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Synthesis of iron orthophosphate catalysts by solution and solution combustion methods for the hydroxylation of benzene to phenol

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ABSTRACT

Iron orthophosphate was prepared by solution and solution combustion method for use as a catalyst in the hydroxylation of benzene to phenol. The products of each method were structurally identical. The morphology and size of the catalyst were significantly influenced by the synthesis method. The catalytic activity of the catalysts in the liquid phase hydroxylation of benzene was studied. The yields of the solution combustion synthesized and solution synthesized iron orthophosphate were 24.52% and 8.90%, respectively, under optimized conditions. The iron orthophosphate synthesized by the solution combustion method exhibited better catalytic performance characteristics than the one prepared by the solution method.

1. Introduction

Iron phosphate has shown good catalytic properties for different catalytic reactions. Both Bronsted and Lewis acid sites are present [1] and responsible for catalytic reactions, such as oxidation [2], oxidative dehydrogenation [3], and ammoxidation reactions [4]. The tetrahedral coordinated iron active site surrounded by phosphate groups contribute to the selective oxidation of methane [5,6]. Iron phosphate exhibits a unique selectivity for oxidative dehydrogenation reactions, such as the formation of pyruvic acid from lactic acid [3]. Both iron phosphate and transition metal doped iron phosphate were used for methyl acetate formation [7]. To broaden the range of this material's applications, many synthesis routes have been developed [8], such as solid state reactions [9], hydrothermal synthesis [10], and a microwave technique [11]. The solution combustion method has emerged as an attractive technique for the rapid, low temperature production of high purity, homogeneous, crystalline powder materials [12]. The basis of this technique is an exothermic redox reaction between a fuel and an oxidizer. Other advantages of this method are its low energy requirement, low time requirement and simple equipment [13].

Phenol is one of the most important intermediates for many industrial products, including petrochemicals, plastics, phenol-aldehyde resins, bisphenol A, epoxy resins, and aniline [14,15]. Currently, phenol is mainly manufactured by a three step cumene process. However, this reaction is a multistep process that requires large amounts of energy and produces acetone as a byproduct [16]. The direct hydroxylation of benzene to phenol is an attractive, economic, one-step method. Nitrous oxide [17,18], hydrogen peroxide [19,20], oxygen [21], and mixtures of oxygen and hydrogen [22,23] have been used as oxidants. Because of its environmental and economic advantages, hydrogen peroxide is preferred. The catalytic hydroxylation of benzene using hydrogen peroxide has been studied in the presence of vanadium based catalysts [24,25], zeolites [26], and iron based catalysts [27,28], among others.

In this work, iron orthophosphate was prepared by solution and solution combustion methods and utilized for the hydroxylation of benzene to phenol. The catalysts were characterized by FT-IR, UV–vis XRD, XPS, and surface analysis techniques (BET, SEM). The effect of benzene/H_2O_2 mole ratio, reaction temperature, reaction time, amount of catalyst, and type of solvent on benzene conversion and phenol selectivity was also investigated.

2. Experimental

Iron nitrate $Fe(NO_3)_3.9H_2O$ (Merck 99.5%) as an iron source; diammonium hydrogen phosphate $(NH_4)_2HPO_4$ (Riedel 99%) as a phosphate source and glycine $C_2H_5NO_2$ (Merck 99.7%) as a fuel were used to produce iron orthophosphate. Benzene, hydrogen peroxide, and acetonitrile were used in catalytic reactions and o-cresol was used as an internal standard. All chemicals were of analytical grade and used without further purification.

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2.1. Catalyst preparation

2.1.1. Solution method

The appropriate amount (P/Fe = 1.0 mole ratio) of iron(III) nitrate and diammonium hydrogen phosphate were dissolved in distilled water under continuous stirring. The excess water was completely removed at 100 °C. Finally, the precursor was calcined at 550 °C for 6 h.

2.1.2. Solution combustion method

Iron(III) nitrate as an oxidizer, diammonium hydrogen phosphate as a phosphate source, and the appropriate amount of glycine as a fuel (P:Fe:G = 1:1:1.67 mole ratio) were dissolved in distilled water. The oxidizer to fuel ratio was calculated based on the oxidizing (O) and fuel (F) valencies of the reactants, as reported earlier [29]. The appropriate amounts of the reactants were mixed under constant stirring, and the temperature was raised to 100 °C. The dehydrating combustion mixture was then quickly introduced into a furnace, which was pre-heated to 500 °C for 10 min, during which time it decomposed in a smoldering combustion process to yield iron orthophosphate.

