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Nanocrystalline potassium impregnated SiO_2 as heterogeneous catalysts for the transesterification of karanja and jatropha oil

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ABSTRACT

Potassium impregnated SiO_2 having 1:1 to 1:6 atomic ratio of Si to K has been prepared by sol gel method and evaluated as heterogeneous catalysts for the transesterification of jatropha and karanja oil with methanol. These catalysts are characterized by powder XRD, TEM, SEM-EDX, Hammett indicators, soluble basicity and FT-IR studies. TEM images of the catalyst with 1:6 atomic ratio of Si and K revealed uniform impregnation of 1.4-5.5 nm sized potassium nanoparticles over 50-72 nm sized spherical silica nanoparticles. This catalyst was found to be efficient for the transesterification of jatropha and karanja oil in 0.3 h and 0.75 h respectively.

Keywords: Transesterification, Biodiesel, Heterogeneous catalyst and Solid base catalyst.

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Introduction

Biodiesel, commonly referred as short chain alkyl (methyl or ethyl) esters obtained by the transesterification of triglycerides (main constituent of oil/fats) with methanol.[1] It is renewable, biodegradable and alternative fuel for diesel engine.[2,3] Compared to conventional diesel, biodiesel is technically more competitive because of its low emission profiles, high flash point, excellent lubricity and superior cetane number.[4, 5] Transesterification reaction is generally catalyzed by alkali[6], acid[7] and enzymes[8]. It can be carried out under non-catalytic conditions in supercritical methanol using 675 K temperature, 65MPa pressures and 42:1 alcohol to oil molar ratio, limiting its application to industrial scale.[9,10] Applicability of enzymes is economically limited because of high price of the enzymes, very large reaction volumes and slow reaction rates. Usually, production at industrial scale is carried out with the use of homogeneous alkali catalysts (KOH, $NaOC_2H_5$) when free fatty acids (FFAs) content and moisture content in feedstock are < 0.5 and 0.1 wt.% respectively and homogeneous acidic catalysts viz., H_2SO_4, HCl etc. with higher FFAs/moisture content. However, acidic catalysts involve longer reaction times and higher molar ratio of methanol than stoichiometric amount. Furthermore, the acid catalysts are more corrosive than basic ones, limiting their application in industries. Though still challenging, heterogeneous basic catalysts can provide solution for most of the problems associated with homogeneous catalysis[11-14]. Various types of heterogeneous basic catalysts for the transesterification of vegetable oils/animal fat are (a) alkaline earth metal oxides, (b) active metal supported metal oxides, (c) hydrotalcites and mixed oxides, and (d) mesoporous based catalysts. Among alkaline earth metal oxides, calcium oxide has been extensively used for transesterification reactions as it is non toxic and cost effective, and possesses relatively high basic strength[15-17]. Further, its catalytic activity can be improved by wet-impregnation of active metals salts viz., Li, K and Na[18-20]. But these catalysts suffer the problem of reusability. Recent interest showed the use of waste mollusk shells and eggs shells as catalysts for biodiesel preparation. These calcite shells upon heating at higher temperature are converted to CaO[21]. Hydrotalcites (HTs) or Layered Double Hydroxides (LDHs) are anionic and basic clays found in nature with the general formula $[M_{(1-x)}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}$ $(A^{n-})_{x/n}.yH_2O$ where $M^{2+}$and M^{3+} are divalent and trivalent cations and A^{n-} is the interlayer anion. Pioneering work on HTs as catalysts for the synthesis of biodiesel have been provided by Helwani et al.[22] Since then a variety HTs have been used as catalysts as well as supports for exogenous catalytic species. These catalysts without any modification require comparatively higher reaction temperatures. They can be converted into corresponding mixed metal oxides upon calcination. Mixed oxides i.e. the oxides containing two or more different kinds of metal cations, represent an interesting class of heterogeneous catalysts and catalyst supports for alkali, rare earth and noble metals[23]. First commercial heterogeneous catalyst based on mixed oxides for biodiesel production was developed by French Institute of Petroleum (IFP)[24]. The IFP patent is a mixed oxide of spinel (AB_2O_4) type having composition of $ZnAl_2O_4$, xZnO, yAl_2O_3 (with range of x and y being 0–2)[25]. Another subsequent IFP patent reported the sensitivity of the catalyst to water that could be used with less than 1000 ppm of water content, implying the use of refined feedstock with the catalyst[26].

One of the major hurdles faced by biodiesel industries is the use of edible oil as a raw material, which is not recommended as it leads to global food problem, deforestation and ecological imbalance while changing the virgin forests and arable lands to large scale biofuel production. Transesterification of soybean bean oil[27] and rapeseed oil[28] has been carried out with commercially available sodium silicate as heterogeneous catalyst after a series of treatments that is dehydration, calcination, trituration followed by passing through 120 / 200 mesh sieves. Wang et al.[29] also demonstrated conversion of soyabean oil into biodiesel in 2 h at 65 °C by the use of lithium silicate prepared by solid state reaction of SiO_2 and $LiNO_3$.

