Catalytic activity of niobia supported graphene oxide for esterification of oleic acid

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Biodiesel has been obtained from esterification of oleic acid with methanol using niobia loaded graphene oxide (GO). Different weight percentages of niobia (1, 3, 5 and 7 wt.%) have been loaded on GO by the wet impregnation method. The synthesized materials have been characterized by XRD, FT-IR, Raman spectroscopy, TGA, BET surface area, NH_3-TPD, ICP-OES, SEM and HR-TEM studies. The catalytic activity of niobia supported on GO has been tested for esterification of oleic acid with methanol for biodiesel production. The maximum yield of methyl oleate (96.4%) is obtained at the reaction conditions of 150 °C, 0.5 g of 5 wt% of niobia on GO catalyst, 1:9 molar ratio of oleic acid:methanol and time 4 h. Influence of solvents (ethanol, propanol, butanol) has been tested for comparative study with same reaction conditions. Based on the catalytic studies, niobia supported GO has good catalytic activity for esterification of oleic acid reaction with good reusability.

Dependency on fossil fuels has serious implications on world economy and environmental pollution because of rising atmospheric CO_2 emissions from diesel engines. Hence, there is a need to produce renewable resources to mitigate depleting fossil fuels reserves, increasing environmental concerns and energy demands for transportation purpose[1]. Biodiesel comprising fatty acid alkyl esters is renewable, biodegradable, eco-friendly and sustainable, and can be produced from low cost materials[2]. Biodiesel can be obtained either by transesterification of vegetable oils or esterification of long chain fatty acids with alcohol in the presence of a suitable catalyst. Homogeneous catalysts like alkali and acids cause problems like difficulty in the separation of the catalyst from the reaction mixture, high free fatty acids in the feedstock producing undesirable saponified products and corrosion of equipment. In addition, cost of production increases and generates large amount of waste water from the separation process[3,4]. In order to overcome these problems, heterogenised metal complexes has been developed which are economical and environmental friendly. Some of the heterogeneous catalysts are NaX zeolites loaded with KOH, niobium containing MCM-41, Amberlyst 15, WO_3/ZrO_2 and sulphonated mesoporous carbon[5-9]. In the esterification process, the support plays a crucial part for the catalytic performance. Catalysts mostly rely on the active sites, capable of chemisorbing the reactants and the formation of surface intermediates of adequate strength[10]. Usually alumina or silica is used as a support for the reaction. Nowadays carbon black or charcoals are also used as a support to carry out the reaction. In this connection, GO a two-dimensional sheet of sp^2 hybridized carbon assembled in hexagonal lattice, has found applications in sensors, supercapacitors, batteries, nanoelectronics and nanocomposites[11,12]. In addition, GO is also used as support due to its characteristics like large surface area, high thermal and mechanical stability with good electrical properties[12,13]. The dispersion of the catalytic species and mass transfer of the reaction has been performed by GO. It can also access the active sites present in the catalytic species with limited mass transfer resistance[14]. GO can be synthesized by exfoliation of graphite oxide containing carboxylic acids present at the edges and carboxyl groups at the basal planes. Nanocomposites are formed using these oxygenated functional groups by nucleation of metal ions[15,16]. Recently, the use of GO as support for the metal oxide in catalysis for the Fe_3O at GO composite for reduction of nitroarens[17] has been reported. Other studies have reported copper-nickel/graphite bimetallic nanocomposite catalyst for synthesis of methyl carbonate[18], Co_3O_4 nanocrystals on graphene

for oxygen reduction reaction[19], epoxidation of olefins by GO supported copper (salen) complex[14], Pd complex immobilized on GO for ester synthesis[20] and methanol electrooxidation by Pt nanoparticle on reduced GO[12].