2.2. Catalyst characterization

Fourier transform infrared spectra (FTIR) were recorded on a PerkinElmer Spectrum One instrument using the KBr pellet method over the wavenumber range 400–4000 cm^{-1}. X-ray diffraction (XRD) measurements were obtained on a Rigaku DMAX-2200 X-ray diffractometer with Cu Kα radiation. UV–vis spectra were recorded using a Shimadzu UV-3600/UV–vis-NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Scientific instrument, with Al Kα

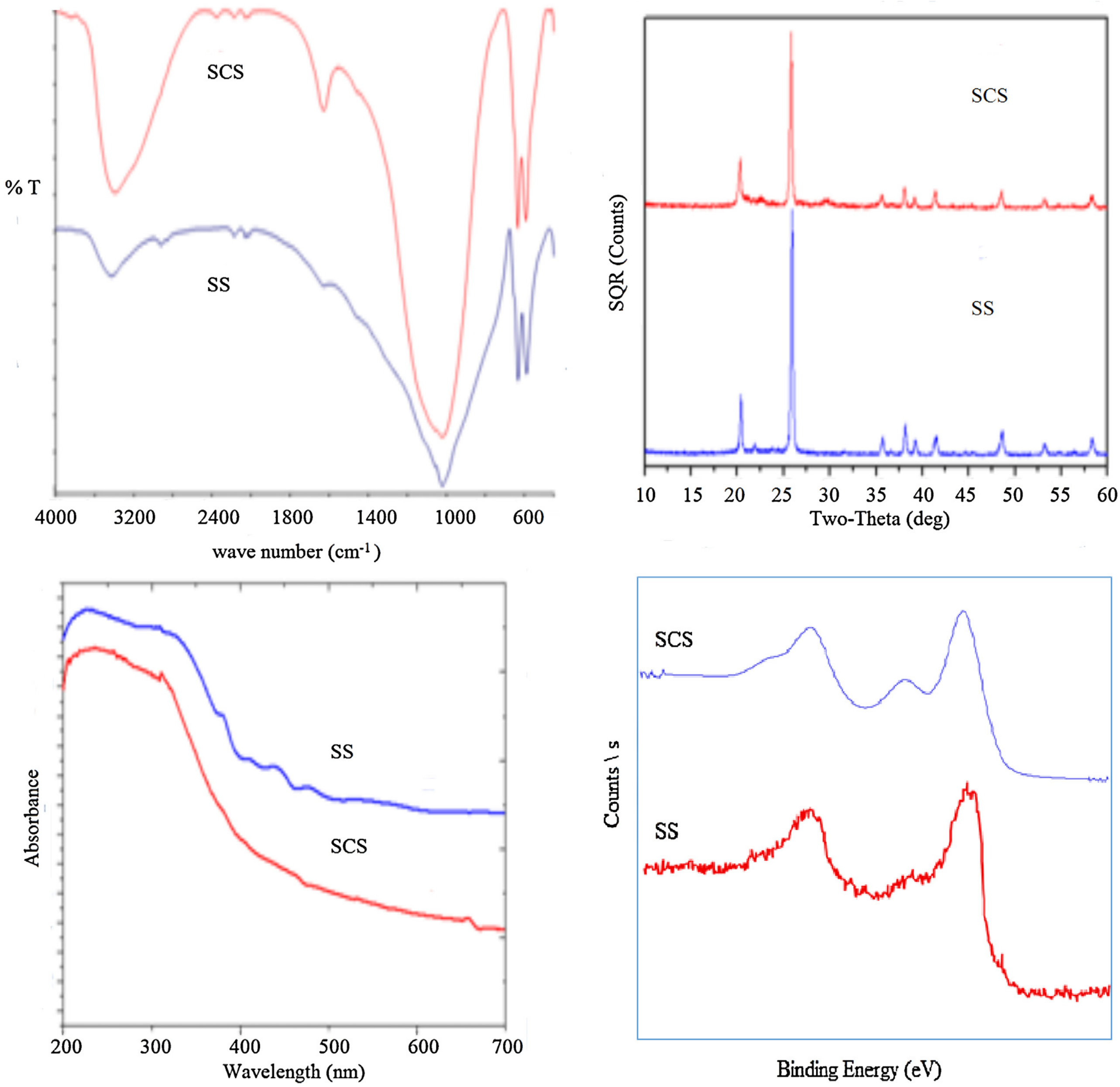

Fig. 1. (a) FT-IR spectra, (b) XRD diffractograms, (c) UV–vis spectra and (d) XPS spectra (Fe_{2p}) of catalysts prepared by solution synthesis (SS) and solution combustion synthesis (SCS).