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Microporous and Mesoporous Materials



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The use of deposited nanocarbon for characterization of zeolite supported metal catalyst

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ARTICLE INFO

Article history: Received 22 July 2012 Received in revised form 5 October 2012 Accepted 9 November 2012 Available online 22 November 2012

Keywords: Zeolite supported metal catalyst Nanocarbon Specimen preparation Nanoparticle Metal-support interaction

ABSTRACT

Zeolite supported metal catalysts are widely used while the electron beam sensitive zeolite makes the characterization of the catalysts using electron microscope (EM) very difficult. Herein a sacrificial-zeolite specimen preparation (SZSP) technique is developed for the EM analysis of the catalyst. The metal particles are transferred from the zeolite support to the deposited nanocarbon generated in the metal catalyzed hydrocarbon reaction. SAPO-34 zeolite with Al₂O₃ binder supported Pt catalyst is employed as the model catalyst. The propane dehydrogenation reaction is carried out to deposit the nanocarbon overlayer which the Pt particles are transferred to as the new support for EM observation. The original catalyst, the deposited nanocarbon, as well as the Pt particles on the new support are characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope. The nanocarbon deposited on SAPO-34 and Al₂O₃ are of different morphologies and structures. The as-observed distribution of Pt particles on the new support suggests the enrichment of Pt on SAPO-34. The shape and size of the Pt particles as well as the strong Pt–SAPO-34 interaction are directly observed.

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1. Introduction

Zeolites have a porous structure that can confine molecules in small spaces. The zeolite affords large surface area and large cage with small window structure. This provides the space confinement and strong metal-support interaction for metal nanoparticles with high dispersion, good stability, and adjustable acidic strength when it is used as a catalyst support. The support of metal, such as platinum, on a porous support provides a way to obtain highly dispersed catalyst with metal nanoparticles. The as obtained metal/zeolite catalysts being used on a large scale for refining of petroleum, conversion of automobile exhaust, hydrogenation of carbon monoxide, hydrogenation and dehydrogenation of hydrocarbons, and many other processes [1-5]. The reactivity and selectivity of a metal catalyst depends greatly on their size, shape, and the metal-support interactions [6-9]. Up to now, a family of zeolites, such as ZSM-5, SAPO-34, X-zeolite, Y-zeolite, Beta, L-zeolite, SBA-15, as well as MCM-41, are widely used as supports for Pt based catalysts [10-14]. Both the size and shape of platinum nanoparticles have crucial influence on the catalytic performance. Well characterizing the size and distribution of metal and detecting the metal-support interaction is the first step to understand the heterogeneous catalysis science of metal/zeolite.

Among the current available techniques to characterize the size, shape, and fine structure like the arrangement style of metal atoms in the nanoparticles, electron microscopy is the most powerful tool [15–20]. However, the nonconductive zeolite is very sensitive. The electron beam damage especially under the strong beam used in transmission electron microscopy (TEM) is very obvious when the zeolite specimen was prepared according to the routine specimen preparation. The electron beam irradiation leads to destruction of the framework and finally makes it amorphous in very short time (usually less than 1 min). The structure destruction of the zeolite promotes the *in situ* fast sintering of small Pt particles, therefore, it is very difficult to obtain clear images of the originally highly dispersed metal nanoparticles on zeolite through routine TEM specimen preparation technique [10,21–23].

Continuous efforts have been paid to improve the stability of zeolite under the electron beam for electron microscopy observation. Various strategies, such as removing zeolitic water, replacing Al by Si (dealumination, effective for aluminosilicate zeolites), and introduction of heavy ions by ion exchange method, have been explored. The loading metal on the zeolite may be reconstructed and the current investigation results are very sensitive to experimental conditions as the deterioration of the modified zeolite structure always presents just in a lower rate [24–27]. Up to now, the most efficient and effective way to avoid electron beam damage of the specimen during TEM analysis of zeolite supported metal catalyst is the removal of the zeolite support by acid/alkali solution

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Fig. 1. Schematic representation of the SZSP process of zeolite supported Pt catalyst using deposited nanocarbon as the new support.

