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Acetalization of glycerol with acetone to bio fuel additives over supported molybdenum phosphate catalysts

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ABSTRACT

The acetalization of glycerol with acetone was carried out over a series of molybdenum phosphate catalysts supported on SBA-15 with varying MoPO loadings ranging from 5-50 wt%. These catalysts were characterized by X-ray diffraction, FT-IR, Laser Raman Spectroscopy, Ultraviolet–visible diffuse reflectance spectroscopy (UV DRS), NH_3-TPD analysis, ex-situ pyridine adsorbed FT-IR analysis and pore size distribution measurements. The XRD results of unsupported MoPO show the formation of $(MoO_2)_2P_2O_7$ phase and this phase is present in a well dispersed state on the SBA-15. Raman spectra reveal the presence of MoPO species in the form of $(MoO_2)_2P_2O_7$ phase in the samples above 40 wt% MoPO/SBA-15. The presence of both isolated tetrahedrally and isolated octahedrally coordinated Mo centers in the unsupported and supported MoPO are confirmed by the UVDRS findings. Ammonia TPD analysis suggests that the total acidity increased with MoPO loading and acidity of the catalysts was proved to be detrimental to assess the catalytic performance. The conversion and selectivity during the acetalization depends strongly on the reaction time, catalyst loading and glycerol to acetone molar ratio. Acetalization of glycerol suggests that 40 wt% MoPO/SBA-15 sample exhibited better catalytic properties than other catalysts investigated. The catalytic properties are well correlated with the acidic functionalities of the catalysts.

1. Introduction

In recent years due to the gradual declining of petroleum reserves, the world energy crisis has become an important topic to explore other possible alternate sources of energy [1–3]. Hence, the use of biofuels has attracted significant attention as a renewable and biodegradable fuel in recent years from researchers in both academic and industries. Biodiesel is generally produced by transesterification of vegetable oils with methanol, where glycerol is the main by-product [4]. This glycerol cannot be utilized for food and pharmaceutical industries due to its high contamination with methanol. However, it can be converted into value added chemicals by different catalytic processes involving oxidation, hydrogenolysis, etherification, dehydration, esterification and acetalization [5–7].

Among various catalytic processes of glycerol conversion, acetalization is found to be one of the most important chemical transformations of glycerol into high value oxygenated fuel additives [8]. This improves the quality of diesel by reducing the emissions of carbon monoxide and unregulated aldehydes. The acetalization of glycerol with acetone produces branched oxygenated compounds, namely (2,2-dimethyl-[1,3]dioxane-4-yl)-methanol (solketal) and 2,2-dimethyl-[1,3]dioxane-5-ol. Solketal is an excellent component in the formulation of gasoline, diesel and biodiesel fuels. The acetals of glycerol have numerous applications in fragrances, pharmaceuticals, detergents, lacquer industries, cosmetics and also as ignition accelerators and antiknock additives in combustion engines [9–11]. Glycerol acetals can also be used as a basis for surfactants [12]. Acetalization of glycerol with acetone is an acid catalysed reaction (Scheme 1) and conventionally carried out using mineral acids as catalysts. In view of stringent environmental requirements, it is essential to develop an effective and inexpensive solid acid catalyst for the acetalization of glycerol.

Different types of solid acids such as amberlyst, zeolites, supported metal oxides, metal phosphates and supported heteropoly acids have been recently reported as the catalysts for glycerol acetalization [13,14]. Umbarkar et al. [15] studied the acetalization of glycerol with various carbonyl compounds using mesoporous MoO_3/SiO_2 catalyst and extensive investigation was made to determine the physicochemical and acidic properties. Molybdenum oxide promoted with ZrO_2 and SnO_2 were also employed earlier for the acetalization of glycerol [16,17]. SBA-15 supported molyb-

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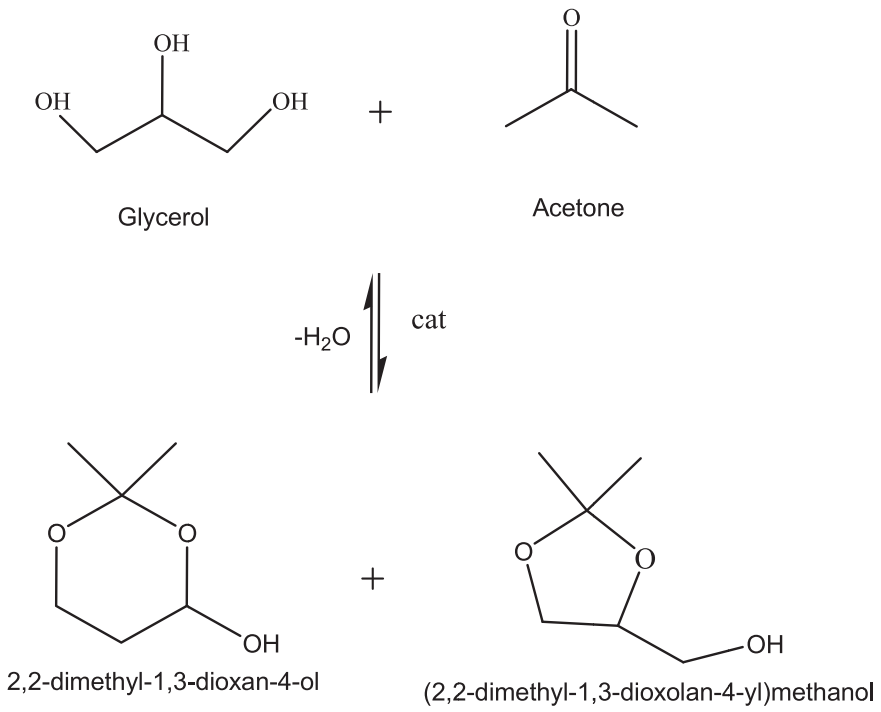

