

SOL-GEL SYNTHESIS OF Fe-Co SUPPORTED SILICA NANOPARTICLES FOR THE CATALYTIC OXIDATION OF PHENOL

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ABSTRACT

In this study, Fe-Co nanoparticles supported silica rice husk were successfully prepared at different pH via sol-gel technique. The prepared materials were characterized by Powder X-Ray Diffraction (PXRD), N₂ adsorption-desorption and Ammonia Temperature Programme Desorption (Ammonia-TPD) analyses. Type IV isotherm with H1 hysteresis loop was exhibited by all the materials. High textural properties, BET surface area and excellent acidity were shown by Fe-Co nanoparticles synthesized at pH 7. The presence of Fe₂O₃ and Co₃O₄ was confirmed from the PXRD analysis. The performance of the materials was evaluated in the solventless oxidation of phenol at 333 K and the activity follows the trend as such: Fe-Co7 (87.9%) > Fe-Co3 (84.3%) > Fe-Co9 (76.2%) which strongly correlates with the high acidity properties and surface area of Fe-Co7.

Keywords: Silica; Rice husk; Nanoparticles; Oxidation; Phenol

INTRODUCTION

Nanotechnology offers the application of nanosized (1-100 nm) materials in various fields such as electronics, magnetism and catalysis. Among metal nanomaterials, Fe and Co have gained huge interest among global researchers due to the existence of two 4s outermost electrons and unsaturated 3d electron shell, which promotes to their rich physicochemical properties such as good strength, magnetic and catalytic performance [1].

Rice is one of the major crops in Malaysia. According to the Paddy Statistics of Malaysia, 720 million metric tonnes of rice were produced in 2011, in which rice husk (RH) accounts 20% of this amount [2]. Silica is the major constituent of RH with 15-20 wt.% [3]. Silica RH exhibits a unique nanoporous structure and large surface area [4]. Taking the advantage of this nanoporous structure, hence, in this study, silica RH was used as the precursor for the fabrication of bimetallic Fe-Co nanoparticles.

Since the properties of nanoparticles are generally controlled by their mean size, thus it is vital to control the synthesizing procedure during nanoparticle production. However,

so far, the focus on the investigation of size dependent properties such as the effect of pH is still lacking. Thus, it has been a challenge to develop a cheap, facile and eco-friendly synthesis route to produce Fe-Co nanoparticles. Most of the methods reported in literatures showed severe drawbacks. For example, recently, Kosma and co-workers [5] had developed Fe-Co nanoparticles supported on hydroxyapatite using chemical vapor decomposition. Nevertheless, this procedure is complicated, involves tedious synthesizing route and requires large quantity of organic solvent. Furthermore, surfactant assisted ball-milling technique also results in the difficulty in controlling the nanoparticles sizes' and their shapes [6]. On contrary, sol-gel is acknowledged as a simple and eco- friendly route for the preparation of metal nanoparticles [7].

Global development substantially increases the discharge of wastewater containing phenolic compounds into water bodies and causes a huge environmental threat to human, aquatic, flora and fauna. Hydroxylation of phenol with hydrogen peroxide appears as an effective approach for the treatment of contaminated water sources due to its operation at low temperature, eco-friendly and produces water as the only by-product [8]. To date, most of the catalysts tested in the phenol oxidation reported tedious preparation route [9] and low reaction rate [10]. Thus, the search for a new and cheap heterogeneous catalyst with high activity in less reaction time is always sought after. Hence, in this study, Fe-Co nanoparticles synthesized at different pH were characterized and evaluated in the liquid-phase oxidation of phenol.

EXPERIMENTAL

Reagents and Raw Materials.

Nitrate based salts ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HmbG Chemicals, 98.5%) and ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, QRec, >99.0%) were used as the metal sources. Sodium hydroxide (NaOH, QRec, 99%) and nitric acid (HNO_3 , QRec, 65%) were used during the alkaline and acid treatment stages. AR grade ethanol and phenol were purchased from QRec and used as procured. Rice Husk (RH) was supplied by BERNAS, a local rice mill in Simpang Empat, Perlis, Malaysia.

Pre-treatment of RH and Extraction of Silica.