[28–30]. HF is usually used attributed from its good dissolution capacity of the metal oxides, especially SiO_2 , in zeolites. However, without the steric restriction and metal-support interaction of the support, sintering of small Pt particles occurs quickly under strong

electron beam [10]. Therefore, a new electron beam damage free support with good electron beam transparency, thermal and electronic property is highly required to stabilize the metal nanoparticles. Furthermore, as the agglomeration of small Pt particles is a spontaneous process in absence of the confinement of support, the new support should be generated before removal of the zeolites.

In this work, an *in situ* generated nanocarbon overlayer in metal catalyzed reaction [9,31] is chosen as a novel support for TEM characterization of metal nanoparticles on zeolites by a facile sacrificial zeolite specimen preparation (SZSP) strategy. As shown in Fig. 1, the metal/zeolite catalyst was used as catalyst for the heterogeneous reaction. The nanocarbon is deposited on the metal nanoparticles and the meso/micro-pore of the zeolites. The zeolites were further removed by acid/alkali treatment and a nanocarbon supported metal specimen was available. The coverage of this nanocarbon sheet provides space confinement for small Pt particles to maintain their stability under electron beam. This technique applies the catalytic characteristics of Pt particles to its electron microscopy characterization.

To demonstrate the proof of the concept, an industrial Pt based catalyst with SAPO-34 zeolite and 20 wt.% γ -Al₂O₃ binder as the



Fig. 2. (a) XRD spectra of the Pt–Sn/SAPO-34–Al catalyst, (\bullet) chabazite (CHA), and (*) γ –Al₂O₃; (b) SEM and (c) TEM image of the mixture of SAPO-34 and Al₂O₃ supported Pt catalyst; (d) partial amplification of the region (1) in TEM image (c); (e) partial amplification of the region (2) in TEM image; (f) HRTEM images and FFT of the Al₂O₃ particles in the mixture of SAPO-34 and Al₂O₃ supported Pt catalyst; (g) TEM images of the SAPO-34 crystal in the mixture of SAPO-34 and Al₂O₃ supported Pt catalyst.

Fig. 3. (a) Raman spectrum and (b) TG–DTA curve of nanocarbon deposited on the catalyst by 5-h propane dehydrogenation reaction. (Reaction conditions: *T*: 863 K; WHSVC₃H₈: 2.8 h^{-1} ; H₂/C₃H₈ = 0.25.) TEM image of (c) the chain-like coke sphere deposited over Al₂O₃, (d) the graphene-like sheet of coke deposited over the external surface of SAPO-34, and (e) the onion-like coke sphere deposited over Al₂O₃ using the SZSP strategy. (f) TEM image of the entrapped filamentous carbon with Pt particles deposited over the external surface of SAPO-34 using the SZSP strategy and (g) the EDS elemental analysis spectrum of this region.

support and Sn as the promoter was employed as the model catalyst. Dehydrogenation of propane to propylene over the catalyst was carried on to lead to the formation of the nanocarbon overlayer on Pt particles. The SZSP process was used to transfer the Pt particles to the nanocarbon overlayer for further characterization. This technique can serve as a new method to investigate the size, shape, and metal-support interaction for catalysts with zeolites as support.

2. Experimental

2.1. Catalyst preparation

The SAPO-34 was prepared according to the procedure reported in the literatures [32,33]. The as-synthesized SAPO-34 zeolite was palletized with γ -Al₂O₃ (20 wt.%) by Huier Green Chemical Tech-

nology Corporation (Beijing, China) to get SAPO-34 + γ -Al₂O₃ support (labeled as SAPO-34–Al). Pt–Sn/SAPO-34–Al was prepared by consecutive impregnation of Sn followed by Pt according to the procedure reported in the literatures [34]. The contents of Pt and Sn were 0.5 and 1.0 wt.%, respectively.