On the other hand, the potential of non-edible oils has been explored less in comparison to edible oils which may be due to the lack of efficient catalytic systems[30]. There are several non-edible oil seed species such as karanja (*Pongamia pinnata*), jatropha (*Jatropha curcas*), neem (*Azadirachta indica*), mahua (*Madhuca indica*), simarouba (*Simarouba indica*) etc., which can be utilized as a source for the production of oil. Among these, karanja is grown in certain parts of India and Australia. Its seed kernels contain 27-39 % of oil and its annual production of oil in India is 200 million tonnes, of which only 6% is being used in the soap and leather tanning industries[31]. *Jatropha curcas* is also equally potent feedstock for biodiesel production having 27-40 % oil content in the seeds[32]. Fuel properties of biodiesel obtained from both jatropha and karanja oil are quite comparable to those of ASTM biodiesel standards[33].

The production of biodiesel from Karnaja oil at industrial scale has been proposed by Vivek et al.[34] involving the neutralization of FFAs content of oil prior to transesterification. Meher et al.[35] also reported neutralization of karanja oil with appropriate amount of potassium hydroxide followed by filtration before transesterification. Patil et al.[33] reported the preparation of biodiesel from jatropha and karanja oil via two steps viz., esterification of FFAs followed by alkali catalyzed transesterification using KOH. Literature survey reveals that the preparation of biodiesel from low grade feed stocks (non-edible oils or animal greases) require complicated procedures of pre-treatment/neutralization by acids/alkalis, filtration of resulting salt, washing and drying after acid catalyzed esterification and alkali catalysed transesterification. We are reporting the preparation of biodiesel in a single step from the non-edible oils (jatropha and karanja) using newly developed potassium impregnated silicon dioxide catalyst.

1. Experimental section

1.1. Materials and Methods

Tetraethylorthosilicate (TEOS) and Pluronic P123 of 99.9% purity were purchased from Sigma Aldrich. Ethanol, methanol, potassium hydroxide, hexane, ethyl acetate, Hammett indicators viz., neutral red, bromothymol blue, phenolphthalein, 2,4-dinitroaniline, and 4-nitroaniline of GR grade were obtained from Loba Chemicals Pvt. Ltd and used as such without further purification. Jatropha and karanja oil was purchased from Medors Biotech Pvt. Ltd. New Delhi (India). Their FFAs content was determined by reported method [36] and was found to be 22.4 and 11.2 mg KOH/g for karanja and jatropha oil respectively. Moisture content of both oils was determined by Karl Fisher method using AF7LC Orion Coulometric autotitrator and was found to be in the range of 0.01-0.02 wt%.

1.2. Catalyst Preparation

Silicon dioxide impregnated with potassium having Si: K in 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6 atomic ratio was prepared by sol-gel method and designated as Si: K-X (X being the atomic ratio of Si to K). In a typical method of impregnation, calculated amount of KOH was dissolved in a mixture of 40 ml of 1:1 mixture of ethanol and deionized water followed by the addition of 10 g of Pluronic P123. After 2 h of stirring, 10 g of TEOS was added drop wise and the mixture was stirred for another 2 h. Gel, so obtained was dried at 80^{o}C for 48 h followed by heating at 0.25^{o}C/min upto 550^{o}C and maintained the temperature for 6 h.

1.3. Catalyst Characterization

All the prepared catalysts were characterized by powder XRD, Transmission electron microscopy (TEM), SEM-EDX (Scanning electron microscopy) and FT-IR. Basic site strengths and soluble basicity of the prepared catalysts were determined by Hammett indicators[37,38] and acid-base titration[14].

Powder XRD were carried on PANalytical X'pert using Ni-filtered Cu Kα radiation in steps of 0.0170° with a scan step time of 15.5 s in the 2θ range of 10–80°. Identification of the crystalline phases was made with the help of Joint Committee on Powder Diffraction Standard (JCPDS) files. TEM were recorded on Hitachi (H-7500) 120 kW. SEM-EDX measurements were taken on Jeol (JSM-7600F). FT-IR spectra were recorded in KBr matrix using iS10, Thermo Scientific in the range of 500-4000 cm^{-1}. Basic site strength of the catalyst was determined by observing change in colour of respective Hammett indicators when 25 mg of the catalyst was shaken with 5 ml of 0.02 M methanolic solution of each Hammett indicator.

