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Combined small- and wide-angle X-ray scattering studies on oxide-supported Pt nanoparticles prepared by a CVS and CVD process

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ABSTRACT

Various model oxide-supported metal catalyst particles (Pt nanodots supported on silica, titania and alumina) prepared by a CVS/CVD process at atmospheric pressure have been studied by using a self-developed SAXS and WAXS laboratory system. It has been shown that simultaneous SAXS and WAXS analyses offer a structural insight into the complexity of the supported metal catalysts, allowing quantitative study on the morphological characteristics of the synthesized oxide-supported catalyst particles and fine structures, including primary particles, internal subunits, mass fractal dimension of the aggregates, surface roughness, and crystallite properties as well as the Pt nanodots. The oxide support particles under study cover a size range of 55–150 nm and the Pt nanodots are in the size range of 1.8–15.8 nm. The SAXS and WAXS results were compared with those by TEM and the XRD reference database, and a good agreement has been found. Experimental findings indicated that SAXS appears to be more effective than WAXS for determining the Pt dot size, especially for Pt dots smaller than 2–4 nm due to the overlapping effect of the scattering signals at wide angles and the resultant difficulty in discerning the broad WAXS peaks of small Pt dots from the support background. The morphological modification of the support particle surface by mixing a certain amount of alumina into the other oxide support particles during the synthesis process has been observed through quantitative determination of the surface fractal dimension describing the surface roughness using SAXS. Simultaneous quantitative characterization of support particle structures and metal catalyst nanoparticles helped to better understand how synthesis conditions influence the resulting structures of the support particles and how this in turn affects the catalyst properties like the agglomeration or sintering of metal nanoparticles on the supports, to further optimize the synthesis process and prepare better supported metal catalyst nanoparticles.

1. Introduction

Catalytic processes using metal catalysts are of great importance in a variety of industrial applications such as automobile emission control and chemical production. To utilize the metal catalysts with high thermal stability more efficiently, the metal catalysts are mostly dispersed in the form of small particles or thin layers on the supports so that the catalytic activity characteristic of the catalyst surface area can be increased as compared with the bulk materials. The noble metal catalysts like Pt and Pd, often used in the catalytic studies such as methane combustion [1], may interact with both reducible (e.g. TiO_2) and non-reducible (e.g. SiO_2 and Al_2O_3) oxide support particles [2,3]. The metal–support interaction may have drastic effects on the catalytic properties of the metal phase deposited on the support particles. Due to the large active surface area, supported metal nanoparticles have been widely used for metal-catalyzed reactions. Early work suggested that many so-called "structure-sensitive" or "demanding" reactions, such as hydrogenolysis of neopentane using supported Pt catalyst [4], show a definite dependence on the metal particle size. The smaller supported metal particles show higher specific activity than the larger ones. Knowledge of the morphologies and surface structures of the support particles and finely deposited metal particles is fundamental to elucidate the mechanism of the metal–support interaction and to better understand the metal particle agglomeration process termed sintering. In order to optimize the properties of the supported catalyst, the control over support composition and roughness as well as the metal particle size are important parameters during the catalyst preparation.

In recent years, numerous preparation methods dependent on the base materials have been developed to prepare the supported metal nanoparticles for catalytic applications. As described in the literature [5,6], most common methods for preparing supported metal catalysts require a combination of different unit operations such as impregnation or ion-exchange, coprecipitation and deposition precipitation, separation, washing, drying, calcination and reduction. As compared to the conventional liquid-phase methods, a gas-phase method called chemical vapor synthesis and chemical vapor deposition (CVS/CVD) has

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been recently developed to prepare solvent-free high-purity supported metal nanoparticles [7–9], showing certain advantages such as no utilization of stabilizers, no need of washing, drying and purification, as well as possible rapid continuous synthesis of catalysts on the support particles. Many attempts have been made to gain useful and fundamental information on the prepared supported metal nanoparticles. Among them, particle size analysis of the supported catalysts acts as a most direct way to predict the effective surface area available for catalytic activity. Proper catalyst support materials help to stabilize metal catalysts against sintering on the particle surface at high temperature. Thus, during the synthesis process quantitative characterization of the support particle structures, surface roughness and supported metal nanoparticles can help to study the possible factors influencing the properties of catalysts, to further optimize the synthesis process and to design and prepare improved metal catalyst nanoparticles with expected properties.

In principle, the structural information on the metal catalyst nanoparticles deposited on the support particles can be obtained by using a variety of measurement techniques [10,11], such as electron microscopy techniques including scanning or transmission electron microscopy (SEM, TEM, HR-TEM) [12,13] and atomic force microscopy (AFM) [14], X-ray techniques including X-ray photoelectron spectroscopy (XPS) [15], X-ray absorption near edge spectroscopy (XANES) [16] and extended X-ray absorption fine structure spectroscopy (EXAFS) [17,18], wide-angle X-ray diffraction (WAXS or XRD) [19,20] and small-angle X-ray scattering (SAXS) [21–23], magnetic methods [24], gas chemisorption [25] and low pressure impaction [26]. It is worth noting that, depending on the supported metal catalysts under investigation, it is often required to combine several characterization methods so as to obtain sufficient structural information. Among these techniques, electron microscopy has often been recognized as an indispensable tool to characterize the structures of supported metal catalysts, giving direct visualization of the catalyst morphology. However, due to its inherent local measurement this technique can be time-consuming so as to get sufficiently statistical results by analyzing many individual micrographs. Besides, the electron beam irradiation in the TEM can lead to the structural change of certain supported catalysts, e.g. SiO_2-supported bismuth oxide reported by Weis et al. [27]. TEM requires a high level of skill in preparing the TEM samples which should be truly representative of the bulk materials under study. SEM can also provide an overview of the sample morphology but the resolution is typically limited. Compared to these traditional methods, the non-invasive X-ray scattering technique unlike TEM allows quick analysis and yields statistical structural information on the particle systems from a macroscopic amount of sample without extended pretreatment which may change the state of the supported metal catalysts.