In this study, esterification of oleic acid with methanol has been carried out using GO as a support for niobia. Effects of reaction temperature, time, amount of catalyst, oleic acid: methanol ratio and various alcohols (ethanol, butanol and propanol) are optimized in the batch reactor for the conversion of oleic acid. It was found that niobia supported GO exhibits high catalytic activity and also outstanding stability even after intensive reuse.

Materials and Methods

Graphite powder and niobium oxalate were purchased from Sigma Aldrich and Alfa Aesar respectively. Sodium nitrate ($NaNO_3$), sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl) (35%), oleic acid and ethanol were purchased from Merck and used as such without any further purification. Methanol was purchased from Sigma Aldrich and was distilled before use. Methyl oleate (MO) was used as internal standard for GC.

Characterization

Powder XRD patterns were obtained with PANalytical XPert diffractometer using Cu Kα radiation at the wavelength of 1.5406 Å. FT-IR spectra were recorded on a Perkin Elmer (Spectrum RX1) instrument using KBr pellet technique in the range 4000–400 cm^{-1}. Raman spectroscopy was recorded at the wavelength of 532 nm on Witec Confocal Raman instrument. Thermal analysis was carried out under oxygen atmosphere using a high resolution TA Instrument, SDT Q600 at a heating rate of 10 °C min^{-1} in the temperature range from 100 to 800 °C. Surface area was calculated by the BET method while pore volume and average pore size were calculated by BJH method (Quanta chrome 2010-09). The N_2 adsorption desorption isotherms were obtained at liquid nitrogen temperature. SEM was used to study the surface morphology of the synthesized samples using Carl Zeiss MA 15/EVO 18 scanning electron microscope. Morphology of the samples was analysed by HR-TEM with EDAX recorded on a JEOL 3010 instrument. Samples were dispersed in ethanol solution and a drop of the suspension was placed on a carbon coated Cu grid and

allowed to dry at room temperature. Elemental analysis was by ICP-OES using a Perkin Elmer (optima 5300 DV) instrument.

Preparation of niobia loaded GO catalyst

GO was synthesised by modified Hummer's method[21] from graphite powder. About 1.0 g of graphite powder was added to a mixture 23 mL of H_2SO_4 (98%) and 0.5 g of $NaNO_3$ in a 500 mL RB flask and stirred in an ice bath for 3 h. After stirring, 3.0 g of $KMnO_4$ was gradually added under vigorous stirring while the RB was kept in ice bath, making sure the temperature maintained was below 20 °C. Then the temperature was raised to 35 °C for 2 h with stirring. About 40 mL of deionised water was slowly added and the mixture was heated to 98 °C for 15 min. The reaction was terminated by adding 140 mL of water to the mixture and 40 mL H_2O_2 (50 wt.%) was slowly added under stirring. The suspension was washed with aqueous HCl (1:10 volume ratio) and deionised water for several times. The precipitate was collected by centrifugation which was dispersed in water for sonication. It was again centrifuged, filtered, dried at ambient temperature to obtain GO.

Different amounts of niobia were loaded on GO by wet impregnation method. GO (1 g) was added to a mixture of 25 mL ethanol and niobium oxalate (1, 3, 5, 7%) in the reactor. The mixture was sonicated and again stirred at RT for 6 h. The resultant mixture was dried at 100 °C for 12 h and the solid was calcined at 300 °C for 5 h. The obtained materials with 1, 3, 5 and 7 wt.% of Nb_2O_5 on GO were denoted as 1Nb-GO, 3Nb-GO, 5Nb-GO and 7Nb-GO respectively.

