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Synthesis and Characterization of $AlCl_3$ Impregnated Molybdenum Oxide as Heterogeneous Nano-Catalyst for the Friedel-Crafts Acylation Reaction in Ambient Condition

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Aluminum trichloride ($AlCl_3$) impregnated molybdenum oxide heterogeneous nano-catalyst was prepared by using simple impregnation method. The prepared heterogeneous catalyst was characterized by powder X-ray diffraction, FT-IR spectroscopy, solid-state NMR spectroscopy, SEM imaging, and EDX mapping. The catalytic activity of this protocol was evaluated as heterogeneous catalyst for the Friedel-Crafts acylation reaction at room temperature. The impregnated $MoO_4(AlCl_2)_2$ catalyst showed tremendous catalytic activity in Friedel-Crafts acylation reaction under solvent-free and mild reaction condition. As a result, 84.0% yield of acyl product with 100% consumption of reactants in 18 h reaction time at room temperature was achieved. The effects of different solvents system with $MoO_4(AlCl_2)_2$ catalyst in acylation reaction was also investigated. By using optimized reaction condition various acylated derivatives were prepared. In addition, the catalyst was separated by simple filtration process after the reaction and reused several times. Therefore, heterogeneous $MoO_4(AlCl_2)_2$ catalyst was found environmentally benign catalyst, very convenient, high yielding, and clean method for the Friedel-Crafts acylation reaction under solvent-free and ambient reaction condition.

Keywords: $MoO_4(AlCl_2)_2$ Nano-Catalyst, Friedel-Crafts Acylation, Solvent-Free and Ambient Condition, Green Chemistry.

1. INTRODUCTION

Friedel-Crafts acylation reactions of aromatic compounds with acid chlorides are considered as fundamental and very important processes in organic synthesis as well as in industrial chemistry.[1–4] Traditionally, these reactions require large amount of anhydrous strong Lewis acids, such as $AlCl_3$, $TiCl_3$, $FeCl_3$, or $SnCl_4$, more than stoichiometric amounts.[5–8] These methods suffer from toxicity and corrosion of the catalysts, generation of a large amount of waste, and difficult purification of products.[9–11] Moreover, these catalysts are highly moisture sensitive and hence moisture-free reaction conditions are required to achieve the optimal yields of the desired aromatic ketones.[1–4] With the increasing emphasis on green chemistry, environmentally benign processes should be developed to improve the green credentials of the reaction.[12–18] For the development of greener processes, moisture-insensitive and easy to handle solid acid catalysts are desired.[19–22] Furthermore, the use of solid acid catalysts offers facile catalyst recovery and recycling, as well as product separation. At the same time, the catalyst recovery also decreases contamination of the desired products with hazardous or harmful metals.[8–13]

Indeed, solid supported catalysts are attracting more consideration in organic reactions because of their ease of handling in work-up procedure, good selectivity, high yields, low cost, and reusability in comparison with their homogeneous catalysts for Friedel-Crafts acylation reaction.[1–5] Several solid acid catalysts

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have been investigated for the Friedel-Crafts acylation reactions, such as metal triflate loaded SBA-15, mesoporous superacid catalyst, zeolite, hybrid zeolitic mesostructured materials, modified clay, nafion-silica composite materials, mesoporous sulphated zirconia, and mesoporous AlKIT-5.[14–25] Although interesting results have been achieved for the Friedel–Crafts acylation reaction, they have not led to any very important industrial application. Friedel-Crafts acylation reaction could be performed under solvent-free reaction condition using a solid heterogeneous catalyst without addition of co-catalysts in mild reaction conditions such process would be eco-friendly and safe.[19–22]

