Silicomolybdic Heteropolyanions Supported in Situ: An Effective Solid Catalyst for Acetylation of Glycerol

*Dr. Deepa Saxena

Abstract

A potential reaction for the creation of high-value compounds and fuels is the acetylation of glycerol. It is crucial to provide a catalyst for this process that is effective and long-lasting. This study looks at the usage of in-situ supported silicomolybdic heteropolyanions (SiMoHPAs) as a solid catalyst for glycerol acetylation. Investigating SiMoHPAs' catalytic activity, stability, and selectivity in glycerol acetylation processes is the goal.

Keywords: Silicomolybdic, solid catalyst, in situ acetylation, glycerol

Introduction

Increased interest in using biomass-derived feedstocks for the manufacture of important chemicals and fuels is a result of the worldwide desire for sustainable and renewable resources. A significant byproduct of the manufacturing of biodiesel, glycerol is a cheap, readily available molecule generated from biomass that has a lot of potential for adding value via different chemical processes. Glycerol acetylation in particular offers a desirable route for the production of glycerol esters, which have uses in the pharmaceutical, cosmetic, and lubricant sectors.

A well-known chemical process called acetylation involves adding an acetyl group (-COCH3) to a molecule. When referring to glycerol acetylation, this procedure involves esterifying one or more of the hydroxyl groups of glycerol with acetic anhydride or acetyl chloride to produce glycerol monoacetate (GMA), diacetate (GDA), or triacetate (GTA), respectively. Due to its potential use as an intermediary in the production of speciality compounds including medicines, fragrances, and food additives, GMA is highly important.

For the glycerol acetylation process to be economically viable and sustainable, an effective and eco-friendly catalyst must be created. Mineral acids (such as sulfuric acid) and strong Lewis acids (such as tin- or titanium-based catalysts) are the conventional catalysts employed in acetylation processes. The downsides of these catalysts are their corrosiveness, high energy consumption, and low selectivity.

Heteropolyacid-based catalysts have attracted a lot of interest lately for a variety of catalytic uses, including glycerol acetylation. A family of polyoxometalate compounds known as heteropolyacids has distinctive structural features and high acidity, which makes them desirable candidates for catalytic processes. Due to their high acidity and redox characteristics, silicomolybdic heteropolyanions (SiMoHPAs) in particular have shown remarkable catalytic activity in a number of chemical reactions.

This study looks at the usage of SiMoHPAs supported in situ as a potent solid catalyst for acetylating glycerol. SiMoHPAs are stabilised more effectively and may be separated and recycled more easily when they are supported in place on a solid substance. The SiMoHPA catalyst's catalytic activity, stability, and selectivity will be assessed under a variety of reaction circumstances, including temperature, reaction duration, catalyst loading, and the molar ratio of acetic anhydride to glycerol.

The research results from this study will help build efficient and sustainable catalytic methods for using glycerol obtained from biomass and producing compounds with added value. In comparison to traditional catalysts, the use of SiMoHPAs as solid catalysts for glycerol acetylation has the potential to result in higher selectivity, less environmental impact, and improved process economics. Additionally, the knowledge acquired from this study will help us understand heteropolyacid catalysis better and will serve as a foundation for designing and improving catalyst systems for additional biomass conversion activities.

Experimental

Material

Ammonium heptamolybdate (AHM), ethyl silicate (ETS-40), iso-propyl alcohol (IPA), 50% aqueous hydrogen peroxide, and 25% ammonia (NH_3) solution were all of AR grade (99.8%) and were purchased from S.D. Fine, Thomas Baker, LOBA, and Merck chemicals, India.

Thomas Baker, India provided the acids, ethanol (absolute), and glycerol of AR grade (99.8%). The compounds weren't further purified before usage.

