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Shape-controlled synthesis of Pt particles and their catalytic performances in the *n*-hexadecane hydroconversion

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ABSTRACT

The platinum nanocrystals with truncated octahedral, spherical and cubic morphologies were synthesized and well dispersed onto the ZSM-22 support, in order to investigate the shape effect of Pt crystals on *n*-hexadecane hydroconversion. It is found that the crystal facets of Pt nanoparticles play more profound roles in determining the catalytic properties. The reaction test shows that both the conversion of *n*-hexadecane and selectivity of iso-hydrocarbons are higher for the catalysts with octahedron nanoparticles of Pt that are predominantly enclosed by Pt {111} crystal facets than those with spherical and cubic morphologies of Pt, whose surfaces consist of more Pt {100} facets. Combined with the results of CO-IR and TPHD, it is suggested that the activity and selectivity of the reaction are well correlated to the fractions of exposed Pt {111} crystal facets, which possess more activated surface defect sites and higher amounts of activated hydrogens either on the Pt surface or in the Pt phase. Meanwhile, the catalyst activity and selectivity are found to be highly sensitive to the Pt particle size. Smaller Pt particles have higher activity and lower isomerization selectivity.

1. Introduction

The catalytic hydroconversion of n-paraffin is an important reaction to improve the quality of diesel and gasoline with high octane number [1–4]. Hydroisomerization of light hydrocarbons can yield high octane fractions for gasoline blending, while hydroisomerization of long-chain alkanes can be employed for improving the low-temperature fluidity of middle distillates (e.g., jet fuels and diesels) or lubrication oils [5–7]. Platinum-supported catalysts, which are commonly employed for hydrotreating of oil fractions, are extensively used [8–11]. The activities and selectivities of a catalyst strongly depend on the shape (morphology) and size (dimension) of Pt crystals, and therefore synthesis of highly active Pt nanostructures of well-controlled shapes and sizes is one of the most attractive goals due to their potential application in heterogeneous catalysts[12–15]. Recently, a variety of methods have been reported for the synthesis of nano-structured Pt with different sizes and shapes, such as photochemical, pulse-radiolytical, thermal methods, electrodeposition processes, supercritical CO_2 deposition, toxic reducing agents, wet chemical, sonochemical, hard and soft template assisted approaches, etc [16–18]. In particular, it was found that the use of linear polymers like polyacrylate solution, poly(N-vinyl-2-pyrrolidone), sodium polyacrylate, P123 and polyvinyl alcohol can control the size and shape of the nanoparticles without affecting their inherent catalytic activity [12,19,20]. Reportedly, polymers can stabilize metal nanoparticles through the steric bulk of their framework and also by binding weakly to the nanoparticle surface through heteroatoms that act as ligands [18,21].

Alkane hydrogenolysis rates showed sensitivity to metal nanocrystals size [22–24]. Previous research unambiguously suggested that the structure dependency of reactivity is more important for nanocrystals smaller than 10 nm, in particular, particle size of less than about 2 nm to be crucial for activity [25–27]. However, there is no consensus on the reason for this effect. Some argue that low-coordinatively unsaturated metal atoms presented in small particles are more active, another explanation is electronic effects based on the particle size or combinations of the two [28]. Recently, the formation of Pt with particular morphologies, including cubic,

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tetrahedral, octahedral, hexagonal, polyhedral, spherical, irregular prismatic, icosahedral and cuboctahedral have also been reported. In addition, many investigations presented some close relationship between shapes and the catalytic properties of metal nanocrystals, which were performed on the exposed facets of metal polyhedral nanocrystals. For instance, Somorjai et al. [29,30] found that only cyclohexane were produced on Pt (100) or Pt nanocubes enclosed by {100} planes, whereas both cyclohexane and cyclohexene could be obtained over Pt (111) or cuboctahedrons enclosed by both {111} and {100} planes in Benzene hydrogenation reaction. They also observed that Pt nanocubes enhanced ring-opening ability and thus showed a higher selectivity to n-butylamine as compared to nanopolyhedra for pyrrole hydrogenation [22]. El-Sayed and co-workers [31–35] discovered that the average rate constant in the Suzuki cross-coupling reaction increased exponentially as the percentage of surface atoms at the corners and edges increased. Besides, Lee's reported [36,37] that the isomerization of trans 2-butene to their cis counterparts was promoted by (111) facets of platinum and that such selectivity was reversed on more open surfaces. They also pointed out that the dehydrogenation of cyclohexene was found to be faster on Pt (111) than on Pt (100) single-crystal surfaces and surface-science investigations on the isomerization of unsaturated olefins strongly suggest that selectivity toward the formation of the cis-isomer may be favored by Pt (111) facets [36].

Some works have been carried out to study the catalytic behaviors of different shapes, but there are few reports on what are the factors contributed to the effect. In this study, the Pt nanocrystals with octahedral, spherical and cubic morphologies, which are typically enclosed by equivalent {111} and {100} facets were synthesized and supported on ZSM-22 as the model catalysts. The *n*-hexadecane hydroconversion performance of catalysts was tested in a fixed-bed reactor. The catalysts were characterized by H_2 chemisorption, Transmission Electron Microscope (TEM), FT-IR spectroscopy of adsorbed CO, Temperature-programmed hydride decomposition (TPHD) techniques to investigate the reason for the different isomerization performance caused by shapes.

