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Catalytic conversion of substituted and un-substituted cyclohexanone into corresponding enones and phenols by nanocatalysts under acid or base-free reaction conditions

Mazloom Shah [a,b,*], Fan Zhang [a,c], Ashfaq Ahmad [b]

[a] Key Laboratory of Tropical Plant Resources and Sustainable Use, Biomass Group, Xishuangbanna Tropical Botanical Garden Chinese Academy of Science, Kunming 650223, PR China
[b] Department of Chemistry, Women University of Azad Jammu and Kashmir, Bagh 12500, Pakistan
[c] University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

The catalytic conversion of substituted and unsubstituted cyclohexanones to the corresponding enones and aromatic alcohol catalyzed by Pd, Pd-1, Pd-cube, Cu, Ni, Ag@Pd and Ni-Sn nanocatalysts has been studied in the presence of O_2 as the oxidant without using any additives i.e. acid or base or ligand. The optimization of experimental parameters for dehydrogenation of cyclohexanones was established to achieve maximum yield of the product by using Pd nanocatalyst. The conversion of cyclohexanone, cyclohexenone, 3-methyl cyclohexanone and 3-methyl cyclohexenone catalyzed by Pd nanocatalyst at 80 °C, 10 atm O_2 pressure after 24 h, led to a 79%, 49%, 62% and 25% yields of desired products, respectively. Then, the conversion of substituted and unsubstituted cyclohexanones investigated in the presence of various nanocatalysts i.e., Pd-1, Pd-cube, Cu, Ni, Ag@Pd and Ni-Sn nanoparticles and was compared their percentage yields.

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1. Introduction

The conversion of cyclic ketones into corresponding aromatic alcohol is a fundamental reaction in organic chemistry. Phenols and its derivatives are versatile synthetic intermediates due to their application in the preparation of polymers, pharmaceuticals, dyes and bulk chemicals [1]. In this regard, a variety of methods and catalyst system have been well documented for the catalytic dehydrogenative aromatization of ketones to aromatic alcohol, however, these protocols use undesirable stoichiometric reagents such as DDQ (2,3-dichloro-5,6-dicyano-1,4- benzoquinone), use stepwise procedures such as bromination/dehydrobromination, low product yields, require harsh reaction conditions, limited access to starting materials, and formation of isomeric products [2–16]. The dehydrogenation of cyclic ketone affords corresponding cyclic-enone or aromatic alcohol via removal of 1 or 2 equivalent of H_2, respectively. Hirao et al. represented oxidative aromatization of a variety of substituted cyclohexenones catalyzed by NH_4VO_3 or $VOSO_4$ with Bu_4NBr/HBr and trifluoroacetic acid (TFA) as additives [5]. Recently, the group of Stahl reported a Pd- based homogeneous catalyst system using O_2 as the terminal oxidant for the dehydrogenative aromatization of substituted cyclohexanones in the presence of *p*-toluenesulfonic acid and 2-(*N*,*N*-dimethylamino)pyridine. More recently, a thorough investigation of the Pd $(TFA)_2$/2-Me_2Npy-catalyzed dehydrogenation of cyclohexanones and cyclohexenones, showing that an initial, highly active molecular Pd (II) species generate soluble Pd nanoparticles that serve as the active catalyst during steady-state dehydrogenation of the substrate [17–19]. In contrast, no effective heterogeneous catalytic method for aromatization of substituted and unsustituted cyclic ketones exist. The advantage of a heterogeneous catalyst lies in its easy separation from the reaction mixture by simple filtration and possibility to be recycled several times.

Here we report the conversion of cyclohexanone to the corresponding cyclohexenone and phenol catalyzed by Pd, Pd-1, Pd-cube, Cu, Ni, Ag@Pd and Ni-Sn nanocatalyst in the presence of O_2 as the oxidant without using any additives i.e. ligand or acid or base. The effect of various parameters such as catalyst concentration, solvent, temperature, O_2 pressure and reaction time on catalytic conversion of cyclohexanone to the cyclohexenone and phenol has also been investigated. Furthermore, Pd nanocatalyst was

* Corresponding author at: Department of Chemistry, Women University of Azad Jammu and Kashmir, Bagh 12500, Pakistan.
E-mail address: shahmazloom@yahoo.com (M. Shah).

