

In situ Formed Supported Silicomolybdc Heteropolyanions: Efficient Solid Catalyst for Acetylation of Glycerol

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Abstract

Present work deals with the extended applicability of the *in situ* generated supported silicomolybdc heteropolyanions from the sol-gel synthesized MoO₃/SiO₂ catalyst for the acetylation of glycerol. The best results were obtained at 118°C using a glycerol: AcOH molar ratio of 1:10 with 100% glycerol conversion in 2 hr and 76% selectivity for triacetin when the reaction was continued for 20 hr.

Keywords: Acetylation; Glycerol; *In situ*; Silicomolybdc; Solid catalyst

Introduction

In recent times, valorization of glycerol into fuel oxygenates by means of esterification is gaining considerable attention, of which the esterification of glycerol with acetic acid (AcOH) is one of the important alternatives. The products of the reaction are monoacetin, diacetin and triacetin which find multitude of industrial applications. The triacetin has a range of applications from cosmetics to fuel additives [1,2]. The monoacetin and diacetin are commercially employed in cryogenics and as raw material for the production of biodegradable polyesters [3]. Traditionally, the acetylation of glycerol is carried out over mineral acids as homogeneous catalyst. In that case the effluent disposal leads to environmental hazards. These problems can be overcome by using heterogeneous catalysts. There are reports which describe the use of solid acid catalysts including zeolites, amberlyst and niobic acid for acetylation of glycerol [4]. Goncalves et al. reported the use of acid exchange resin, amberlyst-15 which showed 97% conversion of glycerol in 30 min at 110°C with maximum selectivity for monoacetin [5]. One more report describes the use of amberlyst and dowex ion exchange resins. In their case only monoacetin was obtained as a major product [6]. Another report studies amberlyst 15, HZSM-5 and HUSY as solid catalyst showed around 85% of combined selectivity for di- and triacetin [7]. In a report when solid catalysts like K-10 montmorillonite, HZSM-5 and HUSY were used for the reaction, hydroxyacetone was obtained as a byproduct. Melero et al. showed the use of sulfonic acid functionalized mesoporous silica providing up to 90% glycerol conversion and over 80% of combined selectivity for di- and triacetin in 4 hr at 125°C when AcOH to glycerol molar ratio of 9:1 was used [8]. In a recent report the use of dodecamolybdophosphoric acid encapsulated in USY zeolite was studied for acetylation of glycerol. In this case, the catalytic activity increased with the increase in the amount of heteropolyacid immobilized on USY zeolite [9]. Studies on the use of dodecatungstophosphoric acid immobilized in the silica matrix for acetylation reaction was also reported by Ferreira et al. [10]. In this case AcOH to glycerol molar ratio was 1:16 and the reaction temperature was 120°C. Maximum selectivity was observed for diacetin with 87% conversion of glycerol in 7 hr. A very high selectivity for triacetin of 87% was reported using acidic ion exchange resin and MgSO₄ at room temperature for 72 hr [11]. Yang and Lu used SO₄²⁻/ZrO₂-TiO₂, and obtained >85% yield for triacetin, referring the best activity of the catalyst at 450°C [12]. Another literature reported a very high yield of 93.6% was for triacetin at 130°C using sulfated zirconia as solid acid [13]. Liu et al. used *p*-toluenesulfonic acid/C and obtained triacetin yield of 92% [14], Li et al. used ionic liquids ([HSO₃⁻pmim] [PTSA]) and the optimum operating conditions were glycerol/AcOH

ratio of 1:8, catalyst amount of 10.5% of the total weight of reactants, 6 hr reaction time and reaction temperature was 120°C [15].

