Promotion effects of alkali- and alkaline earth metals on catalytic activity of mesoporous Co$_3$O$_4$ for 4-nitrophenol reduction

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A B S T R A C T

Mesoporous cobalt oxides doped with alkali (Li, Na, K, Cs) and alkaline earth (Mg, Ca) metals were synthesized and evaluated for their catalytic activity in the reduction of 4-nitrophenol. The prepared materials were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), Brunauer–Emmet–Teller (BET) and hydrogen temperature programmed reduction (H$_2$-TPR) analyses. The characterization techniques used showed the materials to consist of mono-dispersed nanoparticle aggregates with connected, well defined intra-particle voids and the crystalline phase of the cobalt oxide to be cubic Co$_3$O$_4$, while the pore diameters ranged from 12.1 to 19.2 nm depending on the metal ion dopant. The reduction of 4-nitrophenol was chosen as a well-controlled model reaction allowing us to determine the catalytic activity as a function of alkali or alkaline earth dopant. Calcium doped cobalt oxide was found to be the most catalytically active with an apparent rate constant of 3.76×10^{-3} s^{-1} and the order with respect to dopant was Ca > Cs > Mg > Li > K > Na. From characterization of the catalysts by SEM, TEM and H$_2$-TPR promotion effects of the dopants were found to be due to electronic changes in the catalysts as a result of doping rather than structural changes. The kinetics of the most active calcium doped catalyst was modeled in terms of Langmuir–Hinshelwood kinetics. The Langmuir–Hinshelwood surface rate constant for Ca-doped Co$_3$O$_4$ was 5.47×10^{-5} mol m^{-2} s^{-1} compared to the undoped Co$_3$O$_4$ at 5.33×10^{-6} mol m^{-2} s^{-1}. Activation energies were calculated to be 51.3 kJ mol^{-1} and 50.7 kJ mol^{-1} for undoped and Ca-doped Co$_3$O$_4$.

1. Introduction

Mesoporous metal oxides (MMOs) [1,2] have received immense attention in catalysis due to them having multiple oxidation states as compared to the conventional mesoporous silica and aluminosilicates [3–6]. Mesoporous cobalt oxides are extensively used in a wide range of catalytic applications as cobalt is both relatively less expensive compared to noble metals and offers catalytic activity comparable to the noble metals [7,8]. In order to improve the catalytic properties of the MMOs, dopants and promoters are often incorporated into the materials [9–12].

Alkali and alkaline earth promoted cobalt oxides have been reported to have improved catalytic activity towards various reactions including the decomposition of NO$_x$ species [13–16] and various redox reactions [9,17,18]. The mechanism of alkali and alkaline earth promotion has been proposed to be due to the metal dopants being structural [19] or electronic promoters [13,20–22] in the various catalytic properties. In their research on N$_2$O decomposition using alkali and alkaline earth doped catalysts, Xue et al. [13] found that the catalytic activity was greatly increased and that the promotion effect was in the order Li < Na < K < Rb < Cs < Mg < Ca < Sr, Ba. The promotion effect of alkali and alkaline earth metals on the catalytic reduction of 4-nitrophenol using mesoporous cobalt oxide was investigated in this study. Nitro-aromatic compounds are toxic organic species which are produced as by-products in the pharmaceutical, agrochemical, urethane, textile and dye chemical industries [23,24]. There is always, therefore, a need to develop economic and green catalysts for the remediation of sources contaminated with these toxic organic compounds by reducing them to the less toxic amines. Precious metals such as gold, palladium, platinum and ruthenium have been used extensively as catalysts [25–28] for this reduction. Since precious metals are expensive, there is a need to replace them with non-precious metals such as cobalt.

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Mesoporous cobalt oxides were catalytically active in the reduction of 4-nitrophenol, with the activity dependent on the morphology of the catalysts [29]. Literature reports by Sahiner et al. [24] and by Mandlimath et al. [30] have also shown that cobalt oxides are catalytically active in the reduction of 4-nitrophenol. In this work doping cobalt oxide with alkali and alkaline earth metals enhances the catalytic activity in the 4-nitrophenol reduction when compared to the undoped cobalt oxide. Furthermore, the catalytic activity of the calcium-doped catalysts on the reduction of 4-nitrophenol by borohydride in aqueous solution, proceeds via a Langmuir–Hinshelwood (L–H) model [31–33]. We present a full kinetic analysis of the heterogeneous-catalyzed reduction of 4-nitrophenol with sodium borohydride using calcium doped mesoporous cobalt oxide catalysts. There is no reported detailed kinetic analysis of the reduction of 4-nitrophenol using alkali and alkaline earth doped mesoporous cobalt oxide catalysts.

2. Experimental

2.1. Materials

All chemicals used were reagent-grade and used as received. Cobalt(II) nitrate hexahydrate ($\geq 98\%$) [$Co(NO_3)_2 \cdot 6H_2O$], 1-butanol, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO20-PPO70-PEO20 or Pluronic P123, av. $M_n = 5800$), sodium borohydride ($NaBH_4$, $\geq 96.0\%$), 4-nitrophenol ($\geq 99.5\%$), $LiNO_3$ ($\geq 99.0\%$), $NaNO_3$ ($\geq 99.0\%$), KNO_3 ($\geq 99.0\%$), $Mg(NO_3)_2 \cdot 6H_2O$ ($\geq 99.0\%$) and $Ca(NO_3)_2 \cdot 4H_2O$ ($\geq 99.0\%$) were all purchased from Sigma-Aldrich. Concentrated nitric acid (68–70% HNO_3) was purchased from Rochelle Chemicals (RSA).

