



Mesoporous titanosilicate Ti-TUD-1 catalyzed Knoevenagel reaction: An efficient green synthesis of trisubstituted electrophilic olefins

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ABSTRACT

A new, efficient and green methodology has been developed for the Knoevenagel condensation using catalytic amount of mesoporous titanosilicate catalyst Ti-TUD-1, under mild conditions at room temperature. The method generates trisubstituted electrophilic olefins in high yields within short reaction time. The mesoporous nature of the catalyst having high surface area helps in binding the substrate to the active site. The advantage of this catalyst is its reusability with almost consistent reactivity thereby making it viable for industrial applications.

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1. Introduction

In recent times attention has been focused on the development of eco-friendly solid acid/base catalysts for organic synthesis. The advantage of these catalysts lies in their high atom efficiency, extreme selectivity and simple work-up procedure without generating any organic waste. Development of catalysts for C–C bond formation in organic synthesis following green approach always provides a challenge. One such example is the versatile Knoevenagel condensation reaction [1,2], a useful method for the synthesis of active dipolarophiles which finds application in 1,3-cycloaddition reactions [3]. The reaction also has wide application in the synthesis of drugs [4], polymer sciences [5], and natural products [6].

The classical Knoevenagel condensation involves the condensation of aldehydes/ketones with active methylene compounds in the presence of organic bases like pyridine, piperidine and ethylenediamine [7–9]. Normally malononitrile, cyanoesters, β -ketoesters, malonic acids, malonates are used as the active methylene components containing two electron withdrawing groups (EWG). However, the procedure results in a large amount of organic wastes due to polymerization and self condensation reactions. Hence, comes the necessity and importance of developing a clean and

environment friendly catalytic methodology. Supported porous solid acids would be an effective solution of the problem. In continuation to our exploration of green synthetic methodology using porous solids [10,11], we would like to report here the efficiency of the mesoporous titanosilicate catalyst Ti-TUD-1 [12,13] towards the classical Knoevenagel condensation reaction. The catalyst has high surface area and Ti, being in a highly dispersed state on the silica surface, is catalytically highly active. We are the first to report the use of this catalyst in the Knoevenagel condensation reactions at room temperature with high selectivity and quantitative yields (Scheme 1).

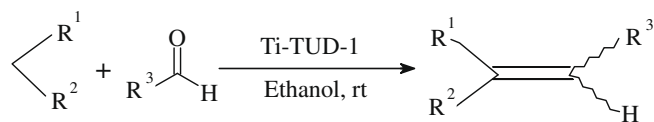
2. Experimental

2.1. General

The NMR spectra (¹H and ¹³C NMR) were recorded on a Bruker Avance 300 MHz and Bruker Avance 75.5 MHz spectrometer and TMS was used as the internal standard. Infrared spectra were recorded in KBr pellet in reflection mode with a Perkin–Elmer RX-1 FT-IR spectrophotometer. X-ray powder diffraction study was carried out on a Philips PW-1830 X-ray diffractometer at a voltage of 35 kV and a current of 25 mA using Cu K α radiation ($\lambda = 154$ nm) at the scanning rate of 1°/min in the 2θ range 0–5° and 10–70°. SEM was performed with a Hitachi-S 3400N microscope at an operating voltage of 15 kV. The sample was coated with gold for effective imaging before being charged. TEM images were obtained from a JEOL JEM-2100 Transmission Electron Microscope at an operating

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$R^1, R^2 = \text{CN}; R^3 = \text{Aryl, Cinnamyl, Furoyl}$

Scheme 1. Knoevenagel condensation reaction.

voltage of 100 kV. The sample was prepared by placing one drop of the dispersed solution of the catalyst in acetone as solvent on a carbon coated copper grid followed by drying over air. The emission fluorescence spectrum was recorded on a Perkin–Elmer spectrophotometer. Melting points (uncorrected) were determined on a Koffler Block apparatus. Synthetic grade chemicals from Acros and E-Merck were used for the preparation of the catalyst and from Spectrochem for carrying out the organic reactions. Analytical TLC was performed using E-Merck aluminium-backed silica gel plates coated with silica gel G. For column chromatography 60–120 mesh silica gel was used from Merck. All the solvents used in the reaction were distilled and dried over Na_2SO_4 .