Owing to the past reports on acetylation of glycerol using solid acids, we thought to perform extended research to evaluate the applicability of the MoO₃/SiO₂ catalyst synthesized by sol-gel method in our group in order to achieve maximum selectivity for triacetin. MoO₃/SiO₂ with varying MoO₃ loading (1, 10 and 20 mol %) were synthesized by novel sol-gel technique without using any surfactant or template. Extensive characterization of SiO₂ and MoO₃/SiO₂ catalysts was performed and is reported earlier [16,17]. Briefly, a very high BET surface area of 896 m²/g with a pore volume of 0.936 cm³/g and a pore size distribution of 42 Å was obtained for SiO₂, clearly indicating the mesoporous nature of SiO₂. However, 20 mol% MoO₃/SiO₂ showed a surface area of 217 m²/g with a pore volume of 0.37 cm³/g, an average pore diameter of 67.9 Å, and total acidity of 0.94 mmol/g. The TEM analysis of 20MS revealed the uniform distribution of MoO₃ nanoparticles of 0.6-1.5 nm size on the SiO₂ support along with bulk crystalline orthorhombic α-MoO₃. The Raman spectroscopic studies demonstrated that along with the presence of silicomolybdc heteropolyanions, bands corresponding to α- and β-MoO₃ were observed on the MoO₃/SiO₂ catalyst surface [17].

Our earlier studies revealed that silicomolybdc heteropolyanions are formed *in situ* due to the higher reactivity of MoO₃ and SiO₂ nanoparticles formed (Scheme 1), during the sol-gel method in presence of moisture or water in the reaction mixture which are found to be catalytically active species for various reactions like nitration [16], acetalization [17] transesterification [18], esterification of ethanol and AcOH when sol-gel synthesized MoO₃/SiO₂ is used as solid acid catalyst [19]. There are also several patents that report about the appreciable selectivity for triacetin using solid acid catalysts. All the reports suggest the higher selectivity for triacetin under at higher temperature, high catalyst loading or longer reaction times.

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Experimental

Material

All the reagents viz., ammonium heptamolybdate (AHM), ethyl silicate (ETS-40) (Chemplast, Chennai, CAS registry no. 18945-71-7), *iso*-propyl alcohol (IPA), 50% aqueous hydrogen peroxide, 25% ammonia (NH₃) solution, were of AR grade (99.8%) and were obtained from S.D. Fine, Thomas Baker, LOBA and Merck chemicals, India. Acids, ethanol (absolute) and glycerol of AR grade (99.8%) were obtained from Thomas Baker, India. The chemicals were used without further purification.

Catalyst synthesis

The MoO₃/SiO₂ catalyst (20 mol %) was prepared by the sol-gel technique as previously reported [16]. In brief, the catalyst was synthesized by dissolving AHM (14.11 g) in water (40 mL) at 80°C. This hot solution was added dropwise to the dry IPA solution of ETS-40 (48 g) with continuous stirring. The resultant transparent greenish gel was dried at RT and calcined at 500°C in air in a muffle furnace for 5 hr. For comparison, high-surface area SiO₂ was also prepared by adding ETS-40 (52 g) to dry IPA (30 g); to this mixture NH₃ solution (25%, 0.02 g) was added slowly with continuous stirring. The transparent white gel thus obtained was air dried and calcined in a muffle furnace at 500°C for 5 hr. Similarly catalysts with 1 and 10 mol% molybdenum oxide loadings were prepared.

High surface area SiO₂ catalyst was prepared for comparison by adding 52 g ETS-40 to 30 g dry IPA; to this mixture 0.02 g ammonia solution (25%) was slowly added with constant stirring. The transparent white gel thus obtained was air dried and calcined in a muffle furnace at 500°C for 5 hr.

Catalyst characterization

The 20 mol% MoO₃/SiO₂ and SiO₂ were extensively characterized using powder XRD, BET surface area, NH₃-TPD, FTIR, FTIR of adsorbed pyridine, Raman, and TEM analysis has been discussed in our earlier reports [16,19]. The identification of *in situ* formed catalytically active species was performed by isolation and characterization of the different fractions of the MoO₃/SiO₂ catalyst in detail using XRD, BET surface area, NH₃-TPD, FTIR, FTIR of adsorbed pyridine, Raman, EDAX and TEM analysis and has been discussed in our earlier report.