New and improved catalytic protocols continue to attract the attention of industries/chemical laboratories due to a very high importance of the aromatic ketones which are key intermediates in several fields including fine chemicals and pharmaceuticals.[1–5] Hence, there is still a demand for developing new synthetic methods for carrying out the Friedel-Crafts acylation, which deal with moisture-insensitive catalysts and efficient product/catalyst isolation procedure.[14–25] Solvent-free Friedel-Crafts acylation reaction with impregnated heterogeneous catalyst leads to new eco-benign reaction procedures that save and maintain green reaction procedure.[14–19] The Lewis acids such as $TiCl_3$ and $FeCl_3$ impregnated with some other metals such as molybdenum which shows the complex formation with Lewis acids are unique heterogeneous catalysts for the Friedel–Crafts acylation reaction.[14–25] These catalysts have their original Lewis acidity and they gain the heterogeneous property with impregnation with other metals and such catalysts were utilized in organic reactions.[8–12] These reactions shows various advantages over traditional reactions in organic solvents, such reactions are reducing the load of organic solvent disposal and enhance the rate of many organic reactions and reuse of catalyst.[5–12] Therefore, the development of an environmental benign heterogeneous catalytic using impregnation method which is more efficient, highly selective, and less expensive for the Friedel-Crafts acylation reaction under solvent-free condition is highly anticipated.

In the present study, we report preparation of heterogeneous $AlCl_3$ impregnated molybdenum oxide nano-catalyst and its application to Friedel-Crafts acylation reaction under solvent-free condition. The prepared heterogeneous catalyst was characterized by using different analytical and spectroscopic methods. The fruitfully prepared and characterized catalyst was utilized in acylation reaction. As results, the catalyst showed 84% yield of respective acylated product in 18 h reaction time at room temperature in solvent-free condition. In addition, effect of amount of catalyst and other solvent effects with this protocol were determined. We have also evaluated the possibility of regeneration of catalyst and recyclability test in Friedel-Crafts acylation reaction.

2. EXPERIMENTAL DETAILS

2.1. Preparation of $MoO_4(AlCl_2)_2$ Catalyst by Impregnation Method

Ethanol (20 ml) was taken in a two necked round bottom flask under nitrogen atmosphere. Anhydrous aluminum chloride ($AlCl_3$) (1.89 g, 0.014 mol) (Aldrich, 99.0%) was added into it and stirred at room temperature till a clear solution formed. Ammonium molybdate (1.25 g, 0.0101 mol) (Aldrich, 99.0%) was added to it under nitrogen atmosphere. The reaction mixture was stirred under reflux at 100 °C and kept under nitrogen atmosphere by passing nitrogen gas (99.999%) at the rate of 10 ml/min for 12 h. Ethanol was evaporated on rotary evaporator at 80 °C and solid dry mass was obtained. The obtained solid mass was calcined in nitrogen atmosphere at 400 °C up to two hours. The HCl gas librated during reflux process was determined by acid base titration and librated amount of HCl in millimole was estimated and then the catalyst was tested for the Friedel-Crafts reaction.

2.2. Catalyst Characterization

FT-IR spectra of prepared catalysts were taken on a Varian 2000 IR spectrometer (Scimitar series) by using KBr disc method. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation ($\lambda = 1.5406$ Å) with a 2° min^{-1} scan speed and a scan range of 10–60° at 30 kV and 15 mA. The surface morphology of $MoO_4(AlCl_2)_2$ catalyst was studied by scanning electron microscopy (SEM) using a Hitachi, S-3500N SEM instrument. Energy Dispersive X-Ray spectrometry (EDX) were determined using SEM instrument combined with an INCA instrument for energy dispersive X-ray spectroscopy scanning electron microscopy (EDX-SEM), with scanning electron electrode at 20 kV. The prepared acylated

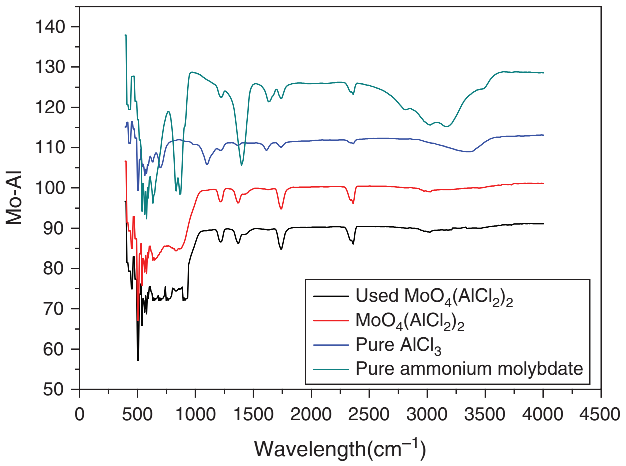


Figure 1. FT-IR analysis of $MoO_4(AlCl_2)_2$ catalyst.

