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Hydrogenolysis of sorbitol over Ni supported on Ca- and Ca(Sr)-hydroxyapatites

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ABSTRACT

Ca-hydroxyapatite (HAP) was synthesized with different morphologies, in needle (N), sphere (S) and rod (R) shapes. A partially Sr-substituted sample (Ca(Sr)-hydroxyapatite) with the stoichiometric composition of $Sr_{0.6}Ca_{9.4}(PO_4)_6(OH)_2$, and possessing a rod shaped morphology was also hydrothermally synthesized (SrHAP-R). The samples were characterized by X-ray diffraction, Fourier-Transform infra-red spectroscopy (FT-IR), scanning and transmission electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS) and surface area measurement. Nickel (6 wt%) was loaded on the samples by an impregnation method. Rod-shaped hydroxyapatite (HAP-R) was more crystalline than the others. FT-IR results showed characteristic bands for $(PO_4)^{3-}$ and O—H vibrations. XPS results indicated Ni to be in the 2+ state, and O 1s satellite features revealed a phosphoric oxide environment in all the samples. The catalytic activities of the Ni-containing samples were tested in the hydrogenolysis of sorbitol into ethylene and propylene glycols in an aqueous medium in a stirred high pressure reactor at different process conditions. The most active catalyst was Ni/SrHAP-R. The catalyst was reusable many times with only a minor activity loss.

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Introduction

Ca-hydroxyapatite (HAP; $Ca_{10}(PO_4)_6(OH)_2$) is an important member of the apatite family and has been investigated extensively for applications in medicine due to its similarity to the mineral component of bones and teeth enamel and its good biocompatibility [1]. It has also been investigated for use in diverse applications as catalyst [2–5] and catalyst support [2,4,6,7], as sensor [8], in pollution-control [9,10] and in drug delivery [11]. A variety of techniques have been reported for the synthesis of HAP to obtain samples with desired particle size, morphology, porosity and substituents [12–21]. Moreover, the Ca^{2+} cations of HAP can be substituted with Zn, Mg, Sr, La, Cd, Pb, Cu, and Fe ions.The substitution of ions into pure HAP alters the crystal structure to a degree, and causes changes in some of its properties, including thermal stability, phase stability, solubility and surface reactivity [22]. Sr is quantitatively incorporated into HAP where its substitution for Ca leads to a linear increase in the lattice constants due to the greater ionic radius of Sr. Sr-substituted HAP (Ca(Sr)-hydroxyapatites) has also been reported to exhibit good thermal stability at high temperatures between 600 and 900 °C [23].

Though petroleum derived hydrocarbons are presently the raw materials for a vast majority of industrial chemicals, biomass derived oxygenate intermediates are expected to replace these in the future for sustainability reasons [24,25]. To achieve the goal of transforming biomass into chemicals, suitable catalysts and processes will need to be developed. One route for the transformation of lignocellulosic biomass into chemicals involves the separation of cellulose, its break-down into intermediate platform chemicals like glucose and sorbitol, and their conversion into bulk chemicals like the widely used ethylene and propylene glycols.

Many studies on the transformation of sorbitol into ethylene glycol (EG), propanediol (PD) and glycerol (G) have been reported over the years [26–35]. We had earlier reported studies on Ni, Pt and Ru supported on NaY, and Ni supported on fly ash [36–38]. Our studies have been directed towards the production of ethylene and propylene glycols. An examination of the literature reveals that different supported metal catalysts have been used in the hydrogenolysis of polyhydric alcohols, Ni and Ru being the most preferred metals, and SiO_2, carbon, Al_2O_3 and MgO being the supports [26,30,31,32–34]. The reaction has also been found to proceed better in the presence of a basic promoter like an alkaline earth hydroxide, especially $Ca(OH)_2$ [27,30,35–39].

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We are now presenting our studies on the synthesis of Ca-HAP with different morphologies and a partially Sr-substituted HAP (SrHAP-R), and their use as supports in Ni catalysts useful for the hydrogenolysis of sorbitol into glycols. The use of HAP as support has been prompted by the reasons that it is stable in aqueous medium, and being a basic material is less likely to cause the formation of hydrocarbons as has been reported in the case of acidic supports [40]. Three Ni/HAP samples, containing 6 wt% Ni, were prepared using HAP with different morphologies, needle (HAP-N), spheroid (HAP-S) and rod (HAP-R).Ni (6 wt%) was also loaded on the Sr-substituted HAP-R (Ni/SrHAP-R).The HAP samples were prepared by different methods [2,3,16] and were well characterized by physicochemical techniques. The Ni/HAP catalysts were tested in the hydrogenolysis of sorbitol into glycols in an aqueous medium. The reusability of the most active catalyst (Ni/SrHAP-R) was examined.