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tested for conversion of cyclohexenone, 3-methyl cyclohexanone and 3-methyl cyclohexenone at optimized reaction conditions for cyclohexanone.

2. Experimental

2.1. Materials

L-ascorbic acid ($C_6H_8O_6$), palladium acetate (Pd $(CH_3COO)_2$), potassium bromide (KBr), sodium borohydride ($NaBH_4$), ethylene glycol ($HOCH_2CH_2OH$), polyvinylpyrrolidone with an average molecular weight of 10,000 (PVP), acetone (CH_3COCH_3), ethanol (C_2H_5OH), cyclohexanone ($C_6H_{10}O$), cyclohexenone (C_6H_8O), 3-methylphenol ($CH_3C_6H_4(OH)$), toluene ($C_6H_5CH_3$), ethyl acetate ($CH_3COC_2H_5$), acetic acid (CH_3COOH), dimethylformamide ($(CH_3)_2NC(O)H$), dimethylacetamide ($CH_3C(O)N(CH_3)_2$), 1-methyl-2-pyrrolidinone (C_5H_9NO) were purchased from Sinopherm chemical reagent Co. Ltd., palladium nitrate hydrate ($Pd(NO_3)_2{\cdot}2H_2O$) from Aladdin, Sodium tetrachloropalladate ($Na_2PdCl_4{\cdot}nH_2O$) from Shanxi kaida chemical engineering Co. Ltd., Sodium sulfate (Na_2SO_4) from Shanghai rich joint chemical reagent Co. Ltd., 3-methyl cyclohexanone ($CH_3C_6H_9O$) from Tokyo chemical industry Co. Ltd., copper acetate monohydrate (Cu $(CH_3COO)_2{\cdot}H_2O$) from Shanghai chemical reagent company, *p*-anisaldehyde from Aladdin chemistry Co. Ltd., 3-methyl cyclohexenone ($CH_3C_6H_7O$) from Energy chemical and silver nitrate ($AgNO_3$) and nickel (II) formate dihydrate (Ni $(HCOO)_2{\cdot}2H_2O$) from Alfa Aesar.

2.2. Nanocatalysts preparation

2.2.1. Pd, pd-1 and Ag@Pd coreshell nanoparticles preparation

Pd (Pd-PVP), Pd-1 (Pd-olylamine) and Ag@Pd coreshell nanoparticles were prepared per guidelines reported previously [20,21]. For Pd-1 nanoparticles preparation, 0.424 g oleic acid and 0.401 g oleylamine were put in 50 ml ethylene glycol. Next, metal-precursor solutions, 0.5 mmol Pd $(CH_3COO)_2$ in acetone was added. The reaction mixture was heated at 393 K for 30 min under vigorous stirring. Subsequently, the temperature was raised to 473 K and kept at reflux for 60 min. The nanoparticles were separated from the mixture through extraction with *n*-hexane.

2.2.2. Pd-cube nanoparticles preparation

In case of Pd-cube nanoparticles [22], calculated amount of poly (vinyl pyrrolidone) (PVP), L-ascorbic acid (60 mg), KBr (300 mg) and Na_2PdCl_4 (57 mg) were dissolved in 11 ml of water. The resulting solution was heated at 353 K in air under magnetic stirring for 3 h and then cooled to room temperature. Nanoparticles were collected by centrifugation and then washed four times with a water-acetone mixture.

