Synthesis of Stable Lithium Modified Mesoporous Catalyst for Oligomerization of Biodisel-Drive Glycerol to Diglycerol

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Biodiesel is an alternative fuel option for future, which comes from pure renewable resources. The rapid growth of the biodiesel industry will result in overproduction of low value glycerol and create a superfluity of this impure by-product. The synthesis of lithium modified mesoprous catalyst for dilyglycerol production via oligomerization of low value biodiesel drive glycerol is reported. This reaction of selective glycerol conversion to diglycerol was studied in a heterogeneous catalysis under solvent free system, using alkaline mesoporous catalysts. Mesoporous materials SBA-15 was synthesized by using P123 and TEMOS as the template. Lithium in the form of LiOH was loaded over prepared SBA-15. The basic strength of prepared samples of SBA-15 was found increasing but structure of mesoporous was found destroying after LiOH loading. The mesoporous structure of prepared SBA-15 was found stable after doping it with 20 % alumina before loading with LiOH. This stability of mesoporous structure was observed very sensitive with alumina doping. These samples were well characterized by surface area, pore volume, pore size, basic strength, and transmission electron microscope (TEM) measurement of prepared samples. The glycerol conversion and dilyglycerol production yield was noted maximum 92 % and 74.5 % over prepared stable lithium modified SBA-15 catalysts. Industrially, the findings attained in this study might contribute towards promoting the biodiesel industry through utilization of its by-products.

1. Introduction

The development of value added chemicals production requires new basic heterogeneous catalysts as well as optimisation of the materials used at present. The great majority of studies involving the catalytic activity of basic catalysts have used either alkali-exchanged zeolites or zeolites impregnated with sodium metal clusters or alkali oxides (Dartt and Davis, 1994). Ordered mesoporous silicas, such as MCM-41 (Kresge et al., 1992) and SBA-15 (Zhao et al., 1998) are attractive materials because of their high surface area and ordered arrays of uniform channels. There are many research reports on their separation, catalysis, etc. Among the ordered mesoporous materials, SBA-15 is a unique; it has ordered mesopores as well as disordered interchannel micropores in the mesopore wall (Yang et al., 2003). In addition, Zhang and co-workers were also found these type of structural observations related to micropore and mesopore walls with in the material of SBA-15 (Zhang et al., 2006). Current research is directed towards the design of mesoporous material SBA-15 for basic components (Glocheux et al., 2013). The main problem with these materials is their poor alkali-resistance correlated with different factors.

Alkaline metal oxides are often used to improve the base strength of a solid catalyst due to their strong basic behaviour. Mesoporous solid strong bases can be prepared by impregnation of mesoporous material with alkali metals or alkaline earth metals. Some previous researchers (Kloestra et al., 1997), worked on preparation of strong bases mesoporous solid especially MCM-41 with cesium acetate solution. Although, the prepared bases materials showed poor stability because cesium oxide can react with the silica host and damage the mesoporous frame works (Kloestra et al., 1997). As lithium is strongest alkali metal in first alkaline metal group and stand at top position due to lighter. It can be used as the guest to generate strong basicity on various porous hosts, such as MCM-41 and zeolite (Clacens et al., 2002). Aiming at forming

strong basic strength on mesoporous silicas, SBA-15 was introduced as the host to disperse LiOH. The obtained material exhibited considerable basic strength but the mesostructure of SBA-15 was destroyed completely during preparation process of sample as our previous study (Muhammad Ayoub and AZ Abdullah, 2011). Hence, generation of strong basicity on mesoporous silicas with stable structure of mesoporous material is still an open question up until now.

There are two main factors which are considered to hinder the generation of strong basicity on mesoporous silicas. First factor is the weak host-guest interaction between silica and the base precursors, which leads to the difficulty in the decomposition of the base precursors to strongly basic species in the form of their oxides. It is already reported that only a small amount of alkali salt can be decomposed on silica even if the sample was activated at the high temperature of 600 °C (Sun et al., 2008a). The second factor is the poor resistance of mesoporous silicas against alkali. These are factors which results in the collapse of the mesoporous structure after the formation of strongly basic species (Sun et al., 2008b).

