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Platinum embedded within carbon nanospheres for shape selective liquid phase hydrogenation

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ARTICLE INFO

Article history:

Received 22 October 2012

Accepted 6 February 2013

Available online 18 February 2013

ABSTRACT

Reactant shape selective catalysis occurs when substrates of different sizes and shapes are consumed at different rates over catalysts that combine molecular sieving transport processes with reaction. By contrast the same substrates react at nearly equivalent rates over catalysts that have large, open pores that do not induce any form of molecular sieving. Here we describe the design and synthesis of reactant shape selective catalysts for liquid phase hydrogenation reactions. Using an emulsion polymerization of furfuryl alcohol, we have made catalysts that consist of microporous carbon nanospheres within which are embedded platinum nanoparticles. The porosity of the carbon spheres was found to be a key parameter affecting catalyst activity and selectivity; porosity was varied by adding pore forming agents, such as polyethylene glycol with different molecular weights, during synthesis, or by mild oxidation of the as-synthesized catalyst using carbon dioxide. In addition to increasing porosity to reduce mass transfer limitations, a synthesis of smaller carbon spheres (<200 nm) was devised to reduce the micropore diffusion length. Decreasing the particle size of the catalyst by adjusting the surfactant composition during polymerization, improved the effectiveness factor by approximately one order of magnitude making it as active as a comparable standard metal catalyst.

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1. Introduction

Porous carbon materials are used commercially as heterogeneous catalyst supports for fine chemicals synthesis because of their combined physical and chemical properties [1,2]. They possess high surface area, chemically variable surfaces and high stability. These properties makes carbon suitable as a support for dispersing transition metal nanoparticles [3–6]. Carbon-supported catalysts figure prominently in electrocatalysis and fuel cells [7–10]. In contrast to carbons derived from natural precursors, synthetic, polymer-derived carbons can be prepared reproducibly with high purity, and they can be modified systematically to control their total porosity, their

pore size distribution and their level of surface functionality and they have been known to be molecular sieves for some time [11–13]. These types of nanoporous carbon have been studied as catalyst support media for a number of different reaction types [14–18].

Shape selective catalysis has been demonstrated mostly in zeolites due to their well-ordered pore structure [19]. Zeolite-based shape selective catalysts with controlled pore structure and acidity have been used in applications such as selective toluene methylation, naphthalene hydrogenation and isomerization reactions [20]. Herein, we examine the liquid phase hydrogenation of alkenes with platinum embedded within nanoporous, molecular sieving carbon. Because the platinum

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<http://dx.doi.org/10.1016/j.carbon.2013.02.024>

particles are larger than the pores by an order of magnitude or more, by embedding them in the carbon, they cannot move; they are immobilized and frozen in place [16,21]. Thus they do not sinter or agglomerate. By embedding, we invert the usual catalyst structure. Instead of the particles being supported on an activated carbon surface residing within a pore, the platinum particles reside within the polyfurfuryl alcohol derived nanoporous carbon (PFA-NPC). The pores that are in the vicinity of the metals end at the metal particle surfaces. In this way the locus of catalytic activity is at the junction of a pore and a portion of the platinum particle surface. In principle, the reaction that takes place at this junction of pore and particle must be subject to the maximal level of steric factors that can be imposed by the walls of the pore.

To fully realize this potential for shape selective catalysis with the platinum embedded within PFA-NPC (Pt-Em-PFA-NPC) materials, their activity must approach that of platinum supported on activated carbon catalysts. It has been shown that Pt-Em-PFA-NPCs are active for the gas phase hydrogenation of ethylene, propene, 1-butene, but to be of interest for fine chemicals synthesis, these catalysts must be useful for reactions of larger molecules [15,16]. In reaction engineering terms, the effectiveness factor of the Pt-Em-PFA-NPC catalysts must be sufficiently close to that of a standard supported platinum catalyst. We know from first principles that to increase the effectiveness factor, we must decrease the Thiele Modulus. In the case of an isothermal reaction with first order kinetics in a spherical catalyst this means that the radius of the sphere must be small enough to reduce the diffusion length, and that the diffusivity must be large enough to significantly lower internal mass transfer resistance. Put another way the magnitude of the characteristic time for diffusion within the catalyst, $\theta_{\text{diffusion}}$, must be small relative to the magnitude of the characteristic time for chemical reaction θ_{reaction} , according to Eq. (1),

$$\phi = \frac{R}{3} \sqrt{\frac{\rho k \tau}{D \varepsilon}} = \frac{1}{3} \sqrt{\frac{R^2 \rho k \tau}{D \varepsilon}} = \frac{1}{3} \sqrt{\frac{\theta_{\text{diffusion}}}{\theta_{\text{reaction}}}} \quad (1)$$