1.4. Catalytic activity

All the prepared catalysts were tested for transesterification of karanja and jatropha oil with methanol for optimizing the Si: K ratio for efficient catalytic activity. For the jatropha oil, 6 wt.% of catalyst and 1:60 oil to methanol molar ratio and for the karanja oil, 8 wt.% of catalyst and 1:80 oil to methanol molar ratio was used along with stirring at 65°C. Progress of the reaction was monitored on TLC using solvent system; hexane: ethyl acetate:: 24:1 v/v. After the completion of reaction/stipulated time period, methyl esters were quantified by a reported method[39] using ^{1}H NMR (400 MHz FT-NMR Cryo Spectrometer Bruker). Various reaction parameters viz., catalyst amount, oil to methanol molar ratio and reaction temperature were optimized by determining the "time period" for obtaining biodiesel i.e., > 96.5% methyl esters. Catalytic activity was also investigated in the presence of additional 0.5-1.5 wt.% of moisture. The turnover frequency (TOF) of the catalysts was calculated using the following formula[40]

$$\mathrm{TOF} = \frac{\mathrm{mol}_{\mathrm{FAME}}}{\mathrm{B} \times \mathrm{A} \times \mathrm{T}}$$

where mol_{FAME} is the moles of FAME produced at time T, B is the basic sites (mmol/g) of catalyst obtained by acid base titration and A is the amount of catalyst.

2. Results and discussion

2.1. Catalyst Characterization

2.1.1. Powder XRD

Powder XRD patterns of Si: K-X (X=1-6) are shown in Fig. 1. In Si: K-1, no sharp peak was observed supporting the amorphous nature of silica. There is formation of coesite (a polymorph of silicon dioxide having monoclinic crystal symmetry, JCPDF 73-1748) supported by the appearance of peaks at 25.8^o and 28.7^o in all other prepared catalysts. In Si: K-2, peaks at 29.8^o, 30.3^o, 34.3^o, 37.0^o and 43.8^o support the formation of $K_2Si_2O_5$ (JCPDS: 49-0163) as major phase. Other peaks at 31.6^o, 32.1^o, 34.21^o and 43.4^o also support the presence of $K_6Si_3O_9$ (JCPDS: 84-0366). Similar diffraction patterns were observed for the other catalysts (Si: K-X, X=3-6) supporting the formation of $K_6Si_3O_9$ (JCPDS: 84-0366) as major phase and $K_2Si_2O_5$ (JCPDS: 49-0163) as minor phase. Akbar et al.[41] reported formation of $Na_2Si_2O_5$ as major phase along with minor phases of α, β, γ- $Na_2Si_2O_5$ and Na_2SiO_3 in Na doped SiO_2 prepared by similar (sol-gel) method using Na and Si in 50:50 atomic ratio.

2.1.2. Basic site strength and soluble basicity

Pure silicon dioxide is amphoteric[42] in nature and its basic site strength was found in the range of $6.8 < H\_ < 7.2$. The basic site strength of all potassium impregnated silicon dioxide catalysts (Si: K-X, X=1-6) were found to be in the range of $9.8 < H\_ < 15.0$ and these catalysts did not show any change in site strength upon storage in air even after 48 h. Wang et al.[29] reported similar site strength for lithium silicates. Although, CaO demonstrated comparatively high basic strength of $15 < H\_ < 18.4$, but it showed reduction upon storage in air[29].

Soluble basicity (total basic sites) of Si: K-X (X=1-6) was determined by acid-titration and was found to be 6.4, 7.4, 8.2, 12.1, 15.6 and 19 mmol of HCl/g of the catalyst for X= 1, 2, 3, 4, 5, and 6 respectively. Increase in basicity was found to be a function of potassium concentration in the catalyst.

2.1.3. TEM

The TEM images (Fig. 2) reveal almost spherical nano deposits of K species ranging from 0.7-5.2 nm that are uniformly dispersed throughout silica matrix. It is evident that with increase in amount of potassium for X = 2, 4 and 6 in Si: K-X, there is appreciable change in size of K nanospecies embedded in silica matrix with average particle size of 1.8, 2.2 and 3.5 nm, respectively (S.I.-Fig.1-3) along with increased concentration of number of K species. The spherical silica nanoparticles in Si: K-2 and Si: K-6 were found to be in the range of 14-41nm and 50-72 nm, respectively. Their average particle size increases from 26.8 nm to 66.8 nm (S.I.-Fig 4-5), hence surface area per-particle increases from 168.3 to 419.5 nm^2 with the increase in X from 2 to 6.

The impregnation of potassium has been further confirmed by SEM-EDX (S.I.-Fig. 6) demonstrating the presence of 85.59 % (atomic percentage) of potassium and 14.41% (atomic percentage) of silicon. These amounts correspond to the expected atomic ratio 1:6 of Si and K respectively.

2.1.4. FT-IR

FT-IR spectra of Si: K-X (X=2-6) are shown in Fig. 3. Bands at 3200-3600 and 1653 cm^{-1} are due to stretching and bending vibration of silanol groups respectively and are in agreement to those reported by Innocenzi et al.[43] due to its strongly bounded nature. Peaks at 1017 cm^{-1} and 901 cm^{-1} relate to the bending and stretching vibrations of Si-O respectively. Similar spectrum for silica has been reported by Guo et al.[27] Band at 1403 cm^{-1} can be assigned to C-O vibration of carbonates.