The objective of this work is to demonstrate the effects of strong metal hydroxide on the porous structures of SBA-15. The basic and structural properties of the obtained materials were well characterized by various approaches. It is verified that the mesoporous structure of SBA-15 was totally destroyed by adding 10 wt % of LiOH over SBA-15 but basic strength of material was enhanced on this newly prepared fluffy structure of SBA-15. This structure was stabilized with alumina coating of suitable amount prior to lithium loading. This prepared basic catalyst was observed for selective conversion of glycerol to diglycerol over oligomerization process.

2. Experimental Methods

Materials Synthesis: Mesoporous silica SBA-15 was synthesized according to the reported method as follows Zhao et al., (1998). Briefly, 4 grams of triblock copolymer P123 (EO20PO70EO20, M = 5,800, Aldrich) was dissolved in 90 ml of water and 60 ml of 4M HCl aqueous solution with stirring at 40°C for 2 h. A 8.5 g portion of tetraethyl orthosilicate (TEOS) was then added to the homogeneous solution and stirred at this temperature for 22 h. Finally, the temperature was heated to 100 °C and held at this temperature for 24 h under a static condition. The prepared sample was recovered by filtration, washed with water, and air-dried at room temperature. The removal of the template was carried out at 550 °C in air for 6 h.

Alumina coating over prepared material SBA-15 was performed using an impregnation method. The required amount of alumina precursor, i.e. aluminium nitrate was dissolved in 10 mL of deionised water and 10 mL of ethanol. After complete dissolution of magnesium nitrate, 2 g of the previously prepared SBA-15 support was added and kept under stirring for 24 h. Then, it was allowed to settle for 4 h. The mixture was subsequently dried using a rotary evaporator and then air dried in an oven at 100 °C for 4 h. The prepared sample was then calcined at 550 °C in air for 6 h. The resulting samples are denoted as Alx/SBA-15 where x represents the calculated mass percentages 10 or 20 wt% of alumina.

The alkali metal LiOH, was introduced by wet impregnation. An identical amount of LiOH (namely 10 wt %) was used for all samples. The required amount of LiOH was dissolved in deionized water, followed by addition of host SBA-15 or Alx-SBA-15. After stirring at room temperature for 24 h, the mixture was evaporated at 80 °C and subsequently dried at 100 °C for 4 h. The obtained solid was calcined at 550 °C for 5 h in air. The resulting samples are denoted as $LiOH_{10}/Alx$-SBA-15. The catalysts were characterized using BET surface area, pore volume, basic strength and TEM images techniques. The N_2 adsorption-desorption isotherms were measured using a Belsorp II system at - 196 °C. The samples were degassed at 300 °C for 4 h prior to analysis. The BET surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. Base strengths of the catalysts (H_) were determined using Hammett indicators. The TEM images of the prepared samples were analysed using a Phillips CM 12 transmission electron microscope equipped with an image analyser and operated at 120 kV.

3. Results And Discussion

Nitrogen adsorption-desorption isotherms of the LiOH on SBA-15 in different metal loadings are given in Figure 1. These data were obtained directly from the nitrogen adsorption-desorption isotherms characterized by a sharp nitrogen uptake at high relative pressure. The isotherm showed that the prepared SBA-15, Al_{10}/SBA-15 and $LiOH_{10}$-Al_{20}/SBA-15 samples exhibited nitrogen adsorption-desorption behaviours that are in agreement with uniform mesoporous ordering, all in terms of type IV with H1 hysteresis loop at the high relative pressure. With hysteresis loop of type H1, the two branches are almost vertical and nearly parallel. Such loops are often associated with porous materials which are known to

have very narrow pore size distributions or agglomerates of approximately uniform spheres in a fairly regular array (Ayoub and Abdullah, 2014).

