

Research Note

Catalytic dehydroisomerization of *n*-alkanes to isoalkenes

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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

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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].

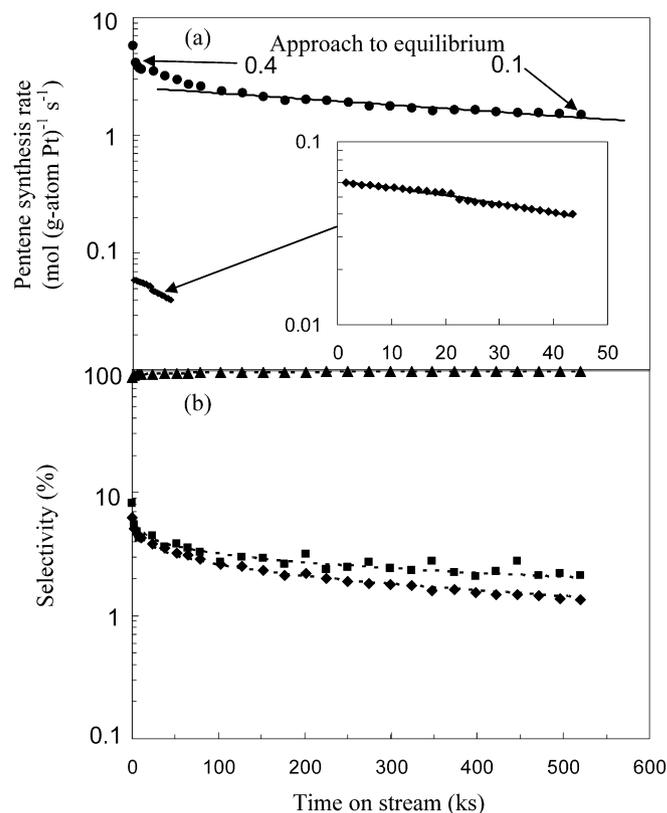


Fig. 1. (a) Pentene formation rates during *n*-pentane dehydroisomerization on (●) Pt/Na-[Fe]ZSM-5 at 673 K (*n*-pentane partial pressure: 25 kPa; H₂ partial pressure: 0 kPa; space velocity: 12 mol (g-atom Pt)⁻¹ s⁻¹) and (◆) Pt/SAPO-11 at 773 K (*n*-pentane partial pressure: 26 kPa; H₂ partial pressure: 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].

Table 2
Double-bond and methyl-shift isomerization. Approach to equilibrium from *n*-pentane during *n*-pentane dehydroisomerization on Pt/Na-[Fe]ZSM-5 at 673 K^a

Time on stream (h)	η_i^b					
	<i>n</i> -Pentenes			Isopentenes		
	1-Pentene	<i>trans</i> -2-Pentene	<i>cis</i> -2-Pentene	3-Methyl-1-butene	2-Methyl-1-butene	2-Methyl-2-butene
0.8	0.47	0.45	0.39	0.39	0.38	0.42
140	0.15	0.14	0.12	0.09	0.08	0.09

^a Reaction conditions: *n*-pentane, 25 kPa; space velocity: 12 mol (g-atom Pt)⁻¹ s⁻¹.

^b Approach to equilibrium from *n*-pentane:

$$\eta_i = \frac{[P_{\text{pentene}(i)}][P_{\text{H}_2}]}{[P_{n\text{-pentane}}]} \times \frac{1}{K_{\text{eq},i}}$$