Esterification of oleic acid

The catalytic activity of the samples was tested in a 100 mL Teflon coated autoclave reactor for esterification reaction. Oleic acid (10 g) was taken in the reactor and to this, methanol and niobia loaded GO (0.5 g) were added. The stirring speed for all the reactions was maintained at 600 rpm and heated to different temperatures (80, 100, 120 and 150 °C). After the reaction was completed, the autoclave was cooled to room temperature and catalyst was recovered using Whatmann filter paper. The methanol present in the filtrate was removed by distillation at 100 °C. The resulting solution was analysed by proton nuclear magnetic spectroscopy (^{1}H NMR) and gas chromatography (GC). The ^{1}HNMR was recorded on a Bruker 500 MHz spectrometer. GC analysis was

performed on Shimadzu GC 17A chromatograph system equipped with 30 mm×0.25 mm of rtx5 column. The oven temperature was set as 100-180 °C at 20 °C min^{-1} and 180-250 °C at rate of 10 °C min^{-1} with holding time for 3 min.

Results and Discussion

Characterization of Nb-GO

Figure 1 illustrates that the wide angle XRD patterns of GO and niobia loaded GO. GO shows an intense peak at 2θ range of 10.9° due to (001) reflections corresponding to interplanar spacing of 0.81 nm which coincided well with the data reported in the literature[13]. This is an indication of insertion of oxygen in the graphitic layer. A broad diffraction peak in the 2θ range of 26.5° due to (002) plane appears in niobia loaded GO (Fig. 1(curves 2-4)). The GO nanosheets are partially reduced and the ordered crystalline structure is restored[22]. The (001) plane of GO disappeared in the XRD pattern of niobia loaded GO. The 7Nb-GO catalyst shows characteristic diffraction peaks at 23.16, 28.91, 37.18, 50.94 and 55.71° (2θ) corresponding to (001), (100), (101), (110) and (111) planes (Fig. 1(curves 5)). The diffraction patterns and intensities match well with those of niobium oxide (JCPDS 07-0061). The crystalline peak of 7Nb-GO indicates that niobia has been successfully dispersed into the GO.

The FT-IR spectra of GO and niobia loaded GO (Supplementary Data, Fig. S1) show a broad peak at 3406 cm^{-1} due to –OH stretching vibration of C-OH group, while the stretching vibration of C=O in carboxylic acid is found at 1723 cm^{-1}. Weak intense peaks at around 2925 and 2852 cm^{-1} is attributed to –CH$_2$ stretching vibration, and the peaks at 1382 and 1217 cm^{-1} are assigned to –OH deformation vibration and epoxy symmetry stretching vibration of C-O respectively. Alkoxy C-O stretching vibration is at around 1034 cm^{-1} and the peak at 1585 cm^{-1} is due to skeletal vibration of unoxidized graphitic domain[23].

In the Raman spectrum (Supplementary Data, Fig. S2) of pristine graphite, a sharp G band appears at 1565 cm^{-1} due to first order scattering of the E_{2g} mode of graphite. The Raman spectrum of GO exhibited typical well defined two main groups of band at 1585 cm^{-1} (G band) and 1325 cm^{-1} (D band). The G band corresponding to E_{2g} mode of graphite is related to the sp^2 carbon atoms in the two dimensional hexagonal lattices, while the D peak is assigned to breathing mode of aromatic rings arising due to defect in the sample[24]. The niobia loaded GO catalysts also contain both G and D peaks at 1585 cm^{-1} (G band) and 1325 cm^{-1} (D band). The I_D/I_G ratio was used to evaluate the graphitic character of the carbonaceous materials. The calculated I_D/I_G values are 0.95, 0.96, 0.98, 1.01 and 1.00 for GO, 1, 3, 5 and 7Nb-GO samples respectively. The I_D/I_G ratio of niobia loaded GO shows a higher value than GO, which is due to the presence of metal oxide in the graphene sheets[25]. This suggests a decrease in the average size of the sp^2 domains, which leads to partial reduction of GO.