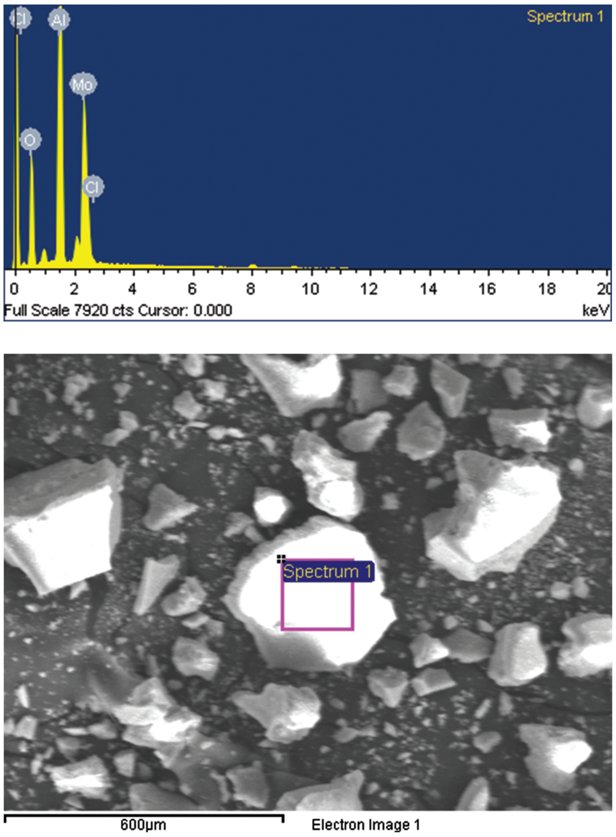


Figure 2. EDX pattern of catalyst $MoO_4(AlCl_2)_2$.

products were compared with the authentic samples and characterized by the ^1H NMR and ^{13}C NMR spectroscopy on Bruker spectrometer 400 MHz at ambient temperature.

2.3. Friedel-Crafts Acylation Reaction

The Friedel-Crafts acylation of Anisole (1 g, 9.26 mmol) (Aldrich, 99.0%) with propionyl chloride (5 equiv.) (Aldrich, 99.0%) using the prepared $MoO_4(AlCl_2)_2$ (5 wt%, 10 mg) catalyst was carried out in a magnetically stirred two-necked round bottom flask fitted with a guard tube ($CaCl_2$), activated at 150 °C for 2 h. The present reaction mixture stirred at room temperature up to the completion of reaction. Reaction progress was monitored by thin layer chromatography (TLC). After completion of the reaction, reaction mixture was filtered and solid catalyst was separated out. The separated solid catalyst can be recycled in next attempt of Friedel-Crafts acylation reaction. The reaction mixture was washed with dichloromethane (DCM) and water, the same process was done triplicate and collected the organic layer. The organic layer was then dried over anhydrous sodium sulfate and concentrated on rotary evaporator and crude acylated product was obtained and purified on column chromatography.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

FTIR spectroscopic analysis of $MoO_4(AlCl_2)_2$ catalyst, pure ammonium molybdate, and pure $AlCl_3$ catalyst were performed in order to determine any alterations in the FT-IR pattern of $MoO_4(AlCl_2)_2$ upon grafting process and results are showed in Figure 1. The prepared catalyst scanned IR range between 400–4000 cm^{-1} and showed major peaks at 1720, 1373, 1199, 910, 994, and 621. The peaks at 994 and 910 resembles the presence of Mo=O and Mo–O–Mo vibrational stretching in $MoO_4(AlCl_2)_2$ catalyst.[26] In addition, the similar peaks we observed in

