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Selective Acetalization of Glycerol with Acetone Over Nickel Nanoparticles Supported on Multi-Walled Carbon Nanotubes

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Abstract The use of multi-walled carbon nanotubes for catalytic applications is acquiring great interest. In this work, heterogeneous catalysts were prepared by incorporating nickel nanoparticles into MWCNTs and were characterized by BET, surface acidity, FTIR, XRD, Raman spectroscopy, and TEM analysis. The Ni-containing catalysts have presented unique catalytic performance in the selective formation of glycerol ketal and acetal via the solventless acetalization with acetone. The formation of glycerol acetal via glycerol ketalization with acetone can be considered as one of the earlier attempts in this field. Experimental investigations revealed that at 40 °C,

Ni(1.8)/MWCNTs facilitated the conversion of 96 % glycerol with corresponding selectivity of 72 and 28 % toward ketal and acetal, respectively, within 3 h. The unique catalytic performance of this catalyst is mainly attributable to its high acidity and the structural characteristics. The stability of the catalytic activity was examined upon recycling the catalyst for four consecutive batch runs.

Keywords MWCNT · Glycerol · Bioadditives · Biodiesel · Oxygenates

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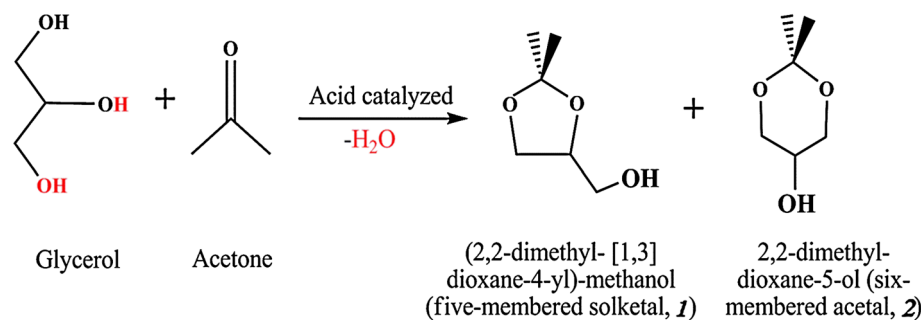
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1 Introduction

Glycerol is an abundant carbon-neutral renewable feedstock for the synthesis of different biomaterials as well as a source for a variety of valuable commodity chemicals [1, 2]. As it is the by-product of biodiesel industry with a portion of 10 wt%, a superfluity of this natural polyol has been generated. Thus, it seems imperative to find more economical destinations for this glycerol via the transformation to value-added chemicals for sustainable and profitable biodiesel production. The synthesis of glycerol-based fuel additives could assist in improving the economy of biodiesel industry and contribute toward replacing the conventional tertiary alkyl ethers (MTBE and ETBE). In particular, glycerol acetal and ketal have colossal potential applications as surfactants, disinfectants, flavouring agents, and fuel additives [3, 4].

The synthesis of these cyclic compounds is usually performed via the acid catalyzed acetalization or ketalization of glycerol with an aldehyde or ketone [5]. As shown in Scheme 1, glycerol acetalization with acetone produces branched oxygenated compounds namely (2,2-dimethyl-

Scheme 1 Acetalization of glycerol with acetone over Ni/MWCNT catalyst to produce (2,2-dimethyl-[1,3] dioxane-4-yl)-methanol and 2,2-dimethyl-dioxane-5-ol



[1,3] dioxane-4-yl)-methanol (five-membered solketal, **1**) and 2,2-dimethyl-dioxane-5-ol (six-membered acetal, **2**). Solketal is an important component for the formulation of gasoline, diesel and biodiesel blends [4]. As fuel additives, the main function of these components is as octane enhancers (anti-knocking agents). Despite that an additive is often added in less than 1 % to the base fuel, it provides an advantage to the chemical industry to produce it in hundreds of tons with respect to fuel consumption.