2.2. Catalyst preparation

The mesoporous titanasilicate Ti-TUD-1 was prepared following a simple and modified synthetic procedure. Modifications were done in terms of tuning of porosity development mechanism where a non-hydrothermal sol–gel technique was used and higher content of structure directing template. Tetraethyl orthosilicate (TEOS) and titanium (IV) butoxide were used as the precursor for silica and titanium, respectively. In the typical procedure titanium butoxide was added slowly to the TEOS

solution. A mixture of triethanolamine (TEA) and water was added to a stirring solution and then triethyl ammonium hydroxide (TEAOH) (20% aqueous solution) was added dropwise to pH 10. The final molar ratio of the reagents was 1.0 $\text{SiO}_2:m \text{TiO}_2$ ($m = 0.01, 0.03, 0.05$):3.0 TEA:0.3 TEAOH:15 H_2O . The clear solution was aged for 24 h at room temperature. It was then dried at 115 °C for 16 h and finally calcined at 700 °C for 12 h at the rate of 2 °C/min under the flow of air. The nature of the as synthesized calcined product was glassy crystalline.

2.3. Typical reaction procedure

The aldehyde (0.2 g, 1.0 equiv.) and active methylene compound (0.14 g, 1.1 equiv.) were taken in a 50 mL round bottom flask. Five millilitres solvent was added and stirred at room temperature. Then the catalyst (0.02 g) was added and stirring was continued under normal atmosphere till the starting materials were no longer present (by TLC technique). The reaction mixture was separated from the catalyst by centrifugation. After drying under vacuum, the crude product was purified by column chromatography using 60–120 mesh silica gel and appropriate mixture of ethyl acetate/hexane as eluent. The purified products were characterized by IR spectroscopy, ^1H NMR and ^{13}C NMR spectrometry and elemental analysis.

3. Results and discussion

3.1. Characterization of the catalysts

Mesoporous Ti-TUD-1 (Ti/Si mole ratio = 0.01, 0.03, 0.05, referred to as catalysts Ti-1-TUD-1, Ti-3-TUD-1, Ti-5-TUD-1, respectively) catalysts were prepared by non-hydrothermal sol–gel

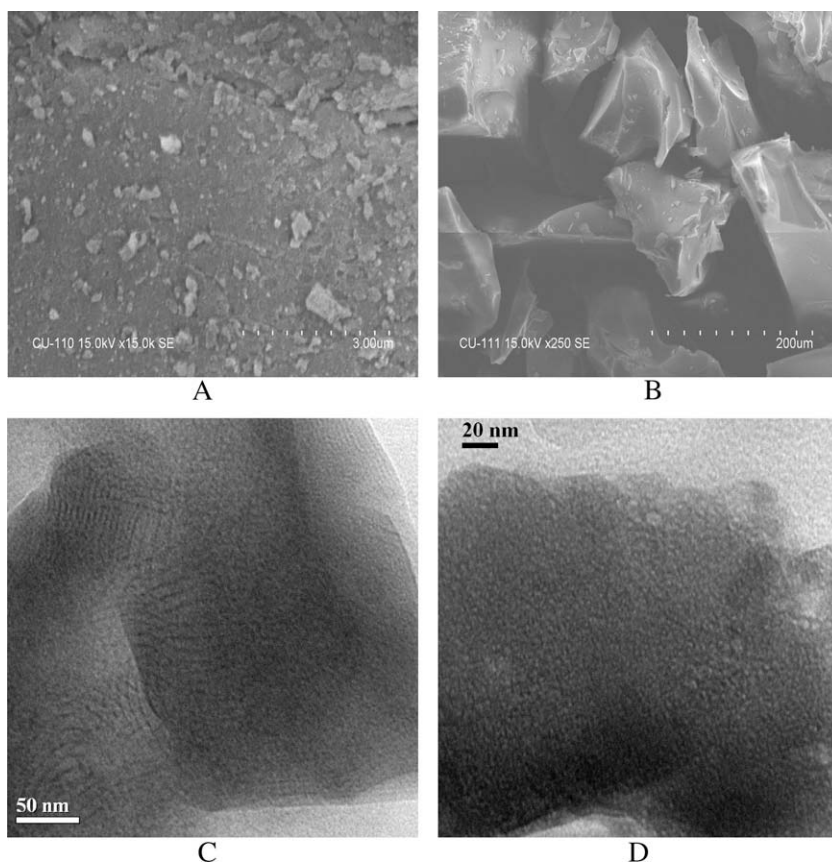


Fig. 1. SEM images of the surface morphology (A and B); TEM images of the lamellar channels (C) and porous surface (D) of the catalyst Ti-3-TUD-1.

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