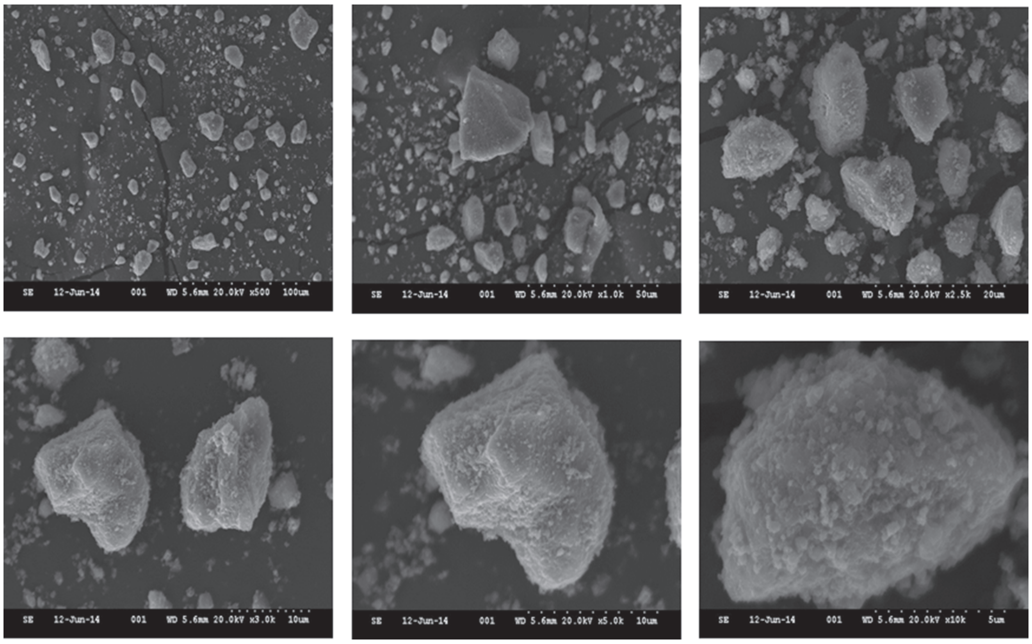


Figure 3. Scanning electron microscopic analysis of $MoO_4(AlCl_2)_2$ catalyst.

pure ammonium molybdate spectra. On the other hand, the absence of broad band between 3400–3600 cm^{-1} and absence of sharp peak at 900 cm^{-1} indicates the absence of hydroxyl and amine groups in prepared $MoO_4(AlCl_2)_2$ catalyst.[27] Peaks at 638, which attributed for the Al–Cl bonding is present in the both pure $AlCl_3$ spectrum and IR spectrum of catalyst.[27] Which indicate the presence of aluminum impregnation on prepared $MoO_4(AlCl_2)_2$ catalyst. To study the structural modifications in recycled catalyst, we also carried out the IR spectra of recycled catalyst and all similar types of bands were also observed in recycled catalyst after being used in 6th cycle.

In order to determine the stoichiometry of $MoO_4(AlCl_2)_2$ we performed EDX scanning, Figure 2 shows the EDX pattern of prepared catalyst $MoO_4(AlCl_2)_2$. At higher magnification, elemental composition was obtained by EDX analysis. An extremely homogeneous distribution of Al, Mo, Cl, and O elements throughout the $MoO_4(AlCl_2)_2$ catalyst was observed by EDX mapping. The weight percent ratio and atomic ratio calculated from EDX analysis were equal to the expected stoichiometry for $MoO_4(AlCl_2)_2$. These results show that the aluminium grafted molybdenum catalyst was prepared successesfully and it was agreed with the secondary support of IR, XRD diffraction and SEM analysis.

The morphology and structure of $MoO_4(AlCl_2)_2$ catalyst were investigated using SEM analysis. Figure 3 shows the morphology of catalyst, which exhibit well-defined nanostructure with ten and five microns in size. The SEM images show that well dispersed powder throughout the surface. In addition, we observed the surface of our $MoO_4(AlCl_2)_2$ catalyst which indicate the amorphous $AlCl_3$ impregnated on molybdenum oxide, which exhibited the active component disperses very evenly on the surface of $MoO_4(AlCl_2)_2$ catalyst. In 100 μm and 50 μm pictures we can see the overall particle shapes of catalyst, these particles shapes can be seen close rambles in picture 20 μm and 10 μm. At 10 μm and 5 μm we can see the catalyst particle surface which specify the impregnated $MoO_4(AlCl_2)_2$ catalyst.