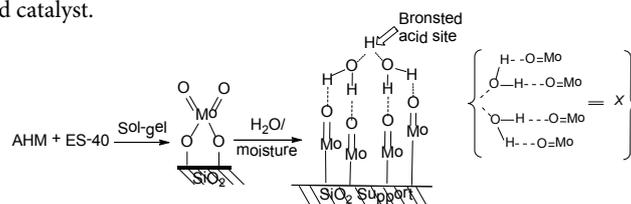
Esterification of glycerol

The esterification of glycerol with various acids was carried out in a 50 mL round bottom flask fitted with a reflux condenser. In a typical esterification experiment the reactor was charged with glycerol (1 mmol), acid (3 mmol) and catalyst (MoO₃/SiO₂, 10 wt% w.r.t. glycerol). The reaction was carried out at 100°C for 8 hr. All the reactions were monitored by GC. Prior to use the GC method was calibrated using external standard method. Samples were withdrawn at regular time intervals and analyzed using GC - Perkin-Elmer AutoSystem XL equipped with FFAP column (50 m length, 0.25 mm internal diameter and 1 μm film thickness) and with flame ionization detector.

Results and Discussion

MoO₃/SiO₂ with varying MoO₃ loading (1, 10 and 20 mol %) were synthesized by novel sol-gel technique without using any surfactant or template. Extensive characterization of SiO₂ and MoO₃/SiO₂ catalysts was performed and is reported earlier [16,17]. Briefly, a very high BET 75 surface area of 896 m²/g with a pore volume of 0.936 cm³/g and a pore size distribution of 42 Å was obtained for SiO₂, clearly

indicating the mesoporous nature of SiO₂. However, 20 mol% MoO₃/SiO₂ showed a surface area of 217 m²/g with a pore volume of 0.37 cm³/g, an average pore diameter of 67.9 Å, and 80 total acidity of 0.94 mmol/g. The TEM analysis of 20MS revealed the uniform distribution of MoO₃ nanoparticles of 0.6-1.5 nm size on the SiO₂ support along with bulk crystalline orthorhombic α-MoO₃. The Raman spectroscopic studies demonstrated that along with the presence of silicomolybdc heteropolyanions, bands corresponding to α- and β-MoO₃ were observed on the MoO₃/SiO₂ catalyst surface [17]. Our earlier studies revealed that silicomolybdc heteropolyanions are formed *in situ* due to the higher reactivity of MoO₃ and SiO₂ nanoparticles formed (Scheme 1), during the sol-gel method in presence of moisture or water in the reaction mixture which are found to be catalytically active species for various reactions when sol-gel synthesized MoO₃/SiO₂ is used as solid acid catalyst.



Scheme 1: *In situ* formation of SiO₂ supported silicomolybdc heteropolyanion in presence of moisture or water.

In continuation to these studies, the study of the esterification of glycerol was carried out using various acids. The esterification of glycerol occurs through consecutive reaction steps initially from monoglyceryl ester to di and ultimately to triglyceryl ester (Scheme 2). Sol-gel synthesized 20 mol% MoO₃/SiO₂ was used as catalyst for the esterification of glycerol, owing to its high Bronsted acidity and high catalytic activity as observed in our earlier studies. The results are shown in Table 1.



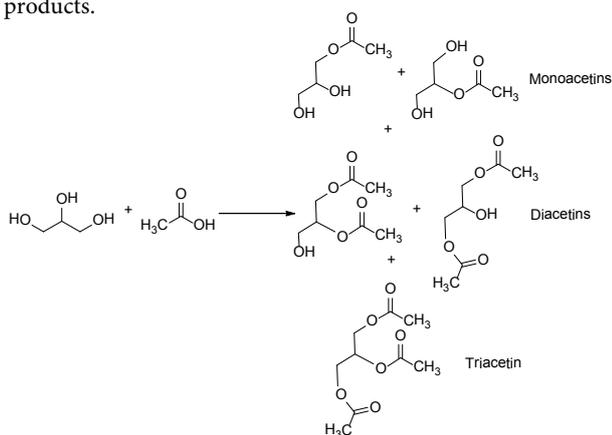
Scheme 2: Esterification of glycerol with acid.