Experimental

Catalyst preparation

HAP of three different shapes were synthesized following published procedures [2,3,16]. The Ca:P mole ratio was maintained at the stoichiometric value of 1.67 in all sample preparations. The synthesis conditions are summarized in Table 1. The Ca/P ratios of the synthesized samples were 1.60–1.62 (Table 2). A partially Sr substituted sample (**SrHAP-R**) with a nominal composition of $Sr_{0.6}Ca_{9.4}(PO_4)_6(OH)_2$ was also prepared by the precipitation method using a mixed solution of $Sr(NO_3)_2$ and $Ca(NO_3)_2$. Nickel (6 wt%) was loaded on the calcined (600 °C, 1 h) HAP and SrHAP-R samples by incipient wet impregnation using a solution of $Ni(NO_3)_2{\cdot}6H_2O$ containing the required amount of the metal. A loading of 6 wt% Ni was found to be most suitable based on studies using Sr-HAP-R (Table S1) and earlier studies [36–38]. The $Ni(NO_3)_2$ loaded samples were dried at 110 °C for 12 h, and then calcined at 450 °C (4 h). Finally, the catalysts were reduced at 400 °C for 4 h prior to use. X-ray fluorescence spectroscopic analysis of the final samples gave a Ni loading of 5.6 ± 0.2 wt% for the samples.

Catalyst characterization

XRD patterns of the calcined catalysts were obtained using a RigakuMiniflex II instrument with CuKα as the radiation source. Surface areas and pore volumes of the samples were calculated from the N_2 adsorption-desorption isotherms obtained at liquid N_2 temperature (Micromeritics, ASAP 2020). The samples were evacuated at 350 °C for 4 h prior to the surface area measurements. The pore volume of the samples were obtained from the amount of liquid N_2 adsorbed/condensed at a p/p_0 of 0.99. XRF analyses were carried out using a PriminiRigaku (RIX 3100) wavelength dispersive X-ray fluorescence spectrometer equipped with Rh X-ray tube, 40 kV generator and 8 position crystal changer. Usually about 1 g of sample was loaded on the XRF sample holder. The presence of functional groups was investigated by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were collected on a Perkin-Elmer Spectrum 100 FTIR spectrometer in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} using KBr-HAP wafers. Scanning electron micrographs and elemental analysis were recorded using FEI, Quanta 200 SEM unit. The morphology of the samples was also studied by transmission electron microscope (TEM, JEM-2010, JEOL Ltd). Samples were mounted on aluminium stubs using conductive glue, and were then coated with a thin layer of carbon.

XPS (X-ray Photoelectron Spectroscopy) measurements were carried out using a multi-probe system (Omicron Nanotechnology, Germany) equipped with a dual Mg/Al X-ray source and a hemispherical analyser operating in constant analyser energy (CAE) mode. The spectra were obtained with 50 eV pass energy for the survey scan and 20 eV for individual scans. The Mg Kα X-ray source was operated at 300 W and 15 kV. The base pressure in the analysing chamber was maintained at 1×10^{-10} mbar. The data were processed with the Casa XPS program (Casa Software Ltd., U.K.). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mix of Gaussian and Lorentzian functions in a 70/30 ratio. The peaks were calibrated by taking the adventitious carbon's C 1s line as 284.7 eV.

Hydrogenolysis of sorbitol

Hydrogenolysis of sorbitol was carried out in a 120 mL stainless steel (SS) autoclave using 40 g of an aqueous solution of 15 wt% sorbitol. After the aqueous mixture of sorbitol was introduced into the autoclave, it was purged thoroughly with pure nitrogen and the H_2-reduced catalyst (powder) kept in N_2 atmosphere was added. The autoclave was next purged by flowing H_2 at room temperature. The contents were then stirred (300 rpm) and the autoclave pressurized with H_2 to 50 bar and heated to the reaction temperature with necessary pressure adjustment to keep the pressure below 60 bar. Once the desired temperature was reached, the pressure

Table 1
Conditions used in the preparation of HAP with different morphologies.

Sample	Synthesis conditions			Morphology of HAP	Synthesis method [Reference]
	Organic agent	Temp. (°C)	pH		
HAP-N	Sodium citrate	40	10	Needle	[2]
HAP-R	–	100	>12	Rod	[3]
HAP-S	Triethanolamine	100	12	Sphere	[16]

Table 2
Structural characteristics and composition of HAP samples and catalysts.

Sample/ Catalyst	Lattice constants		Unit cell volume	2θ (°) for reflection			Relative crystallinity[a]	Composition[b]	
	a (Å)	c (Å)	(Å^3)	100	002	211		Ca(+Sr)/P ratio	Ni or Sr (wt%)
HAP-N	9.45	6.86	530.4	11.02	25.90	31.48	0.33	1.60	–
HAP-S	9.50	6.85	535.2	10.80	26.00	31.78	0.58	1.62	–
HAP-R	9.57	6.88	545.9	10.66	25.82	31.72	0.55	1.62	–
SrHAP-R	9.62	6.92	554.6	10.56	25.76	31.80	0.52	1.62	5.6(Sr)

[a] Method described in text.
[b] By inductively coupled plasma analysis.

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