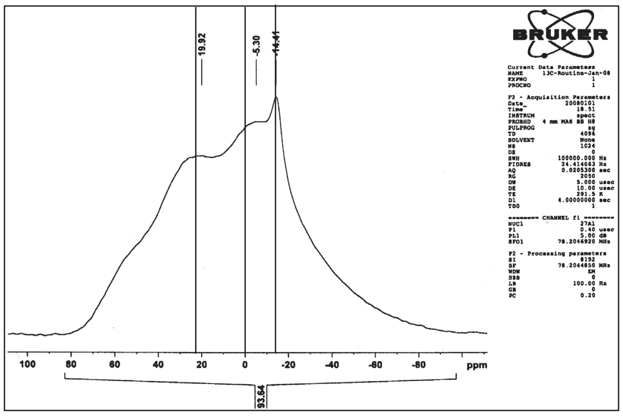


Figure 4. ^{27}Al solid state NMR analysis of $MoO_4(AlCl_2)_2$ catalyst.

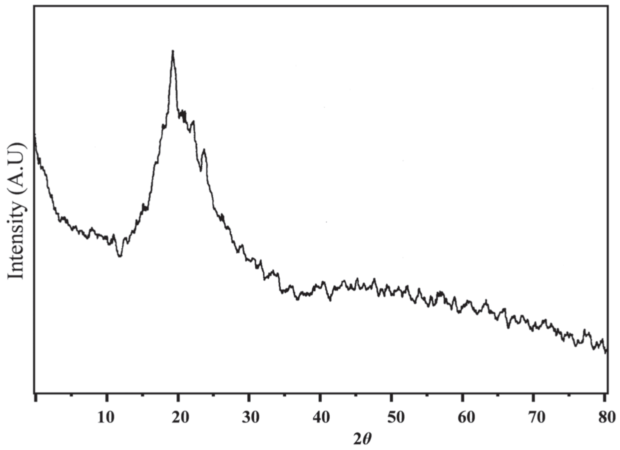
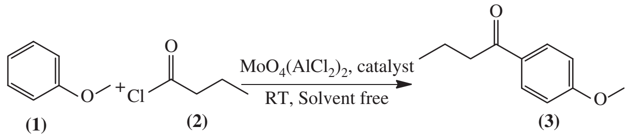


Figure 5. XRD analysis of $MoO_4(AlCl_2)_2$ catalyst.

The ^{27}Al NMR in the solid state method is uniquely suitable to the study of Al chemistry and thus for characterization of Al in various states of complexation and good tool for the determination of the aluminium coordination number in complexes. It is well known that ^{27}Al NMR in the solid state shows a signal between −10 and +20 ppm for coordination number six and between +55 and +85 ppm for coordination number four. The ^{27}Al spectrum of $MoO_4(AlCl_2)_2$ catalyst represented in Figure 4. The ^{27}Al solid state NMR spectrum of $MoO_4(AlCl_2)_2$ catalyst at 25 °C showed a clear single line spectrum at −12.01 ppm, which showed the highly active tetrahedral form of ^{27}Al is present in the catalyst. The absence of peak in the range of +55 and +85 ppm attributed the absence

