

Research Note

Catalytic dehydroisomerization of *n*-alkanes to isoalkenes

Xuebing Li, Enrique Iglesia *

Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462, USA

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Abstract

An equilibrated mixture of pentene isomers was produced by dehydroisomerization of *n*-pentane on catalysts consisting of Pt clusters within [Fe]ZSM-5 channels. These catalysts showed high isomerization rates, excellent stability even without added H₂, and isopentene selectivities above 60%. Metal sites on Pt clusters dehydrogenate *n*-alkanes and *n*-alkenes formed undergo skeletal rearrangements with high selectivity on weak acid sites prevalent in Na-[Fe]ZSM-5 after reduction of exchanged Pt cations. Zeolite channels inhibit side reactions and sintering processes that cause rapid deactivation on unprotected Pt clusters.

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1. Introduction

Alkenes are useful intermediates in the synthesis of many chemicals. One of these, methyl-*tert*-butyl ether, produced via isobutene-methanol reactions and useful as a fuel additive, has raised concerns about its solubility and permanence within aquifers [1]. *tert*-Amyl methyl and larger ethers are less soluble and degrade more rapidly; as a result, they have emerged as attractive alternatives. The synthesis of these molecules requires higher isoalkenes, which can be produced via catalytic dehydroisomerization of *n*-alkanes. The selective direct dehydroisomerization of *n*-butane to isobutene has been reported [2–9], but corresponding reactions of larger *n*-alkanes occur concurrently with side reactions and remain largely unexplored [10,11].

We have shown previously that Pt/Na-[Fe]ZSM-5 catalyzes dehydrogenation of C₂–C₄ alkanes with unprecedented reactivity and stability [12,13]. The synthesis of *n*-alkenes from larger *n*-alkanes required the rigorous titration of all residual Brønsted acid sites in the catalysts using Cs [14]. These acid sites, however, catalyze alkene isomerization via monomolecular pathways [15]. We exploit here these isomerization pathways and the remarkable reactivity and stability of encapsulated Pt clus-

ters in alkane dehydrogenation to catalyze the direct dehydroisomerization of *n*-pentane to equilibrated mixtures of pentene isomers. These catalysts exhibit excellent reactivity, selectivity, and stability even in the absence of H₂ in the reactant stream.

2. Experimental

The synthesis of Pt/Na-[Fe]ZSM-5 has been previously reported [12–14]. Na-[Fe]ZSM-5 precursors were prepared by exchanging NH₄-[Fe]ZSM-5, synthesized by known methods [15], three times with 0.1 M NaNO₃ solutions (EMD Chemicals, >99%) at 353 K for 15 h. Pt cations were then grafted by exchange with [(NH₃)₄Pt](NO₃)₂ solutions (6.25 × 10⁻⁵ M; Aldrich, 99.995%) for 12 h at 353 K, and subsequent filtration, rinsing with deionized water, and treatment in flowing dry air (Praxair, extra dry, 1.67 cm³ s⁻¹) for 12 h at 723 K (0.017 K s⁻¹). [Fe]ZSM-5 crystals were ~0.5 μm in diameter (transmission electron microscopy). This sample contained 0.12 wt% Pt and 0.28 wt% Fe with a Si/Fe atomic ratio of 340 (from inductively-coupled plasma emission spectra). Al was present in trace amounts (0.06 wt%).

The Pt dispersion (0.58) was measured from volumetric uptakes of strongly chemisorbed H₂ (4–40 kPa) at 298 K using a Quantasorb chemisorption analyzer (Quantachrome Corp. Autosorb-1), after treating samples (1 g, 180–250 μm diameter) in He (0.5 cm³ s⁻¹) at 573 K for 1 h, then at 573 K in

* Corresponding author.

E-mail address: iglesia@berkeley.edu (E. Iglesia).

H₂ (0.5 cm³ s⁻¹) for 2 h, and finally in dynamic vacuum at 573 K for 1 h. Strongly chemisorbed hydrogen by subtracting from total uptakes those measured after evacuation at 298 K, which correspond to weakly-held hydrogen, after extrapolating both adsorption and backdesorption isotherms to zero H₂ pressure. A H:Pt adsorption stoichiometry was used to calculate the number of Pt surface atoms.

n-Pentane reaction rates and selectivities (25 kPa, Aldrich, 99%) were measured at 673 K and ambient pressure in two types of reactors; one was a tubular reactor with plug-flow hydrodynamics and the other a gradientless recirculating batch reactor (206 cm³ volume). Both reactors were certified to be free of mass or heat transfer corruptions. Catalysts (0.1 g in flow and 0.001 g in batch reactors, 180–250 μm aggregates) were treated for 2 h in 40% H₂ (Praxair, 99.999%, 0.20 cm³ s⁻¹) in He (Praxair, 99.999%, 0.30 cm³ s⁻¹) at 673 K. *n*-Pentane (25 kPa) was added to He flow with a syringe pump (Teledyne Isco, Model 500 D). Reactants and products were separated by gas chromatography (HP 5890 II; HP-1 capillary column; 50 m × 0.32 mm) and detected by flame ionization. The approach to equilibrium for each pentene isomer (η_i) from *n*-pentane was calculated from measured rates and thermodynamic data [16] and used to correct measured net rates and determine forward dehydroisomerization rates [14].