On the other hand, the shapes of the curves for other $LiOH_{10}$/SBA-15 and $LiOH_{10}$-Al_{10}/SBA-15 samples do not agree with the type IV isotherm but more of type I that is a characteristic of microporous material. Hence, LiOH loading led to the collapse of some mesoporous structures of SBA-15 which causes a drop in porosity and exhibiting a decrease in the hysteresis loop (Chris et al., 2003). This porosity was not sustained even 10 % alumina coating before lithium loading. Although, after 20 % alumina coating prior to lithium loading sustained the structure of SBA-15 and showed comparative high porosity. Therefore, it can be concluded from this figure that 20 % alumina coated SBA-15 support successfully preserved its mesoporous structure after loading of LiOH.
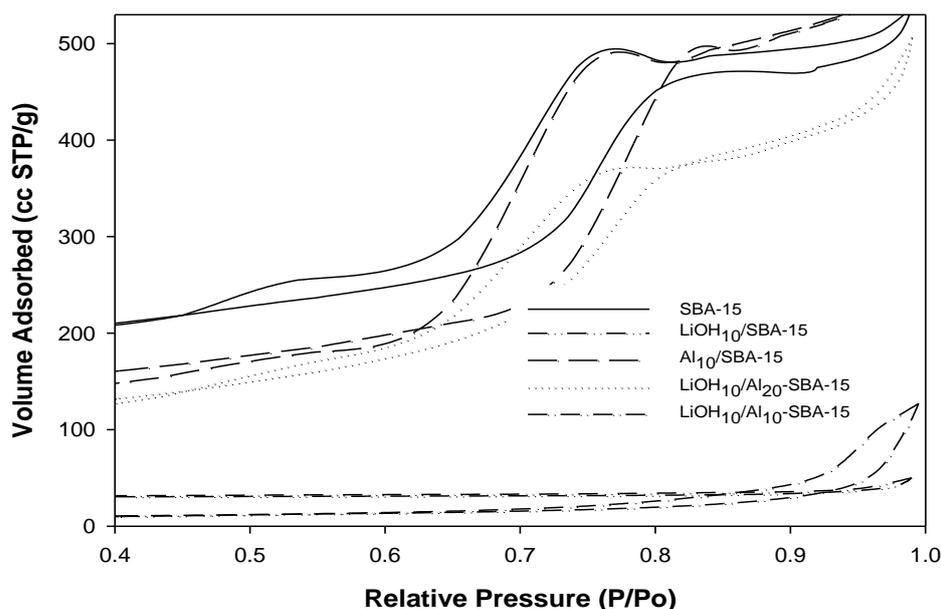

Figure 1: Nitrogen adsorption-desorption isotherms for different prepared materials

The physical characteristics of prepared materials are shown in Table 1. It can be seen in this table that the basic strength of the prepared samples increased after loading alkali metal LiOH (10 wt%). The basic strength of SBA-15 was noted H_ < 4.0, however after loading 10 wt % LiOH, it was noted 4.8 < H_ < 9.3. This basic strength of prepared materials was found further increased by coating alumina prior to lithium loading ($LiOH_{10}$-Al_{10}/SBA-15) which was noted 9.3 < H_ < 15. The basic strength of Al_{10}/SBA-15 was noted in the range of 4.8 < H_ < 6.8. In the same table it is also clear that surface areas of prepared samples were sharply decreased after loading alkali metal over SBA-15. A decrease in surface area, pore size and pore volume after coating with alumina and loading LiOH can be further observed from the data given in this Table 1. As clearly noted, the BET surface area, mesoporous area and pore dia of the prepared samples $LiOH_{10}$/SBA-15 and $LiOH_{10}$-Al_{10}/SBA-15 was sharply decreased while it was significantly persistent by $LiOH_{10}$-Al_{20}/SBA-15. The decrease in surface area and pore size might happen due to destruction of mesoporous structure of SBA-15 support in the presence of strong alkali lithium which cannot preserve even 10% coating of alumina prior to this lithium loading (Ayoub and Abdullah, 2011). The surface area of sample Al_{10}/SBA-15 was found to slightly decreased after coating with alumina. Sample $LiOH_{10}$-Al_{10}/SBA-15 also showed sufficiently high surface area, mesoporousity and pore dia which was found to be sufficient compare to the parent SBA-15. It is determined that mesoporous area and pore volume also sharply decreased along with decreasing surface area of these samples. Obviously it is indicating that there is no anymore mesoporous structure present inside these samples. Overall, the surface area analysis of these samples revealed that the mesoporous structure of samples $LiOH_{10}$/SBA-15 and $LiOH_{10}$-Al_{10}/SBA-15 were totally destroyed while this structure seemed to be still intact in $LiOH_{10}$-Al_{20}/SBA-15 sample.

