Short Communication

The action mechanism of ethanol in preparation of supported nano-sized Ru catalyst via supercritical fluid deposition

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ABSTRACT

Ru catalysts supported on activated carbon (AC) were prepared by supercritical fluid deposition (SFD) with ethanol added and their catalytic performance in butanone hydrogenation was investigated. The effects of ethanol amount on Ru particle size were systematically studied. As the amount of ethanol increased, Ru mean particle sizes always decreased firstly, then increased. And the minimum mean particle size of Ru was obtained at 10 ml ethanol. The catalysts with smaller Ru mean particle size presented higher catalytic activity. These results demonstrated that the role of ethanol may not be only co-solvent but also anti-solvent and extractant during the preparation of Ru/AC.

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1. Introduction

Supported metal nanoparticles (NPs) are of great interest with respect to their wide applications in catalysis [1–3], and their unusual properties are directly related to the specific particle size and shape, metal dispersion, metal loading and the electronic properties of metal in their host environment [4]. Unfortunately, metal NPs are unstable because they tend to agglomerate which is the main reason resulting in the loss of their catalytic activities [5,6]. Consequently, how to control the size and dispersion of metal nanoparticles is an important issue and a serious challenge in the synthesis of supported metal catalysts.

Recently, the supercritical fluid deposition method has been employed to prepare highly dispersed metal nanoparticles supported on porous materials like activated carbon (AC) [7], carbon nanotubes (CNTs) [8,9], alumina (Al_2O_3) [10,11] and other matrixes [12]. This method involves the transportation and deposition processes in supercritical fluids (SCFs), that is, the dissolution of metal precursor in supercritical fluids (SCFs), the diffusion and impregnation of SCF solution into the pores of the supports and the adsorption of metal precursor onto the walls of the pores, followed by thermal or chemical reduction to form metal nanoparticles. Supercritical fluids (SCFs) have unique properties such as gas-like diffusivities, liquid-like densities and dissolving capacities, low viscosities, near-zero surface tensions and tunability [13]. These properties are favorable for the penetration and diffusion of precursors into pores of supports and result in the highly dispersed metal nanoparticles supported on subtrates. Among all supercritical fluids,

supercritical carbon dioxide ($SCCO_2$) is the most promising because it exhibits many favorable properties such as abundance, low cost, non-flammability, non-toxicity and in particular its relatively moderate critical pressure and temperature values ($T_c = 31.1$ °C, $P_c = 7.38$ MPa).

In the SFD process, the dissolution of metal precursors in SCFs is the first step and also the prerequisite to obtain highly dispersed metal nanoparticles. But the low solubility of most metal precursors in $SCCO_2$ leads to the poor metal utilization and subsequent high cost [14]. In order to solve the problem, many researchers tried to add polar solvents as co-solvents to improve the dissolution of metal precursors in SCFs [15–17]. The effect of polar solvent on the supercritical deposition process can be reflected by the critical point of binary systems [16,18], the polarity of $SCCO_2$ [19,20] and the interactions between polar solvents and the metal precursors [17]. Zhang et al. [18] measured the critical point properties of binary systems including CO_2 and a common solvent such as methanol, ethanol and toluene and found that the performance of supercritical fluid (SCF) as a solvent can be greatly affected by the addition of an entrainer to the system. Özel et al. [16] investigated the influence of the addition of polar solvents on the critical point of CO_2 using the stainless steel supercritical fluid extraction system and found the appropriate linear relationships between the concentration of polar solvent and critical point including critical temperature and critical pressure. In the case of the polarity of $SCCO_2$, the addition of polar solvents can result in the generation of induced dipole and subsequently enhance the polarity of $SCCO_2$. And many authors have deeply investigated the effect of polar solvent on the polarity of $SCCO_2$ in the case of experiments and theoretical calculation [20] and proposed several theories [19]. Ohashi et al. [17] investigated the solubilities of $Cr(acac)_3$ in $SCCO_2$ with the aid of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and

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3,5-bis(trifluoromethyl)phenol (BTMP) respectively. And they reported that the improvement of the solubility might be attributed to the generation of hydrogen bonding between metal precursors and co-solvents. In conclusion, many researchers have proposed and investigated the co-solvent role of polar solvents in the supercritical deposition process. But for the complex supercritical deposition system, the role of polar solvent is probably complicated.

In the present work, we systematically investigated the influence of ethanol and its addition amount on the whole supercritical fluid deposition system. And besides co-solvent, we also tried to understand the role of polar solvent from the perspective of anti-solvent and extractant, which is scarcely reported in the published papers. These results in this paper would be helpful to design the deposition experiments and control the size and morphology of metal nanoparticles. Moreover, activated carbon, acknowledged as a representative porous support, was employed in this work to take into consideration the particle deposition inside the support pores.

2. Experimental

2.1. Materials

Ruthenium(III) acetylacetonate (Ru(acac)$_3$, 99%) was purchased from Heraeus, Shanghai, and Jiangsu Industrial Additives Co., respectively. AC from Tangshan New Activated Carbon Co., China, was used as the support for the Ru NPs. Prior to use, the AC was dried under vacuum at 100 °C and 10 mbar for 8 h to remove any adsorbents on the surface. Ethanol (99.9%), ethyl acetate (99.9%) and butanone (99.9%) were purchased from Tianjin Jiangtian Chemical Technology Co. Acetaldehyde aqueous solution (40%) was supplied by Tianjin Standard Co. and CO$_2$ (>99.9%) and H$_2$ (99.999%) were provided by Tianjin Liufang Gas Co. With the exception of the AC, all the gases, reagents and materials were used as received without further treatment.