2.2. Catalytic activity

2.2.1. Transesterification

A series of transesterification reactions were performed at 65°C using 8 wt.% and 6 wt.% of Si: K-X (X=1-6) with 1:80 and 1:60 oil to methanol molar ratios for the karanja and jatropha oil respectively and results are shown in Table 1. Among all the prepared catalysts, Si: K-6 catalyst has demonstrated best performance. The activity of the catalysts increases with the increase in amount of potassium from X = 1 to 6. Increase in amount of potassium resulted the generation of catalytic sites and increase in basicity of catalysts which could be attributed to the formation of $K_6Si_3O_9$ as major phase. Catalytic sites which are possibly Lewis basic sites (O^{2-}) might have generated by interaction of potassium nanospecies with SiO_2. Turnover frequency was calculated at 50 % conversion level for the catalysts resulting in yield > 96.5% and is shown in Table 1. It increases with the increase in amount of potassium, suggesting that the number of K nanoparticles impregnated in silica may be rate determining factor. However, change in average particle size (1.8 to 3.5 nm) of potassium species for transesterification may not be significant (TEM, Table 1), but more number of impregnated K nanoparticles in silica matrix may led to observed enhanced catalytic activity to biodiesel. Another decisive factor could be the per-particle surface area of the spherical silica matrix which increases from 168.3 to 419.5 nm^2 with increase in amount of potassium for X= 2 to 6.

The higher reaction time for the karanja oil may be due to its higher FFAs content, possibly due to blocking and neutralization of basic sites. This may happen due to strong interactions of highly polar acetate (–COO$^-$) functional group of FFAs with K species on surface of the catalyst resulting in the partial blocking of the active sites. The reaction involving the use of KOH as homogeneous catalyst with oil having FFAs content > 0.5 wt.% (e.g. karanja and jatropha oil) resulted in saponification instead of biodiesel formation. However, with Si:K-6 catalyst, transesterification of jatropha and karanja oil having 5.6 and 11.3 wt.% of FFAs respectively, yielded > 97% conversion into fatty acid methyl esters. Morover, the homogeneous contribution of less than 5 % for Si: K-6 catalyst was observed by refluxing the catalyst with optimized amount of methanol for 30 min followed by filtration and using the methanol so obtained for transesterification of jatropha oil under optimized reaction conditions, as per reported method[40].

2.2.1.1. Effect of catalyst amount

Transesterification reactions were carried out by using different amount of catalyst (Si: K-6) with 1:60 and 1:80 oil to methanol molar ratios (with jatropha and karanja oil respectively) at 65°C and results are shown in Fig. 4. The time period for completion of reaction for jatropha oil decreases from 1.75 to 0.3 h with increase in catalyst amount from 3 to 6 wt.%. Further increase in amount (upto 7 wt.%) did not show any significant change in the reaction time. Hence, 6 wt.% of catalyst was used for optimizing other reaction parameters. For the karanja oil, 8 wt.% of catalyst showed the minimum reaction duration of 0.75 h and further experiments were performed with this amount of the catalyst.

2.2.1.2. Effect of methanol to oil molar ratio

Transesterification reactions were performed by varying the methanol to oil molar ratios from 20:1 to 90:1 for karanja oil and from 20:1 to 70:1 for jatropha oil at 65°C till the completion of reaction (Fig. 5). The jatropha oil showed decrease in time period for the completion of reaction from 0.83 h to 0.3 h with increase in methanol: oil molar ratio from 20:1 to 60:1 and further increase did not show any marked reduction in reaction time. The karanja oil showed variation in the reaction time of completion from 1.5 h to 0.75 h with increase in molar ratio from 20:1 to 80:1 for methanol to oil respectively. Further increase in molar ratio did not show reduction in reaction time. Hence, 80: 1 and 60: 1 molar ratios of methanol to oil were selected for karanja and jatropha oils respectively for optimizing other parameters.

2.2.1.3. Effect of Temperature

Transesterification of karanja and jatropha oil was not complete at temperatures lower than 50 and 45°C respectively. For jatropha oil, reaction time of completion decreases from 2.25 h to 0.3 h with the increase in temperature from 45 to 65°C and for the karanja oil, time period decreases from 5 h to 0.75 h with increase in temperature from 50 to 65°C (Fig. 6). At 65°C, the minimum time period of 0.3 h and 0.75 h was observed with jatropha and karanja oils respectively. The increase in temperature resulted in increased rate along with improvement in the miscibility of polar alcoholic media with non-polar oily phase.