In terms of catalysts used, glycerol acetalization with acetone is conventionally performed using strong mineral acids as homogeneous catalysts such as H_2SO_4 , HF, HCl or *p*-toluene sulphonic acid. Supported heteropolyacids, Amberlysts, promoted Zirconia, Zeolites, and others are good examples of the previously used heterogeneous catalysts for glycerol acetalization [6–8]. However, heteropolyacids and ion exchange resins (Amberlyst) exhibit drawbacks such as solubility in polar media, poor thermal stability, hindrance by limited accessibility, poor regeneration ability and low specific surface area [9]. Thus, the development of an effective, thermally stable and affordable catalyst is a necessity to perform the acetalization process well. In addition, the selective performance toward the formation of glycerol acetals from acetone is still challenging. In addition, several studies were reported with explicit drawbacks such as the use of hazardous solvents, employing high molar ratio of glycerol to acetone [8], and the long reaction duration to achieve only 80 % of glycerol conversion [10]. These studies motivated us to investigate the performance of nickel nanoparticles supported onto MWCNTs as a selective solid acid catalyst toward the formation of **5** and **6** via the acetalization of glycerol with acetone.

2 Experimental

2.1 Materials

Anhydrous glycerol (>99 %) and HPLC-grade acetone (≥ 99.8 %) were purchased from Sigma-Aldrich, Malaysia. Nickel (II) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HNO_3 and

H_2SO_4 were supplied by Merck, Malaysia. Hydrochloric acid (HCl 37 %) from Mallinckrodt, USA was used.

2.2 Synthesis of the Ni/MWCNTs Catalysts

The MWCNTs were synthesized using a gas mixture comprising $\text{C}_2\text{H}_4/\text{N}_2/\text{H}_2$ (1:1:2) in a fluidized-bed reactor over 5 % $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst at 650 °C for 30 min. The detailed synthesis procedure can be found in our earlier contribution [11]. An acid treatment for the as-obtained MWCNTs was employed to remove the amorphous carbon and metallic impurities introduced by the preparation process. In a round-bottom flask, 4 g of raw MWCNTs were oxidized by immersing in 400 ml solution of HNO_3 and H_2SO_4 (ratio of 1:3) and refluxing the mixture at 90 °C for 6 h under constant stirring (250 rpm). This process entails the thermal decomposition of the functional oxygenated groups attached to the CNTs and thereby, provides the necessary oxygen to produce NiO nanocrystals. After filtration, the sample was then thoroughly washed with deionized water up to the neutrality the rinse water and subsequently dried at 130 °C for 12 h. Afterwards, the catalyst was prepared by incipient wetness method as follows: 1 g of purified MWCNTs was impregnated with an aqueous solution containing the desired amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The suspension was then dried at 110 °C for 8 h and subsequently calcined at 400 °C in a closed cup crucible. The obtained samples were denoted as Ni(x)/MWCNTs, where x refers to the weight percentage of nickel in the sample. The as-synthesized materials were characterized by BET surface area using Micromeritics ASAP 2020 instrument (USA), surface acidity, FTIR analysis (Perkin–Elmer System 2000 spectrometer), XRD (Bruker D8 Advance) with $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) over the 2θ range of 5°–90°, TEM images over Philips CM120 instrument) at 120 kV, and Raman spectroscopy to analyze the degree of graphitization of CNTs (Renishaw Raman using an Ar^+ ion laser at 514.5 nm excitation).

2.3 Catalytic Activity

Glycerol acetalization experiments were performed in a 50 mL round bottom glass flask under nitrogen flow