Catalyst synthesis

According to a prior publication [16], the solgel approach was used to create the MoO_3/SiO_2 catalyst (20 mol%). In a nutshell, the catalyst was created by combining AHM (14.11 g) and water (40 mL) at 80°C. With constant stirring, this hot solution was added dropwise to the dry IPA solution of ETS-40 (48 g). The resulting translucent, greenish-blue gel underwent RT drying and a five-hour calcination process at 500°C in air in a muffle furnace. For comparison, high-surface area SiO_2 was also created by combining dry IPA (30 g) with ETS40 (52 g), and then progressively incorporating NH_3 solution (25%, 0.02 g) while continuously stirring. The resulting translucent white gel was air dried before being calcined at 500°C for five hours in a muffle furnace. The same way, catalysts loaded with 1 and 10 mol% molybdenum oxide were created.

To make a high surface area SiO_2 catalyst for comparison, combine 30 g of dry IPA with 52 g of ETS-40. Slowly add 0.02 g of ammonia solution (25%) to this mixture while stirring continuously. The resulting translucent white gel was air dried before being calcined at 500°C for five hours in a muffle furnace.

Characterization of the catalyst

In our prior studies [16,19], we detailed the thorough characterization of the 20 mol% MoO_3/SiO_2 and SiO_2 utilising powder XRD, BET surface area, NH_3-TPD, FTIR, FTIR of adsorbed pyridine, Raman, and TEM examination. In our earlier report, we discussed how to isolate and characterise the various

MoO_3/SiO_2 catalyst fractions in detail using XRD, BET surface area, NH3-TPD, FTIR, FTIR of adsorbed pyridine, Raman, EDAX, and TEM analysis to identify in situ formed catalytically active species.

Glycerol esterification

In a 50 mL round bottom flask equipped with a reflux condenser, glycerol was esterified with different acids. A typical esterification experiment included adding glycerol (1 mmol), acid (3 mmol), and catalyst (10 wt% relative to glycerol) to the reactor.

For eight hours, the reaction was conducted at 100°C. The GC continuously monitored each response. The GC technique was calibrated using an external reference procedure before usage. GC - Perkin-Elmer AutoSystem XL fitted with FFAP column (50 m length, 0.25 mm internal diameter, and 1 m film thickness) and flame ionisation detector was used to analyse samples that were taken out at regular intervals.

Results and Discussion

A one-of-a-kind sol-gel process was utilized to make MoO_3/SiO_2 with fluctuated MoO_3 stacking (1, 10 and 20 mol%) without the need of a surfactant or format. SiO_2 and MoO_3/SiO_2 impetuses have gone through broad portrayal, which has been recently depicted [16,17]. Basically, SiO_2 was found to have an incredibly high Wagered 75 surface area of 896 m2/g, a pore volume of 0.936 cm3/g, and a pore size circulation of 42, in this manner showing its mesoporous nature. Be that as it may, 20 mol% MoO_3/SiO_2 had a surface area of 217 m2/g, 0.37 cm3/g of pore volume, 67.9 of normal pore breadth, and 0.94 mmol/g of complete corrosiveness. The TEM examination of 20MS showed that mass translucent orthorhombic - MoO_3 and MoO_3 nanoparticles with sizes going from 0.6 to 1.5 nm were both conveyed consistently on the SiO_2 substrate. Raman spectroscopy examinations showed that groups relating to - and - MoO_3 were seen on the MoO_3/SiO_2 impetus surface notwithstanding the presence of silicomolybdic heteropolyanions [17]. Our previous exploration showed that the development of silicomolybdic heteropolyanions happens in situ because of the greater reactivity of MoO_3 and SiO_2 nanoparticles made (Plan 1) during the sol-gel technique within the sight of dampness or water in the response blend. These nanoparticles are viewed as chemically dynamic species for different responses when sol-gel orchestrated MoO_3/SiO_2 is utilized as a strong corrosive impetus.
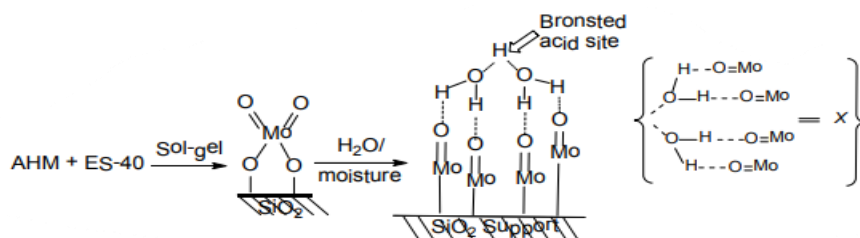
Figure 1 shows the in-situ production of a silicomolybdic heteropolyanion supported by SiO_2 in the presence of moisture or water.