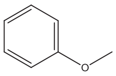
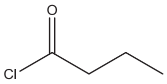
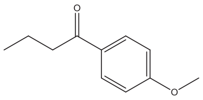
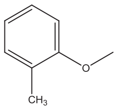
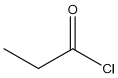
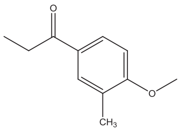
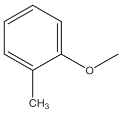
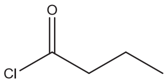
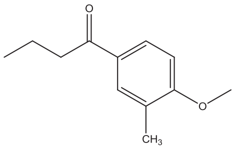
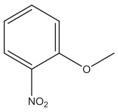
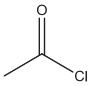
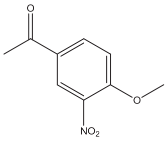
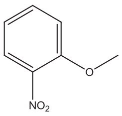
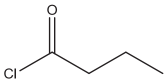
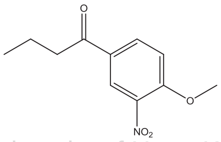
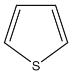
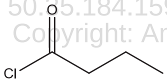
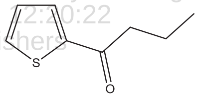
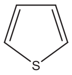
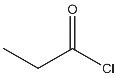
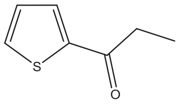
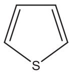
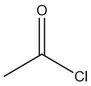
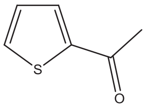
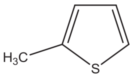
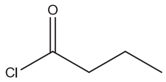
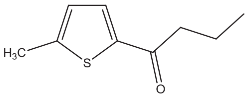
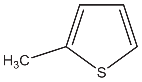
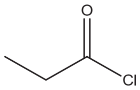
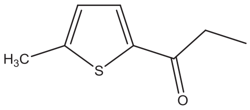
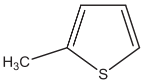
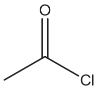
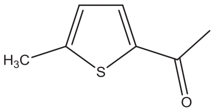
Table I. Friedel-Crafts acylation reaction using $MoO_4(AlCl_2)_2$ in solvent-free condition and effect of other solvents[a].



Entry	Solvent	$MoO_4(AlCl_2)_2$ (equiv)	Temperature	Time (h)	Yield[b] (%)
1	–	–	rt	48	–
2	–	1.0	rt	12	86
3	–	0.5	rt	14	86
4	–	0.4	rt	14	85
5	–	0.3	rt	14	86
6	–	0.2	rt	15	86
7	–	0.1	rt	18	84
8	Benzene	0.1	rt	12	27
9	Tetrahydrofuran	0.1	rt	18	42
10	1,4-dioxane	0.1	rt	18	22
11	Methanol	0.1	rt	12	48
12	Dichloromethane	0.1	rt	12	31
13	Acetonitrile	0.1	rt	18	24

Notes: [a] All reactions were carried out on 1.0 mmol scale of substrate with 0.1–1.0 equiv. of $MoO_4(AlCl_2)_2$ catalyst, accordingly in 4.0 ml solvent and without solvent. [b] Yield refers to the isolated product.

Table II. Preparation of various acylated derivatives using $MoO_4(AlCl_2)_2$ catalyst in solvent-free condition[a].

Sr. No	Ar-H	Acid Halide	Time (h)	Product	Yield[b](%)
1			18		84
2			16		72
3			14		72
4			16		80
5			22		67
6			8		87
7			12		81
8			6		76
9			9		71
10			14		69
11			18		76

Notes: [a]All reactions were carried out on 1.0 mmol scale of substrate with catalyst (except Entry 1) and without addition of any co-catalyst and solvent; [b]Yield refers to the isolated product.

of octahedral form in the prepared $MoO_4(AlCl_2)_2$ catalyst. According to a study, the peak at 0.0 ppm is attributed to six-coordinate Al species. This peak appears from air contamination when the catalysts were placed in an NMR cell. This cell was manipulated under ambient air and it does not protect entirely the catalyst from moisture.

Figure 5 shows the 2-D X-ray diffraction spectra of $MoO_4(AlCl_2)_2$ catalyst. We performed the XRD pattern between 0–80°, to determine the crystalline structure of catalyst, unfortunately catalyst does not have any strong diffraction peaks in the range of $2\theta = 0$–$80°$. The broad hump at the range of $2\theta = 18$–$25°$ is belong to the molybdenum oxide. It can be seen that all the XRD patterns of the catalysts are like crystalline and amorphous which suggest that $AlCl_3$ is impregnated on molybdenum, in which molybdenum showed crystalline phase and $AlCl_3$ showed the amorphous phase in prepared impregnated $MoO_4(AlCl_2)_2$ catalyst.