2.2. Fabrication and characterization of the supported Ru NPs

2.2.1. The preparation of the ruthenium catalyst precursors

The ruthenium precursor (0.2 g) was dissolved in ethanol and then the solution was mixed with AC (~5 g). Subsequently, the mixture was placed in an autoclave (Parr 4575, 500 ml), into which CO$_2$ was added until the desired pressure (8.0 MPa) was achieved. The desired temperature (80 °C) was set and 4 h later the product was removed from the autoclave and dried under vacuum for 4 h. This product was the catalyst precursor. For the purpose of comparison, catalysts (Ru(acac)$_3$ on AC) were also prepared using the ethanol impregnation method with the same conditions that were used for the SFD.

2.2.2. Reduction of the ruthenium catalyst precursors

The ruthenium catalyst precursors were reduced in H$_2$–N$_2$ (V%, 10%–90%) for 3 h in a fixed bed reactor at 350 °C. The resulting products were stored in a desiccator.

2.2.3. Characterization of the catalysts

The structure and morphology of the synthesized catalysts were examined by high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G2F20). The average size and size distribution of the Ru NPs were determined from the HRTEM images with statistical analysis, where the total number of Ru NPs in every HRTEM image was 100.

The nitrogen adsorption–desorption isotherm of the samples was measured with a Micromeritics Tristar 3000 using nitrogen at 77 K. Specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method.

The dispersion of the Ru NPs was determined from measuring the consumption of H$_2$, which was carried out with an AutoChem II 2920 chemisorption analyzer (Micromeritics).

The ruthenium real content of the prepared catalysts were determined by using Varian 700-ES series inductively coupled plasma-optical emission spectroscopy (ICP-OES). Before ICP determining, each sample needs to be calcined at high temperature to get rid of activated carbon, subsequently reacted with excess strong alkaline at high temperature and finally dissolved in a certain amount of H$_2$SO$_4$ (60%, wt.%). The following is the reaction equation of Ru:

$$Ru + O_2(heat) \rightarrow RuO_2 \tag{1}$$

$$RuO_2 + 2KOH + KNO_3 \rightarrow K_2RuO_4 + KNO_2 + H_2O. \tag{2}$$
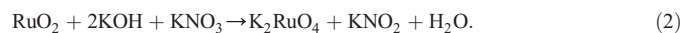
2.3. Catalytic activity measurements

The catalytic activity for hydrogenation was determined in a stirred autoclave (Parr 4575). The feed stock simulated a reaction mixture of the industrial synthesis of ethyl acetate using ethanol. It includes acetaldehyde (0.36%, mol%), butanone (0.23%, mol%), H$_2$O (1.67%, mol%), ethanol (74.09%, mol%), and ethyl acetate (23.65%, mol%). The reaction condition of the hydrogenation of butanone includes a pressure of 4 MPa, a temperature of 85 °C and the mass ratio of catalyst to feed 1%. When the reaction time reached to 3 h, the reaction mixture was sampled and analyzed by GC–MS (Agilent 5973-6890).

3. Results and discussion

3.1. TEM and BET characterization

A series of catalysts were prepared by SFD with different addition amounts of ethanol and their morphology was observed by TEM, shown in Fig. 1. All the Ru/AC samples displayed similar morphology except for slight differences in average sizes of metal particles, which was related with the addition amount of ethanol.

In comparison with Ru nanoparticles prepared in the presence of ethanol, the Ru nanoparticles (Fig. 1A) prepared without ethanol tended to aggregate seriously. It was reported that adding a small amount of a polar solvent such as ethanol to SCCO$_2$ could increase the solubility of organometallic compounds [21]. At this time, ethanol played a co-solvent role. Because in the process of dissolution, the addition of co-solvent tuned the polarity of SCF solution, thus improved the solubility of precursor in SCCO$_2$. But with the addition amount of ethanol rising, ethanol would play different roles in the supercritical fluid deposition process.

In order to discuss the action mechanism of ethanol in SFD better, we calculated the solubility of ethanol in SCCO$_2$ under the experimental condition. Eq. (3) is the solubility equation of ethanol in SCCO$_2$ under different temperatures [22]. According to the relevant equations and figures in reported literatures [22,23], the maximum volume of ethanol dissolved in SCCO$_2$ (80 °C, 8 MPa, 500 ml) is about 10.5 ml.

As shown in Fig. 1B, the Ru nanoparticles were seriously aggregated together at 2 ml ethanol, which was undesirable for their catalytic performance. The probable explanation might be that not all Ru(acac)$_3$ dissolved in the SCCO$_2$–ethanol (2 ml) system, which made some Ru(acac)$_3$ not diffuse into the pores of AC without the aid of SCCO$_2$. And when the amount of ethanol increased from 5 ml to 10 ml, the CO$_2$, ethanol and Ru(acac)$_3$ formed a single-phase solution. In this process, the ethanol played an anti-solvent role more than a co-solvent and the supercritical anti-solvent (SAS) mechanism might be in charge of the decreasing size. The supercritical anti-solvent is based on the fast dissolution of organic solvent in SCCO$_2$ [24]. One solid solute, which is slightly soluble in SCCO$_2$, dissolves in one organic solvent that has a large solubility in SCCO$_2$ forming a homogenous solution. When the solution mixes with the SCCO$_2$, the organic solvent quickly dissolves in the