2.2.3. Ni, Cu and Ni-Sn nanoparticles preparation

For preparation of Ni nanoparticle 0.24 g Ni $(HCOO)_2{\cdot}2H_2O$ and calculated amount of PVP were dissolved in 35 ml of ethylene glycol and the solution was heated to 342 K while stirring until the formation of a completely homogeneous blue solution. Once at this temperature, 0.15 g of $NaBH_4$ was added under magnetic stirring. The resultant solution was refluxed at 468 K for 2.5 h [23]. In case of Cu nanoparticle preparation calculated amount of Cu $(CH_3COO)_2{\cdot}H_2O$ and PVP were added in 70 ml of ethylene glycol and the solution was heated to 323 K while stirring until the formation of a completely homogeneous solution. Once at this temperature, 0.34 g of $NaBH_4$ was added under magnetic stirring. The resultant solution was refluxed at 463 K for 2.5 h. In case of Ni-Sn nanoparticle preparation calculated amount of Ni $(HCOO)_2{\cdot}2H_2O$, $SnCl_2{\cdot}2H_2O$ and PVP were added in 35 ml of ethylene glycol and the solution was heated to 323 K while stirring until the formation of a completely homogeneous blue solution. At 323 K, 0.18 g of $NaBH_4$ added under magnetic stirring and resultant solution was refluxed at 471 K for 2.5 h. The nanoparticles were precipitated in acetone, washed with acetone, ethanol and dried in air at room temperature.

2.3. Catalytic reaction of substituted and un-substituted cyclohexanones

In catalytic reaction, catalyst (2.8–5.1 mol%), cyclohexanones (0.5 mmol), DMSO (0.5 ml) and stir bar were added to a 10 ml schlenk tube. O_2 was bubbled through the solution for 10 min at room temperature. The reaction was heated in an oil bath to 80 °C with vigorous stirring under a balloon of O_2 for given time. After the completion of the reaction, the reaction mixture was filtered.

In case of using high pressure reactor, catalyst (2.8–5.1 mol%), the substituted or un-substituted cyclohexanones (0.5 mmol) and DMSO (1 ml) were placed in a reactor. After purging the pressure reactor with O_2, the reactor was loaded with given O_2 pressure (25 °C). The reaction was heated to 80 °C with vigorous stirring for given time. After the completion of the reaction, the reaction mixture was filtered. Then, the residue was extracted with ethyl acetate. The products were identified with GC–MS and quantified by GC analysis.

2.4. Instrumentation

The crystalline nature of the materials prepared was determined by X-Ray Diffraction (XRD) using a Rigaku TTR-III diffractometer operated at 200 mA and 40 kV with a monochromated Cu Kα radiation (λ = 1.541 Å) – step size = 0.02, time per step = 10 or 20 s/step, the scan rate was 8 °/min. The average crystallite size of nanoparticle was calculated from XRD using Scherrer equation: $L = K\lambda/\beta\cos\theta$, where L is the average crystallite size, K is the Scherrer constant related to the shape and index (*hkl*) of the crystals, λ is the wavelength (0.15406 nm) of the X-rays, β is the additional broadening (in radians) and θ is the Bragg angle, respectively. SEM studies were performed on a JSM-6700F scanning electron microscope. TEM analyses were performed on a JEM-2011 transmission electron microscope operating at 200 kV. The microstructure and chemical composition of the bimetallic nanoparticles were analyzed by using a High-resolution transmission electron microscope (HR-TEM) (JEM-2010) which was operated at the accelerating voltage of 300 keV, equipped with EDS. GC–MS analyses were performed by using a Thermo Finnigan Trace GC coupled to MS IS2 MSD. Gas chromatographic analysis of reactions was conducted with a Shimadzu GC-17A gas chromatograph with a DB-Wax column.

3. Result and discussion

3.1. Nano-catalysts characterization

The synthesis conditions used for the preparation of metallic Pd, Pd-1, Pd cube, Cu and Ni nanoparticles and bimetallic Ag@Pd, and Ni-Sn nanoparticles are summarized in Table 1. Nanoparticles were evaluated by powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). SEM, TEM and EDX were used to analyze morphology and elemental composition of nanoparticles while Nanoparticles crystal phases were identified by XRD. XRD patterns of Pd before and after reaction, Pd-1, Cu, Pd-cube, Ni, Ni-Sn and Ag@Pd nanoparticles are shown in Fig. 1(d) and Fig. 3(c). Four diffraction peaks at 2θ = 39.21, 45.87, 68.11 and 82.07° correspond to the (111), (200), (220) and (311) crystal planes of metallic Pd [24,25], confirming the formation of Pd nanoparticles. The diffraction peaks in XRD pattern of Ag@Pd nanoparticles

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