3. Results and discussion

Fig. 1 shows *n*-pentane dehydroisomerization rates (per Pt atom) and selectivities (on a carbon basis) on Pt/Na-[Fe]ZSM-5 as a function of time-on-stream (673 K, 25 kPa *n*-pentane; flow reactor, 140 h). Forward pentene formation rates decreased from 5.7 mol (g-atom Pt)⁻¹ s⁻¹ (25% *n*-pentane conversion) after 0.8 h on stream to 1.5 mol (g-atom Pt)⁻¹ s⁻¹ (11% *n*-pentane conversion) after 140 h (Fig. 1a). Measured pentene formation rates are compared per Pt atom, because dispersion data were unavailable in the comparative previous report [10]. These rates are ~30 times greater on Pt/Na-[Fe]ZSM-5 than on Pt/SAPO-11 (0.5 wt% Pt) [10] at similar values (0.35) of the approach to equilibrium for pentenes from *n*-pentane even though the latter rates were measured at higher temperature (773 vs. 673 K) [10] (Table 1). The higher rates on Pt/Na-[Fe]ZSM-5 apparently because of the higher dispersion and resistance to sintering of encapsulated Pt clusters prepared by grafting of Pt precursors onto Na-[Fe]ZSM-5. Undesired hydrogenolysis re-

actions are also inhibited on small Pt clusters because of their requirement for large Pt ensembles [17].

First-order deactivation constants on Pt/Na-[Fe]ZSM-5 (0.004 h⁻¹) are similar to those observed for C₂–C₄ alkane dehydrogenation on these catalysts [12,13] and ~10 times smaller than for *n*-pentane dehydroisomerization on Pt/SAPO-11 even though H₂ was present to stabilize the catalysts in the latter study [10] (Table 1, Fig. 1). We conclude that encapsulation of small Pt clusters within constrained environments in [Fe]ZSM-5 channels also inhibits chain growth reactions that form unsaturated organic residues responsible for deactivation when Pt clusters are present within less protected environments [18].

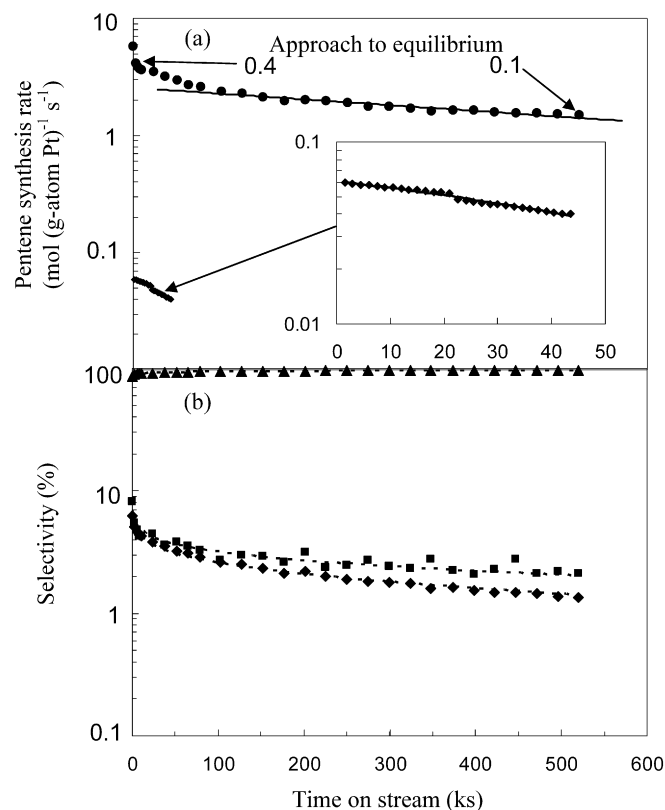


Fig. 1. (a) Pentene formation rates during *n*-pentane dehydroisomerization on (●) Pt/Na-[Fe]ZSM-5 at 673 K (*n*-pentane partial pressure: 25 kPa; H₂ partial pressure: 0 kPa; space velocity: 12 mol (g-atom Pt)⁻¹ s⁻¹) and (◆) Pt/SAPO-11 at 773 K (*n*-pentane partial pressure: 26 kPa; H₂ partial pressure: 44 kPa; space velocity: 0.24 mol (g-atom Pt)⁻¹ s⁻¹) [10]. (b) Selectivities to (▲) pentenes, (◆) cracking products and (■) oligomerization products during *n*-pentane dehydrogenation on Pt/Na-[Fe]ZSM-5 at 673 K in the absence of H₂.

Table 1
Catalytic performance of Pt-based catalysts for *n*-pentane dehydroisomerization

Catalyst	Reaction conditions		<i>n</i> -Pentane conversion (%)	Measured pentene synthesis rate ^a	Pentene selectivity (%)	First-order deactivation rate constant (h ⁻¹)
	Reactants (kPa)	<i>T</i> (K)				
Pt/Na-[Fe]ZSM-5 (this study)	<i>n</i> -Pentane (25) H ₂ (0)	673	16	1.9	95	0.004
Pt/SAPO-11 [10]	<i>n</i> -Pentane (26) H ₂ (44)	773	24 ^b	0.06	94 ^b	0.04 ^b

^a mol (g-atom Pt)⁻¹ s⁻¹.

^b Obtained from Fig. 5, Ref. [10].

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