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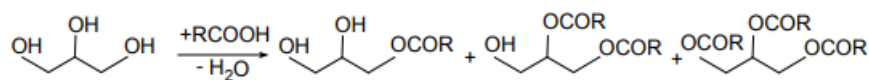
Figure 2: Esterification of glycerol with acid.

Equations 1 and 2 illustrate the results of calculations to determine the products' selectivity and glycerol conversion, respectively. Glycerol esterification with AcOH demonstrated a maximum conversion of 68% and a high monoacetin selectivity of 81.3%.

Moreover, a very low selectivity of 16.5% and 2.2%, respectively, for the production of di- and tri-esters was noted. With 100% monoester selectivity in every instance, the conversion dropped for the remaining acids in the following order: AcOH > Propionic Acid > Pentanoic Acid > Hexanoic Acid > Heptanoic Acid. Two components, the inductive effect and the steric effect, may be used to explain this.

| 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 shows the esterification of glycerol with various acids using a 20 mol% MoO3/SiO2 catalyst.

The ability of an acid to release electrons as the alkyl chain lengthens causes the inductive effect. The inductive effect makes it easier for carbonyl oxygen to protonate, but it also makes the carbonyl carbon less electrophilic, which leads to an alcohol nucleophilic assault that is energy-hampered and rate-limiting. The steric barrier rises with molecule size and causes electronic repulsion between the reactants' non-bonded atoms. The carboxylic acid's steric effect grows as the alkyl chain length increases, which limits the carboxylic acid's ability to operate. These elements therefore lower the carbonyl carbon's electropositivity, which lowers the substrate's activity. With the exception of AcOH, 100% selectivity for monoester was achieved in each example. The goal of the esterification of glycerol with AcOH was to maximise selectivity for triacetin, which is the most intriguing product

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from the standpoint of fuel applications because it can be combined with fuels derived from petroleum to improve either cold and viscosity properties (biodiesel) or anti knocking properties (gasoline). To optimise the reaction conditions, the impact of several reaction parameters including temperature, catalyst loading, and the molar ratio of AcOH to glycerol were carefully investigated. It was shown that the reaction conditions significantly influenced both the products' selectivity patterns and the conversion of glycerol.
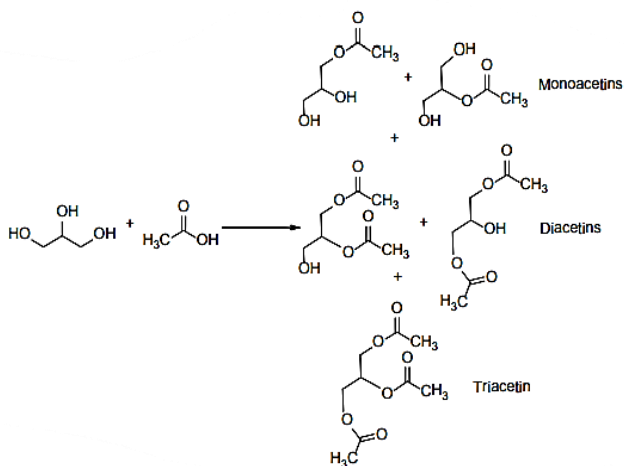
Figure 3: Acetylation of glycerol.

The impact of the molar ratio of AcOH to glycerol on glycerol conversion and product selectivity was first investigated. Table 2 presents the outcomes.