Thermal stability of the samples was determined by thermogravimetric analysis. Figure 2 illustrates the TG curves of GO and niobia loaded GO. The initial weight loss at 100 ºC in thermogram of GO was due to physically adsorbed water molecule with a further weight loss (~25%) between 150 ºC and 280 ºC due to
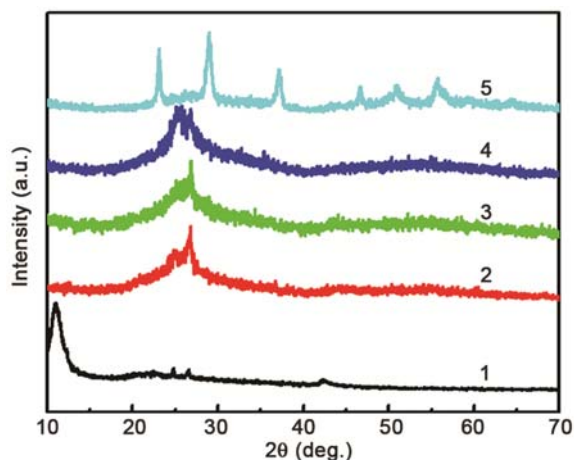

Fig. 1 — Wide angle XRD patterns of (1) GO, (2) 1Nb-GO, (3) 3Nb-GO, (4) 5Nb-GO and (5) 7Nb-GO.
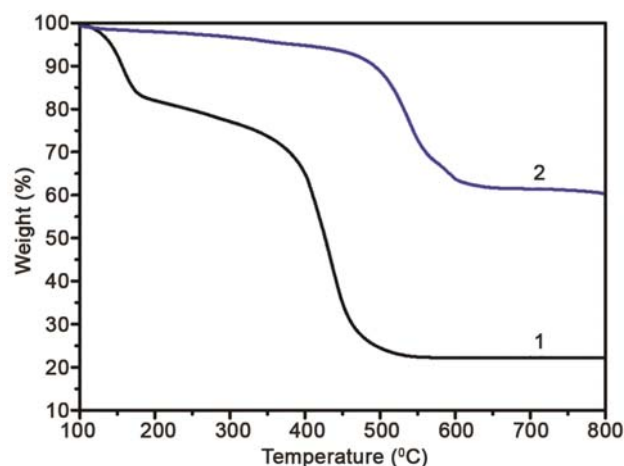

Fig. 2 — TG curve of (1) GO and (2) 5Nb-GO.

chemically adsorbed water molecule and removal of acidic functional groups to give CO, CO_2, and H_2O residues[26]. Finally, the weight loss between 400 ℃ and 600 °C was due to decomposition of graphitic carbon. However, in the case of niobia loaded GO, there is no weight loss observed in the range of 150–280 ℃ as the oxygen containing functional groups are removed during calcination process. The results confirm that metal oxide loaded GO has higher thermal stability than GO.

Figure 3 shows the nitrogen adsorption–desorption isotherms for GO and niobia loaded GO catalysts. The BET surface area, pore volume, and average pore size of catalyst are listed in Table 1. The isotherms exhibit type IV with a hysteresis loop in the relative pressure range of pressure (P/P_0) range 0.4-1.0 for GO and niobia loaded GO[27]. A marginal difference was observed in the isotherm for niobia loaded on GO which is due to the presence of metal oxide on the surface of GO. As expected, the BET surface areas for niobia loaded GO decreased with increase in the loading of niobia on GO. Surface area, pore volume and pore size of GO was 137 m^2/g, 0.13 cm^3/g and 4.0 nm respectively. Elemental analysis for niobium content in niobia loaded GO catalyst measured by ICP-OES analysis is above given in Table 1.

The NH_3-TPD profile of 5 and 7 wt.% niobia loaded GO, show a peak at low temperature range of 150-250 °C, representing the weak acidic sites of all the catalysts (Fig. 4). A high intensity peak is observed at 600-700 °C due to strong acidic sites in the catalyst. The intensity of desorption peak at higher

temperature increased with increase in niobia loading on GO. The results suggest that after niobia loading on GO, 7 wt.% of Nb-GO possesses strong acidic sites which arise from Bronsted acidic sites of niobia[28]. The acidity of 5 and 7 wt.% Nb/GO is found to be 83 and 126 μmol/g respectively. Furthermore, the results suggest that niobia was loaded on the framework of GO.

