BAEYER-VILLIGER OXIDATION OF CYCLIC KETONES OVER IRON-CONTAINING MESOPOROUS MCM-48 SILICA MATERIALS

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Abstract
Fe-MCM-48 mesoporous material was found to be a highly active catalyst for the Baeyer-Villiger oxidation of several cyclic ketones. The catalyst could be reused several times without any loss of activity.

Keywords: Baeyer-Villiger oxidation, iron, mesoporous MCM-48

INTRODUCTION

The discovery of M41S class of materials in 1992 by Mobil scientists [1] is considered a major breakthrough in the class of porous solids. Since then ordered mesoporous materials having different pore morphologies have been synthesized [2-5]. These materials have drawn much attention to the field of catalysis, owing to their regular channel of pores, high surface area, and high thermal stability.

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The Baeyer-Villiger oxidation (BVO) is a versatile oxidation reaction that has been applied for the synthesis of a wide variety of compounds, ranging from pheromones, to polymers, steroids and antibiotics. Aerobic BVO of ketones in the presence of sacrificial aldehydes were reported [6, 7] using Fe₃O₄ and Fe-MCM-41 under heterogeneous conditions. A drawback of the MCM-41 type of materials is the unidirectional pore system. In this respect, the cubic MCM-48, with its interwoven and continuous 3D regular pore system provides favorable mass-transfer kinetics and seems to be a better candidate for catalytic applications than MCM-41. To the best of our knowledge, no report exists on the use of a cubic MCM-48 support for the Bayer-Villiger oxidation of cyclic ketones. Thus, it is very important to examine the feasibility of a high surface area support such as MCM-48, for catalytic reactions. Here, we wish to report the successful aerobic BVO of several cyclic ketones to corresponding lactones in the presence of sacrificial benzaldehyde using highly dispersed Fe³⁺-containing cubic MCM-48 mesoporous materials.

EXPERIMENTAL

Siliceous MCM-48 and Fe-containing MCM-48 were prepared according to a modified Stöber synthesis [8]. A typical preparation of siliceous MCM-48 is as follows. In a polypropylene bottle (125 mL), 1.2 g of cetyltrimethylammonium bromide (CTAB), 50 mL deionized water, 25 mL ethanol, 6 mL of aq. NH₃ and 1.8 mL of tetraethyloxysilicate (TEOS) was added and the mixture stirred for 4 h. The composition of the initial gel is 0.41 CTAB: 11 aq. NH₃: 1.0 TEOS: 53 Ethanol: 344 H₂O. The Fe³⁺-containing MCM-48 mesoporous material was prepared in an analogous manner as described above, except for the required amount of Fe(NO₃)₃·9H₂O was added to the synthesis gel immediately after solubilizing the surfactant in water. The precipitate obtained was filtered and washed extensively with deionized water. The white powder obtained was dried in an air oven at 353 ± 10 K overnight. The dried powder was then ground finely and then calcined in static air at 823 K at a heating rate of 3 K/min to remove the surfactant molecules.

Characterization

The powder X-ray diffraction studies of the calcined mesoporous samples were performed using a Scintag Pad V X-ray diffractometer, with DSMNT data acquisition and analysis software. The diffuse reflectance (DR) spectrum of Fe-MCM-48 was recorded using a Cary 100 Bio UV-Vis spectrophotometer equipped with a Harrick DR praying mantis accessory. N₂ isotherms were taken