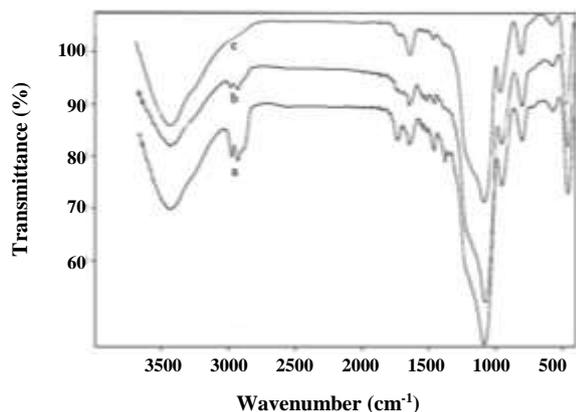


Fig. 2: FT-IR spectra of a) As-synthesized Ca/SBA-15 (DS), b) Ethanol extracted Ca/SBA-15 and c) Calcined Ca/SBA-15.

incorporation into the SBA-15 decreases in the presence of organic template; for example, calcined Ca/SBA-15 WI (fifth row) in comparison to a catalyst prepared by ion exchange method (sixth row). It may result from the polymeric template that plugs the channels of SBA-15 and limits the metal loading, so metal incorporation occurs mainly at pore mouth.

Furthermore, calcium content in extracted Ca/SBA-15 WI is less than the calcined sample. The mesoporous SBA-15 is typically known to have considerable micropores within its wall. The micropores are formed due to the interactions of PEO chains between different micelles. After calcination of surfactant the PEO chains are dehydrated, the amount of micropores decreases and the pore sizes increase.

The amount of calcium after extraction decreased in comparison to a template containing Ca/SBA-15 DS. This was an expected result because of the calcium leaching from the support under the solvent extraction process.

Transesterification

Currently, the majority of biodiesel fuel is commonly produced following a traditional transesterification of triglyceride and free fatty acid from vegetable oils and animal fats with short chain alcohol over homogeneous liquid catalysts. Owing to its relatively low costs and quite a predictable reaction, methanol is the most commonly used acyl acceptor in transesterification reactions. One of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically, a 3:1 specific molar ratio of methanol is needed in the reaction. For any alcohol, an excess amount

of alcohol (at least 1.6 times) is required for complete conversion and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time, but recovering glycerol becomes more difficult. Also, traces of methanol if present in biodiesel may cause serious damage to conventional fuel systems and engine rubber-made components. In some studies that Ca/SBA-15 has been used as a basic catalyst [7-9], a high molar ratio of methanol to oil (i.e. 20:1 or 40:1) was needed for oil transesterification but for the current study, we used CH₃OH/oil molar ratio 6:1.

One thing to be noted here is that the Ca/SBA-15 catalyst showed a much lower catalytic activity than the values for pure CaO reported in many research papers [24]. This may be explained by the better solubility of CaO in methanol and/or glycerol compared with CaSiO₃. Thus, the homogeneous system has more activity than the heterogeneous system in the transesterification reaction, which of course faces the leaching problem. In the practical application point of view, Ca/SBA-15 catalyst is better than CaO. For the transesterification reaction, it is important to find a more stable catalyst rather than a more active catalyst.

Fig. 3 shows the yields of FAME (fatty acid methyl ester) for the transesterification of canola oil with methanol. Compared with Ca/SBA-15 samples prepared by DS method, the Ca/SBA-15 (WI) showed better catalytic activity. The basic property of the catalysts is considered a key factor yielding biodiesel, so the greater activity of an impregnated sample can be justified by the presence of a higher concentration of basic sites. Furthermore [P123]SBA-15 and calcined SBA-15 without calcium incorporation were not active for the reaction as only 4 and 8% FAME was obtained, respectively. It is known that pure SBA-15 contains weak acidic sites. This confirms the role of calcium as an active basic site in the transesterification reaction.

Calcined Ca/SBA-15 (WI) had the highest activity with biodiesel yield of 83 % (Fig. 4). Actually, the calcined catalysts exhibited higher yields compared to solvent extracted ones, because the calcination process leads to the formation of calcium oxide. Apart from the influence of the calcium amount on basicity, base strength of solid base catalysts correlates to surface oxygen species of the catalysts, which were reported to be active centers of transesterification reaction [12].