Table 1: Physical characteristics of prepared materials with different metal loadings

Sample	Basic Strength $(H\_)$	BET surface area (m^2/g)	Mesopore area (m^2/g)	Pore size (A)	Pore volume (cc/g)
SBA-15	$H\_ < 4.0$	674	571	59.3	0.73
$LiOH_{10}/SBA-15$	$6.8 < H\_ < 9.3$	70	45	15.9	0.09
$Al_{10}-SBA-15$	$4.8 < H\_ < 6.8$	456	415	38.7	0.59
$LiOH_{10}/Al_{10}-SBA15$	$9.3 < H\_ < 15$	97	74	19.5	0.13
$LiOH_{10}/Al_{20}-SBA15$	$9.3 < H\_ < 15$	329	307	34.4	0.47

The preservation of the structure of prepared SBA-15 and $LiOH_{10}/Al_{20}-SBA-15$ materials were also confirmed by TEM images, which show hexagonal structure and clear straight channels as shown in Figure 2 (a) and (d). It was noted that the silica particles were actually made up of an array of straight channels of meso size range. However, with the decreasing amount of alumina (from 20 to 10 %) in sample $LiOH_{10}/Al_{10}-SBA-15$, the ordering of the SBA-15 support was observed to deteriorate after LiOH loading like in the case of $LiOH_{10}/SBA-15$ sample as also observed previous research studies (Ayoub and Abdullah, 2011). This might be caused by significant destruction of the overall structure of $LiOH_{10}/SBA-15$ as shown in Figure 2 (b). It can be observed from these results that the quantity of alumina coating over mesoporous material was an important factor for loading LiOH, and the mesoporous structure could be preserved by high coating of alumina (around 20 % and above) before loading with LiOH. Subsequently, it can be concluded that sample $Al_{20}-SBA-15$ successfully preserved its mesoporous structure after loading LiOH.

The collapsed and sustained behaviors of prepared samples were also observed by TEM images of these samples. TEM images of sample SBA-15 and $LiOH_{10}/SBA-15$ are shown in Figure 2(a) and (b). For SBA-15, the TEM image shows well-ordered hexagonal pores with clear channel tubing inside the structure. However, with 10 wt % LiOH loading, the ordering of the SBA-15 support was observed to deteriorate and the LiOH seemed to disperse on the outer surface of the SBA-15 walls. The same behavior was observed by sample $LiOH_{10}-Al_{10}/SBA-15$ as shown in Figure 2(c). Thus, it was clear that the dispersion status depended on the metal loading. It might due to the higher amount of LiOH that led to the easier LiOH particle diffusion into the SBA-15 pores implying that a larger amount of LiOH was located inside the pores of the support and the excess LiOH blocked the pores mouth. This type of metal dispersion over the surface pores of material is also discussed by Zhang et al. (2007). On the other hand, the structure preservation was found in sample $LiOH_{10}-Al_{20}/SBA-15$ that showed some clear straight channels which is a property of mesoporous SBA-15 as shown in Figure 2 (d). It can be observed from these results that the amount of alumina coating over mesoporous material was an important factor for loading LiOH, and the mesoporous structure could be preserved by coating with alumina (with specific amount around 20 %) before loading with LiOH. Subsequently, it can be concluded that sample $LiOH_{10}/Al_{20}-SBA-15$ successfully preserved its mesoporous structure after loading LiOH.