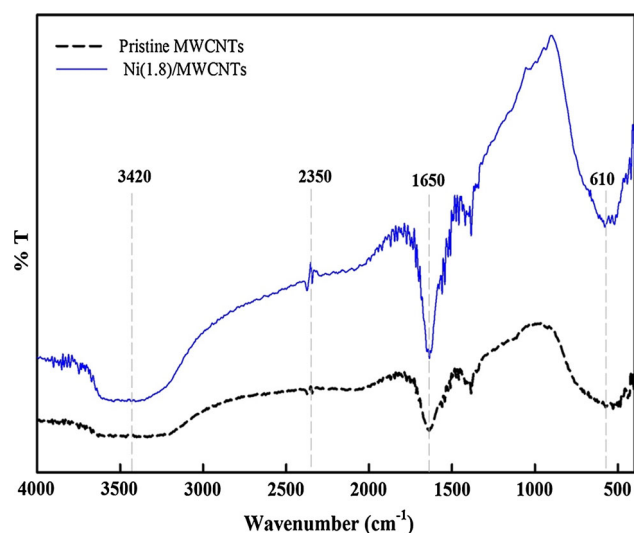


Fig. 1 FTIR spectra of the pristine MWCNTs and Ni(1.8)/MWCNTs catalyst

conditions and constant stirring (530 rpm). Typically, 0.30 g of the catalyst, 5.0 g of glycerol and 23.9 mL of acetone (1:6 molar ratio of glycerol to acetone) were mixed and the reactions were performed at 40 °C. In some experiments, a molar ratio of 1:4 of glycerol to acetone was used. For comparison, blank experiment, without adding catalyst, was also carried out under the same reaction conditions. The reaction progress was monitored by withdrawing samples at specific time intervals and analyzing them by gas chromatograph (GC; Shimadzu 2010 plus, Japan) equipped with a flame ionization detector (FID) and a capillary column (ZB5-HT; 30 m × 0.25 mm × 0.25 μm).

3 Results and Discussion

3.1 Characterization of the Catalysts

The pristine MWCNTs material possessed a total surface area of 231 m²/g, which reduced to 207 m²/g as 1.8 wt% of Ni was introduced. This reduction might be attributable to the partial occlusion of the surface channels due to the intercalation of metallic species. The catalyst surface acidity was measured by the neutralization titration method [12]. The surface acidity was found to be a function of Ni loading; being the catalyst with highest metallic loading is of the strongest acidity. The acidity values were 464, 712, 1083, and 1209 μmol g⁻¹ for the oxidized MWCNTs, Ni(0.6)/MWCNTs, Ni(1.8)/MWCNTs, and Ni(2.2)/MWCNTs catalysts, respectively. The relatively-high acidity values are possibly attributable to the carboxylic acid functionalities that would be formed concomitantly during the preparation of NiO particles.

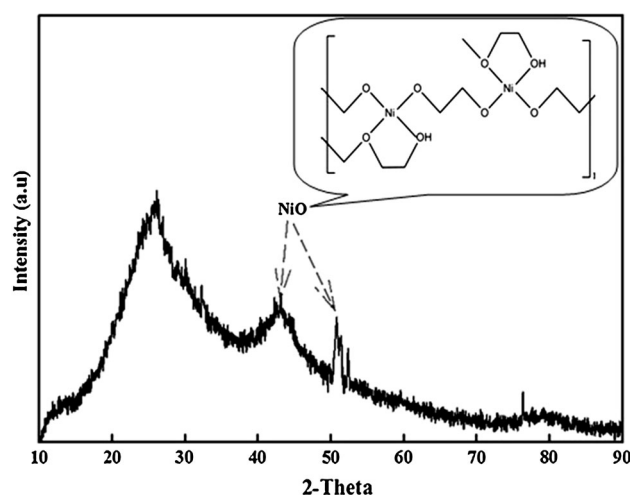


Fig. 2 XRD pattern of Ni(1.8)/MWCNTs catalyst

The FTIR spectra of the pristine and the functionalized MWCNTs are presented in Fig. 1. The bands at 3,420 and 1,650 cm⁻¹ are assigned to the vibration modes of hydroxyl and carbonyl groups, respectively [13]. The shoulder at about 2,350 cm⁻¹ is attributable to the adsorption of atmospheric CO₂, which is found to be weak in the spectrum of MWCNTs. This might explain the hydrophobic nature of the pristine MWCNTs which does not adsorb much of the atmospheric guest species. On the contrary, the hydrophilic nature of Ni(1.8)/MWCNTs is manifested as the band is stronger and more intense. This could merely explain the adsorption capacity of this catalyst, which is an important property of catalytic materials.