Scheme 1. Schematic representation of acetalization of glycerol with acetone over MoPO/SBA-15 catalysts.

denum oxide has been studied for oxidation reactions such as oxidation of propene and oxidation of ethane [18,19]. The promotion of molybdenum oxide to basic material enhances activity of the catalyst due to an increase of the strong acidic character [20,21]. However, the presence of both Brønsted and Lewis acid sites in phosphated metal catalysts makes them to use as selective and active catalysts for acid-catalysed dehydration [22–25], ketalization of ketones with diols [26] and also in the isomerisation reactions.

Molybdenum phosphate was employed as a catalyst for the ammoxidation of picoline, oxidation of propane and oxidation of ethane [27–29] because of their ability to stabilize metal ion in various oxidation states, i.e., M^{6+}, M^{5+}, M^{3+} and even mixed valences such as M^{5+}/M^{6+}. These materials are built up from the linkage of PO_4 tetrahedral with $(MoO_6)^{6-}$ octahedral [30]. Moreover, these materials (MoPO) have received increasing attention in the last decade for the use as new cathode materials for lithium and sodium batteries [31]. Hence, in the present work, we have employed this material in the acid catalysed reaction such as glycerol acetalization reaction. The use of unsupported molybdenum phosphate catalyst has disadvantages such as low surface area and low pore size. Therefore, molybdenum phosphate is supported on mesoporous support such as SBA-15 in order to impart stability of the catalyst and dispersion of the active phase. SBA-15 is a purely siliceous mesoporous molecular sieve with high thermal stability and having potential to use as a catalyst support for the active phase in various applications. This material possesses a high surface area (700–1000 $m^2\,g^{-1}$) which should promote a high dispersion of the active phase with pore diameter in the mesoporous range (2–7 nm) [32].

In the present work, we have investigated the efficiency of molybdenum phosphate catalyst supported on SBA-15 for the acetalization of glycerol with acetone to produce bio fuel additives. The reaction was systematically investigated by varying several reaction parameters to optimise the conditions to find a catalyst exhibiting high activity/selectivity with fairly good stability. These catalysts were characterized by X-ray diffraction, pore size distribution, FT-IR, Raman, UV-DRS and NH_3-TPD methods. Our results provide a basis mainly for correlating the catalyst acidity by varying MoPO content on SBA-15 support and the effect of various reaction parameters such as the molar ratio of acetone to glycerol, catalyst amount and reaction time.

2. Experimental

2.1. Catalyst preparation

The mesoporous SBA-15 support was prepared by the procedure described elsewhere [33,34]. Briefly, it involves using a tri-block copolymer poly-ethylene glycol–block-poly-propylene glycol–block-poly-ethylene glycol (P123, average molecular mass ≈5800 g, Aldrich) as a template. About 2 g of P123 copolymer was dissolved in a mixture of 15 g of water and 45 g of 2 M followed by addition of 0.2 g of cetyl trimethyl ammonium bromide (CTMABr) and 5.9 g of tetraethyl orthosilicate (TEOS) with continuous stirring of the contents. The final molar ratio of the synthesis mixture was 1 TEOS:0.02 CTMABr:3.1 HCl:115 H_2O:0.012 Polymer. The synthesis mixture was introduced into a Teflon lined autoclave, sealed and kept at 100 °C for 24 h. Subsequently, it was cooled, filtered and washed with deionised water and ethanol to remove the excess template from the mixture prior to calcination in air at 500 °C (5 °C /min) for 5 h.

The molybdenum phosphate was prepared by the procedure described elsewhere [35,36]. Typically, the white Mo (VI) containing precursor material was prepared by dissolving 7.5 g of MoO_3 (99.5%, Aldrich) in 22.5 cm^3 85% H_3PO_4 (331 mmol, Aldrich) at approximately 180 °C. The solution was then cooled to room temperature and 200 cm^3 of 15.8 M HNO_3 (Fisher) was added to it and refluxed further for 12 h. Upon cooling, small crystallites of the target compound was precipitated from the solution. These crystals were vacuum-filtered, washed with acetone, dried in air and subsequently calcined at 550 °C (5 °C /min) for 6 h.

Molybdenum phosphate supported on SBA-15 was prepared by impregnation method by adding required amount of aqueous solu-