Hence, optimized reaction conditions for jatropha oil are: 1:60 oil to methanol molar ratio with 6 wt.% of the catalyst at 65°C for 0.3 h of reaction time and for karanja oil: 1:80 oil to methanol molar ratio with 8 wt.% of catalyst at 65°C for 0.75 h of the reaction time. With soyabean oil, optimized reaction time of 2 h and 1 h is reported with lithium orthosilicate[31] and calcined sodium silicate[15] as catalysts. However, these catalysts are expected to take lesser time with edible oils due to their low FFA content. The Na doped SiO_2[41] having δ-$Na_2Si_2O_5$ as major phase along with minor phases of α, β, γ- $Na_2Si_2O_5$ and Na_2SiO_3 required 0.75 h for 99% conversion of non-edible oil. Hence, variation in reaction time with different catalysts could be due to different preparation conditions and resulting various crystalline phases. The presence of mixed phases as in Na doped SiO_2 and in the present work favours better catalytic activity. Shree et al.[44] also reported that a particular ratio of magnesia and zirconia showed better activity for transesterification of jatropha oil due to the formation of strong basic sites and smaller crystallite size of zirconia.

2.2.1.4. Effect of moisture on catalytic activity

The moisture resistance of the catalyst (Si: K-6) was studied for transesterification of jatropha oil with methanol in the presence of additional water content of 0.5 -1.5 %. Biodiesel (methyl esters >96%) was obtained even in the presence of 0.5 and 1 wt.% of moisture content in 0.8 h and 1.2 h, respectively. Conversion of more than 96% was not obtained in the presence of 1.5 wt.% of moisture during reaction time of 6 h. Hence Si: K-6 indicated the tolerance of 1wt.% of moisture. Babu et al.[45] reported the catalytic activity of mixed oxides of La and Mg for transesterification of sunflower oil containing 5 wt.% of FFA also showed tolerance toward water content. It has been observed that when homogeneous KOH and NaOH catalysts are used for the transesterification of triglycerides in the presence of moisture > 0.06 wt.%, soap is produced instead of desired methyl esters, where as Si: K-6 catalyst produced methyl esters even in the presence of 1 wt.% of moisture. Potassium species were found to be in the impregnated/heterogeneised form in the Si: K-6 catalyst and these remain insensitive to moisture content present in the reaction mixture.

2.2.1.5. Reusability

Reusability experiments were performed using Si: K-6 catalyst with jatropha oil under optimized reaction conditions. The catalyst was separated from the product by filtration, washed with methanol, dried and activated at 550°C before reuse for the next run. It showed 42% and 30% conversion during first two recycles respectively. In order to investigate the loss in catalytic activity, EDX spectra of Si: K-6 catalyst after 2nd reuse (Fig. 7a) was recorded which confirms the presence of silica and potassium in 3: 8 atomic ratio. Elemental mapping studies (Fig. 7b) and STEM image (Fig. 8) of the same sample confirm uniform dispersion of potassium nanospecies over silica nanoparticles. Powder XRD and soluble basicity of Si: K-6 catalyst was also measured after both catalytic runs. Powder XRD diffraction patterns of reused catalysts (S.I.-Fig. 7) showed diffraction patterns corresponding to $K_6Si_3O_9$ (JCPDS: 84-0366) as major phase and $K_2Si_2O_5$ (JCPDS: 49-0163) as minor phase as that observed in the fresh catalyst. Hence, catalysts structure did not showed any significant change upon repeated use. Soluble basicity of the catalyst after 1st run decreases from 19 to 7.3 mmol HCl/g and in subsequent two runs, it did not show marked variation (that is 7.1 and 6.8 mmol HCl/g). The abrupt decrease in basicity after first run may be due to neutralization and interaction of surface sites with free acids as described earlier. Later the basicity did not show much variation and the conversion decreases from 42 % to 30 %. However, the soluble basicity of Si: K-6 with cotton seed oil after first three recycles was found to be 18.2, 17 and 15 mmol of HCl/g. Hence, FFA content seems to be responsible for change in soluble basicity.

The reusability of Si: K-6 catalyst was also tested with cotton seed oil having 0.2 wt.% FFAs content. The catalyst demonstrated 95%, 92.5% and 92% conversion during 1st three recycles showing better reusability compared to that found with jatropha oil. Moreover, soluble basicity of the catalyst after first three reuses with cotton seed oil was found to be 18.2, 17 and 15 mmol of HCl/g. Thus, catalyst reusability was negatively affected by the presence of FFAs content in the triglyceride.

3. Conclusion

Nanospecies of potassium have been successfully impregnated over SiO_2 by sol-gel method. These species generate basic sites over silica nanoparticles and resulted in solid basic catalyst. Transesterification of jatropha and karanja oil with methanol using Si: K-6 catalyst at 65°C, resulted in conversion of more than 97 % biodiesel in 0.3 h and 0.75 h respectively. The Si: K-6 catalyst also showed the formation of biodiesel in presence of additional 1 wt.% of the moisture with jatropha oil. The same catalyst also demonstrated remarkable reusability with cotton seed oil.

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Table 1 Turnover frequency and time period for conversion (> 97%) of jatropha and karanja oil into biodiesel by using Si: K-X, (X = 1-6) catalysts.