ϕ = Thiele Modulus; R = radius of the spherical particle (cm); ρ = density of the particle (g/cm^3); k = first order rate constant ($\text{cm}^3/\text{g s}$); τ = tortuosity; D = diffusivity of reactant within the catalyst (cm^2/s); ε = void fraction within the catalyst.

In this paper we use the Thiele modulus as a guide for improving the activity of the embedded platinum catalysts for hydrogenation of longer chain and bulkier alkenes in the liquid phase. To assess the effectiveness of the changes that were made in the catalyst structure, hydrogenation reaction rates were used as measures of the extent of improvement in the effectiveness of embedded catalysts. By comparing the hydrogenation rates of linear alkenes with increasing chain lengths, or with a branching methyl group, we were able to assess how the changes that we made in the catalyst structure affected the relative activities and reactant shape selectivities of the embedded catalysts. We then took the ratio of the rate of any given hydrogenation reaction over an embedded platinum catalyst to the rate of reaction over a supported platinum catalyst to compute an “effectiveness factor”. This allows us to place these effectiveness factors for the new catalysts on a general plot of effectiveness factor

versus the Thiele modulus in order to progressively solve the catalyst design problem.

2. Experimental

2.1. Materials

Pluronic F-127, which is a tri-block copolymer consisting of poly(ethylene oxide) as the hydrophilic part and poly(propylene oxide) as the hydrophobic segment, was purchased from Sigma-Aldrich and was used as received. Ethanol and distilled water were used as solvents and hydrochloric acid solution (HCl, 36.5 wt.%) was used as the polymerization initiator. Furfuryl alcohol (FA) (98% purity) was purchased from Sigma-Aldrich and used as received as the monomer. All the alkenes (and alkanes) that were used for the experiments were purchased from Sigma-Aldrich. N-undecane which was used as the main solvent in catalysis was purchased from Alfa-Aesar and was used as received. Platinum acetylacetonate ($\text{Pt}(\text{acac})_2$) was purchased from Strem Chemicals and was used for synthesizing platinum nanoparticles.

2.2. Catalyst synthesis

2.2.1. Supported control catalyst

An emulsion polymerization approach adapted from Yao's work [22] was used to synthesize carbon spheres with controlled size [23] and these were used as the support for the platinum; this is the supported catalyst that we take as the control in this study. For a typical synthesis, 6 g of surfactant (Pluronic F-127) were dissolved in a mixture of ethanol and water (40 cc ethanol and 12 cc water). The mixture was magnetically stirred to form a homogeneous solution. After complete dissolution of solid, 2.8 g HCl was added as the polymerization initiator. This step was followed by adding FA to the solution, drop wise. The polymerization proceeded for 12 h. The first step, polymerization under mild conditions, was followed by a rapid polymerization and cross-linking under forcing conditions that were catalyzed by concentrated sulfuric acid. To do this, 5 M sulfuric acid was added to the polymerized solution and the mixture was heated to 90 °C until all the solvent evaporated. The viscous brown residue of high polymer furfuryl alcohol was then washed and centrifuged several times with a copious excess of distilled water. The solid that resulted was dried in an oven overnight. To transform these polyfurfuryl alcohol (PFA) spheres to carbon, pyrolysis was done under argon atmosphere at 800 °C. To synthesize the supported catalyst, these spheres were “activated” and then used as the support for platinum. We refer to the carbon spheres after activation as ACS for activated carbon sphere. The activation of the carbon spheres was carried out under flowing CO_2 at 900 °C. The activation process was stopped once the mass of the carbon was 55% of the original mass, which is to say after 45% of the original pyrolyzed mass was removed. This process increases the porosity of the carbon spheres and also increases the available surface area for dispersing the platinum nanoparticles. More details on the carbon spheres can be found elsewhere [22,23].

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