Figure 2 shows the XRD pattern of the as-synthesized Ni(1.8)/MWCNTs catalyst. The strong diffraction peak at $2\theta = 25.1^\circ$ and the weak peak at $2\theta = 43.6^\circ$ are ascribed to (002) and (100) diffraction patterns of typical graphite, respectively [13]. The results indicated that MWCNTs were well graphitized. The XRD peaks at 2θ of 44.2° and 51.2° are assigned to the face-centered cubic phase of NiO [14]. The presence of nickel oxide in the catalyst structure was toggled as the pattern unveiled the formation of monoclinic NiO phase, as obtained from EVA software. There is no observable peak in the XRD spectra that corresponds to the presence of pure Ni. The average crystallite size of NiO has been determined by the Debye–Scherrer formula based on the half-band width of the peak at $2\theta = 51.2^\circ$ due to Ni(200) planes.

The TEM images of the pristine MWCNTs and the Ni(1.8)/MWCNTs catalyst are shown in Fig. 3. The synthesized MWCNT has possessed a uniform wall thickness with the outer diameter of 18 nm and the inner of about 9 nm. It can be also seen (Fig. 3c) that the metallic Ni species were preferred to allocate between the outer and

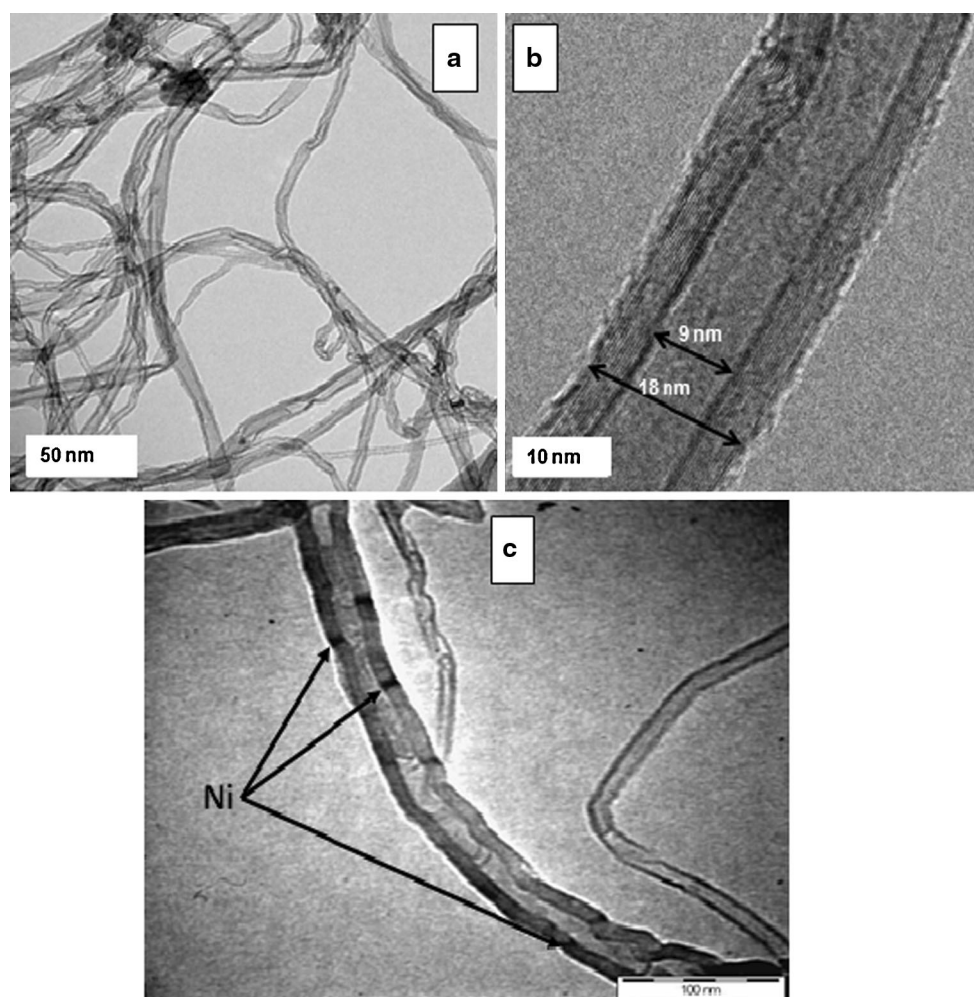


Fig. 3 TEM images of MWCNTs (a, b), Ni(1.8)/MWCNTs catalyst (c)