Although numerous studies on the supported metal catalysts have been carried out by using X-ray scattering techniques in the past, various porous materials have been mostly used as carriers to support metal catalyst particles. As regards the substrate, alternatively, nonporous nanometer- or sub-micrometer-sized oxide particles synthesized by an aerosol-based CVS and sintering process have been gradually used as catalyst carrier materials [8,9,28,29]. Besides the continuous catalyst film [27,30], small metal catalyst dots deposited on the support particle surface are often used because of a large ratio of the active catalyst surface to the used catalyst mass. Therefore, in this work we focus on the case of the catalyst dots rather than the continuous catalyst film deposited on the oxide support particles. Some recent reports on the simultaneous SAXS and WAXS experiments on the supported metal catalyst particles in various processes can be found in the literature [31–35] and mostly they were based on the synchrotron X-ray source. To the best of our knowledge, so far there have been no reports on simultaneous SAXS and WAXS studies on the oxide-supported metal catalyst nanoparticles synthesized by a combined CVS/CVD process at atmospheric pressure. In our previous studies it has been shown that our simultaneous small- and wide-angle X-ray scattering laboratory setup can be applied to extract information on the nanostructured particles (SAXS) as well as the crystalline structures (WAXS) in different synthesis processes such as metallic nanoparticles generated by electrical discharges in inert gases [36–38] and silica-magnetite core-shell nanocomposites synthesized using the modified Stöber sol–gel method [39].

In the present paper, we extend the investigation to the model oxide-supported metal catalyst nanoparticles prepared by a CVS/CVD process at atmospheric pressure. To this end, a self-developed SAXS and WAXS laboratory system is used to investigate various oxide-supported Pt particles (Pt nanodots supported on silica, titania and alumina) which are used as model catalyst systems. We show how simultaneous SAXS and WAXS analyses offer a structural insight into the complexity of the supported metal catalysts, allowing quantitative study on the morphological characteristics of the synthesized oxide support particles and fine structures, including primary particles, internal subunits, mass fractal dimension of the aggregates, surface structure, and crystallite properties as well as the Pt nanodots deposited on the oxide support particles. Some factors affecting the Pt dot size are discussed. Additionally, the morphological modification of the support particle surface by mixing a certain amount of alumina into the other oxide support particles during the synthesis process is observed from the SAXS measurement. The SAXS and WAXS results are compared with those by TEM and the XRD reference database.

2. Experimental section

2.1. Sample preparation

A typical continuous CVS/CVD process, as already described in the literature [8,9] and shown in Fig. 1, has been used for the preparation of oxide support particles (silica, titania and alumina) by the CVS and sintering processes and supported Pt nanoparticles by the subsequently combined CVD process at atmospheric pressure. The control of gas flow rates and temperatures in the experimental setup was realized by flow indicator controllers and temperature indicator controllers, respectively. A nitrogen–oxygen mixture was used as carrier gas and the precursors used for silica, titania and alumina were tetraethylorthosilicate (TEOS), titanium (IV) isopropoxide (TTIP) and aluminium tri-sec-butoxide (ATSB), respectively. For preparing binary oxide support particles, for example, by mixing of a certain amount of alumina into silica to modify the surface structure, two bubbling systems ran in parallel by adjusting the ratio of two precursor vapors. The evaporated precursor from the bubbling system was mixed with oxygen and nitrogen and fed into a CVS tube reactor at 1000 °C. The precursor decomposed, oxidized and nucleated to oxide particles, which were highly fractal structures and were subsequently sintered/coalesced into solid spherical particles in a second tube furnace at 1500 °C. If the sintering temperature was lower, then it would be hard to obtain the solid spherical particles. In a second step the synthesized oxide particles were dried in the aerosol state with a diffusion dryer, mixed with the evaporated platinum precursor and then fed into a CVD reactor at 380 °C. The chemical decomposition reaction of the Pt precursor took place on the oxide support particles in the CVD reactor, leading to the Pt nanoparticles on the oxide support particles. The aerosol particles prepared in the respective synthesis steps (CVS, sintering and CVD) were sampled for simultaneous SAXS and WAXS studies. For comparison with the SAXS results, the prepared samples were additionally characterized by TEM (Philips CM12 microscope operating at 120 kV). The TEM micrographs were acquired to provide an overview of the particle shape and size, and analyzed using the imaging software ImageJ.

2.2. SAXS/WAXS measurements

A self-developed small- and wide-angle X-ray scattering laboratory camera, as shown in Fig. 2, has been used to study various oxide-