Nearly 30.0 g of RH was weighed and added into a 1 L beaker containing 500 mL of 1 M HNO_3 and mechanically stirred for 1 day. Later, the treated RH was washed thoroughly with distilled water until the filtrate reaches a pH of 4.5-5.0. Then, the RH was dried at 383 K for 18 h and later weighed and denoted as RH- HNO_3 . Next, RH- HNO_3 was stirred with 400 mL of 1.0 M NaOH for 24 h. Later, it was suction filtered yielding sodium silicate and the residue was subsequently oven dried at 383 K for 18 h and weighed. The dried residue was labeled as RH-NaOH. The extracted silica was calculated based on the mass difference between RH- HNO_3 and RH-NaOH.

Synthesis of Fe-Co Nanoparticles.

A simple acid-base titration was carried out by titrating the prepared sodium silicate against 130 mL of 3.0 M HNO_3 containing 10wt.% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 15wt.%

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ until reaches required pH of 3, 7 and 9. The gel was left for ageing in the mother liquor for 48 h. Then, it was centrifuged, washed with 100 mL of water and ethanol mixture (1:1 v/v) and finally suction filtrated into soft gel which was later oven dried at 383 K for 18 h. After drying, the samples were hand ground into fine powder and denoted as FeCo_x ($x = 3, 7$ or 9).

Characterizations of Fe-Co Nanoparticles.

The synthesized samples were subjected for the powder XRD analysis (PANalytical Xpert PRO MRD, Bruker) in the range $2\theta=10-90^\circ$ at a scan rate of 0.05° . Isotherms and the textural data were recorded on Micromeritics ASAP2020 at -195°C . The acidity strength of the materials was investigated by TPD (TPDRO 1100) using ammonia as the probe molecule from 50 to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Catalytic Test in the Phenol oxidation.

In a typical run, 1.88 g phenol (10 mmol) and 0.02 g nanoparticles was added into a 50 mL flask set at 333 K. 2.28 g aqueous H_2O_2 (20 mmol) was added slowly in 10 min to initiate the reaction. After 0.5 h, sample was withdrawn, added with $1\ \mu\text{L}$ acetophenone as an internal standard prior analysis by GC (Agilent, 7890A) with the following program: Initial oven temperature $-433\ \text{K}$; ramp of $25\ \text{K}/\text{min}$; final temperature $-503\ \text{K}$ for 10 min and ramp of $25\ \text{K}/\text{min}$. Similar reaction was repeated in the absence of catalyst and the progress of activity was monitored by GC. Product identification was done by injecting the standards under the similar GC program.

RESULTS AND DISCUSSION

N_2 adsorption-desorption and ammonia TPD analysis.

The N_2 sorption isotherm and hysteresis loop of Fe-Co nanoparticles are displayed in Figure 1.

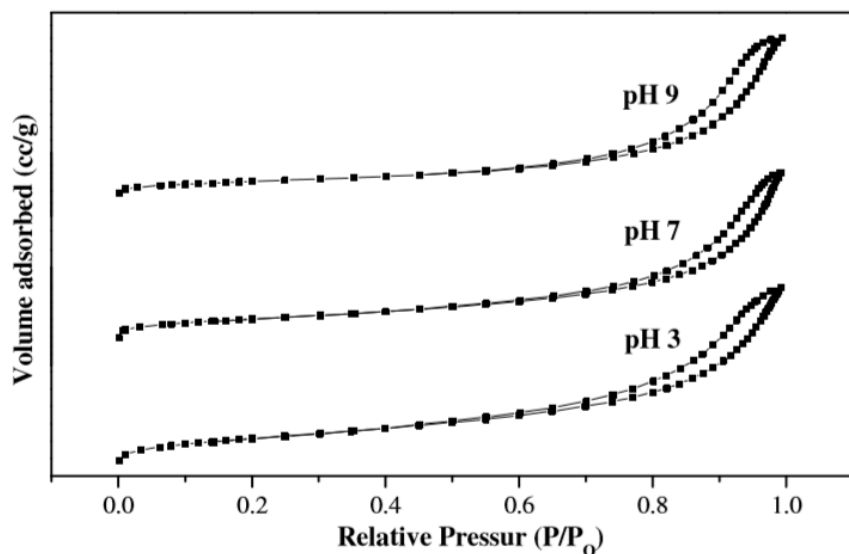


Figure 1: Hysteresis loops and isotherms of Fe-Co nanoparticles

It clearly showed that the isotherm type and hysteresis loop was not affected throughout the pH variation studies. According to the IUPAC classification, the isotherms of Fe-Co3, Fe-Co7 and Fe-Co9 were of Type IV with a H1 hysteresis loop. Type IV isotherm has a high energy of adsorption and normally observed for mesoporous solids. The presence of the hysteresis loop of type H1 is normally observed for aggregates and agglomerates with uniform and regularly packed material [11]. Sharp inflection point observed at P/P_0 of 0.45-0.60 for all the materials relates to capillary condensation in mesopores. Table 1 presents the physical characteristics of the synthesized materials based on the BJH and BET models together with the TPD acidity data.

