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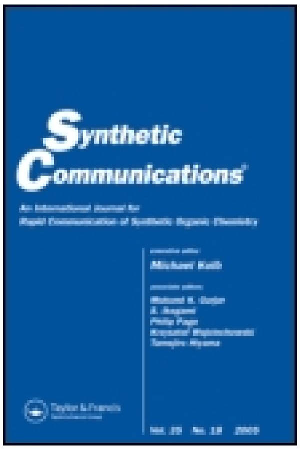

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ECO-FRIENDLY Pt-Mo/ZrO$_2$ SOLID ACID CATALYST FOR SELECTIVE PROTECTION OF CARBONYL COMPOUNDS

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ECO-FRIENDLY Pt–Mo/ZrO_2 SOLID ACID CATALYST FOR SELECTIVE PROTECTION OF CARBONYL COMPOUNDS

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ABSTRACT

An easy method for protection of carbonyl compounds has been carried out in excellent yields under catalysis of Pt–Mo/ZrO_2 in toluene at 383 K.

The carbonyl function, as present in aldehydes and ketones, is the most versatile functional group in organic synthesis. During a synthetic sequence a carbonyl group may have to be protected against encounter by various reagents such as acidic, basic, oxidizing and reducing agents. One of the most useful protecting methods of carbonyl compounds is acetalization or thioacetalization[1] and the protective groups are acyclic or cyclic acetals and ketals. Recently, different catalytic systems such as $SOCl_2$–SiO_2,[2] HY Zeolite,[3] Mg–ZnTf,[4] natural clay,[5] and modified days such as Montmorlonite-KSH[6] and Ce-Montmorlonite[7] have been attempted for effecting the acetalization or thioacetalization reactions. However, most of these reported catalysts show many disadvantages such as a rapid catalyst deactivation, production of wasteful products, low product yields, and severe reaction conditions. In view of the environmental concern, there is a global

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* Corresponding author.

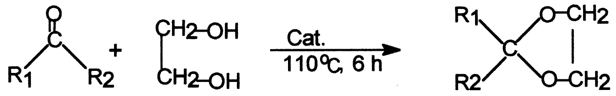
effort to replace the conventional catalysts by new solid acids, which can be easily separable from the products, less toxic, and reusable. In this communication we report an efficient eco-friendly Pt–Mo/ZrO_2 solid acid catalyst for selective protection of various aldehydes and ketones including α, β unsaturated carbonyl compounds with ethane-1,2-diol as protecting group.

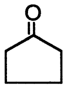
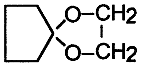
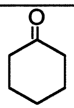
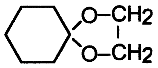
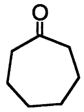
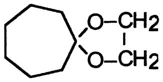
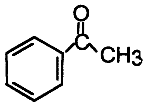
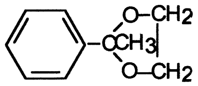
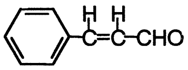
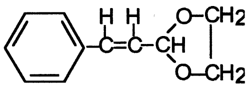
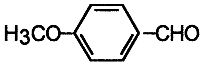
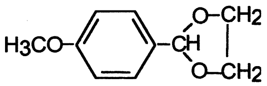
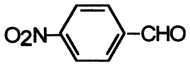
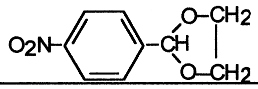
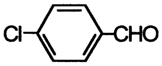
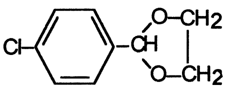
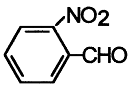
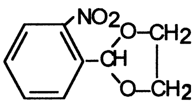
The importance of sulfated ZrO_2 as a solid super-acid for various catalytic applications has been identified recently.[8] However, the sulfated zirconia undergoes rapid deactivation due to loss of sulfate ions during activation and catalytic run. Very recent investigations reveal that WO_x-ZrO_2 and MoO_x- ZrO_2 are another set of alternative catalysts in reactions requiring stronger acid sites.[9–11] The major advantage of tungsten or molybdenum modified zirconia over sulfated ZrO_2 is that there is no loss of SO_4^{2-} ion during thermal activation and catalytic run, hence, less deactivation. The present study discloses that Pt-MoO_3/ZrO_2 is an interesting and multifunctional catalyst, much superior to the earlier reported catalysts. The use of a reusable heterogeneous catalyst in achieving selective protection of carbonyl compounds is very significant from the point of view of its commercial implications.

