Catalysis Communications 59 (2015) 145–150

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Fabrication of $CuCr_2O_4$ spinel nanoparticles: A potential catalyst for the selective oxidation of cycloalkanes via activation of C_{sp3}–H bond

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ARTICLE INFO

Article history:
Received 11 August 2014
Received in revised form 22 September 2014
Accepted 17 October 2014
Available online 28 October 2014

Keywords:
$CuCr_2O_4$
Nanoparticles
Cycloalkanes
H_2O_2
Selective oxidation

ABSTRACT

We report here preparation of $CuCr_2O_4$ spinel nanoparticle catalyst, mediated by cationic surfactant CTAB in hydrothermal route. XRD revealed the formation of $CuCr_2O_4$ spinel phase and TEM showed the particle size of 30–60 nm. The catalyst was speculated to be highly active for selective oxidation of cyclohexane to cyclohexanone with H_2O_2. A cyclohexane conversion of 70% with 85% cyclohexanone selectivity was achieved over this catalyst at 50 °C temperature. Moreover, the catalyst did not show any significant activity loss even after 8 reuses and proved its efficacy in the oxidation of other cycloalkanes also.

1. Introduction

The selective transformation of inert C–H bonds of alkanes into useful functional groups is of much potential interest because alkanes are less expensive and more readily available than the current petrochemical feedstocks [1]. The catalytic hydroxylation of alkanes under mild conditions remains a major challenge in industrial and synthetic chemistry [2] because alkanes are relatively inert and the inertness arises from the constituent atoms of alkanes all being held together by strong and localized C–C and C–H bonds, so that the molecules have no empty orbitals of high energy that could readily participate in a chemical reaction. The oxidation of cyclohexane represents a typical example for this type of reactions which have become the theme of several researches these last years [3]. The oxidation of cyclohexane produces cyclohexanol and cyclohexanone (collectively called KA oil or "olone"), which are further used to produce adipic acid and caprolactum, which in turn are the starting materials for the synthesis of nylon-6 and nylon-66 polymers, respectively [4]. That means, selective oxidation of cyclohexane is the center-piece of the commercial production of Nylon. The conventional industrial process for C–H oxidation to a mixture of K and A, the so-called KA-oil (6×10 t/y), employs soluble cobalt or manganese salts as homogeneous catalysts under severe conditions (140–180 °C and 10–20 atm of air) and produces KA-oil with 75–80% selectivity, limiting the conversion to 5–7% in order to prevent overoxidation of the target products [5]. Apart from low conversion, this process also produces several byproducts, such as mono- and dicarboxylic acids, esters, and other oxygenated materials. This low conversion and selectivity, leaching of metal, and over-oxidation of products in the existing catalytic systems reinforce the need for new catalytic systems, including heterogeneous catalyst and clean oxidant [6]. Therefore, the selective oxidation of cyclohexane at mild condition with high energy efficiency has become a challenge to the researchers [6]. To overcome this problem, many researchers came forward and applied certain oxidants like H_2O_2 [7] TBHP [8] and molecular O_2 [9]. Although oxidation of cyclohexane with the greenest oxidant molecular oxygen has demonstrated important progress, these systems display shortages and their applications are limited; either H_2O_2 or TBHP and even NHPI was used as co-catalyst to accelerate the initiation step of the oxidation or a large amount of organic solvent was used. That is why, the technology with which cycloalkanes has been oxidized by O_2 to produce their corresponding oxygenates has not been improved well up to now. Therefore, a mammoth task in this field is to design the heterogeneous catalyst that affords the primary product with high selectivity at cost of high conversion of the hydrocarbon. Our previous report indicated that, Cu (II) nanoclusters supported on nanocrystalline Cr_2O_3 catalyst efficiently convert cyclohexane and furnish high yield of cyclohexanone [10]. But, the catalyst suffers severe leaching; therefore a catalyst that is devoid of leaching properties is highly demanding in case of liquid phase reactions, since the efficacy of a heterogeneous catalyst is evaluated in terms of its recyclability and stability. Very recently, we have accomplished an unprecedented and efficient oxidation of toluene over $CuCr_2O_4$ spinel nanoparticle catalyst using H_2O_2 in acetonitrile under normal atmosphere [11]. But the catalyst has not been well explored for the selective catalytic oxidations of other hydrocarbons by virtue of C^{sp3}–H activation, which is considered as a challenging topic in contemporary chemical research [12]. In this paper, we focus on the

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http://dx.doi.org/10.1016/j.catcom.2014.10.015
1566-7367/

preparation and characterization of recyclable $CuCr_2O_4$ spinel nanoparticles and its catalytic application on the oxidation of hydrocarbons especially the C5–C8 cycloalkanes and cycloalkanes containing benzylic C–H bonds following an environmentally benign oxidation protocol using H_2O_2 as oxidant. A cyclohexane conversion of 70% with 85% cyclohexanone selectivity was achieved over this catalyst at 50 °C temperature. The catalyst was proved to be highly efficient for the oxidation of other cycloalkanes as well.

