IRANIAN JOURNAL OF CATALYSIS

Supercritical water impregnation of CuO nanoparticles on silica-support as new catalyst

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Received 26 February 2012; received in revised form 21 May 2012; accepted 21 June 2012

ABSTRACT

In our current study, supercritical water impregnation (SCWI) was introduced as a unique catalyst preparation method by employing the high diffusivity property of supercritical water. The method allows nano-particles to place on support surfaces in extremely dispersed conditions. The silica-based nanocatalyst granules for this purpose were prepared by initial impregnation of highly porous silica (500 m^2/g) in aqueous nitrate solutions, followed by hydrothermal decomposition of the nitrates to oxides at supercritical condition. The prepared sample prior to undergoing characterized by X-ray diffractometry, transmission electron microscopy, and nitrogen adsorption analysis (BET). Although the catalytic properties of the CuO in silica supports were not evaluated, the procedure of employing supercritical water in comparison to other routes to deposit metal oxide particles on hydrophobic surfaces inside support structures offers promise for catalyst preparation without the use of toxic or noxious solvents.

***Keywords**: CuO nanoparticles, Supercritical water impregnation, Hydrothermal synthesis, Silica template.*

1. Introduction

One of the most investigated nano metal oxide from catalytic aspect is CuO, an advanced material with wide applications in alkylation, cracking, dehydrogenation and oxidation reactions [1–4], catalysts for the water–gas shift reaction [5], steam reforming [6], and CO oxidation at low-temperature for treatment of automobile exhaust gases [7]. In addition, applicability of the CuO nano powder in formulations of heat transfer of nano-fluids has been reported [8].

Although a great deal of efforts for developing the efficient techniques for preparation of copper oxide nanoparticles suggested [9-12]; but the control over particle size and size distribution remains a key problem associated with their manufacture by conventional techniques. In particular, the trend of nanoparticles to aggregate, and the difficulty of controlling their morphology and individual particle sizes are well documented [13]. In addition, for many catalytic applications, straight treatment, processing and continual employ of nanoparticles is hard if they are not stabilized in bulk solid matrices [14]. Accordingly, a key confront in this area is to develop a wide-ranging methodology that not only allows tailoring of size and composition of nanoparticles, but also facilitates handling of the ultra-fine particles through their ‘implantation’ into a range of porous bulk materials.

Among the synthesis methods of nano-catalyst supports composites, conventional impregnation is the most widely used route for preparing supported catalysts. Such catalysts are usually prepared by imbibing the support in a solution of the catalyst precursor, followed by drying, calcination, and reduction at high temperatures. Unfortunately, the later may result in objectionable changes such as sintering that lead to changes in the active catalyst distribution [15]. In addition, numerous impregnation steps may be necessary to obtain the desired quantity of catalyst on the support [16]. It is also well known that the catalytic activity is powerfully reliant on the particle shape, size, and size distribution [17, 18]. However, conventional impregnation techniques often do not give adequate control of particle shape, size and size distribution [19-20].

Lately supercritical water impregnation (SCWI) of metal oxide nanoparticles has received significant consideration as a medium for synthesizing metal oxide particles via hydrolysis and dehydration of metal salts. [21-23]. Earlier study have revealed that the high reaction rates and low metal oxide solubility in supercritical water can lead to high

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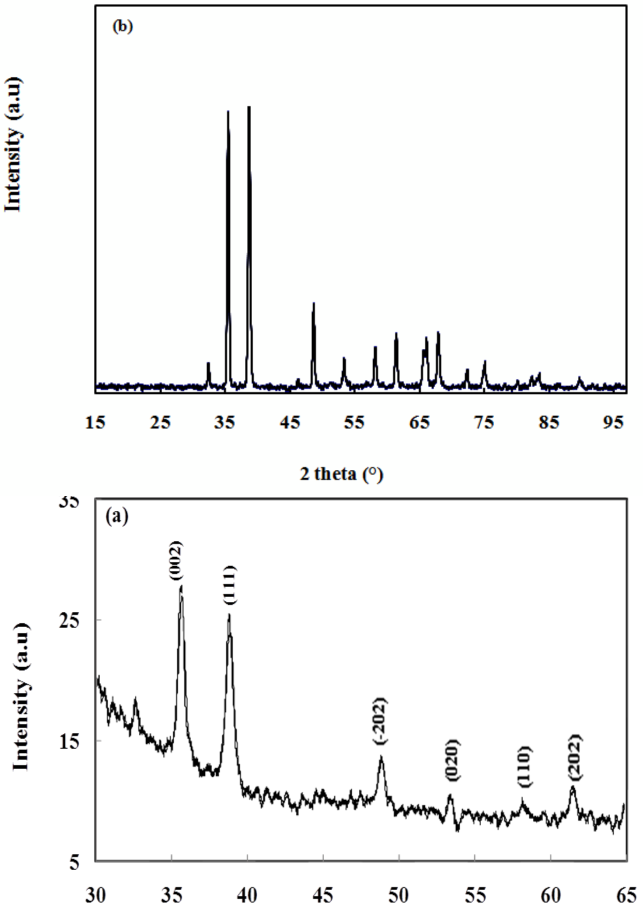