Table 1 : The textural properties and summary of data obtained from BJH, BET and Ammonia TPD analysis.

Samples	S_{BET} ($m^2 g^{-1}$)	Average Pore volume ($cc g^{-1}$)	Average Pore diameter (nm)	Total acidity ($\mu mol/g$)
Fe-Co3	181.5	0.41	9.40	2853.7
Fe-Co7	238.9	0.68	11.8	3355.5
Fe-Co9	149.6	0.50	14.4	3118.5

Accordingly, Fe-Co7 exhibited higher BET surface area and pore volume which were $238.9 m^2 g^{-1}$ and $0.68 cc g^{-1}$ respectively. However, the BET surface area of Fe-Co3 and Fe-Co9 showed reduction of 24% and 37% respectively in comparison to Fe-Co7. Similar decreasing trend was shown with respect to pore volume. In addition, referring Table 1, upon increasing the pH, the pore diameter was found to shift progressively to wider diameter. Accordingly, Fe-Co7 registered the highest acidity followed by Fe-Co9 and Fe-Co3. The greatest acidity strength at pH 7 could be due to the strong interaction between Fe, Co with silica compared to other pHs.

PXRD analysis.

The high angle PXRD pattern of the nanoparticles is shown in Figure 2. The amorphous characteristics of silica was clearly evidenced by the presence of peak at $2\theta = 23^\circ$. However, serious deterioration was observed at this region upon increasing pH from 3 to 9. This presumably was due to the changes in morphology from amorphous to crystalline nature. Less intense crystalline peaks attributed to spinel Co_3O_4 and Fe_2O_3 were observed for all samples, suggesting the well dispersion of metal species on the silica support. Similar behavior was reported in the case of CoFe/SBA-15 prepared by incipient wetness impregnation [12]. However, the intensities of these signals were higher in Fe-Co7 compared to Fe-Co3 and Fe-Co9.

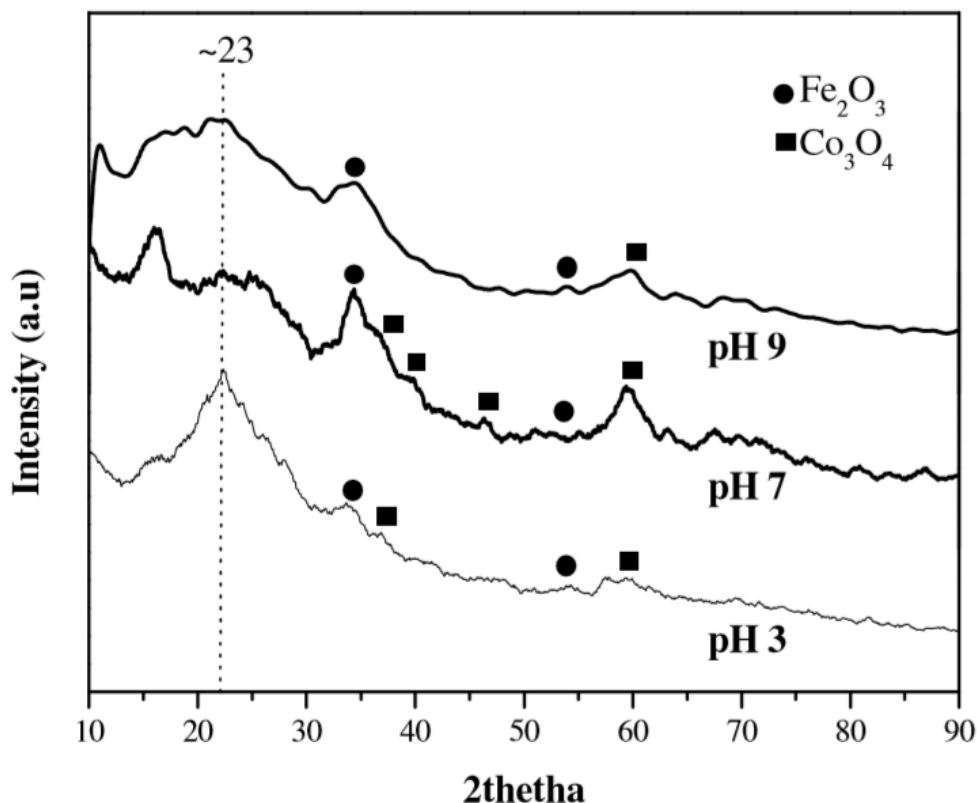


Figure 2: High angle PXRD pattern of the materials

Catalytic evaluation in phenol hydroxylation.