SEM images of GO presented in Fig 5(a) reveal that the material consists of randomly aggregated, corrugated and also folds on the surface of GO. It confirmed that the two dimensional GO can be produced by exfoliation of graphite as reported in literature[29]. The 7 wt.% niobia loaded GO shows sheet-like structure but the layer of sheets are more corrugated compared with starting GO sheets, which may be due to the introduction of metal oxide. This is also accordance with the TEM images discussed below. The HR-TEM images of GO and niobia loaded

Table 1 — Textural properties of GO and 1, 3, 5 and 7 Nb-GO

Catalyst	Surface area $(m^2/g)^a$	Pore size $(nm)^a$	Niobium $(wt.\%)^b$	I_D/I_G ratio^c
GO	137	4.0	-	0.95
1Nb-GO	130	3.8	0.8	0.96
3Nb-GO	113	3.7	2.7	0.98
5Nb-GO	63	3.7	4.5	1.01
7Nb-GO	37	3.6	6.8	1.00

^{a}Values obtained from nitrogen adsorption-desorption isotherm studies.
^{b}Values obtained from ICP-OES analysis.
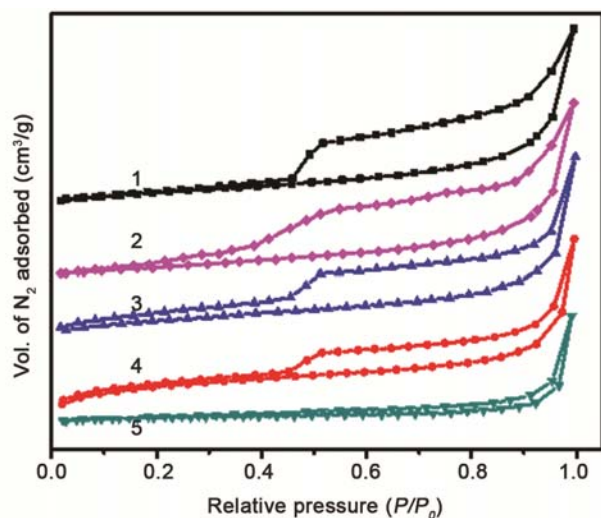^{c}Values obtained from Raman spectroscopy.

Fig. 3 — Nitrogen adsorption- desorption isotherms of (1) GO, (2) 1Nb-GO, (3) 3Nb-GO, (4) 5Nb-GO and (5) 7Nb-GO.
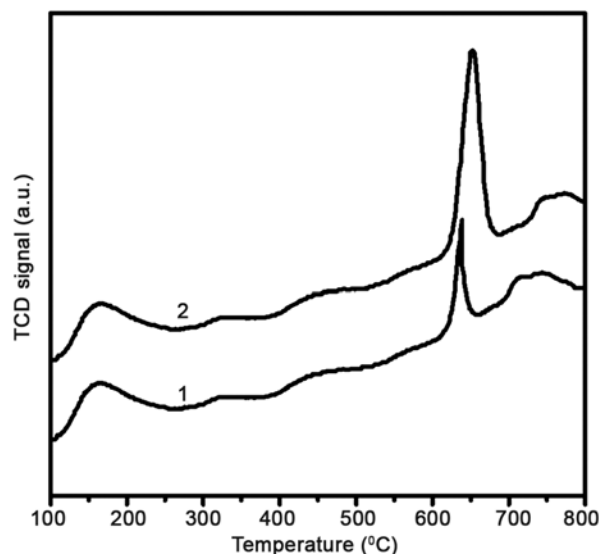