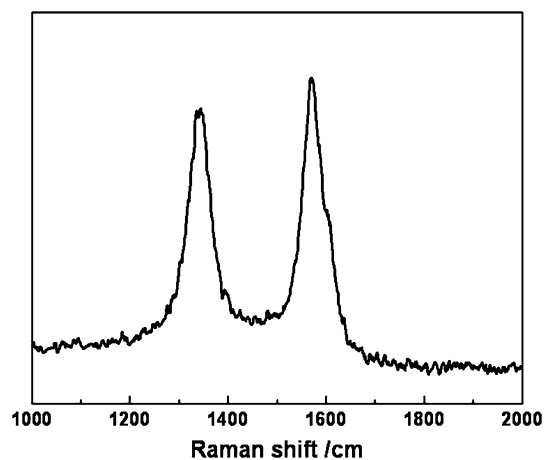


Fig. 4 Raman spectroscopy analysis of the as-synthesized MWCNTs

inner diameters of the MWCNT. This was believed to be one of the reasons of the stability of the catalytic activity under the acetalization reaction conditions.

The Raman spectrum for the as-synthesized MWCNTs is shown in Fig. 4. The spectrum showed two typical peaks at $1,334$ and $1,591\text{ cm}^{-1}$, which assigned to D-band (disorder band) and G-band (graphite band), respectively. The D-band is ascribed to the Raman allowed A_{1g} phonon. Whereas the G-band could be assigned to the phonon E_{2g} (stretching mode of graphite), which indicates the formation of highly ordered hexagonal lattice of graphite [13]. The relatively high G/D ratio of 1.2 obtained from the Raman spectrum evidently confirms that the synthesized material is of high purity and well graphitized.

3.2 Catalytic Reaction

The selective acetalization reactions of glycerol with acetone were performed in the absence of any organic solvent and under nitrogen atmosphere to avoid oxidation reactions. In our previous work, nickel species have shown selective behavior toward the formation of glycerol

Table 1 Reaction profile (Glycerol conversion and product selectivity) for initial screening experiments using Ni(x)/MWCNTs catalysts. Reaction condition: reaction time of 3 h, molar ratio of glycerol/acetone of 1:6, and reaction temperature of 40 °C

Catalyst	Conversion (%)	Selectivity (%)		
		1	2	Others
Blank test	30	73	0	27
MWCNTs	41	84	0	16
Ni(0.6)/MWCNTs	63	88	5	7
Ni(1)/MWCNTs	71	82	15	3
Ni(1.4)/MWCNTs	84	84	16	0
Ni(1.8)/MWCNTs	96	72	28	0
Ni(2.2)/MWCNTs	79	87	13	0

solketal and acetal (**1** & **2** products) at low reaction temperature of 40 °C and short reaction time of 3 h [14]. Also, it has been reported that the catalytic activity of Ni/AC is lower than that of Ni/CNTs due to the structure collapse of the AC support [15]. Therefore, we focus in this study on improving the products selectivity and economizing the reaction conditions by using Ni/MWCNTs catalyst.

For the uncatalyzed experiment, glycerol conversion did not exceed 30 % with a corresponding selectivity of 73 % toward **5** and 27 % toward side products (mostly non-cyclic products). Higher conversion value of 41 % and improved selectivity values were obtained using the pristine MWCNTs as catalytic material. To this end, it was believed that the catalytic performance of the pristine MWCNTs material is attributable to its carboxylic acid functionalities that resulted in surface acidity of 464 $\mu\text{mol g}^{-1}$. In addition, the increased selectivity toward **1** (from 73 to 84 %) was associated with the decreased selectivity to byproducts, which may explain the shape-selective performance of MWCNTs toward the formation of cyclic products. These results have motivated us to select MWCNTs as catalyst support for the synthesis of **1**. To enhance the formation of **2**, Ni nanoparticles have been added to the catalytic system (as they showed such performance in our previous catalyst [12]).