The conversion of glycerol and selectivity for the products were calculated as shown in equations 1 and 2, respectively. When the esterification of glycerol was carried out with AcOH it showed maximum conversion of 68% with high selectivity of 81.3% for monoacetin. Moreover, the formation of di- and tri-ester was observed with a very low selectivity of 16.5% and 2.2% respectively. In case of other acids, the

Entry	Acid	Glycerol Conv., %	Acetin selectivity, %		
			Mono-	Di-	Tri-
1		68	81.3	16.5	2.2
2		41	100	00	00
3		39	100	00	00
4		35	100	00	00
5		30	100	00	00

Table 1: Esterification of glycerol with various acids using 20 mol% MoO₃/SiO₂ as catalyst. *Reaction conditions: Acid:glycerol-3:1 (molar ratio), Temperature-100°C, Time-8 hr, Catalyst-10% w.r.t. wt. of glycerol.

conversion decreased in the trend- AcOH>propionic acid>pentanoic acid>hexanoic acid>heptanoic acid with 100% selectivity for monoester in all cases. The reason for this can be explained considering two factors - inductive effect and steric effect [20]. The inductive effect is a result of electron releasing capacity of an acid with the increasing alkyl chain. Inductive effect facilitates the protonation of carbonyl oxygen but at the same time reduces the electrophilic character of the carbonyl carbon which in turn results in energy-hindered rate-limiting nucleophilic attack by the alcohol. The steric hindrance increases with increasing molecular size, which induces electronic repulsion between non-bonded atoms of the reactants. As the alkyl chain length in the carboxylic acid increases, its steric effect also increases which constrains the activity of the carboxylic acid. These factors thereby reduce the electropositivity of the carbonyl carbon decreasing the activity of the substrate. In all the cases 100% selectivity for monoester was obtained, except for AcOH. Esterification of glycerol with AcOH was carried out (Scheme 3) with an objective to achieve maximum selectivity for triacetin, which is the most interesting products from a fuel- application point of view, since it can be formulated with petrol-derived fuels to improve either cold and viscosity properties (biodiesel) [21] or anti knocking properties (gasoline) [22]. The effect of various reaction parameters such as molar ratio of AcOH to glycerol, catalyst loading and temperature were thoroughly studied to optimize the reaction conditions. It was observed that the reaction parameters had a strong effect on the conversion of glycerol and selectivity pattern of the products.



Scheme 3: Acetylation of glycerol.

Initially, the effect of molar ratio of AcOH to glycerol was studied on glycerol conversion and selectivity of products. The results are shown in Table 2.

It was observed that even at low AcOH: glycerol molar ratio of 3:1 and 5:1, appreciable glycerol conversion of 67% and 91% was obtained in 8 hr, respectively. However, 100% glycerol conversion was achieved at higher AcOH: glycerol molar ratio of 10:1. It was interesting to note that the selectivity distribution of acetins for different AcOH: glycerol molar ratio was altogether different. At AcOH: glycerol molar ratio of 3:1, a very high selectivity of 81% was achieved for monoacetin whereas only 16% and 3% selectivity was obtained for diacetin and triacetin, respectively. As expected the selectivity of diacetin and triacetin increased to 30% and 19% respectively with decrease in the selectivity for monoacetin (51%) when AcOH: glycerol molar ratio of 5:1 was used. In order to achieve maximum selectivity for triacetin, the AcOH: glycerol molar ratio was increased to 10:1. In this case a very high triacetin selectivity of 50% was obtained compared to lower AcOH: glycerol molar ratio. Therefore all the further studies were

carried out using AcOH: glycerol molar ratio of 10:1. All the above discussed reactions were carried out using 10 wt% (w.r.t. glycerol) catalysts loading. When the reaction was carried out using 5 wt% of catalyst amount (w.r.t. glycerol) only 78% conversion of glycerol was obtained with 73% selectivity for monoacetin in 8 hr. This showed that catalyst loading along with AcOH: glycerol ratio played an important role to attain maximum glycerol conversion and high selectivity for triacetin. To carry out the further parametric studies, 10 wt% catalyst amounts (w.r.t. glycerol) was used for the acetylation reaction. The effect of MoO₃ loading on SiO₂ support was studied on the acetylation and the results are shown in Table 3. The reactions were performed for 8 hr. The acetylation of glycerol was also carried out without catalyst for comparison.