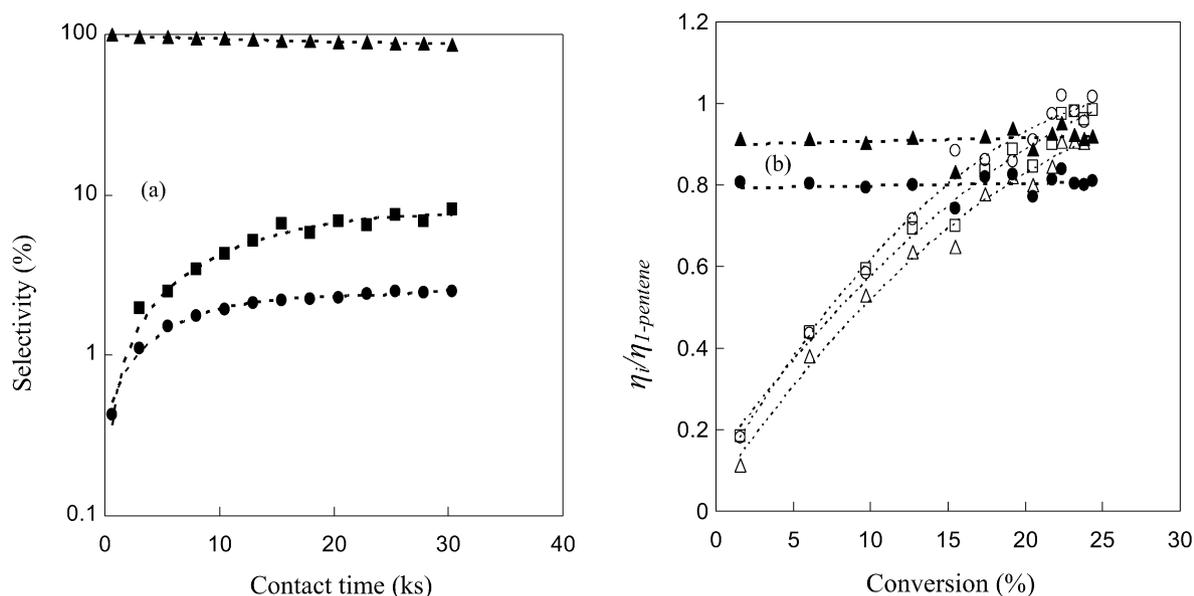
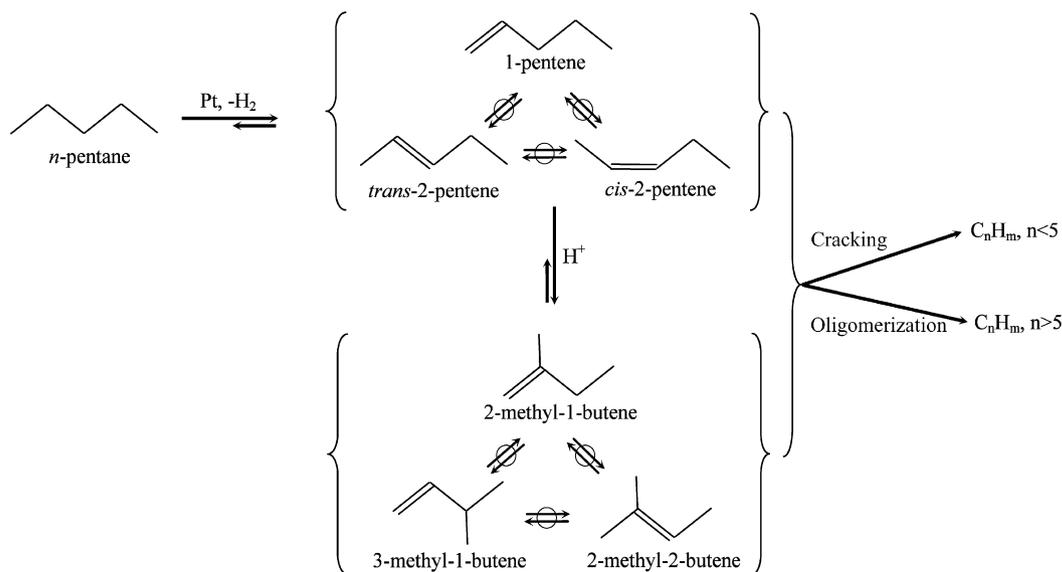