The conversion was obviously increased and the selectivity was shifted towards the formation of **2** over all of all the investigated Ni(x)/MWCNTs catalysts (Table 1). It was found that increasing the Ni content in the catalyst from 0.6 to 1.8 wt% resulted in improving glycerol conversion from 63 to 96 % and the disappearance of the side products. This evidently explains the selective performance of Ni species toward the formation of cyclic products. The prepared Ni(1.8)/MWCNTs catalyst showed the highest conversion value of 96 % with selectivity of 72 and 28 % to **1** and **2**, respectively. This might be due to the presence of well-dispersed metallic active sites and to the strong acidity of

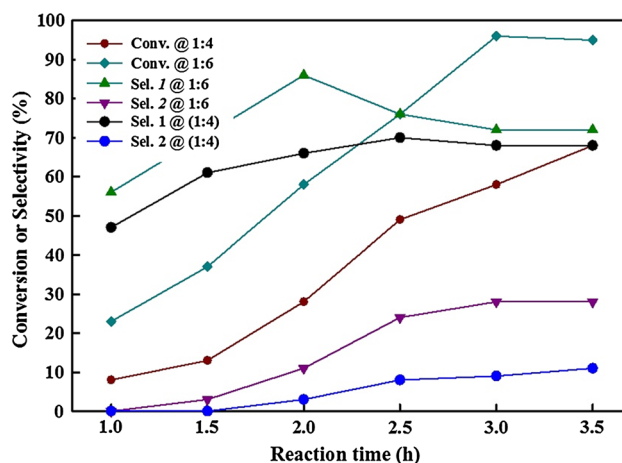


Fig. 5 Glycerol conversion and product selectivity over Ni(1.8)/MWCNTs catalyst at variant reaction time and using two molar ratios of glycerol/acetone (1:4 and 1:6) at reaction temperature of 40 °C

this catalyst. Increasing the Ni content to 2.2 wt% resulted in decreasing the conversion to 79 % and the selectivity toward **2** to 13 %. This could be explained due to the aggregation of Ni species inside and outside the nanotubes at this level of metallic loading (2.2 wt%) and thereby, decreasing the number of the accessible active sites. The aggregation of Ni species is possibly attributable to the saturation of the metal-support anchoring points and the increased metal–metal interactions at a certain level of metallic loading. Thus, the 1.8 wt% of Ni represents the optimum level of metallic loading that shows the best catalytic activity for this reaction.

In fact, the layered structure of MWCNTs with intraspacing suitable for substrates diffusion (where mostly reactions occurred) enhanced the reaction to selectively form **2** and retarded the formation of other undesired cyclic molecules (Table 1). It was reported that the acidic treatment of CNT for 6 h results in increasing the ratio of surface area to volume and greatly enhances the surface energy, which may ensure higher rates of surface diffusion [16]. As a consequence, more functional groups are introduced to the surface of CNTs, resulting in enhancing the interactions between Ni species and CNT walls. Therefore, the outer planes of Ni species might favor the surface diffusion of the reactive molecules more greatly, which could be believed as one of the reasons for the increasing activity of Ni nanoparticles [17].