The esterification occurred in absence of the catalyst, although the glycerol conversion remained much lower compared to the case when MoO₃/SiO₂ was used as catalyst. In absence of catalyst, the esterification led only to higher selectivity for monoacetin (92%) and 8% of diacetin with 36% glycerol conversion. Formation of triacetin was not observed. The esterification was carried out using pure SiO₂ as catalyst and it was found that the glycerol conversion was only 44% with 86% monoacetin and 11% diacetin. Traces of triacetin were observed in this case. Further the reaction was carried out using series of MoO₃/SiO₂ catalysts triacetin was not observed. The esterification was carried out using pure SiO₂ as catalyst and it was found that the glycerol conversion was only 44% with 86% monoacetin and 11% diacetin. Traces of triacetin were observed in this case. Further the reaction was carried out using series of MoO₃/SiO₂ catalysts with different MoO₃ loadings on SiO₂ and it was observed that 100% glycerol conversion was obtained with 1 mol% and 10 mol% MoO₃ loading but there was a notable difference in the selectivity pattern of mono-, di- and triacetin. Only 17% triacetin was obtained when 1 mol% MoO₃/SiO₂ was used as catalyst. However, selectivity for triacetin increased to 33% with gradual decrease in selectivity for monoacetin (36%) and an almost equal amount of diacetin (31%) was obtained when 10 mol% MoO₃/SiO₂ was used as catalyst. A maximum selectivity of 50% was obtained for triacetin when 20 mol% MoO₃/SiO₂ was used as catalyst. The main function of the catalyst in this reaction should be to direct the selectivity to the desired product i.e., triacetin. In this case increase in MoO₃ loading on SiO₂ increased the rate of spontaneous reaction of converting mono- to di- and ultimately to triacetin. We can assume that the traditional Fisher esterification mechanism is operating in case of blank reaction (without catalyst) and the reaction with SiO₂ as

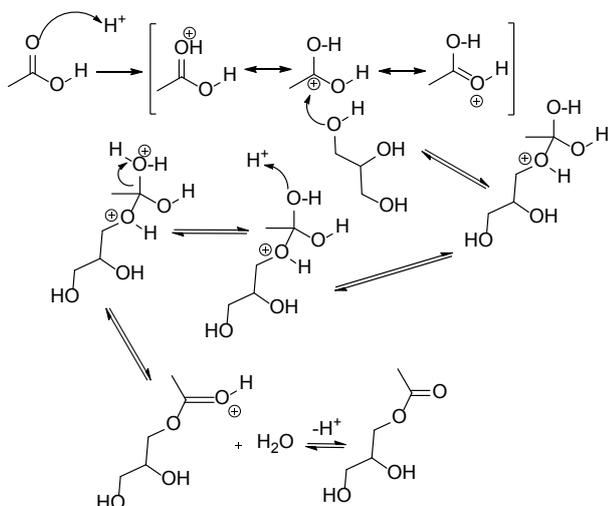
Entry	Molar ratio (AcOH:Gly)	Glycerol Conv., %	Acetin Selectivity, %		
			Mono-	Di-	Tri-
1	3:1	67	81	16	3
2	5:1	91	51	30	19
3	10:1	100	17	33	50

Table 2: Effect of mole ratio of AcOH to glycerol on acetylation of glycerol over 20 mol% MoO₃/SiO₂. *Reaction conditions: Catalyst-10 wt% (w.r.t. glycerol), Temperature-100°C, Time- 8 hr.