2. Experimental

2.1. Materials

ZSM-22 (Si/Al = 100) used as the support of the catalysts was provided by Shanghai Novel Chemical Technology Co., Ltd., China. K_2PtCl_4 (AR) were supplied by Xi'An catalyst chemical Co., Ltd. $H_2PtCl_6·6H_2O$ (AR) was purchased from Tianjin Guangfu Fine Chemical Research Insititute. Poly (vinyl pyrrolidone) (PVP, M_w = 55,000) were purchased from Sigma–Aldrich. Cetyltrimethyl Ammonium Bromide (CTAB) and $NaBH_4$ were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. All Other chemicals used in this study were of analytical grade (purity > 99%). All the chemical reagents were used without further purification.

2.2. Synthesis of Pt nanocrystals with different shapes

Pt truncated octahedral nanoparticles were synthesized according to literature methods [25,38,39]. In detail, 1.5 ml of 0.077 M H_2PtCl_6 and PVP were dissolved in 15 mL mixed solution of deionized water and Ethylene glycol with a volume ratio of 1:4 hosted in a three-neck flask equipped with a reflux condenser and a Teflon-coated magnetic stirring bar. The solution was heated to 90 °C and refluxed for 4 h. The products were collected by centrifugation and washed with acetone once and a mixed solution of deionized water and ethanol with a volume ratio of 1:4 several times to remove excess PVP and physically adsorbed chloridion ions, and then dried in air at 60 °C for 10 h. For the Synthesis of Pt nanospheres, an aqueous H_2PtCl_6 solution (0.077 M, 2.5 mL) were mixed with 10 mL of aqueous D-glucose solution (0.02 M) and stirred for 10 min. Then, an aqueous $NaBH_4$ solution was added dropwise under stirring for another 1 h. The product was washed with water and centrifuged to collect the catalyst [16]. In a typical synthesis of Pt nanocubes, CTAB were used because bromide species selectively adsorbed onto Pt (100) crystal faces and induced the formation of Pt nanocubes. Aqueous solutions of CTAB (100 mM) and K_2PtCl_4 (1 mM) were dissolved in deionized water at room temperature. The solution was heated at 60 °C for about 5 min until the solution became clear. Freshly prepared $NaBH_4$ (30 mM) used as reducing agent were added dropwise. Finally, the reaction continued for 5 h at 60 °C. The products were collected by centrifugation and washed with ethanol several times [40].

2.3. Catalysts preparation

The catalysts studied in this work were prepared by impregnation of the zeolitic supports with the platinum nanoparticle colloid following a previously reported methodology [41]. The impregnation was carried out by mixing a known amount of support with an adequate amount of the purified nanoparticle colloid suspension in order to obtain a final metallic loading of 0.5 wt.%. The mixtures were vigorously stirred for 12 h using a magnetic stirrer to guarantee similar metal loading and distribution in all the catalysts and then the samples were heat treated at 60 °C to remove the solvent. Finally, the catalysts were washed several times with a cold mixture of H_2O/EtOH (50:50, v/v), dried at 60 °C for 12 h and calcinated in air at 200 °C to remove the stabilising agents [36]. The resulting catalysts were denoted as oct-111, sph-111+100 and cub-100.

2.4. Catalyst characterization

TEM measurement was performed with a Tecnai G2 F30 electron microscope operating at 300 kV voltages. The reduced catalysts (in H_2 flow at 300 °C for 1 h) were suspended in ethanol with an ultrasonic dispersion for 20 min and deposited on copper grids coated with amorphous carbon films.

H_2 chemisorption was performed on AutoChem II 2920 equipment (Micromeritics, USA) with a TCD detector at 50 °C. Before the test, the catalysts were in situ reduced by flowing pure H_2 (30 ml/min) at 300 °C for 1 h and then purged with Ar for 1 h. After cooled down to 50 °C, several pluses of H_2 were injected at regular intervals until saturation with H_2 for the sample.

FTIR study of CO adsorption was performed on an infrared spectrometer (VERTEX70, Bruker, Germany), equipped with KBr optics working at the liquid nitrogen temperature. The infrared cell with ZnSe windows was connected to a gas-feed system with a set of stainless steel gas lines, allowing the in situ measurement for the adsorption of CO. At first, the catalysts were reduced in H_2 flow (20 ml/min) at 300 °C for 1 h. Then the system was cooled down to 25 °C in He flow and pretreated in He flow (20 ml/min) at 25 °C to clean the surface for 1 h. The CO-FTIR spectra were recorded following adsorption of CO at 25 °C and subsequently desorption of CO in He flow at a higher temperature.

Temperature-programmed hydride decomposition (TPHD) was used to examine the thermal decomposition of the Pt-H phase that was either adsorbed on or absorbed in the catalyst [42]. A 150 mg of catalyst was reduced in a quartz reactor in a flow of 10% H_2/Ar (20 ml/min) at 300 °C for 2 h. After reduction, the sample was cooled down to room temperature in H_2/Ar flow (20 ml/min) to avoid the thermal decomposition of the Pt-H phase and it was purged with Ar gas (20 ml/min) for 30 min to remove the weakly adsorbed hydrogen. The catalyst temperature was increased from 30 °C to 300 °C at a rate of 5 °C/min under H_2/Ar with a flow rate 20 ml/min. Since the samples had already been reduced, the aim of