It was shown that significant glycerol conversion of 67% and 91%, respectively, was produced in 8 hours even at low AcOH: glycerol molar ratios of 3:1 and 5:1. However, with a greater AcOH:glycerol molar ratio of 10:1, 100% glycerol conversion was attained. It was intriguing to see how diverse the selectivity distribution of acetins was for various AcOH: glycerol molar ratios. A very high selectivity of 81% was obtained for monoacetin at a 3:1 molar ratio of AcOH to glycerol, but only 16% and 3% selectivity were obtained for diacetin and triacetin, respectively. As anticipated, using an AcOH:glycerol molar ratio of 5:1 resulted in an increase in the selectivity of diacetin and triacetin to 30% and 19%, respectively, and a drop in the selectivity for monoacetin (51%). The AcOH:glycerol molar ratio was raised to 10:1 in order to maximise selectivity for triacetin. In this instance, a decreased AcOH: glycerol molar ratio resulted in a very high triacetin selectivity of 50%. Therefore, a 10:1 molar ratio of AcOH to glycerol was used for all subsequent investigations. All of the aforementioned reactions were conducted with catalyst loadings of 10 wt% (relative to glycerol). Only 78% of the glycerol was converted when the reaction was run with 5 wt% of the catalyst

quantity (relative to the glycerol) in 8 hours with 73% monoacetin selectivity. This demonstrated that catalyst loading and the AcOH:glycerol ratio were crucial in achieving maximal glycerol conversion and good triacetin selectivity. The acetylation process was conducted using 10 wt% catalyst concentrations (relative to glycerol) in order to conduct the further parametric tests. The findings of the investigation into the acetylation impact of MoO3 loading on SiO2 support are shown in Table 3. The reactions were run for eight hours. For comparison, glycerol was also acetylated without the use of a catalyst.

Despite the lack of the catalyst, the esterification still took place, but at a considerably lower rate than when MoO3/SiO2 was used as the catalyst. Without a catalyst, esterification produced only increased monoacetin selectivity (92%), 8% diacetin, and 36% glycerol conversion. Triacetin formation was not seen. Pure SiO2 was used as the catalyst in the esterification, and it was discovered that only 44% of the glycerol was converted, while 86% of the monoacetin and 11% of the diacetin were produced. In this instance, triacetin traces were found. Triacetin was not seen when a succession of MoO3/SiO2 catalysts were used to carry out the reaction. Pure SiO2 was used as the catalyst in the esterification, and it was discovered that only 44% of the glycerol was converted, while 86% of the monoacetin and 11% of the diacetin were produced. In this instance, triacetin traces were found. Further, a series of MoO3/SiO2 catalysts with various MoO3 loadings on SiO2 were used to carry out the reaction. It was discovered that 100% glycerol conversion was achieved with 1 mol% and 10 mol% MoO3 loading, but there was a noticeable difference in the selectivity pattern of mono-, di-, and triacetin. With a catalyst concentration of 1 mol% MoO3/SiO2, only 17% triacetin was produced. However, when 10 mol% MoO3/SiO2 was utilised as a catalyst, selectivity for triacetin improved to 33% with a progressive decline in selectivity for monoacetin (36%) and a nearly equivalent quantity of diacetin (31%) was produced. Triacetin was selected with a maximum selectivity of 50% using a catalyst of 20 mol% MoO3/SiO2.

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: Acetylation of glycerol over 20 mol% MoO3/SiO2 is affected by the mole ratio of AcOH to glycerol.**

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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.

The catalyst's primary job in this reaction should be to focus selectivity on the intended end product, triacetin. In this instance, an increase in MoO3 loading on SiO2 accelerated the pace at which monoacetin spontaneously changed into diacetin and then triacetin. In the case of blank reactions (reactions without a catalyst) and reactions using SiO2 as a catalyst, we may infer that the conventional Fisher esterification mechanism is in operation.
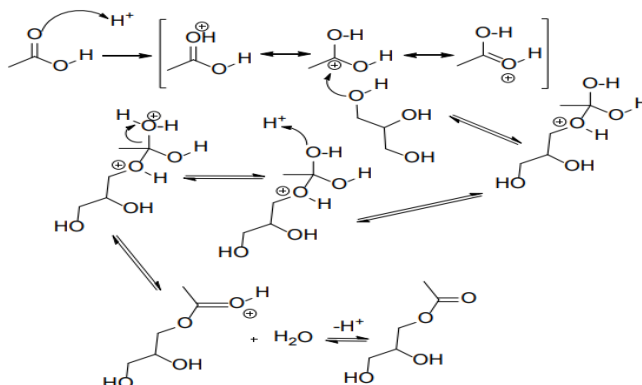
Figure 4: Fisher esterification mechanism of glycerol with acetic acid to monoacetin