Entry	Catalyst	Glycerol Conv., %	Acetin Selectivity, %		
			Mono-	Di-	Tri-
1	--	36	92	08	00
2	SiO ₂	44	86	11	3
3	1 mol% MoO ₃ /SiO ₂	100	56	28	17
4	10 mol% MoO ₃ /SiO ₂	100	36	31	33
5	20 mol% MoO ₃ /SiO ₂	100	17	33	50

Table 3: Acetylation of glycerol with acetic acid using different loadings of MoO₃ on SiO₂. *Reaction conditions: Acetic acid:glycerol-10:1 (molar ratio), Catalyst-10 wt% (w.r.t. glycerol), Temperature-100°C, Time-8 hr.

catalyst (Scheme 4).



Scheme 4: Fisher esterification mechanism of glycerol with acetic acid to monoacetin.

Owing to the appreciable reactivity of $\text{MoO}_3/\text{SiO}_2$ for acetylation of glycerol, acidity seemed to have a dominant influence on the catalytic behavior in this reaction. The NH_3 -TPD showed the global increase in acid strength with increase in MoO_3 loading on SiO_2 from 1 mol% to 20 mol%. Moreover, from the pyridine adsorption studies it was seen that, Lewis acidity increased with incorporation of MoO_3 on SiO_2 and at higher MoO_3 loadings (10, 15, 20 mol%) the formation of Bronsted acid sites was observed which increased in the order $10 < 15 < 20$ mol% MoO_3 indicating the co-existence of both Lewis and Bronsted acid sites in the catalyst [18]. Melero et al. showed a direct correlation between the selectivity of di- and triacetin and the strength of the acid sites of the sulfonic acid functionalized mesostructured materials: the strongest Bronsted acid sites caused the highest selectivity for di- and triacetin [8]. In our case, highest selectivity for triacetin was obtained when 20 mol% $\text{MoO}_3/\text{SiO}_2$ was used as a catalyst. This catalyst showed highest acid strength (0.9 mmol/g) (NH_3 -TPD experiments) with a very high population of Bronsted acid sites (observed from the pyridine adsorption studies) directly correlated to the *in situ* formation of silicomolybdc heteropolyanions. The results are in good agreement with the earlier reported literature. This shows that acid strength and nature of acid sites are an important factor for the product distribution in the acetylation of glycerol. The 20 mol% $\text{MoO}_3/\text{SiO}_2$ showed best results for acetylation of glycerol in comparison to that of the other $\text{MoO}_3/\text{SiO}_2$ catalysts in the series. This catalyst was further used to study the effect of temperature and time-on-stream parameter for the reaction. The reaction of glycerol and AcOH was carried out at increased temperature of 118°C with all other reaction conditions constant and the progress of the reaction was monitored at different time intervals till 20 hr and the results are presented in Figure 1.

It was observed that in 15 min, 26% glycerol conversion was obtained with 100% selectivity for monoacetin. With time glycerol conversion increased to 47.4% after 45 min with 15% selectivity for diacetin without any formation of triacetin. Within 2 hr, 100% glycerol conversion was achieved. The selectivity for monoacetin decreased with time with corresponding increase in di- and triacetin selectivity because di- and triacetin products were formed through consecutive esterification reactions. Though 100% conversion was achieved in 2 hr, the reaction was continued further up to 20 hr to attain maximum selectivity for triacetin. After 20 hr of the reaction a very high selectivity

of 76% was obtained for triacetin. When these results were compared with that of the reaction carried out at 100°C (Figure 2), keeping the rest of the parameters constant, it was observed that 83% glycerol conversion was obtained in 2 hr with 67% monoacetin and 26% and 7% of di- and triacetin, respectively. Maximum glycerol conversion of 97% was achieved after 8 hr and there was no appreciable selectivity for triacetin.