Catalyst	$TOF_{jatropha}$ ($\times 10^{-3}$ h^{-1})	$T_{jatropha}$	$TOF_{karanja}$ ($\times 10^{-3}$ h^{-1})	$T_{karanja}$
Si: K-1	-	NC	-	NC
Si: K-2	6.08	1.25	-	NC
Si: K-3	6.87	1.0	-	NC
Si: K-4	7.06	0.66	1.08	3.75
Si: K-5	7.22	0.50	2.63	1.0
Si: K-6	9.88	0.30	2.90	0.75

$TOF_{jatropha}$, Tourover frequency for jatropha; $TOF_{karanja}$, Turnover frequency for karanja; $T_{jatropha}$, Time period (h) for conversion of jatropha oil into biodiesel; $T_{karanja}$,Time period (h) for the conversion of karanja oil into biodiesel; NC, Not Completed; *reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; catalyst amount, 6 wt % of oil; and temperature, 65 °C; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; catalyst amount, 8 wt % of oil; and temperature, 65 °C.*

Fig. 1 Powder XRD pattern of Si: K-X (X = 1-6) (*, $K_2Si_2O_5$; O, $K_6Si_3O_9$; #, SiO_2).

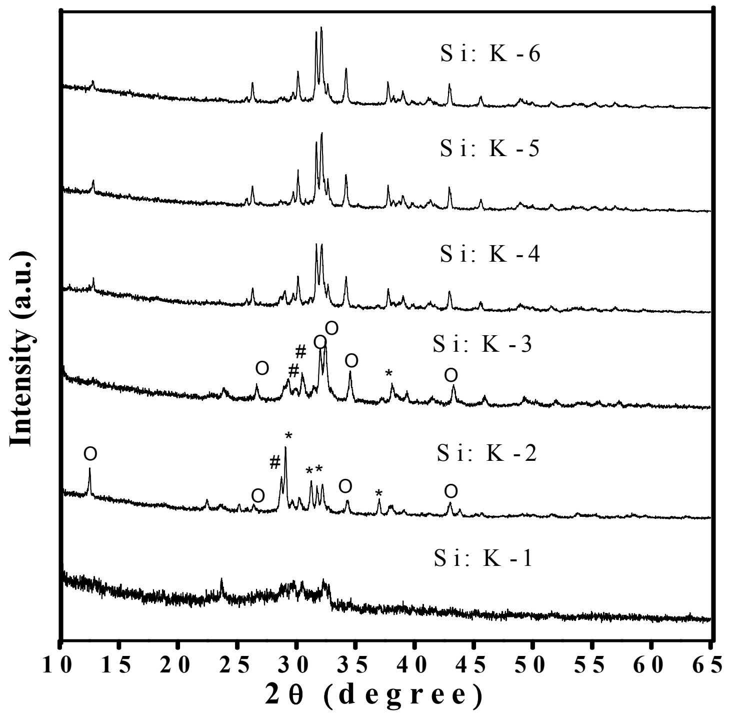


Fig. 2 TEM images of (a) Si: K-2 and (b, c) Si: K-6

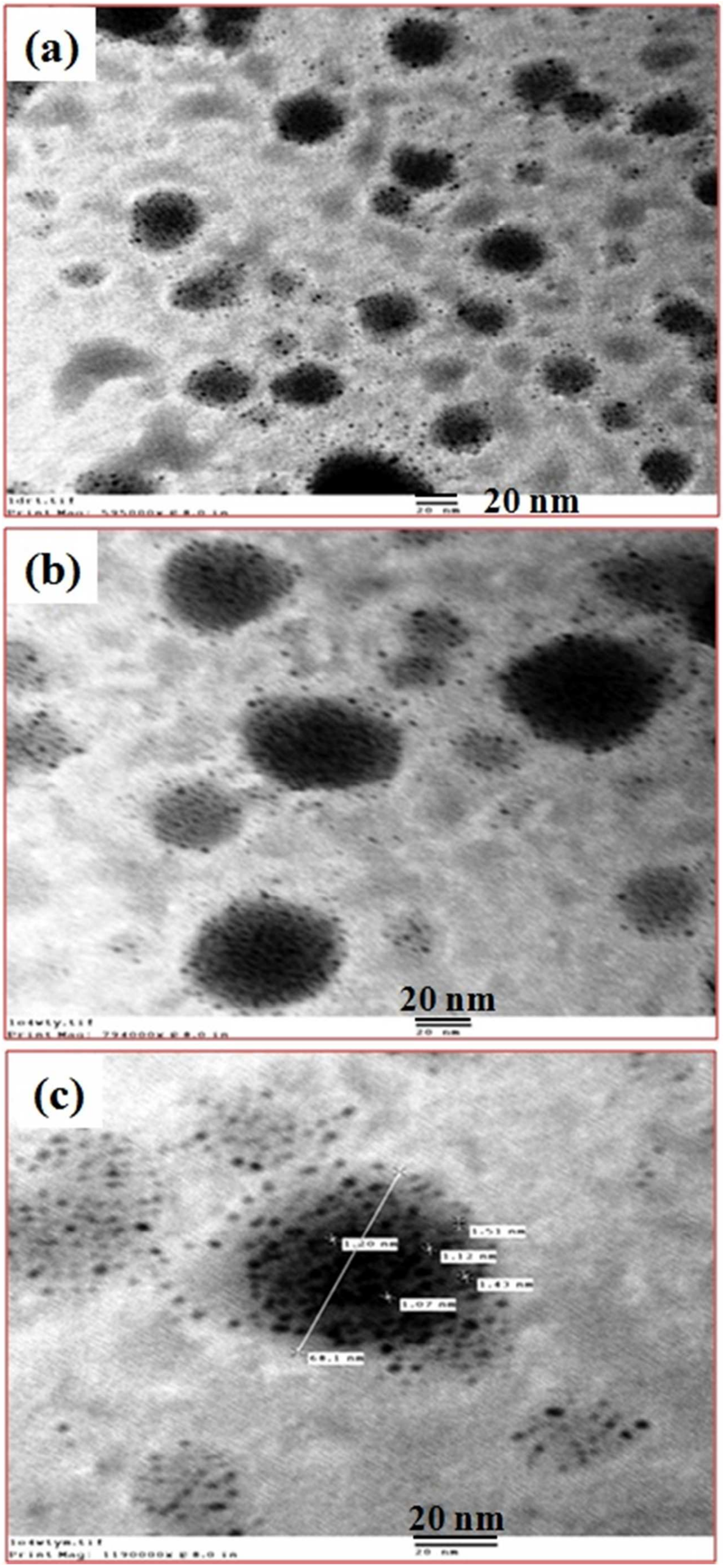


Fig. 3 FT-IR spectra of Si: K-X (X = 2-6).

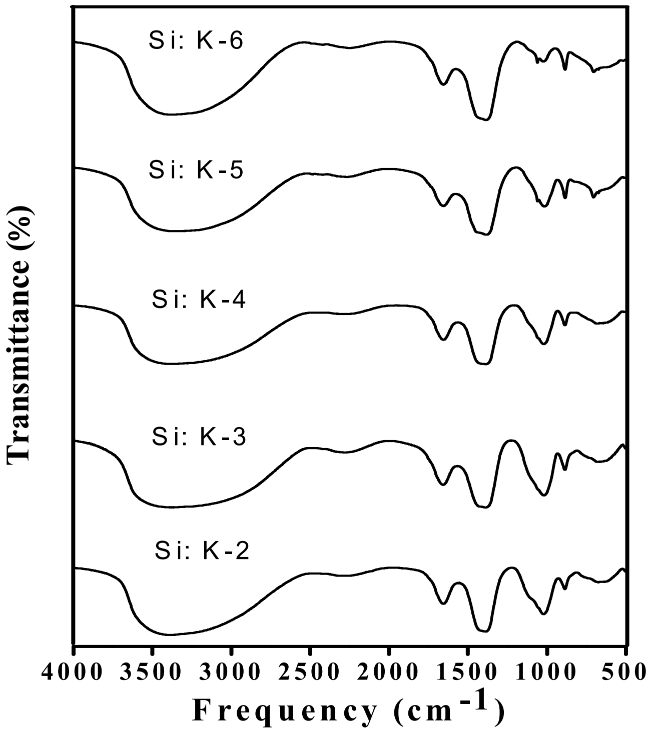


Fig. 4 Effect of catalyst amount *(reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; and temperature, 65 °C; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; and temperature, 65 °C).*

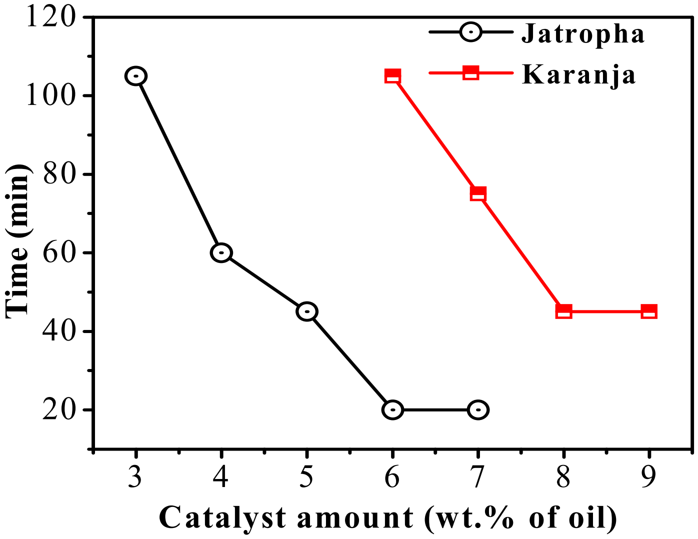


Fig. 5 Effect of methanol to oil molar ratio *(reaction conditions for jatropha oil: catalyst amount, 6 wt % of oil; and temperature, 65°C; reaction conditions for karanja oil: catalyst amount, 8 wt % of oil; and temperature, 65°C).*

