Pt/[Fe]ZSM-5 modified by Na and Cs cations: an active and selective catalyst for dehydrogenation of *n*-alkanes to *n*-alkenes

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Pt clusters within [Fe]ZSM-5 channels provide active and stable sites for the selective catalytic dehydrogenation of *n*-alkanes to *n*-alkenes. Cs and Na cations titrate acid sites and inhibit skeletal isomerization and cracking side reactions.

Linear alkenes are essential intermediates in the synthesis of useful chemicals, such as lubricants[1] and detergent-range alkylaromatics.[2] Alkane dehydrogenation reactions are endothermic and favored by high temperatures and low H_2 pressures; these conditions lead, in turn, to cracking side reactions and fast deactivation, especially for larger alkanes. Pt-based catalysts are among the most active and selective for alkane dehydrogenation.[3] Until this study, high dehydrogenation rates and catalyst stability have required the concurrent presence of H_2 (>200 kPa) and the use of promoters or stabilizers (*e.g.* Cl to enhance Pt dispersion,[4] Sn to improve stability,[5] and Li to neutralize support acid sites[6]).

We previously reported that Pt/Na–[Fe]ZSM-5 materials, prepared by ion-exchange of Pt onto Na–[Fe]ZSM-5, showed unprecedented rates and stability in the selective dehydrogenation of C_2–C_4 alkanes.[7] These materials, when used as catalysts for larger alkanes, gave significant isomerization selectivities, apparently because acidic OH groups form during reduction of exchanged Pt cations by H_2. Here, we report that the titration of these protons with Cs *after* reduction of Pt cations leads to Pt/Na–[Fe]ZSM-5 materials with high selectivity for dehydrogenation of *n*-alkanes to linear *n*-alkenes and also with high rates and excellent catalyst stability. Low deactivation rates (first-order deactivation rate constant: 0.003–0.006 h^{-1}) were achieved at much lower H_2 pressures (7 kPa) than required in previous reports (>200 kPa) and even without H_2.

Pt/Na–[Fe]ZSM-5 catalysts were prepared as previously reported.[7] NH_4^+–[Fe]ZSM-5 was exchanged thrice with 0.1 M $NaNO_3$ solutions (EMD Chemicals, >99%) at 353 K for 15 h to prepare Na–[Fe]ZSM-5 precursors. Pt cations were then exchanged onto these samples by contact with $[(NH_3)_4Pt](NO_3)_2$ solutions (6.25×10^{-5} M; Aldrich, 99.995%) for 12 h at 353 K, filtered, washed with deionized water, and treated in flowing dry air (1.67 $cm^3\ s^{-1}$) for 12 h at 723 K (0.017 K s^{-1}). These samples contained 0.12 wt% Pt, 0.28 wt% Fe, and a Si/Fe atomic ratio of 340 (by inductively-coupled plasma emission spectroscopy). [Fe]ZSM-5 crystals had an average diameter of 0.5 μm (from transmission electron microscopy). *n*-Pentane (25 kPa, Aldrich, 99%) and *n*-heptane (25 kPa, Aldrich, 99%) dehydrogenation rates and selectivities were measured at 673 and 723 K at ambient pressure using a tubular flow reactor with plug-flow hydrodynamics. Samples (0.1 g, 180–250 μm diameter pellets) were treated in 40% H_2 (Praxair, 99.999%, 0.20 $cm^3\ s^{-1}$) in He (Praxair, 99.999%, 0.30 $cm^3\ s^{-1}$) at 673 K for 2 h. Reactant and product concentrations were measured by gas chromatography (HP 5890 II). *n*-Pentane and *n*-heptane reactants were introduced using a high-pressure syringe pump (Teledyne Isco, Model 500 D). Dehydrogenation rates were calculated from measured rates, by correcting for approach to equilibrium for each alkene isomer using thermodynamic data.[8]

Fig. 1 shows pentene formation rates (per Pt) and selectivities (on a carbon basis) on Pt/Na–[Fe]ZSM-5 at 673 K during contact with reactants for 140 h. The selectivity to pentenes increased from 85% to 96% during this period and cracking selectivities concurrently decreased to ∼1%. The selectivity to aromatics also decreased from 8% to ∼2%. This inhibition of cracking and aromatization reactions reflects the slow deactivation of acid sites by unreactive organic deposits during dehydrogenation reactions.[7] These lower selectivities may also reflect, in part, smaller contributions from secondary reactions as the alkane conversion level decreases with time on stream. Pentene formation rates (corrected for approach to equilibrium) decreased from 5.7 mol (g-atom Pt)$^{-1}$ s^{-1} (*n*-pentane conversion: 25%) to 1.5 mol (g-atom Pt)$^{-1}$ s^{-1} (*n*-pentane conversion: 11%) over 140 h. Deactivation was initially rapid (k_d = 0.025 h^{-1}), but became slower with time, with a first-order deactivation constant of 0.004 h^{-1} after 20 h. These deactivation rates resemble those previously reported on Pt/Na–[Fe]ZSM-5 during C_2–C_4 alkane

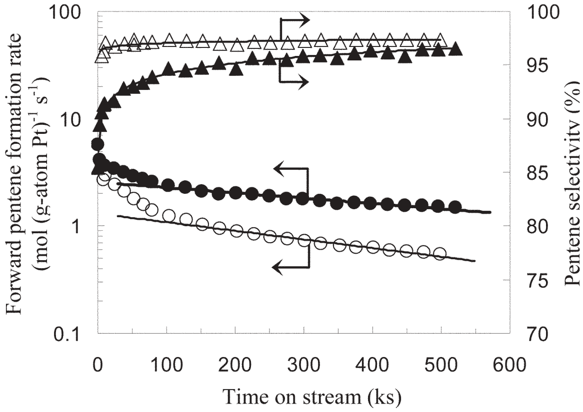

Fig. 1 Forward rates and selectivities for pentene isomers during *n*-pentane dehydrogenation on (●,▲) Pt/Na–[Fe]ZSM-5 and (○,△) Cs–Pt/Na–[Fe]ZSM-5 at 673 K in the absence of H_2. *n*-Pentane partial pressure: 25 kPa; space velocity: 12 mol (g-atom-Pt)$^{-1}$ s^{-1}.