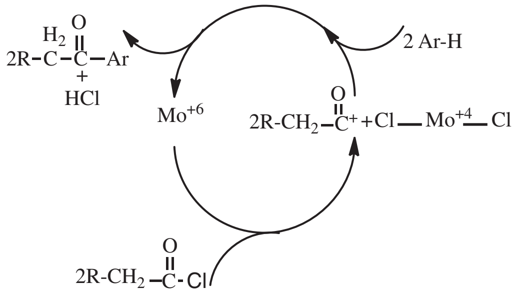
3.2. Friedel-Crafts Acylation Reaction Using MoO_4 $(AlCl_2)_2$ Catalyst

Table I exhibits the Friedel-Crafts acylation reaction of anisole (1) with propionyl chloride (2) using $MoO_4(AlCl_2)_2$ in solvent-free condition as a model reaction using various reaction conditions with catalyst. Initially, we performed catalyst free and solvent-free acylation reaction of (1) and (2) at room temperature for two days and we observed that, this reaction fails to give any desired product (entry 1). Further, to determine the catalytic activity of $MoO_4(AlCl_2)_2$ at room temperature, number of reactions were performed in solvent-free condition. Primarily, we discovered the minimum amount of $MoO_4(AlCl_2)_2$ required for rapid acylation reaction by carrying out the catalyst dosage using 1, 0.5, 0.4, 0.3, 0.2, and 0.1 equiv. of $MoO_4(AlCl_2)_2$ at uniform reaction condition (entry 2-7) and we found that all reactions were progressed efficiently and provide excellent yield of respective acylated product (3) in 18 h reaction time, these reactions showed the significant catalytic activity of $MoO_4(AlCl_2)_2$ catalyst. In view of, the mole economy ratio of catalyst we selected to use 0.1 equiv. of $MoO_4(AlCl_2)_2$ for further study of the Friedel-Crafts acylation reaction under solvent-free condition.

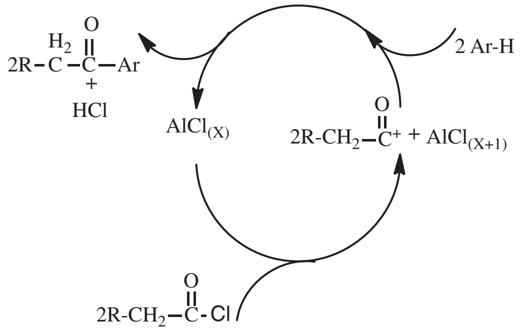
In addition, we also carried out Friedel-Crafts acylation reaction using various solvents with $MoO_4(AlCl_2)_2$ catalyst to study the effect of these solvents on acylation reaction of (1) and (2). Entries 8 and 9 show acylation reaction with prepared catalyst in benzene and tetrahydrofuran and were observed very sluggish reaction and provided only 27% and 48% yield of desired product in respective reaction period. However, solvents such as 1,4-dioxane and methanol were also found to be inactive for this protocol and showed only 22% and 48% yield (entry 10 and 11). On the other hand, Entry 13 shows the acylation results in dichloromethane and acetonitrile in presence of catalyst and was showed 31% and 24% yield of respective acylated products. Therefore, from all these results we conclude that, prepared $MoO_4(AlCl_2)_2$ catalyst is highly efficient for Friedel-Crafts acylation reaction under solvent-free condition.

Table II shows various Friedel-Crafts acylation reaction products of structurally varied arenes and acid chlorides of using optimized reaction condition in presence of $MoO_4(AlCl_2)_2$ catalyst. Entry 1 shows the results of model reaction products which were used to establish the optimized reaction condition. Entries 2, 3, 4, and 5 shows the results of substituted anisole with different structures of acid chlorides, all yields of respective products are efficient in corresponding reaction time with $MoO_4(AlCl_2)_2$ catalyst. In addition, we tried to determine the reaction with five membered arenes "thiophene" with different acid chlorides. Results showed that, present catalyst is able to perform Friedel-Crafts acylation reaction efficiently with five membered rings in good yield at ambient condition (Entries 6, 7, 8). Entries 9, 10, 11 shows the results of acylated products of substituted thiophene with different acid chloride, all reactions were performed smoothly and obtained good to efficient yield with impregnated $MoO_4(AlCl_2)_2$ catalyst in solvent-free condition. These observations encourage us to study the reaction mechanism with prepared $MoO_4(AlCl_2)_2$ catalyst in solvent-free condition.