Fig. 1. The XRD pattern of (a) a nano CuO sample that was synthesized by supercritical decomposition of $Cu(NO_3)_2$ solutions within 1 h. and (b) bulk copper oxide.

supersaturations and the formation of fine metal oxide particles from aqueous solutions of metal salts. However, few studies have exploited the reactive and transport properties of supercritical water to deposit particles on pre-shaped catalyst supports except the recent work of Otsu and Oshima [23].

In the current study, the deposition of nanoparticles of copper oxide on a high porosity silicate is investigated using supercritical water. The objectives are to synthesize and disperse the metal oxide catalyst nanoparticles uniformly on the surface and in the pores of silica- supports using supercritical water. The final aim is to gain general principles for the drawing of nanocomposite catalysts based on catalyst supports, and to derive factors that affect the catalyst during preparation. The silica- support would have the potential to join the best attributes of both homogeneous (highly active and selective) and heterogeneous (easy separation from the reaction media) catalysts. The use of supercritical water to deposit metal oxide nanoparticles on hydrophobic surfaces also offers promise for other-supported catalyst preparation not including the use of toxic or noxious solvents.

2. Experimental

2.1. Supported Catalyst Preparation Methods.

Preparation of the silica supported CuO nanoparticles was carried out in a 200 mL stainless steel batch reactor, especially designed to endure working pressure and temperature of 610 atm and 550 ^{o}C, respectively. The reactor was filled with a 0.1 M precursor solution of $Cu(NO_3)_2$ to one third of its volume, and then to this solution was added about 2g of highly porous silica (surface area: 500 m^2/g). The reactor was heated at 500^{o}C for about 1 h. Afterward, it was removed from the furnace and quenched by the cold water. The CuO-deposited silica particles were separated from the solution by decantation, and underwent a multiple washing-decantation procedure by distilled water. Subsequently, they were spread on some Petri dishes and dried at ambient condition.

For the sake of comparison the CuO micro-powder was synthesized by a two-step calcination procedure. In this process, first the crystalline water of copper (II) nitrate trihydrate was removed by its gentle heating on a hot plate, and then dehydrated $Cu(NO_3)_2$ sample was decomposed by high temperature (i.e. 400ºC) heating for about 22 h. At last, the obtained CuO granules were ground and screened into a fine micronized product.

2.2. Physical characterization

Crystal structure and composition of the CuO samples before and after the reduction step was examined by the X-ray diffractometry (XRD, Philips PW 1800) using the Cu-Kα radiation line.

Size and morphology of the nanoparticles in silica-supported samples was observed by transmission electron microscopy (TEM, LEO 912AB). Surface area of the silica –supported samples was determined by the nitrogen adsorption method (BET, Quantachrome Instruments, Nova 2000e, Boynton Beach, FL).

3. Results and discussion.

3.1. Morphology

Fig. (1a) and (1b) exhibit the XRD patterns of silica-supported CuO, and a specimen of the bulk (non-nanometric) CuO respectively. Whilst no sign of the impurities like $Cu_2(OH)_3NO_3$ or $Cu(OH)_2$ is observed in any of these samples, difference between the sharpness of their XRD peaks indicates that size of their particles differ markedly from each others. According to the Scherer's analysis the sharper is the XRD peaks; the larger is the size of its particles.

3.1. Morphology

Transmission electron microscopy images of silica support itself and silica-supported CuO indicate the nanometric size of their particles (Fig. 2a and 2b). Although in Fig. (2-b) the silica support cannot be differentiated from the

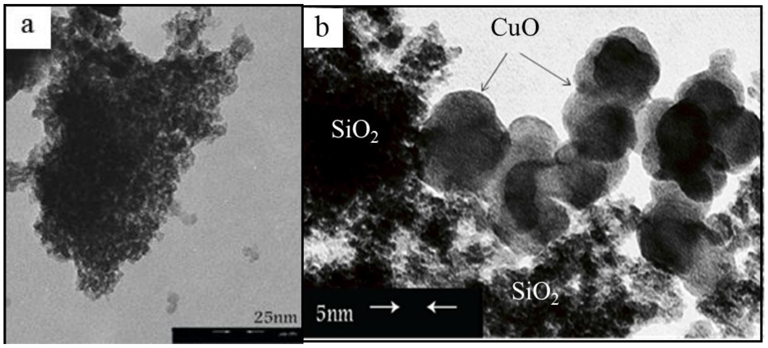

Fig.2. TEM image of the (a) silica alone, (b) silica supported CuO.