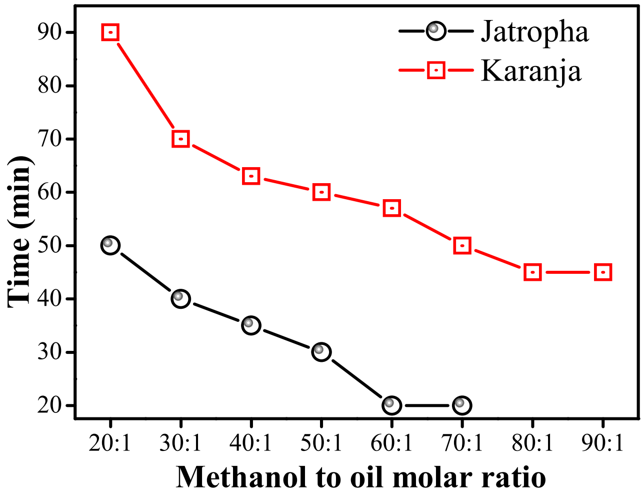


Fig. 6 Effect of Temperature *(reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; catalyst amount, 6 wt % of oil; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; catalyst amount, 8 wt % of oil).*

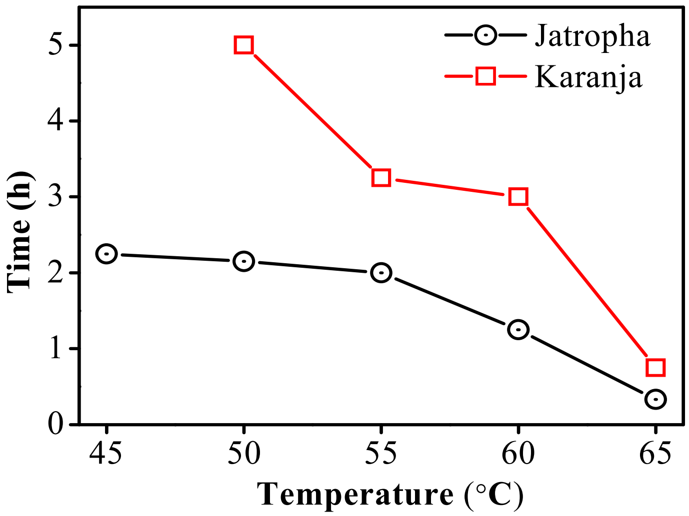
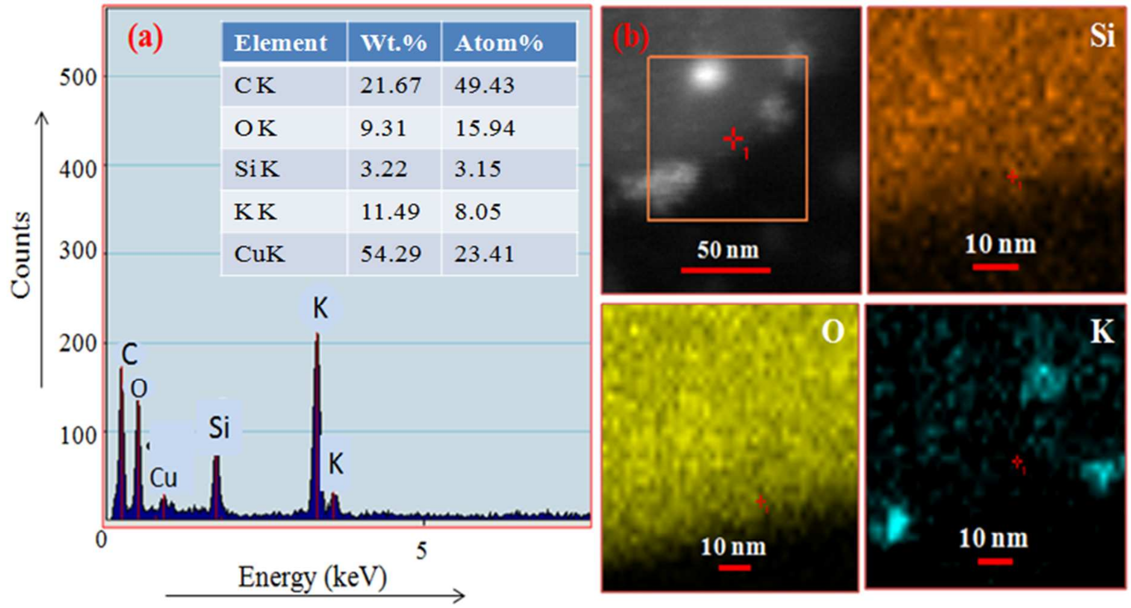


Fig.7. (a) EDX spectra, (b) STEM image and elemental mapping of Si: K-6 catalyst after 2nd reuse with jatropha oil.



Element	Wt.%	Atom%
C K	21.67	49.43
O K	9.31	15.94
Si K	3.22	3.15
K K	11.49	8.05
CuK	54.29	23.41

Fig.8. STEM image of Si: K-6 catalyst after 2nd reuse with jatropha oil.