2.2. Propane dehydrogenation reaction for the nanocarbon overlayer deposition

The propane dehydrogenation reaction was performed in a fixed bed quartz reactor at 863 K over 200 mg catalyst with a particle size of 420–590 μ m. The catalyst was firstly reduced with H₂ at 773 K for 3 h before letting in feed gas. The WHSV_{C3H8} was 5.6 h⁻¹ and the molar ratio of H₂/C₃H₈ in feed gas was 0.25. Analysis of the product stream was performed with a gas chromatograph (GC) (TechComp 7890II). After a 5-h reaction, the spent

catalyst with deposited nanocarbon overlayer on the Pt particles is employed for the sequential SZSP process.

2.3. The SZSP technique for EM specimen preparation

The spent catalyst by a 5-h propane dehydrogenation reaction was dissolved using HF solution. Typically, 30 mg of the spent catalyst was dissolved in 1 mL 20% HF in a Teflon container. The organic compounds were extracted from the water phase by the addition of 1 mL CH_2Cl_2 . After the extraction was finished, the solid contained water phase was centrifuged to get the precipitated nanographene overlayer. Then it was washed with deionized water for 10 times to remove the adhered HF. A drop of the nanographene overlayer suspension was placed on a Cu grid with a perforated carbon film for EM characterization.

2.4. Catalyst characterization

XRD spectra of the catalyst were obtained with a Bruker D8 Advance diffractometer with Cu Ko radiation. A JEOL JSM 7401F scanning electron microscopy (SEM) operated at 3.0 kV was employed to acquire the SEM images and a JEOL JEM 2010 TEM operated at 120 kV with an energy dispersive spectrometer (EDS) attachment (EDAX PV 9800) was employed to acquire the TEM images and EDS spectra. The observations in scanning transmission electron microscope (STEM) mode were performed by using a FEI Tecnai G^2 F20 microscope operating at 200 kV, which was equipped with a high-angle annular dark-field (HAADF) detector in a STEM system for Z-contrasting STEM imaging and EDAX energy dispersive X-ray detector for elemental analysis and mapping. For the EDS mapping acquired by FEI TIA software, the dwell time is 1000 ms/pixel, the map size is 50×50 pixel, and the spot size is 6. The Raman experiments were performed using a Renishaw RM2000 Raman spectrophotometer with a 633 nm excitation source. The deposited coke content and the weight changing rate at coke burning profile were recorded by using a Netzsch STA409 thermogravimetric analyzer using air as the burning gas. The H₂-chemisorption experiments were carried on using Chembet

Fig. 4. HRTEM image and FFT of the Pt particles on the nanocarbonsupport.

Fig. 5. (a) STEM image of the nanocarbon supported Pt nanoparticles. (b) The histogram of Pt particle size distribution based on STEM image.

PULSAR TPR/TPD (p/n 02139-1) (Quantachrome Instruments Corporation). About 50 mg of Pt–Sn/SAPO-34–Al was loaded into a quartz cell and then reduced in flowing 7% H₂/Ar (10 mL min⁻¹). The temperature of the specimen was raised at 5 K min⁻¹ to 773 K and then maintained at 773 K for 2.0 h. The specimen was then flushed in flowing Ar at 813 K for 2.0 h and then cooled down to 318 K. The uptake of chemisorbed hydrogen was then measured by determining the uptake of H₂ from pulses of 4% H₂/Ar using a TCD detector. The pulse size was 1 mL g⁻¹ and the time between pulses was 5 min.