The catalysis of the synthesized materials was compared in the phenol oxidation and the results are illustrated in Figure 3. No catalysis was observed in the absence of the catalysts. Superior activity was exhibited by Fe-Co7 followed by Fe-Co3 and Fe-Co9. In all cases, only catechol and hydroquinone were obtained unlikely to those reported by other researchers [13,14]. The trend in activity was in agreement with the specific surface area as shown in Figure 3. Theoretically, in heterogeneous catalysis system, higher BET surface area provides larger surface for the adsorption of reactants, surface reactions and desorption of products. In view of that, the accessibility of active sites might be high in Fe-Co7 compared to other catalysts. In addition, largest average pore volume (0.68 cc g^{-1}) of Fe-Co7 could promote the diffusion of reactants into the pore cavities and further enhances the catalysis. In addition, surface acidity plays an important role in controlling the conversion rate in phenol hydroxylation. The highest acidity strength of Fe-Co7 (refer Table 1) demonstrates the favorable adsorption and reactions of reactants on the surface which facilitates the catalysis.

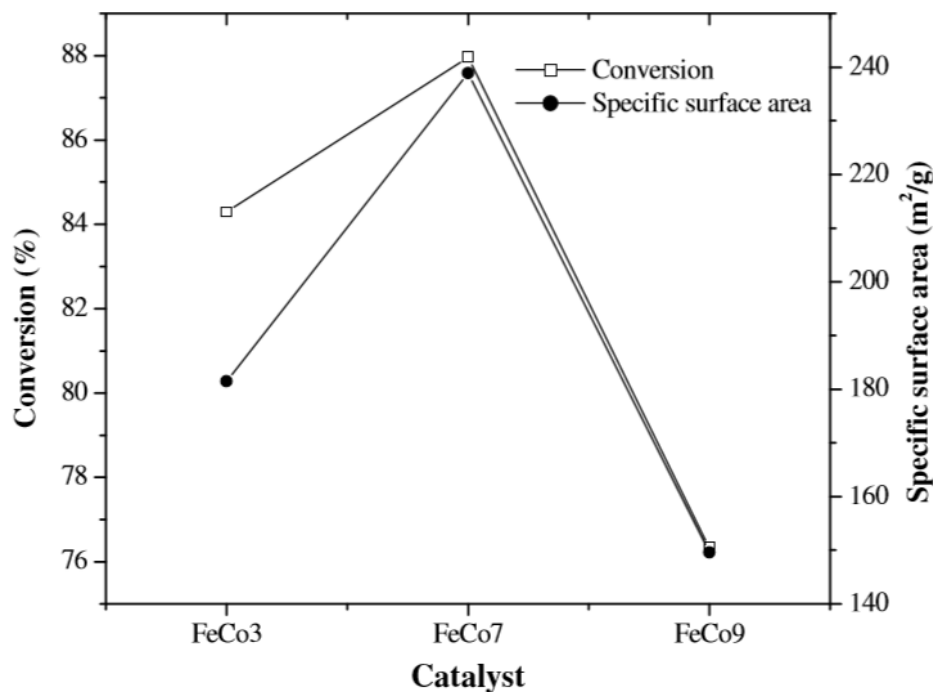


Figure 3: Linear correlation between specific surface area and catalytic activity of the catalysts

CONCLUSION

In this study, cheap agro waste was used to synthesize Fe-Co nanoparticles using facile sol-gel route at different pH. High BET surface area with well dispersion and high acidity were evidenced through the spectroscopic studies. These mesoporous materials were active in the conversion of toxic phenol into valuable dihydroxybenzenes in solventless system in only 30 min. Fe-Co7 appears to be highly active under the reaction condition. To conclude, this study provides a fast and promising method for the utilization of silica rice husk into nanoscale materials for phenol abatement.

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