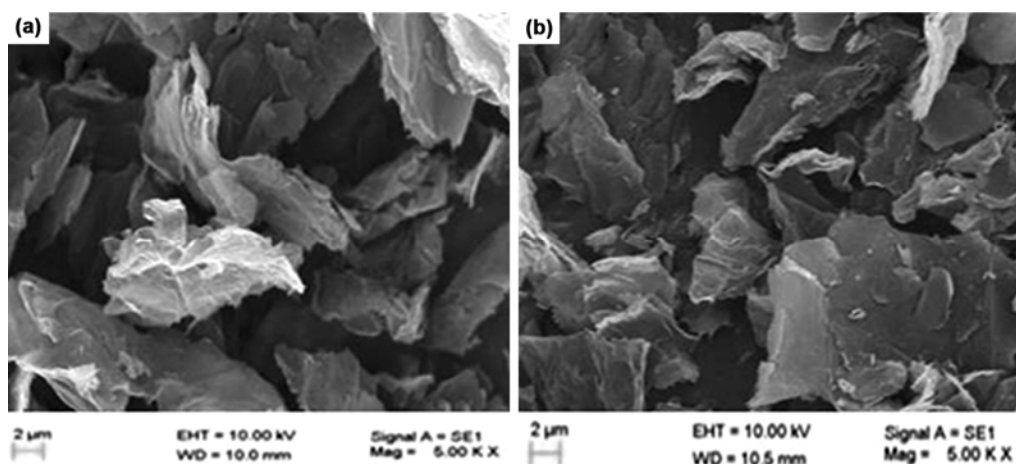Fig. 4 — TPD profiles for (1) 5Nb-GO and (2) 7Nb-GO.

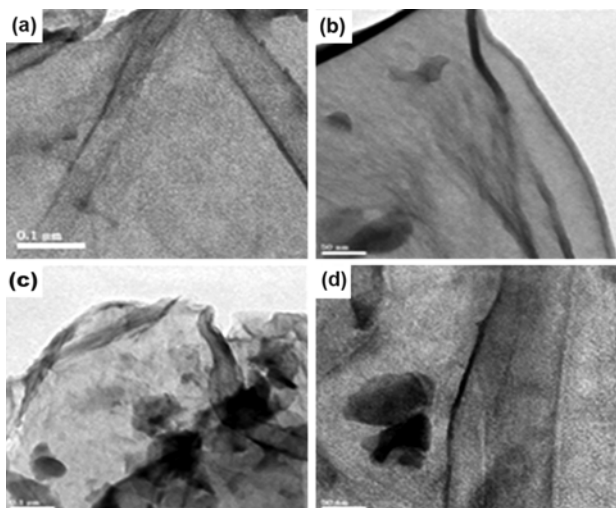Fig. 5 — SEM images of (a) GO and (b) 7Nb-GO.

Fig. 6 — HR-TEM images of (a & b) GO and (c & d) 7Nb-GO at different magnifications.

GO at different magnifications are presented in Fig. 6. The image displayed that niobia loaded GO has a flake like shape with slight wrinkles occurs on the surfaces and it can be identified to be a multi-layer GO sheets. The dark spots in Fig. 6(b) confirm the presence of niobia on the graphitic layer, and may be attributed to non-uniform distribution and non-uniform decoration of metal oxide on the GO surface. It reveals that, niobia was successfully loaded on GO. From the EDAX measurements, the weight percentage of niobium was found to be 6.8% for 7Nb-GO (Fig. 7).

Esterification reaction

In the ^{1}HNMR spectrum of MO, the resonance singlet peak corresponding to the methoxy protons of ester was observed clearly at 3.65 ppm.

(Supplementary Data, Fig. S3) The absence of this distinct peak in the ^{1}HNMR spectrum of oleic acid[30], shows the presence of methyl esters in the MO sample.