3. Results and discussion

3.1. Characterization of the Pt-Sn/SAPO-34-Al catalyst

The XRD pattern of the catalyst is shown in Fig. 2a. The chabazite (topology style of SAPO-34) diffraction lines and the γ -Al₂O₃ diffraction lines are clearly detected. No XRD peaks for the presence of crystalline Pt and Sn phases were detected, which is attributed from their small amount and high dispersion. Fig. 2b shows a SEM image of the catalyst, nano-sized Al₂O₃ agglomerates adhering onto the cubic SAPO-34 zeolite are observed. TEM image at low magnification (Fig. 2c) together with its partial amplifications (Fig. 2d and e) shows a clear adhering structure. The high resolution TEM image (Fig. 2f) indicates that the Al₂O₃ particles are stick-shaped with average length of ca. 15 nm. The nanostructure of the typical Al₂O₃ particle is studied based on the high resolution TEM (HRTEM) image (Fig. 2f) with the Fourier transform (FFT). The crystal faces with interplanar distance 4.57 Å and joint angle of 70.5° are observed, which correspond to the (111) and (1-11)crystal faces of Al₂O₃. A fast crystalline-to-amorphous transformation in the structure of SAPO-34 with bubbles observed under electron beam irradiation (Fig. 2g), which is similar to the beam damage of zeolite reported by other researchers [35]. The SAPO-34 has a three-dimensional pore system with ellipsoidal shaped

(a) (b) 10 nm (c) (d) (d)

Fig. 6. EDS elemental maps of the nanocarbon supported Pt specimen. (a) The HAADF-STEM image and its corresponding elemental maps of (b) Pt, (c) C and (d) O.

cages of 6.7×10 Å² interconnected via 8-membered ring windows with pore apertures of 3.8×3.8 Å² [36,37]. As the ion size of Pt precursor (PtCl²₆) is much larger than the pore, Pt particles were mainly distributed on the external surface of SAPO-34 as shown in Fig. 1 [38]. The Pt dispersion based on the irreversible uptake of the H₂-chemisorption using an adsorption stoichiometry of unity of hydrogen and platinum is 83.9%. Hemispherical particle size is determined from d (nm) = 1.13/D, where D is the metallic dispersion. The calculated particle size is 1.35 nm.

3.2. Transfer of Pt particles to the deposited nanocarbon

3.2.1. Formation of the nanocarbon overlayer

The nanocarbon overlayer on Pt particles was deposited using the propane dehydrogenation reaction over the Pt-Sn/SAPO-34-Al catalyst. The Raman spectrum for the nanocarbon deposited catalyst by a 5-h reaction is presented in Fig. 3a. Two broad bands are observed at 1319 and 1595 cm⁻¹. These features are assigned to the D and G bands, respectively [39]. Compared to that of single crystal graphite (1575 cm⁻¹), the G band shift to higher frequencies, indicating the decrease in graphite crystal size. The Raman peaks are deconvoluted with a Lorenzian lineshape for each of the two peaks and the value of I_D/I_G is 3.23 from which size of the graphite domain is deduced to about 1.36 nm [40]. The content of deposited coke was 10.7 wt.% determined by thermogravimetry/ differential thermal analysis (TG-DTA) with air as the burning gas. The weight changing rate profile (Fig. 3b) indicates two kinds of coke deposited on the spent catalyst. It was known that for Pt based catalyst, deposited coke consisted of two parts: carbonaceous overlayer on Pt particles (graphitic and/or amorphous) and polycyclic aromatic hydrocarbons on the acidic sites of support [31,38]. The first peak is considered to be the oxidation of carbonaceous overlayer [31,38,41]. The profile (Fig. 3b) can be further fitted approximately by two Gaussian functions. The content of carbonaceous overlayer is calculated to be 3.85 wt.%. The molar ratio of C in the carbonaceous overlayer and Pt is 125. The deposited nanocarbon can cover the Pt particles even if 100% dispersion is achieved (the theoretical molar ratio is about 37), indicating that the carbonaceous overlayer generated in propane dehydrogenation can serve as the new support of Pt particles for TEM observation.