Preparation of Catalyst: Zirconium hydroxide was prepared from an aqueous solution of $ZrOCl_2$ (Loba Chemie, GR grade) by adding NH_4OH solution (Ranbaxy, LR grade) drop-wise from a burette upto pH 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 48 h. Ammonium heptamolybdate (J T Baker, England, GR grade) aqueous solution of adequate concentration (9 wt.%) was added to the oven dried hydroxide and the excess water was evaporated on a water bath. The resulting sample was oven dried again at 393 K for 48 h and calcined at 873 K for 6 h in a flow of oxygen. The calcined sample was impregnated with hexachloroplatinic acid (Loba Chemie, GR grade) solution to obtain 0.5 wt.% of platinum containing catalyst by an incipient wetness technique. The resulting sample was oven dried at 393 K for 48 h and calcined at 873 K for 6 h in a flow of oxygen. The X-ray powder diffraction analysis of Pt-Mo/ZrO_2 and Mo/ZrO_2 samples show that the former contains more tetragonal zirconia which is known to be responsible for strong acidity of these catalysts.[12,13]

General Procedure for Protecting of Carbonyl Group: Equimolar ratio of carbonyl compound and ethylene glycol with the Pt-Mo/ZrO_2 catalyst (0.3 g) along with the solvent toluene was heated at 383 K in a round bottom flask provided with a Dean-Stark apparatus having condenser to remove the water from the reaction mixture. After completion of the reaction (*ca.* 6 h), the catalyst was filtered off and the filtrate was concentrated and chromatographed on SiO_2 to obtain the cyclic acetal in good yields. The results are summarized in Table 1. The results thus show that the

Table 1. Protection of Carbonyl Functions with Ethane-1,2-diol in the Presence of Eco-friendly Pt-Mo/ZrO$_2$ Solid Acid Catalyst



Entry	***Substrate***	***Product***	***Yield (%)***[a]
1			98
2			93
3			84
4			87
5			40
6			80
7			65
8			95
9			80

[a] Based on NMR.

Pt-Mo/ZrO_2 will be ideally suited for the selective protection of carbonyl compounds. The main advantage of this catalyst is easy operation and simplicity in the workup, which involves mere filtration of the catalyst and its reusability.

The CH analysis data for various product molecules is as follows: $C_7H_{12}O_2$ (Entry 1): C, 65.62; H, 9.37. Found: C, 65.5; H, 9.43. $C_8H_{14}O_2$ (Entry 2): C, 67.60; H, 9.85. Found: C, 66.5; H, 9.53. $C_9H_{16}O_2$ (Entry 3): C, 69.23; H, 10.25. Found: C, 68.7; H, 9.89. $C_{10}H_{12}O_2$ (Entry 4): C, 73.17; H, 7.31. Found: C, 73.2; H, 7.20. $C_{11}H_{12}O_2$ (Entry 5): C, 75.00; H, 6.81. Found: C, 73.4; H, 7.1. $C_{10}H_{12}O_3$ (Entry 6): C, 63.82; H, 6.38. Found: C, 62.85; H, 6.21. $C_9H_9NO_4$ (Entry 7): C, 65.06; H, 6.02. Found: C, 65.5; H, 5.85. $C_9H_9ClO_2$ (Entry 8): C, 67.60; H, 9.85. Found: C, 65.7; H, 9.61. $C_9H_9NO_4$ (Entry 9): C, 65.06; H, 6.02. Found: C, 64.5; H, 5.95.

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