CuO particles, there are a pieces of evidence which demonstrate that nanometric particles on the upper part of the image are the CuO ones. The TEM image of the pure silica support in Fig. (2-a) show that size of its particles is less than 10 nm, thus particles with sizes around 37 nm in Fig. (2-b) cannot be the silica ones; this argument serves as our evidence.

During formation of the CuO nanoparticles, the porous structure of the silica acts as a scaffold for precipitation of the CuO nanoparticles, and keeps them relatively apart from each other. In this way, silica hinders growth of the micrometric and larger particle. However, this mechanism is only held when concentration of the copper solution is low (e.g. 0.1 M in the current study), because in this case the likelihood of multilayer precipitation of $Cu(OH)_2$ on the outer surface of silica becomes slim.

Surface area of the SiO_2-supported samples and micronized powder for comparison, was measured by the BET method, and results were tabulated in Table 1.

3.2. Reaction Mechanism of synthesized nanoparticles

SCWI in its batch mode is principally consisted of heating of an aqueous solution of a transitions metal nitrate (or other hydrolysable salts) to above (or near) critical temperature and keeping it in that conditions in the presence of support until most of the initial salts decompose to the oxide and deposited on catalyst supports [23]. If conducted under the appropriate conditions, SCWI method produces a nanometric product with a high reaction yield. Hydrothermal conversion of copper (II) nitrate into copper (II) oxide at supercritical conditions proceeds through a complicated pathway. In this mechanism, first Adschirri's reactions including water dissociation and hydrolysis take place [20, 22].

$$H_2O \rightarrow H^+ + OH^- \qquad (1)$$

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \qquad (2)$$

And then a portion of $Cu(OH)_2$ reacts with liquid or gaseous HNO_3 to yield a complex compound named copper hydroxyl nitrate ($Cu_2(OH)_3NO_3$) [24].

$$2Cu(OH)_2 + HNO_3\ (g) \rightarrow Cu_2(OH)_3NO_3 + H_2O\ (g) \qquad (3)$$

$$2Cu(OH)_2 + HNO_3\ (aq) \rightarrow Cu_2(OH)_3NO_3 + H_2O \qquad (4)$$

Afterward, the formed $Cu_2(OH)_3NO_3$ along with un-reacted $Cu(OH)_2$ undergo decomposition reactions to the final CuO product

$$Cu_2(OH)_3NO_3 \leftrightarrow HNO_3\ (g) + H_2O\ (g) + 2CuO \qquad (5)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \qquad (6)$$

Reviewing of the above mechanism reveals that the final CuO product is very likely contaminated with the $Cu_2(OH)_3NO_3$ due to the co-formation of this substance in the hydrothermal synthesis.

4. Conclusion

Supercritical water impregnation of synthesized nanoparticlese on supports has been shown to be an efficient and environmentally benign technique to prepare metal oxide/catalyst supports nano composites. This method has been employed to obtain well-dispersed nanometersized CuO particles in silica- supports. Mechanism for particle formation and deposition of particles has been postulated. Silicate, recognized as an agent porous support, was applied in this work to achieve the particle deposited inside support pores. The major advantage of this method is simultaneous formation and precipitation of the nano particles that allows precise adjustment of their sizes by controlling of the process parameters. Indeed, supercritical water treatment

Table 1. Comparoison of both nano and micro CuO samples Surface areas measured by nitrogen adsorption (BET) test.

	Silica supported nanoparticles	Micronized powder
Surface area(m^2/g)	382	0.49

can be efficient for preparing metal oxide-carbon of nanocomposites for adsorption and catalytic decomposition volatile organic compounds (VOCs) for environmental cleaning. The procedure of employing supercritical water to deposit metal oxide particles on hydrophobic pore surfaces offers promise for supported metal catalyst preparation without the use of toxic or noxious solvents.

Acknowledgement

The authors gratefully acknowledge the Department of Energy Engineering of Sharif University of Technology, Iran for the financial and instrumental support of this project.

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