Figure 5 compares glycerol conversion and the corresponding product selectivity over the Ni(1.8)/MWCNTs catalyst at different reaction durations using varying molar ratios of glycerol/acetone for the reactions performed at 40 °C. It was found that the values of glycerol conversion using molar ratio of glycerol/acetone of 1:6 were higher than those using the ratio of 1:4. This might be explained

Table 2 Catalyst reusability tests and surface acidity values for Ni(1.8)/MWCNTs catalyst recycled four times

Recycle	Glycerol conversion (%)	Selectivity to 1 (%)	Selectivity to 2 (%)	Surface acidity ($\mu\text{mol/g}$)
First	96	72	28	1,083
Second	92	73	27	1,046
Third	91	72	28	1,039
Fourth	91	74	26	1,039

Reaction conditions: Reaction time of 3 h, molar ratios of glycerol/acetone of 1:6, and reaction temperature of 40 °C

by the effect of the extra acetalization agent that drives the reaction toward the acetalization of the remaining glycerol and also favor the formation of **2**. In addition, it is well-established that the six-member cycle it is more stable than the five—one and for this reason; its formation is time-dependent. Anyhow, by comparison with literature reports, the herein obtained results are better (in terms of conversion, selectivity, and reaction conditions) than many other studies employed acetone as the acetalization agent [7, 14]. The selectivity was found to be time-dependent, as it can be seen that the formation of **2** increases by the expense of **1**, which explains the sequential formation of these products.

Reusability tests were performed to ascertain that the catalyst can maintain the same activity upon recycling. The catalyst (Ni(1.8)/MWCNTs) was separated after each catalytic experiment, and regenerated by washing it with ethanol and subsequently dried at 75 °C for 4 h. Then, the regenerated catalyst was reused in another catalytic experiment. This procedure was repeated three times to achieve four recycles. Table 2 presents the values of glycerol conversion and product selectivity obtained upon reusing the Ni(1.8)/MWCNTs catalyst for four recycles. The catalyst showed stable performance with no appreciable change in glycerol conversion and product selectivity. The spent catalyst was characterized by BET and XRD analysis. The surface area has been lowered to 187 m²/g after the fourth recycle, which might be attributable to the partial occlusion of the surface pores and wall channels by the effects of the reaction medium. On the other hand, no appreciable changes have been noticed by XRD pattern compared to that of the fresh catalyst. The spent catalyst has been also characterized by surface acidity after each recycle to provide clear insight about the activity stability. It was found that the surface acidity reduced by 4 % (from 1,083 to 1,039 $\mu\text{mol/g}$ after the fourth recycle), which explains the chemisorbed nature of the surface acidic groups and their stability in polar reaction medium. Moreover, the acidity values may confirm that the surface acidity of this catalyst is attributable to the carboxylic acid functionalities that would be formed concomitantly

during the preparation of NiO particles. Such functionalities are parts of the support system and synergistically interconnected to the NiO species by strong ionic interaction forces, resulting in non-leached catalytic active species.

The stability of the Ni(1.8)/MWCNTs catalyst was also examined by leaching test. First, the catalyst was immersed in acetone and the mixture then heated to the reaction temperature (40 °C) and kept under constant stirring rate for 3 h. Later on, the catalyst was separated from the mixture and 5.0 g of glycerol were added to the in-flask acetone. The liquid mixture was subjected to the same conditions described above, allowing them to react in the absence of the heterogeneous catalyst. Then, the reaction sample was analyzed to determine the values of glycerol conversion, which was found to be 32.7 % and close to that obtained from the blank test 30 % (blank test means the reaction of glycerol with acetone without any catalytic material). It seems that there was no appreciable leaching of the Ni species from the catalyst structure to the liquid phase, which strongly support the claim for the stability of the prepared catalyst.

4 Conclusion

In this work, the classical acetalization of glycerol was modified to obtain five-membered solketal, (**1**) and six-membered acetal (**2**) from acetone as the acetalization agent over the chemo-selective Ni-containing MWCNTs catalyst, in a solventless process. The conversion of glycerol was 96 % with corresponding selectivity of 72 % and 28 % to **1** and **2**, respectively, at the economized reaction conditions of 40 °C, 3 h, and using molar ratio of 1:6. Seemingly, the catalytic activity of this catalyst was mainly attributable to its high acidity, layered structure, and the well-dispersed Ni species. The Ni/MWCNTs catalyst was not only active and selective toward glycerol acetalization, but also could be effectively recycled with maintaining its initial activity.

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