The activities of prepared catalysts for selective glycerol conversion to diglycerol over 2 wt% catalyst at 240 ^{o}C for 8 h are shown in Table 2. The glycerol conversion level was found very low less than 20 % over SBA-15 at given reaction conditions. The glycerol conversion was found to be increased up to 52 % over $LiOH_{10}/$ SBA-15 and it was gradually increased with addition of alumina. The conversion over $LiOH_{10}/Al_{10}-SBA-15$ and $LiOH_{10}/Al_{20}-SBA-15$ was noted about 84 and 92 % after 8 h at 240 ^{o}C. It is also evident from this table that the yield diglycerol were significantly high at addition of alumina in $LiOH_{10}/SBA-15$ and this yield also increased from 57.1 % to 74.5 % by increasing amount of alumina in catalyst from Al_{10} to Al_{20}. The comparison between two tables Table 1 and Table 2 shows that the basic strength and surface area of prepared catalysts have vital role to increase the conversion as well as yield of diglycerol. Actually, this surface area depends on stability of catalyst which can enhanced by addition of specific amount of alumina in prepared catalyst.
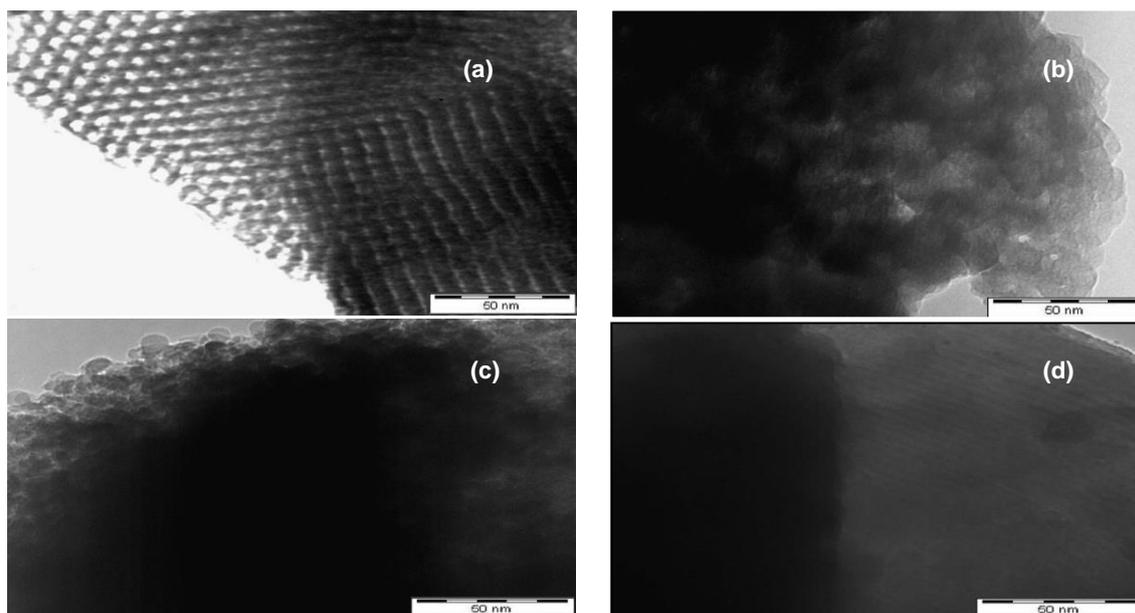
Figure 2: TEM images of a) SBA15 b) LiOH$_{10}$/SBA15 c) LiOH$_{10}$/Al$_{10}$-SBA15 d) LiOH$_{10}$/Al$_{20}$-SBA15

Table 2: Glycerol conversion to diglycerol over 2 wt% of catalyst at 240°C for 8 h

Compound	SBA-15	LiOH$_{10}$/SBA-15	LiOH$_{10}$/Al$_{10}$-SBA-15	LiOH$_{10}$/Al$_{10}$-SBA-15
Glycerol Conversion (%)	17.0	52.0	84.0	92.0
Diglycerol Selectivity (%)	3.0	11.0	48.0	68.5
Others (%)	97.0	89.0	52.0	31.5
Diglycerol Yield (%)	17.6	21.2	57.1	74.5

Overall, the activity and yield of prepared LiOH$_{10}$/ Al$_{20}$-SBA-15 for glycerol conversion to diglycerol was found higher than any homogenous catalyst at the same reaction conditions. The sluggish behaviour of SBA-15 and LiOH$_{10}$/ SBA-15 for conversion of glycerol and diglycerol production might be due to or converted small oligomers to higher oligomers and then again break down to glycerol (Izquierdoa et al., 2013). It might be possible that some other by-products like acroline or some other types of non-polymeric compound produced through other side reactions during this period of oligomerization process.

4. Conclusions

Mesoporous silica support, SBA-15 was successfully prepared with the template of nonionic triblock copolymers (TCP) and tetraethylorthosilicate (TEOS). Severe destruction of the mesoporous structure was detected after loading of LiOH over it. The mesoporous structure of SBA-15 was found to be stable after 20 % coating of alumina prior to LiOH loading. This structure stability was found to be affected by the amount of alumina coating i.e. above 20 %. The basic strength of the prepared sample LiOH$_{10}$/Al$_{20}$-SBA15 was also found to be increased after coating with alumina and subsequently loading it with LiOH. This prepared stable catalyst LiOH/Al$_{20}$-SBA-15 showed high conversion of glycerol about 92 % and maximum yield of diglycerol production 74.5 % with the amount of 2 wt% at 240 ^{o}C for 8 h of reaction time.

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