Fig. 2. (a) Selectivities of (▲) pentenes, (◆) cracking products and (■) oligomerization products during *n*-pentane dehydrogenation on Pt/Na-[Fe]ZSM-5 at 673 K in RRU unit in the absence of H₂. (b) Ratio of ($\eta_i/\eta_{1\text{-pentene}}$) as a function of *n*-pentane conversion: (▲) *trans*-2-pentene, (●) *cis*-2-pentene, (○) 3-methyl-1-butene, (△) 2-methyl-1-butene and (□) 2-methyl-2-butene. *n*-Pentane partial pressure: 25 kPa.



Scheme 1. Possible pathways for *n*-pentane dehydroisomerization on Pt/Na-[Fe]ZSM-5.

The selectivity to pentenes increased from 85 to 96% with increasing time-on-stream (Fig. 1b), while selectivities to smaller molecules, formed by cracking or hydrogenolysis side reactions, and to larger hydrocarbons, formed by oligomerization/dehydrogenation pathways, concurrently decreased. These selectivity trends predominantly reflect weaker contributions from secondary reactions as *n*-pentane conversion decreased with time, but perhaps also the selective deactivation of stronger acid sites, which favor cracking and oligomerization of primary alkene products.

Pentene isomers are essentially in thermodynamic equilibrium with each other during *n*-pentane dehydrogenation on Pt/Na-[Fe]ZSM-5. The approach to equilibrium values (η) are similar for all isomers during the early stages of reaction (0.8 h time-on-stream; Table 2). Thus, skeletal isomerization of pentenes to form branched isomers (3-methyl-1-butene, 2-methyl-1-butene and 2-methyl-2-butene) is fast on acid sites formed in Na-[Fe]ZSM-5 during reduction of grafted cationic Pt precursors. At longer times (140 h), *n*-pentenes (1-pentene, *trans*-2-pentene and *cis*-2-pentene) remain equilibrated with each other via fast hydride shifts, but η values for isopentenes become smaller than for *n*-pentenes, apparently because slower methyl shift reactions cannot reach equilibrium as the number of acid sites decreases with time-on-stream (Table 2). Nevertheless, isopentenes represent more than 60% of all pentene products even after 140 h on Pt/Na-[Fe]ZSM-5 catalysts.

Primary and sequential pathways in dehydroisomerization reactions catalyzed by Pt/Na-[Fe]ZSM-5 were probed by measuring changes in selectivity with contact time in a recirculating batch reactor (Fig. 2). Pentene isomers are almost exclusively formed at low conversions (Fig. 2a), indicating that cracking, oligomerization, and aromatization reactions require secondary reactions of primary pentene products (Scheme 1). All *n*-pentene isomers remain at equilibrium with each other at all contact times, as their constant $\eta_i/\eta_{1\text{-pentene}}$ ratios indicate; this indicates that hydride shifts are fast on acid sites. Isopentene $\eta_i/\eta_{1\text{-pentene}}$ ratios were smaller than for *n*-pentenes and increased with contact times, because isopentenes form via slower skeletal isomerization of *n*-pentenes on Brønsted acid sites (Fig. 2b, Scheme 1).

4. Conclusions

These data show that isopentene isomers (3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene) can be formed via

dehydrogenation of *n*-pentane at 673 K on Pt clusters followed by selective skeletal rearrangement of *n*-pentenes on acid sites present on [Fe]ZSM-5. Alkene selectivities above 95% with excellent stability (deactivation rate constants: 0.004 h^{-1}), even in the absence of co-fed H_2 , were achieved. Reaction rates are more than ten-fold higher than the best values previously reported and allow the use of catalysts with much lower Pt content. These catalysts and insights provide potentially practical routes for the selective synthesis of molecules useful as precursors to fuel additives and chemical intermediates.

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