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Short communication

Highly active InO_x/TUD-1 catalyst towards Baeyer–Villiger oxidation of cyclohexanone using molecular oxygen and benzaldehyde

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ABSTRACT

InOx/TUD-1 is prepared by sol–gel method and characterized by different techniques. On the basis of different characterization results it is found that spongy porous InOx/TUD-1 (In/Si = 8/100) matrix contains small crystallite of indium oxide in +3 oxidation state. InOx/TUD-1 (In/Si = 8/100) catalyst shows good catalytic results for Baeyer–Villiger oxidation of cyclic ketones using molecular oxygen and sacrificial reagent benzaldehyde. The cyclohexanone conversion was found 100% with ε-caprolactone selectivity 100% using polar aprotic solvents e.g. dichloroethane, acetonitrile and benzonitrile in the presence of molecular oxygen.

1. Introduction

Due to wide synthetic utility, Baeyer–Villiger oxidation has drawn much attention globally [1]. It is used to convert readily available ketones to esters or lactones. The studies involving heterogeneous catalytic Baeyer–Villiger oxidation of cyclic ketones using molecular oxygen and benzaldehyde are highly challenging [2–6]. Several works have been done to exploit the chemical property of one of the heterogeneous siliceous TUD-1 material by doping different metal atoms towards different reactions [7–11]. Indium is one of the post-transition metals having strong Lewis acidity in its most stable oxidation state +3 because these species possess a vacant low energy. It has been reported that indium shows high selectivity in catalytic reactions such as Friedel–Crafts alkylation, acylation, Wagner–Meerwein rearrangement, and Diels–Alder reactions [12–15].

Activation of molecular oxygen to perform aerobic oxidation reaction is always demanding from atom economic point of view. Recently, we have observed that indium oxide dispersed on TUD surface can perform styrene epoxidation reaction using molecular oxygen [16]. Being prompted by this result we have explored the catalytic activity of indium oxide dispersed on TUD-1 surface towards Baeyer–Villiger oxidation reaction using benzaldehyde as reductant and molecular oxygen as an oxidant. To the best of our knowledge, there exists no report on the use of InOx/TUD-1 mesoporous materials for the Baeyer–Villiger oxidation using molecular oxygen and sacrificial reagent benzaldehyde.

Herein, we have prepared indium oxide nanoparticle dispersed on TUD-1 matrix by sol–gel technique and carried out Baeyer–Villiger oxidation of cyclohexanone using benzaldehyde as reductant and molecular oxygen as an oxidant. The catalyst has been characterized by FESEM, HRTEM, ^{29}Si-NMR, XRD, elemental mapping, EDS, and CO_2-TPD. The catalytic activity was optimized with indium loading, reaction temperature, O_2 flow rate, solvent and longer time on stream (TOS). An interesting correlation between catalytic activity and catalyst characterization is obtained in this study.

2. Experimental

2.1. Catalyst preparation

The InOx/TUD-1 catalyst was prepared by conventional sol–gel technique as reported in literature [16]. Briefly for the catalyst preparation, tetraethyl orthosilicate, triethanolamine, aqueous solution of indium (III) nitrate hydrate and water were mixed to form a gel mixture which has molar ratios of TEOS:$In(NO_3)_3$:TEA:H_2O:TEAOH (1:0.08:2:11:1). The mixture was kept for about 24 h in stirring condition at room temperature. Then the prepared gel was kept in an oven at 100 °C for 16 h and afterwards the prepared material was calcined at 700 °C for 10 h in a muffle furnace with the heating rate of 2 °C/min. In-SBA-15 (In/Si = 8/100) was prepared by sol–gel method

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using indium nitrate metal precursor as reported in literature [17].The InOx/TUD-1 (In/Si = 8/100) was prepared by physical mixing method keeping InOx/TUD-1 weight ratio closer to the InOx/TUD-1 prepared by sol–gel method (Catalyst preparation S1). 1 wt.% indium doped on alumina and 1 wt.% indium doped on titania is prepared by impregnation method (Catalyst preparation S1).

2.2. Characterizations

High resolution transmission electron microscopy (HRTEM) image of the prepared catalysts was obtained on a JEOL JEM 2100 microscope operated at 200 kV acceleration voltage using lacey carbon coated Cu grid of 300 mesh size. Field emission scanning electron microscopy (FESEM), elemental mapping and electron dispersive X-ray (EDX) measurements were done by a supra 55 (Zeiss, Germany) microscope equipped with an oxford instrument X-max detector and a Gemini beam line attachment. X-ray powder diffraction (XRD) was performed by a Rigaku Ultima 4 diffractometer using Cu K_α radiation (wavelength, k = 1.54056 Å). The average crystallite sizes were estimated considering most intense diffraction peak (222) located at 2θ = 30.50° through Scherrer's formula D = 0.94 k/(βcosθ), where D was the average crystallite size, k was the X-ray wavelength, β was the peak width at half height, and θ Bragg's angle. UV visible measurement was carried out by using a Varian Cary 500 (Shimadzu) spectrophotometer. The spectra were recorded in the range of 200–800 nm wavelength. The temperature programmed CO_2-TPD profiles of the catalyst samples were performed by a ChemiSorb 2720 (Micrometrics, USA) equipped with a TCD detector. The CO_2-TPD profile was obtained by temperature programming under 5.2% CO_2 in He with a flow rate of 20 ml/min from ambient temperature to 1000 °C at a temperature ramp of 10 °C/min. The amounts of CO_2 desorbed in the TPD peak area was evaluated by pulses of CO_2 in a flow of He.