2.2. Synthesis of alkali- and alkaline earth-doped mesoporous cobalt oxides

To synthesize alkali- and alkaline earth-doped mesoporous cobalt oxides a method adapted from the literature was used [34]. In short, $Co(NO_3)_2 \cdot 6H_2O$ (10 g, 0.035 mol) was dissolved in a solution containing P123 (5.0 g, 8.62×10^{-4} mol) and HNO_3 (4.8 g, 0.076 mol) in 1-butanol (34 g, 0.66 mol). An appropriate amount of XNO_3 (X = Li, Na, K) or $X(NO_3)_2$ (X = Mg, Ca) was added to give 2% (mol/mol) of each dopant. The red solution was stirred and then placed in an oven at 50 °C for 12 h to remove the solvent. The formed gel was then placed in an oven at 120 °C for 3.5 h. The obtained powder was washed with ethanol several times, and dried in a vacuum oven. The resulting red powder was calcined at 150 °C for 12 h with a heating rate of 1 °C/min. All heating cycles were performed in air.

2.3. Characterization

Powder X-ray diffraction analyses were performed on a Rigaku Miniflex-600 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) at room temperature. Both low angle ($2\theta = 0.5-8°$) and wide angle ($2\theta = 10-90°$) diffraction patterns were measured. Nitrogen sorption measurements were performed on a Micromeritics Tristar 3000 sorption system. The samples were degassed at 90 °C for 18 h prior to the experiments. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were obtained by the Barrett–Joyner–Haleda (BJH) method from the desorption branch of the isotherms. Scanning Electron Microscopy (SEM) images were taken on a Tescan Vega 3LMH scanning electron microscope with the samples carbon-coated on copper grids using an Agar Turbo Carbon Coater. High resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100F electron microscope with an accelerating voltage of 200 kV. Temperature programmed analyses were conducted on a Micromeritics Autochem II. About 30 mg of material was packed

in a quartz tube reactor. The loaded samples were pretreated in an inert gas flow (Ar) at 200 °C for 1 h to clean the catalyst surface before each test. In H_2-TPR measurements, 10% H_2/Ar was passed through the catalyst bed at a flow rate of 50 ml min^{-1} while the temperature was ramped from 30 °C to 500 °C with a heating ramp rate of 10 °C min^{-1}. XPS data were acquired at room temperature with a SPECS Phoibos 150 electron energy analyser, using a monochromated Al Kα photon source ($h\nu = 1486.71$ eV). The overall energy resolution was set to 0.5 eV for all the spectra. The binding energy was calibrated with respect to the main peak in the C 1s core level (284.6 eV). To counteract the effect of surface charging, samples were irradiated with a low energy electron flood gun during measurements (electron energy: 3 eV).

2.4. Catalytic activity

The kinetic evaluation was performed by detecting the extinction of 4-nitrophenol (4-NP) via UV–vis spectrophotometry using a Shimadzu UV1800 equipped with a CPS-240A Cell Positioner and CPS-Controller for temperature regulation. Stock solutions of 4-NP (1000 μM) and $NaBH_4$ (1.0 M) were first prepared. Initial spectrophotometric scans were performed using the full spectrum range of λ 200–800 nm with readings taken every three minutes, in quartz cuvettes. Subsequently all kinetic measurements were performed in disposable polystyrene cuvettes. In a typical run, the appropriate amount of 4-NP and catalysts was mixed in a 50 ml jacketed flask and the volume made to 25 ml with deionized water. The mixture was then degassed by bubbling with nitrogen for 30 mins. The jacketed flask was then connected to a pre-heated water bath at the desired temperature. Then a 100 fold excess of $NaBH_4$ was added to start the reaction and aliquots of 3 ml were taken at 3 min intervals, filtered and the UV–vis spectrum taken. For the kinetic runs to obtain L–H parameters, two sets of experiments were performed at 25 °C with a constant catalyst amount. The first data set was obtained for a constant $NaBH_4$ concentration while varying the concentration of 4-NP. The second set, k_{app} values were obtained for a run were the concentration of $NaBH_4$ was varied while keeping 4-NP concentration constant. For thermodynamic analysis, the temperature of the water bath was varied from 20 to 35 °C. From the raw experimental data, k_{app} values were determined using the Kinetic Studio software [35] while the L–H fitting of the data was performed using the Origin Pro 8.5 graphing and modeling software [36].

3. Results and discussion

3.1. Synthesis and characterization of mesoporous doped Co_3O_4 catalysts

Mesoporous cobalt oxides doped with alkali (Li, Na, K and Cs) and with alkaline earth (Mg and Ca) metals were synthesized using a method reported in the literature [37]. Powder X-ray diffraction (*p*-XRD) patterns are shown in Fig. 1 (a) for the undoped as well as alkali and alkaline earth metal ion-doped mesoporous cobalt oxide materials. From the *p*-XRD analysis with the Match™ Software, all the materials showed a typical spinel Co_3O_4 pattern (JCPDS 090418) with a cubic crystal system. Crystallite sizes of the materials estimated from *p*-XRD analysis showed an insignificant change upon doping with all the metals, an observation that could be explained by the fact that only a small amount of dopant (2%) was added. From N_2 sorption analysis all doped materials maintained the characteristic Type IV adsorption isotherms, with a Type I hysteresis loop typical of a regular ordered mesoporous structure (Fig. 1b). Doping of the cobalt oxide with the different metal ions resulted in a decrease in the surface area of the materials as summarized