

Pt Nanoparticles Encapsulated in Zeolites for Tandem Aldol Condensation and Hydrogenation of Furfural with Acetone

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Introduction

Tandem catalysis has been known as an effective process intensification strategy for chemical processes.¹ Metal-acid bifunctional catalysts are widely used for tandem reactions because metal and acid sites catalyze a broad but distinct range of reactions.^{2,3} However, not all catalytic materials with both metal-acid sites could mediate the tandem reaction in the desired sequence because reactants are exposed to both acid and metal sites in the beginning of the reaction, and both metal and acid-catalyzed conversions would happen in parallel rather than in desired sequence.^{3,4} Thus, the distribution of catalytic sites can play a crucial role in designing catalysts for tandem reactions. One effective strategy for manipulating the distribution of catalytic sites in metal-acid bifunctional catalysts is to encapsulate metal nanoparticles (NPs) into acid zeolite matrices.^{5,6}

In this study, we report a cationic polymer-assisted synthetic method to encapsulate Pt NPs into HZSM-5 zeolites with >90% of encapsulation degree of the NPs.⁷ The encapsulated catalyst (Pt@HZSM-5) is used for the tandem aldol condensation and hydrogenation of furfural with acetone, and shows hydrogenated aldol adducts with 97% yield.

Materials and Methods

HZSM-5 encapsulated Pt NPs (Pt@HZSM-5) are achieved by introducing polydiallyldimethylammonium chloride (PDDA) into zeolite synthesis solution with PtCl_6^{2-} . For comparison, Pt NPs are loaded on HZSM-5 zeolites (Pt/HZSM-5) of which HZSM-5 is prepared by the same method used in the synthesis of Pt@HZSM-5 except for adding Pt precursors. After running tandem aldol condensation and hydrogenation of furfural with acetone over the prepared catalysts, the reaction product is analyzed on GC/MS (FID detector).

Results and Discussion

The key to the formation of Pt@HZSM-5 is to introduce a cationic polymer into zeolite synthesis solution with anionic metal precursors. The cationic PDDA polymers can electrostatically interact with both anionic Pt precursor (PtCl_6^{2-}) and anionic aluminosilicate building units of zeolites during zeolite crystallization, thereby promoting the encapsulation of the metal precursors into the zeolite matrix (Figure 1).

The ability of Pt@HZSM-5 to mediate tandem reactions is demonstrated using aldol condensation and hydrogenation of furfural with acetone as a model system. Pt@HZSM-5 produces a combined yield of 87% for hydrogenation aldol adduct, i.e., 4-(2-furyl)-butan-2-one (FAc-H, 3%) and FAc-HH (84%) at 160 °C for 20 h (Figure 2). The tandem reaction over Pt@HZSM-5 is

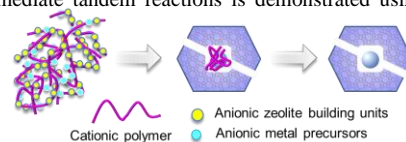


Figure 1. Synthesis scheme for encapsulating metal NPs into zeolites.

accelerated at 180 °C for 3 h. In contrast, Pt/HZSM-5 leads to much lower yields of the target products, and the majority of furfural undergoes decarbonylation (group A) or hydrodeoxygenation (HDO, group B). This is because furfural is directly exposed to Pt NPs on the HZSM-5 from the beginning of the reaction. Additional control experiments with the physical mixture of catalysts, i.e., Pt/SiO₂+HZSM-5 and Pt@Si-MFI+HZSM-5, confirm that these catalysts lead furfural to undergo not only aldol condensation but also its decarbonylation and HDO in parallel.

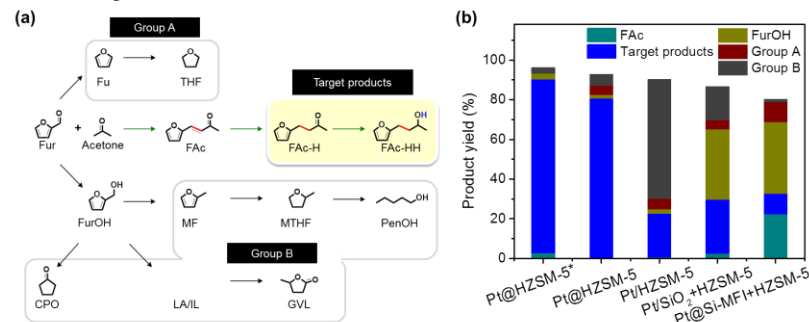


Figure 2. (a) Reaction pathways for tandem aldol condensation and hydrogenation of furfural with acetone, and (b) catalytic results over tested catalysts. Reaction conditions are as follows: 1 mmol furfural, 20 mmol acetone and 2 mL isopropyl alcohol; 600 psi H₂; furfural/Al (mol mol⁻¹) = 43; furfural/Pt (mol mol⁻¹) = 1232; 180 °C for 3 h, except Pt@HZSM-5* (160 °C for 20 h).

Significance

Encapsulation of metal NPs within zeolites is a promising route for tandem reactions which enable multiple sequential reactions to proceed in a single vessel via one-step. We develop a cationic polymer-assisted synthetic strategy to encapsulate Pt NPs into MFI zeolites. The prepared Pt@HZSM-5 selectively mediates the tandem aldol condensation and hydrogenation of furfural and acetone to form hydrogenated aldol adducts with 87% yield. This is the first demonstration that the product distribution is manipulated by tailoring the architecture of catalytic materials via encapsulation.

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