Since MoO3/SiO2 for acetylation of glycerol displays eminent reactivity, sharpness appeared to excessively affect the synergist conduct in this cycle. With an expansion in MoO3 stacking on SiO2 from 1 mol% to 20 mol%, the NH3-TPD exhibited an overall ascent in corrosive strength.18 Moreover, it was found from pyridine adsorption concentrates on that Lewis sharpness expanded with joining of MoO3 on SiO2, and at higher MoO3 loadings (10, 15, and 20 mol%), the development of Bronsted corrosive locales was noted, which expanded in the request 101520 mol% MoO3,

showing the concurrence of both Lewis and Bronsted corrosive destinations in the impetus [18]. Melero et al. shown an unmistakable connection between the strength of the corrosive locales in the sulfonic corrosive functionalized mesostructured materials and the selectivity of di-and triacetin: the most grounded corrosive destinations delivered the best selectivity for di-and triacetin [8]. In our circumstance, utilizing 20 mol% MoO3/SiO2 as an impetus brought about the best selectivity for triacetin. With an exceptionally huge populace of Bronsted corrosive destinations (seen from the pyridine adsorption tests), this impetus exhibited the best corrosive strength (0.9 mmol/g) (NH3 - TPD preliminaries), which was straightforwardly related to the in situ blend of silicomolybdic heteropolyanions. The discoveries are a lot of in accordance with recently distributed material. This shows that the sort of corrosive destinations and their solidarity play a critical part in the item conveyance during the acetylation of glycerol. Contrasted with the other MoO3/SiO2 impetuses in the series, the 20 mol% MoO3/SiO2 impetus showed the best outcomes for the acetylation of glycerol. The effect of temperature and the time-on-stream boundary for the response were likewise concentrated on utilizing this impetus. Glycerol and AcOH were consolidated in a response at 118°C, with any remaining circumstances held steady. The response's advancement was seen throughout 20 hours at different time spans, and the discoveries are displayed in Figure 5.

It was noticed that 26% glycerol change with 100 percent monoacetin selectivity was accomplished quickly. Glycerol transformation expanded with time, arriving at 47.4% following 45 minutes with 15% selectivity for diacetin and no triacetin creation. 100 percent glycerol change was accomplished in under two hours. Because of the consecutive esterification occasions that created di-and triacetin items, the selectivity for monoacetin decreased with time while expanding for di-and triacetin. Despite the fact that a 100 percent change rate was arrived at in just 2 hours, the response was run for 20 extra hours to boost triacetin selectivity. An extremely high selectivity of 76% for triacetin was seen following 20 hours of the response. The discoveries showed that 83% of the glycerol was changed over in 2 hours with 67% monoacetin and 26% and 7% of di-and triacetin, separately, when contrasted with the response that was done at 100°C (Figure 6) while keeping up with different boundaries steady. Following 8 hours, the greatest glycerol change of 97% was reached, and there was no way to see an inclination for triacetin.

As per a writing survey, utilizing microwave or ultrasonic settings considered >90% glycerol transformation and 85% generally speaking selectivity for di-and triacetin. In this case, the response was directed at 100°C with the help of hydroxylated magnesium fluorides as impetuses. At the point when the response was led at 120°C, a 6:1 AcOH to glycerol molar proportion, and 5 wt% impetuses, Reddy et al. detailed the SO42 -/CeO2 - ZrO2 as a promising impetus.