3.2.2. The characterization of Pt nanoparticles entrapped nanocarbon

The spent catalyst with carbonaceous overlayer on Pt particles was dissolved with 20% HF solution to remove the original zeolite support. The polycyclic aromatic hydrocarbons were extracted from the suspension liquid by the addition of CH₂Cl₂. The TEM specimen was then prepared using the nanocarbon contained water phase. A family of the deposited coke morphologies are observed (Fig. 3c and d). The onion-like spheres are agglomerated into chain-like architectures with a pore size of 10-20 nm (Fig. 3c) that are considered to be deposited on the nano-Al₂O₃ particles. There is almost no Pt nanoparticles distributed on these onion-like spheres, which is confirmed by the HRTEM image (Fig. 3e). Another type of coke, graphene-like sheet (Fig. 3d), is considered to be deposited on the external surface of SAPO-34 crystals. The entrapped filamentous carbon with Pt particles on the graphene sheet is deduced from the HRTEM images together with the EDS spectra of this region (Fig. 3f and g). The difference in Pt location in the two types of coke demonstrates that the enrichment of Pt on SAPO-34 in the original SAPO-34 and Al₂O₃ mixture support. The EDS spectrum also demonstrates the successfully transfer of Pt particles from the original support to carbonaceous overlayer with very little amount of P and Al remained.

3.3. The TEM observation of the Pt particles on the nanocarbon

The nanostructure of the Pt particles distributed on the nanocarbon deposited on SAPO-34 crystal is further explored by HRTEM. Fig. 4 illustrates HRTEM images of typical Pt particles with different crystal faces, the indicated reflections in the Fourier transform (FFT) of the particles. The interplanar distance determined from the inverse FFT images is 0.196 and 0.227 nm, which correspond well to the (200) and (111) crystal faces of Pt, respectively.

For highly dispersed metal particles, the particle size distribution (PSD) analysis using STEM is more accurate than using HRTEM [42,43]. Highly dispersed Pt particles can be clearly seen in the dark field STEM image (Fig. 5a). The histogram of PSD of the Pt particles (Fig. 5b) was obtained based on the STEM image. The histogram of PSD can be fitted by one Gaussian function centered at 1.10 nm. The mean particle size is estimated to be 1.16 ± 0.42 nm. The Pt dispersion in the catalyst is also characterized using H₂-chemisorption experiment and the measured value is 83.92%. The calculated size of Pt particles is 1.35 nm from the H₂-chemisorption result, which is in good comparison with the STEM result.

The HAADF STEM imaging which can provide atomic number (Z) contrast information with atomic-scale spatial resolution, and EDS mapping derived from specimen via the SZSP strategy offer the distribution of the main element (Pt. C. O) distribution. The very small Pt nanoparticles distributed on the support show no direct relationship with the C or O element (Fig. 6). The uniform distribution of Pt nanoparticles is proposed to be derived from the strong metal-support interaction (SMSI) between the Pt and SAPO-34 support. This is confirmed by the Pt distribution on the deposited nanocarbon support, in which large amount of Pt can be observed on the carbonaceous overlaver deposited on SAPO-34 support (Figs. 3f, 5, and 6), while no Pt nanoparticles can be found on the nanocarbon deposited on Al₂O₃ support. Further investigation on the detailed mechanism for the SMSI between Pt and SAPO-34 are highly required.

4. Conclusions

A SZSP strategy has been developed through combination of the catalytic characteristics of Pt with its characterization to overcome the difficulty in electron microscopy observation of Pt particles supported on zeolite. The nanocarbon overlayer is generated in the Pt catalyzed hydrocarbon reaction, then the original zeolite support is dissolved in HF or other solution, and the Pt particles are transferred to the nanocarbon overlayer as the new support for TEM observation. The coke deposited on SAPO-34 and Al₂O₃ are of different morphologies and nanostructures. The as-observed distribution of Pt particles on the new support suggests enrichment of Pt on SAPO-34. The shape and size of the Pt particles as well as the mechanism of SMSI between Pt and the original support are directly observed. This offers a novel route to monitor the metal size and the interaction between the metal and support, which shed a light on the mystery science of heterogeneous catalyst and provide new insights on the relationship among the structure, active site, and reactivity.

Acknowledgments

We thank Ling Hu and Tongwei Wu for their help with the transmission electron microscope and the H₂-chemisorption experiment. This work was supported by National Basic Research Program of China (973 Program, 2011CB932602), Research Fund for the Doctoral Program of Higher Education of China (No. 20100002110022) and the IMR SYNL-T.S. Kê Research Fellowship.

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