2.3. Baeyer–Villiger oxidation reaction

Selective oxidation of cyclohexanone was carried out with 2 mmol cyclohexanone (Acros), 6 mmol benzaldehyde (Merk), 10 ml Acetonitrile solvent (Merck) and 0.2 ml internal standard (dodecane) in a two neck 50 ml round bottle. The catalyst (0.05 g) was added to the reaction mixture followed by oxygen supply with a given rate under reflux condition. The reaction was carried for 4 h in a fixed temperature as required. The products were analyzed by gas chromatography (CIC-India) using SE-30 column. In the case of the recyclability test, after washing with acetonitrile and drying, the catalyst was used for a subsequent two cycle Baeyer–Villiger oxidation.

3. Results and discussion

3.1. Characterization results

From FESEM and HRTEM image the sponge like morphology was obtained for InOx/TUD-1 as evident in Fig. 1 (A) & (B). The indium oxide nanoparticles in InOx/TUD-1 were distributed on the TUD-1 surface as observed in HRTEM image. The ^{29}Si NMR spectra of the prepared catalysts were depicted in Fig. 1 (C). These spectra exhibited the Q lines [Q^n: $Si(OSi)_n(OH)_{4-n}$, n = 2–4] attributed to the TUD-1 silica support. In case of TUD-1 catalysts both Q^2, Q^3 and Q^4 bands were present but in case of InOx/TUD-1 (In/Si = 8/100) only Q^4 band ($\equiv SiO)_4Si$ was chiefly found. XRD result of InOx/TUD-1 (In/Si = 8/100) indicated the crystalline cubic indium oxide (JCPDS card reference no. 00-006-0416) having crystallite size in 15 nm range (Fig. 1 (D)). The appearance of absorption band in the region of 300 nm clearly indicates the presence of In_2O_3 nano-particles (Fig. S1). A blue-shift is observed compared to the absorption at 330 nm wavelength of bulk In_2O_3 species. This is due to the weak quantum confinement effect.

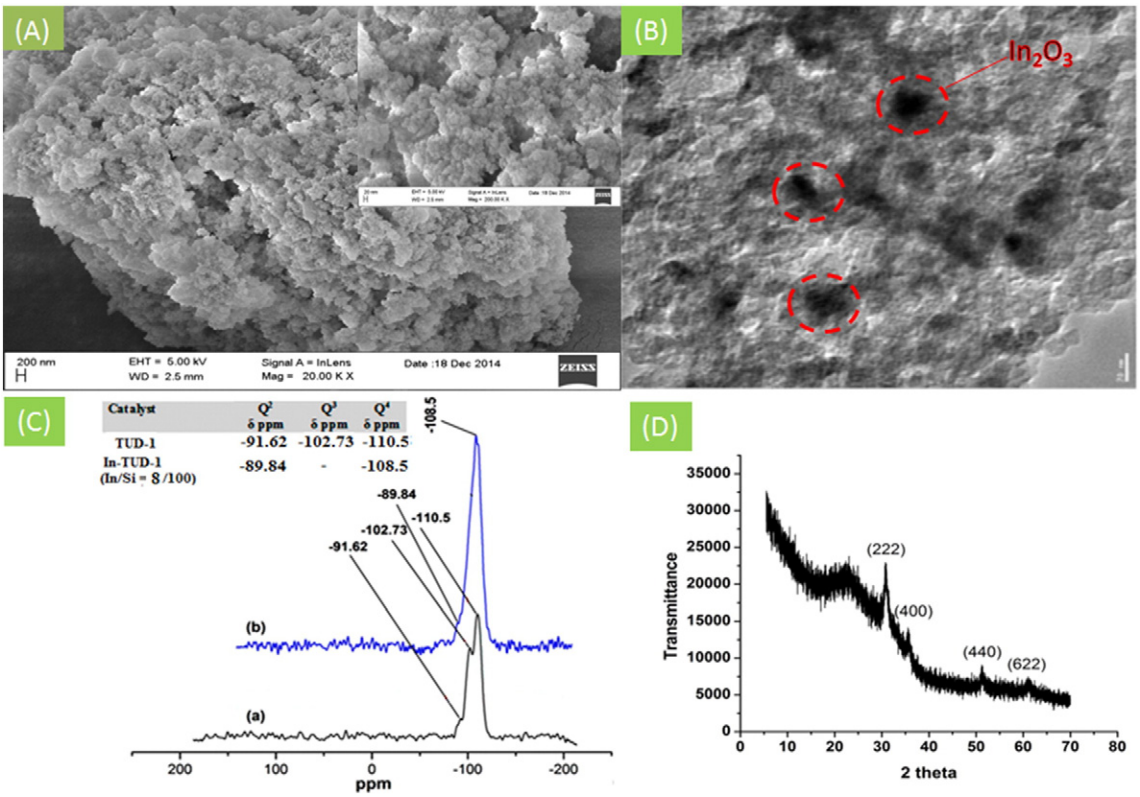

Fig. 1. (A) FESEM image of InO_x/TUD-1 (In/Si = 8/100) viewed at 200 nm and 20 nm (inset) (B) HRTEM image of InO_x/TUD-1 (In/Si = 8/100) (C) ^{29}Si NMR of (a) TUD-1, (b) InO_x/TUD-1 (In/Si = 8/100) and (D) XRD of InO_x/TUD-1 (In/Si = 8/100).