Nonetheless, for this situation, >85% triacetin selectivity was achieved in 40 hours of response time. For the acetylation of glycerol, heteropolyacids upheld on enacted carbon have been depicted. Despite the fact that the response was directed at 120°C with a molar proportion of 1:16 glycerol to AcOH, phosphotungstic corrosive (4.9 wt%) on enacted carbon had the most extreme synergist movement of 85% glycerol transformation in 3 hours. In this case, the most specific method for getting diacetin

was utilized. As indicated by a new report, homogeneous impetuses for the acetylation of glycerol were utilized to accomplish 86-close to 100% selectivity for triacetin. We have not yet seen a report utilizing a strong corrosive impetus and moderate circumstances with magnificent triacetin selectivity. In a few writing discoveries, glycerol transformation at 100 percent took longer selectivity for diacetin and, in many occurrences, response time were achieved. In this example, triacetin was created with >75% selectivity under gentler response conditions than those recently detailed, and 100 percent glycerol change was accomplished in 2 hours.
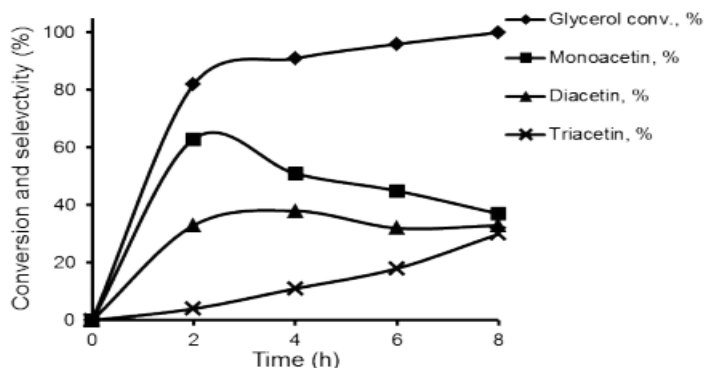
Figure 5: Acetylation of glycerol using 20 mol% MoO3 /SiO2 as catalyst. Reaction conditions: Glycerol-0.0108 mol, Glycerol:acetic acid-1:10 (molar ratio), Catalyst-0.1 g, Temperature- 118°C
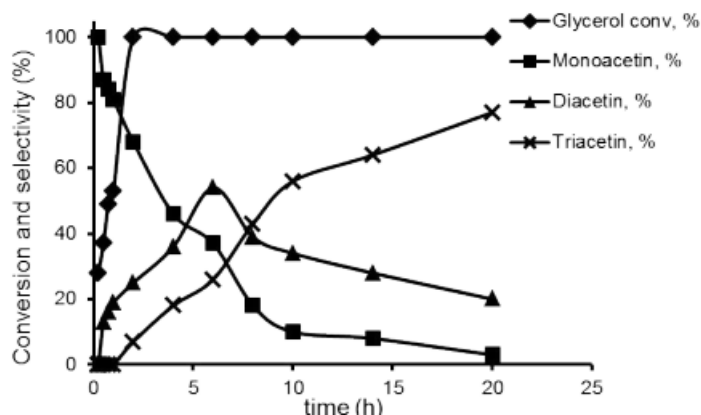
Figure 2: Acetylation of glycerol using 20 mol% MoO3 /SiO2 as catalyst. Reaction conditions: Glycerol-0.0108 mol, Glycerol:acetic acid-1:10 (molar ratio), Catalyst-0.1 g, Temperature- 100°C.

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Conclusion

To achieve 100% glycerol conversion with the highest triacetin selectivity, in situ generated supported silicomolybdic heteropolyanions have been an effective catalyst in the acetylation of glycerol.

This might be seen as yet another prospective use of the supported MoO3/SiO2 heteropolyanions synthesised by sol-gel synthesis as a heterogeneous catalyst for the value-adding of glycerol. The current work addresses the urgent need for building a sustainable process employing a heterogeneous catalyst system; subsequent initiatives include executing the reaction in continuous mode and taking into account metrics like catalyst recyclability and lifetime under reaction conditions.

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