A literature report describes the use of microwave or ultra sound conditions and achieved $>90\%$ glycerol conversion and $\sim 85\%$ selectivity for di- and triacetin collectively. Hydroxylated magnesium fluorides were used as catalysts in this case and the reaction was carried out at 100°C [23]. Reddy et al. reported the $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ as promising catalyst for acetylation of glycerol when the reaction was carried out at 120°C , 6:1 AcOH to glycerol molar ratio and 5 wt% catalysts [24]. However, in this $>85\%$ selectivity for triacetin was achieved in 40 hr reaction time. Heteropolyacids supported on activated carbon were reported for the acetylation of glycerol [25]. Phosphotungstic acid (4.9 wt%) on activated carbon showed highest catalytic activity of 85% glycerol conversion in 3 hr, although the reaction was carried out at 120°C with glycerol: AcOH molar ratio of 1:16. Diacetin was obtained with maximum selectivity in this case. A recent article reported the use of heteropolyacid-based ionic liquids as homogeneous catalysts for the acetylation of glycerol to attain 86-99% selectivity for triacetin [26]. We have so far not come across any report with high triacetin selectivity using solid acid catalyst under mild conditions. In many literature reports, 100% conversion of glycerol was achieved in longer

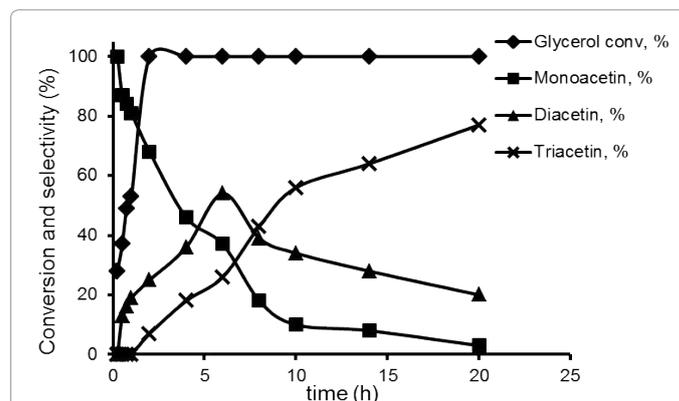


Figure 1: Acetylation of glycerol using 20 mol% $\text{MoO}_3/\text{SiO}_2$ as catalyst. Reaction conditions: Glycerol-0.0108 mol, Glycerol:acetic acid-1:10 (molar ratio), Catalyst-0.1 g, Temperature- 118°C .

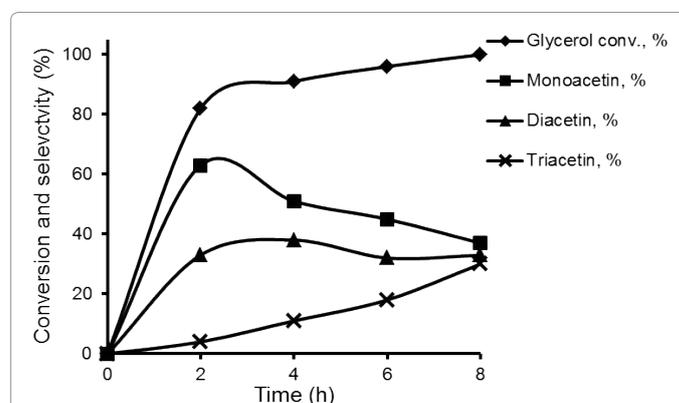


Figure 2: Acetylation of glycerol using 20 mol% $\text{MoO}_3/\text{SiO}_2$ as catalyst. Reaction conditions: Glycerol-0.0108 mol, Glycerol:acetic acid-1:10 (molar ratio), Catalyst-0.1 g, Temperature- 100°C .

reaction time and in majority cases higher selectivity for diacetin was obtained. In present case, 100% glycerol conversion was obtained in 2 hr and triacetin was obtained with >75% selectivity at milder reaction conditions than discussed above.

Conclusion

In situ formed supported silicomolybdic heteropolyanions have played efficient role as catalysts in the acetylation of glycerol order to attain 100% glycerol conversion with maximum selectivity for triacetin. This may be considered as another promising application of the supported silicomolybdic heteropolyanions from sol-gel synthesised $\text{MoO}_3/\text{SiO}_2$ as heterogeneous catalyst for the value-addition of glycerol. The pressing need for developing a sustainable process using the heterogeneous catalyst system in the present study; metrics like catalyst recyclability and longevity under the reaction conditions are being considered and performing the reaction in continuous mode are ongoing projects.

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