The prepared catalysts were used for the esterification of oleic acid with methanol to obtain biodiesel component under heterogeneous conditions. The effects of different reaction parameters such as reaction temperature, reaction time, amount of catalyst, molar ratio of oleic acid:methanol and different alcohols (ethanol, isopropanol and butanol) were studied to optimize the conditions for methyl oleate production. Recyclability of catalyst was studied to establish stability of the catalyst.

The effect of reaction temperature on the yield of MO was studied over 1, 3, 5 and 7 wt.% niobia loaded GO as catalyst at 80, 100, 120, and 150 °C (Fig. 8). Typically, the esterification conditions were 4 h, 0.5 g of catalyst and 1:9 of oleic acid:methanol molar ratio at different temperatures. Esterification reaction proceeds slowly at 80 °C where the yield of methyl esters was 25%. The yield of methyl esters increased up to 96.4 % with increase in temperature up to 150 °C. However, reaction temperature above 150 °C was not advantageous for this reaction, as the yield of ester was insignificant (not shown in figure). Hence, the temperature of 150 °C was taken as the optimum temperature as it gave good yields. For comparison, the reaction was also carried out in the absence of catalyst. The results revealed that the yield of MO was about 46% at 150 °C. In the presence of catalyst, the yield of MO increased significantly. As the yield of MO for the 5% and 7% niobia loaded GO at 150 °C was 96.4 and 97% respectively and hence the former was chosen as a better catalyst for further studies.
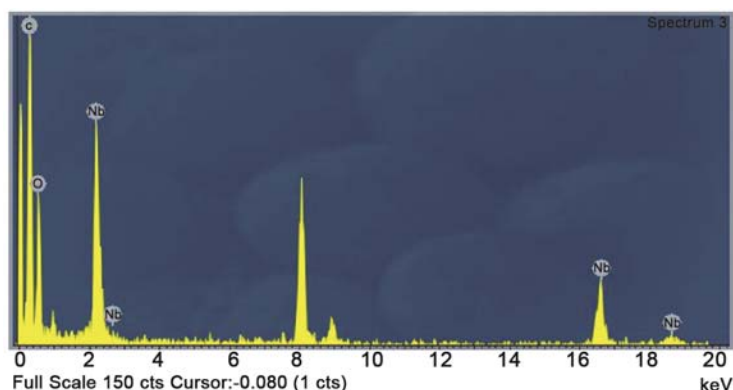
Fig. 7 — EDAX image of 7Nb-GO.

The yield of MO was high over GO with high weight percentage of 5Nb-GO. There was an increase in the yield with the increasing loading of niobia content. This may be because at low percentage of niobia loaded, the catalyst does not have as many active sites as compared to catalyst with high weight percentage of niobia[31]. Among the catalyst studied, 5Nb-GO was chosen for further studies as it gave high yield of MO.

The effect of various reaction times viz., 1, 2, 3, 4 and 5 h, was investigated on the MO yield. The parameters of the reaction were oleic acid: methanol molar ratio 1:9, catalyst 5Nb-GO and reaction temperature 150 °C. It was observed that, MO yield increased with increasing the reaction time yield of 96.4% of MO was achieved at reaction time of 4 h. Hence, this time was chosen for studying the effect of the amount of catalyst. At reaction time above 4 h, no significant change was observed in the MO yield for up to 5 h (Supplementary Data, Fig. S4).