Figure 6 shows the plausible reaction mechanism of Friedel-Crafts acylation reaction with impregnated $MoO_4(AlCl_2)_2$ catalyst under solvent-free condition.



Case-I Reaction Mechanism with Molybdate Oxide



Case-II Reaction Mechanism with Aluminum Chloride

Figure 6. Plausible reaction mechanism of Friedel-Crafts acylation reaction with impregnated $MoO_4(AlCl_2)_2$ catalyst under solvent-free condition.

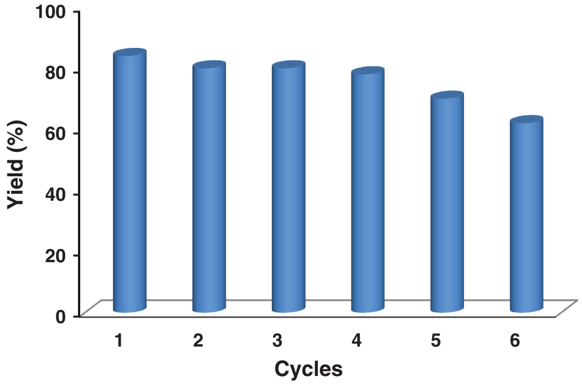


Figure 7. Recyclability test of $MoO_4(AlCl_2)_2$ catalyst in Friedel-Crafts acylation reaction under solvent-free condition.

We believed that the present catalyst could participate in mechanism in two different ways. In case-I, the Mo^{6+} present in $MoO_4(AlCl_2)_2$ catalyst helps to the formation of acyl cation from the acid chloride and molybdenum complex, which on reaction with the aromatic substrate leads to the formation of the acylated product and Mo^{+6} is regenerated as showed in case-I. On the other hand, the $AlCl_x$ present in the catalyst might be helping to the formation of acylated product in presence of $MoO_4(AlCl_2)_2$ catalyst as shown in case-II.

3.3. Recyclability Test of Heterogeneous $MoO_4(AlCl_2)_2$ Catalyst

Catalyst reusability is one of the important factors for economical operation for organic transformation using heterogeneous catalyst, as this can allow reduction in the operating cost and environmental pollution. After first run of Friedel-Crafts acylation reaction, catalyst was removed from the reaction mixture by filtration process. The filtered catalyst was reused directly after washing with ethanol. Catalyst was reused for the next six cycles with the same reaction parameters which were used for fresh catalyst assisted acylation reaction. The results of catalyst reusability study has been depicted in Figure 7 and it was found that almost similar yield can be obtained up to fourth run i.e., acylated yield only marginally decreased from 84 to 78%. After the fifth run, catalyst activity started decreasing significantly and 62% yield of respective product was obtained in sixth run. Hence, the catalyst is efficiently recycled for up-to six cycles without considerable loss in its catalytic activity and selectivity in the Friedel-Crafts acylation reaction under solvent-free condition.

4. CONCLUSIONS

Aluminum trichloride ($AlCl_3$) impregnated molybdenum oxide heterogeneous nano-catalyst was prepared successfully by using simple impregnation method. Properties and morphology of prepared catalyst were characterized by FT-IR, XRD, SEM, EDX, and solid-state NMR spectroscopy. $MoO_4(AlCl_2)_2$ catalyst after successful characterization applied as heterogeneous catalyst for the Friedel-Crafts acylation reaction. The present catalytic system showed 100% conversion and achieved 84% yield of respective acylated product at room temperature using 0.1 equiv. of catalyst in solvent-free condition. Various acylated derivatives were prepared by using optimized reaction condition with $MoO_4(AlCl_2)_2$ catalyst at optimized reaction condition. In addition, a proposed mechanism path way also draw to understand the reaction path way with $MoO_4(AlCl_2)_2$ catalyst. The prepared $MoO_4(AlCl_2)_2$ catalyst can be recycled by simple filtration process at end of the reaction and reused several times without considerable loss of catalytic activity and selectivity. The results demonstrate that the impregnated $MoO_4(AlCl_2)_2$ catalyst is an excellent environmentally benign solid catalyst for the Friedel-Crafts Acylation reaction in ambient condition.

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