2. Experimental

2.1. Preparation of the catalyst

The $CuCr_2O_4$ spinel nanoparticles were prepared hydrothermally by modifying our own preparation method taking nitrate precursors of copper and chromium [13]. All chemicals were used without further purification. All solvents used were of reagent grade. All syntheses were carried out under ambient conditions. In a typical synthesis procedure, an aqueous solution of 2.3 g $Cu(NO_3)_2 \cdot 3H_2O$ (from Sigma Aldrich) was added with vigorous stirring to 7.5 g $Cr(NO_3)_3 \cdot 9H_2O$ (from Sigma Aldrich) dissolved in 40 g deionized water to give a clear dark blue homogeneous solution. By gradual addition of a few drops of ammonia to the solution, the pH of the solution was made 8. An ethanolic solution (10%) of 2.6 g CTAB (from Sigma Aldrich) was added dropwise followed by the addition of 0.6 g hydrazine (from Sigma Aldrich) to the reaction mixture. The reagents were added maintaining the molar ratio of Cu:Cr:CTAB:H_2O:hydrazine = 1:2:0.75:250:1. After stirring, the so obtained homogeneous solution was hydrothermally treated at 180 °C for 24 h in a Teflon-lined autoclave vessel under autogeneous pressure. The solid product was collected by means of centrifugation at 18,000 rpm and dried at 120 °C, for 10 h, followed by calcination at 750 °C for 6 h in air (ramped at 1 °C/min) to get $CuCr_2O_4$ spinel nanoparticles.

2.2. Catalyst characterization techniques

Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_α radiation source using Cu Ka radiation with a wavelength of 1.5418 Å. Diffraction patterns in the 2°−80°region were recorded at a rate of 0.5° (2θ) per minute. The resulting XRD profiles were analyzed to identify the crystal phase of the compound using reference standards. The line width of the most intense XRD peak was taken for estimation of crystallite size by the Scherrer equation. Scanning electron microscopy images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB_6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer. Samples were subjected to scanning electron microscope analysis to understand the shape, size, and morphology properties. The particle size and distribution of the samples were analyzed by TEM, JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. X-ray photoelectron spectra were recorded on a Thermo Scientific K-alpha X-ray photoelectron spectrometer and binding energies (±0.1 eV) were determined. The resulting spectra were analyzed to identify the different oxidation states of the copper and chromium ions present in the sample. Prior to the analysis, the spectra were calibrated with reference to C1s observed at a binding energy of 284.5 eV. Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer; model: PS 3000 uv, (DRE), Leeman Labs, Inc., (USA). Thermogravimetric Analyses (TGA) of the uncalcined catalyst were carried out in a Pyris Diamond, Perkin Elmer Instruments, and Technolohy by SII [(Seiko Instruments INC), USA] instrument-balance by heating 2.15 mg samples at 5 °C min^{-1} in flowing air atmosphere. Fourier transform infra-red (FTIR) spectra were recorded on a Thermo Nicolet 8700 (USA) instrument with the operating conditions: resolution: 4 cm^{-1}, scan: 36, operating temperature: 23–25 °C and the frequency range: 4000–400 cm^{-1}. Spectra in the lattice vibrations range were recorded for wafers of sample mixed with KBr.

2.3. Liquid phase hydroxylation

Liquid phase oxidation reaction was carried out in a two neck round bottom flask, equipped with refrigerant, containing 0.05 g catalyst, 10 ml solvent and 1 g cyclohexane to which H_2O_2 (50% aq. solution) was added dropwise to prevent immediate H_2O_2 decomposition. The flask was then emerged in a preheated oil bath and vigorously stirred with a magnetic stirrer. The reaction temperature was ranged between RT and 100 °C. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis using a syringe. At the end of the reaction, the solid particles (catalyst) were separated by filtration and the products were analzed by Gas Chromatograph (GC, Agilent 7890) connected with a HP5 capillary column (30 m length, 0.28 mm id, 0.25 μm film thickness) and flame ionization detector (FID). Chem Station software was used to collect and analyze the respective GC-data. The relative error of product determination did not exceed ±5%. The cyclohexane conversion and cyclohexanone formation were calculated using a calibration curve (obtained by manual injecting the authentic standard compounds). An anisole solution with a known amount was used as an external standard for analysis. The individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting the authentic standard samples in GC and GC–MS. The C-balance as well as material balance was carried out for most of the experiments. For the reusability test, the catalyst was repeatedly washed with acetonitrile and acetone and dried overnight at 110 °C and used as such, without regeneration. In order to check the metal leaching the mother liquor was then analyzed using ICP-AES.

3. Material balance

We have performed the C-balance for the most of the experiments and have also done the material balance for few experiments. The estimated error in analysis arising due to sampling and handling losses was ±5%.

4. Results and discussion

4.1. Catalyst characterization

The crystalline phase, degree of crystallinity and phase purity were determined by X-ray diffraction (XRD). The X-ray diffraction patterns of the Cu–Cr catalyst (presented in Fig. 1a) showed the typical diffraction lines of the bulk, single phased $CuCr_2O_4$ spinel (JCPDS. 05-0657). No impurity phase such as $CuCrO_2$ and not even cubic or monoclinic $CuCr_2O_4$ was found. The particle size was determined from the full width half maxima of the line broadening corresponding to the diffraction angle of 35.16° by using Scherrer equation and a mean particle size of 38 nm was observed. XRD diffractogram (Fig. 1b) also predicts that, the catalyst retains its spinel phase even after 8 recycles. The $CuCr_2O_4$ spinel nanoparticle catalyst, prepared hydrothermally in the presence of cetyltrimethylammonium bromide (CTAB) surfactant showed a single-phase morphology reflecting an assembly effect of the surfactant as imaged by SEM (Fig. 2a) and it showed the formation of almost homogeneously distributed uniform particles with a size ~35 nm. From SEM-EDAX image, it can be seen that the sample contains only Cu, Cr and O (Fig. 2b). The embedment of the surfactant molecules (CTAB) on the on the uncalcined sample and the generation of stable