The effect of the catalyst amount was studied by varying the amount of catalyst from 0.1-0.7 g (1-7 wt.%) with respect to the weight of oleic acid (Supplementary Data, Fig. S5). The reaction conditions of the experiments were: reaction time 4 h, temperature 150 °C, oleic acid: methanol molar ratio of 1:9 and 5Nb-GO catalyst. The results revealed that MO yield increases with the amount of catalyst and the maximum yield was achieved with the loading of 0.5 g. The increase in the MO yield can be ascribed to an increase in the number of available catalytic active sites. On further increase in the catalyst amount up to 0.7 g, the MO yield became constant which may be due to the attainment of equilibrium. Hence, 0.5 g of catalyst was chosen as the optimum catalyst weight.
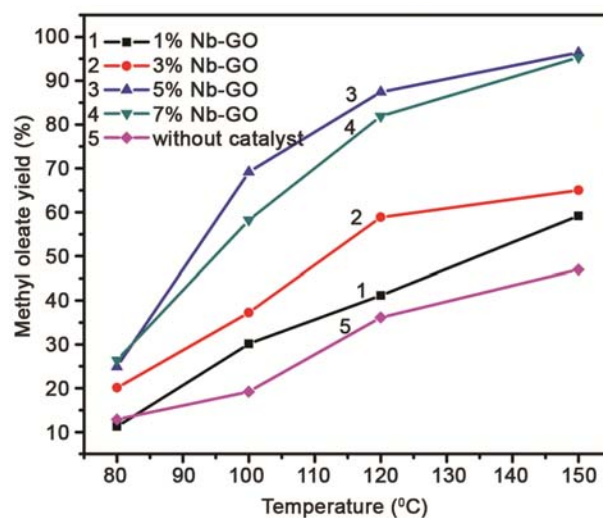

Fig. 8 — Effect of reaction temperature over different catalyst for esterification of oleic acid.

The effect of the mole ratio was carried out by varying the mole ratio of oleic acid to methanol. The reaction conditions were 5Nb-GO catalysts (0.5 g) for 4 h at 150 °C. The results reveal that 96.4% of MO yield was observed with increase in the mole ratio of oleic acid:methanol to 1:9. On further increase in the mole ratio (1:12), the increase in MO yield was not appreciable. Only shift in the chemical equilibrium was identified with increase in alcohol:acid ratio[32]. On increase in molar ratio, there is saturation of active sites of methanol. The completion of the reaction was decreased due to the protonation of the reactant at the active sites[33]. In addition, on further increase in the methanol quantity, more water will be produced which in turn will react with MO to form oleic acid. Hence, molar ratio of 1:9 was selected for esterification of oleic acid (Supplementary Data, Fig. S6).

Various solvents (viz., ethanol, butanol, iso-propanol) was tested in the esterification of oleic acid using 5% of niobia loaded GO and without catalyst (Supplementary Data, Fig. S7). Different alcohols have different reactivities in the esterification reaction. Low methyl oleate yield was observed for the reaction without catalyst. The effectiveness of alkyl ester yield using niobia loaded GO is high which follows the order: ethanol > isopropanol > butanol, which is due to size and type of the alcohol chain influencing the esterification reaction[34]. The results suggest that methanol is a better solvent for oleic acid conversion.

Reusability of the catalyst

Reusability of the catalyst was tested to evaluate the activity and stability of the catalyst. The catalyst was used repeatedly for five cycles. The catalyst was recovered after the each reaction by simple filtration, washed with methanol till to remove the oleic acid, dried at 100 °C for 12 h and reused for a new reaction cycle. The result show that the percentages of MO yield was marginally decreased up to third cycle and again gradually decreased to 79% after 4th cycle. The result show that the catalyst can be recycled reasonably and decrease in MO yield was marginal (Supplementary Data, Fig. S8).

Conclusions

GO was efficiently synthesised and used as a support for niobia. The Nb-GO can be efficiently used as a catalytic support for esterification reaction. The effect of various reaction parameters was optimized for the esterification reaction. Extremely high catalytic activity was observed with the optimum reaction conditions of temperature: 150 °C, time: 4 h, amount 5Nb-GO catalyst: 0.5 g and oleic acid:methanol molar ratio: 1:9. The results shows that GO could be a valuable support for niobia in acid catalysed esterification reactions. This novel heterogenous catalyst exhibited excellent catalytic activity and reusability which demonstrates its potential for industrial applications.

Supplementary Data

Supplementary Data associated with this article, viz., Figs S1-S8, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(04)379-386_SupplData.pdf.

Acknowledgement

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