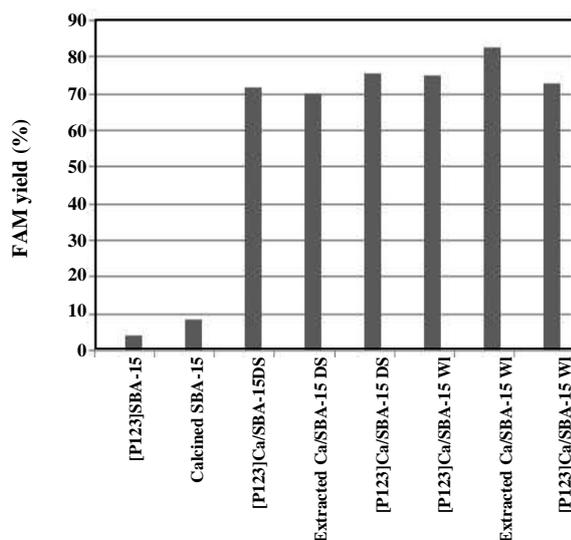


Fig. 3: FAME yield in the transesterification of canola oil with methanol (reaction temperature, 333 K; reaction time, 6 h).

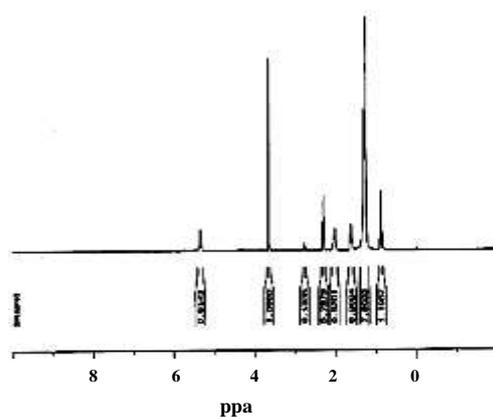


Fig. 4: ^1H NMR spectrum of FAME from canola oil in the presence of calcined Ca/SBA-15 (WI)

These excess strong basic sites were attributed to highly dispersed CaO, which resulted from the decomposition of calcium salt after calcination of Ca/SBA-15, confirming the higher overall basicity of calcium oxide with respect to calcium. In general, Lewis bases show a higher base strength than the corresponding Bronsted bases [20]. In our cases, $\text{Ca}(\text{CH}_3\text{COO})_2$ is considered as a Bronsted base ($-\text{OH}$); while CaO is considered as Lewis base ($-\text{O}-$). The improved catalytic activity of calcined catalysts may be attributed to the greater number of structural oxygen anion on these supports.

As we mentioned, nonionic surfactant, P123 decreases the catalyst basicity. So template containing Ca/SBA-15 showed a much lower catalytic activity

in the transesterification of canola oil. In addition to, this may be explained by the polymeric character of organic template. The catalytic site of Ca/SBA-15 is practically unhindered allowing an easy access of the methanol for proton transfer, while the steric hindrance shown by the P123 in surfactant-containing Ca/SBA-15, is so significant, furthermore in a second step the methoxide ion that is attached to the catalyst surface cannot attack the carbonyl carbon of the triglyceride molecule easily.

Moreover, all catalysts exhibited good activity for transesterification of canola oil and produced a FAME yield in the range of 70–85 %, whereas the calcium loading shows a broad range of values. These results confirm that the activity of a base catalyst cannot be attributed to its basicity or any isolated characteristic alone but is likely to be determined by the combined effects of the various attributes such as pore blockage.

Reusability

Calcined SBA-15 WI and SBA-15 DS catalysts that displayed the best catalytic performance were studied further. After the first test, the used catalyst was filtered, washed with distilled water and methanol respectively to remove glycerol and esteric product. Then the recovered catalyst was charged for the next transesterification run.

EDX analysis was performed to estimate the calcium content of the recovered samples and showed the presence of Ca atomic % = 6.74 and 0.19 for catalysts prepared by impregnation and direct synthesis respectively. This result indicated that there was significant leaching of the calcium from the impregnated catalyst under the reaction condition.

A methyl ester content of 70.6 and 74.8 % was obtained employing calcined SBA-15 WI and SBA-15 DS catalysts, respectively. The catalyst prepared by direct synthesis showed only minor deactivation (from 76.4 % to 74.8 %) with a small loss of calcium. So it has substantial stability under the used experimental conditions. In contrast, the catalytic activity of the reused Ca/SBA-15 WI was found to be lower than the parent catalyst. This deactivation is mostly due to the leaching of CaO from the support in reaction media. The poor stability of this catalyst is attributed to the weaker interaction of calcium species with the silica surface in comparison to the direct-synthesized catalyst, in which, Ca^{2+} is well dispersed in the silica framework.

CONCLUSIONS

In the present study, Ca/SBA-15 catalysts have been synthesized by direct synthesis and impregnation. Then the pluronic template was removed by two different methods; solvent extraction and calcination. The prepared samples were used as a catalyst in the transesterification of canola oil. The results showed that Ca/SBA-15 prepared by wet impregnation was more active for this process, which could be attributed to the presence of strong basic sites on the surface. The catalyst which pores were occluded by the organic template, showed lower activity in the transesterification reaction. So calcination is a better method to remove the pluronic template. The catalyst prepared by direct synthesis was able to be used without significant loss of activity.

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