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Table 1 *n*-Pentane dehydrogenation on Pt/Na–[Fe]ZSM-5 and Cs–Pt/Na–[Fe]ZSM-5 at 673 K[a]

Catalyst	*n*-Pentane conv. (%)	Pentene sel. (%)	η^b						Net pentene formation rate[c]	Forward pentene formation rate[c]
			1-Pentene	*trans*-2-Pentene	*cis*-2-Pentene	3-Methyl-1-butene	2-Methyl-1-butene	2-Methyl-2-butene		
Pt/Na–[Fe]ZSM-5	21	89	0.44	0.42	0.36	0.39	0.35	0.38	2.8	4.5
Cs–Pt/Na–[Fe]ZSM-5	13	97	0.53	0.50	0.43	0.01	0.004	0.005	1.8	3.5

[a] *Reaction conditions*: 673 K, 25 kPa *n*-pentane, balance: He; space velocity: 12 mol (g-atom Pt)$^{-1}$ s^{-1}. [b] Approach to equilibrium from *n*-pentane. [c] mol (g-atom Pt)$^{-1}$ s^{-1}.

dehydrogenation[7] and correspond to a mean catalyst lifetime of 250 h, a value larger than typically reported at the severe conditions required for high alkene yields in alkane dehydrogenation reactions.

[Fe]ZSM-5 zeolites have weaker Brønsted acid sites than their Al homologs.[9] Protons form in Pt/Na–[Fe]ZSM-5 during reduction of exchanged Pt cations. These acid sites catalyze skeletal isomerization of *n*-pentenes at 673 K to form branched pentenes (3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene) and lead to equilibrium distributions of pentene isomers (approach to equilibrium from *n*-pentane ~0.4 for all isomers; Table 1). These protons were titrated after reduction of Pt/Na–[Fe]ZSM-5 by impregnation with a solution of Cs acetate (Cs/Fe = 1). Cs was chosen because it is less mobile than Na under hydrothermal conditions prevalent during drying or regeneration thermal treatments.

These Cs–Pt/Na–[Fe]ZSM-5 samples gave much higher selectivities to linear pentenes (96%) than Pt/Na–[Fe]ZSM-5 (28%). Cracking and aromatic products were not detected after Cs introduction at any time on stream, consistent with the stoichiometric titration of Brønsted acid sites by Cs. Pentadienes (~3% selectivity) became the predominant by-products, because of sequential dehydrogenation reactions of linear pentenes. These dienes react quickly on acid sites *via* Diels–Alder type reactions to give aromatics and unsaturated organic residues and are quickly scavenged on catalysts containing acid sites. Forward pentene formation rates and selectivities are shown in Fig. 1 on Cs–Pt/Na–[Fe]ZSM-5 at 673 K. The deactivation rate constant (k_d = 0.007 h^{-1}) was slightly higher than that on Pt/Na–[Fe]ZSM-5 (0.004 h^{-1}), apparently because of the higher concentrations of polyunsaturated precursors (*e.g.* dienes), which are otherwise scavenged by acid sites on Pt/Na–[Fe]ZSM-5 catalysts. The high reactivity and stability of Pt domains in [Fe]ZSM-5 channels for dehydrogenation reflects in part the small size of encapsulated Pt clusters with 58% dispersion (defined as the percentage of Pt atoms exposed at surfaces; estimated by H_2 chemisorption at 293 K); these dispersion values are significantly higher than in previously reported catalysts based on Pt/Al_2O_3 (20–35% dispersion).[10] Small Pt domains, prepared by anchoring Pt precursors onto exchange sites of [Fe]ZSM-5, give higher reaction rates because of the concomitant higher densities of exposed Pt atoms. These small clusters also inhibit the formation of deactivating residues because oligomerization reactions require larger ensembles and more open environments than those present within the zeolite channels that contain the active Pt clusters in these materials.[11]

We have also examined the more demanding dehydrogenation of larger alkanes (*n*-heptane) on Cs–Pt/Na–[Fe]ZSM-5. These larger alkanes are more reactive in acid-catalyzed cracking and skeletal isomerization than their smaller homologs. *n*-Heptane dehydrogenation at 673 K formed linear heptenes with high selectivity (87% initial combined selectivity to 1-heptene, *trans*-2-heptene, *cis*-2-heptene, *trans*-3-heptene, *cis*-3-heptene). Selectivities to linear heptenes increased with time on stream (to 92% after 100 h) (Fig. 2). Heptadienes were the most abundant by-products, as a result of sequential dehydrogenation of initial *n*-heptene products; their selectivities decreased with time on stream (from initial 12% to 7% after 100 h) because of the concomitant decrease in *n*-heptane conversion with time and of the resulting smaller contribution from sequential reactions of primary *n*-heptene products. Reaction rates were lower with *n*-heptane than with *n*-pentane in the linear region of the rate–time data shown in Fig. 1 and 2, apparently because of the faster initial deactivation observed for the larger alkanes at the high conversion and high diene concentrations prevalent during the initial contact of the catalyst with reactants.

The addition of small amounts of H_2 (7 kPa) to *n*-heptane reactants decreased the prevalent concentration of heptadienes and improved catalyst stability. H_2 typically increases catalyst stability during dehydrogenation reactions,[12] but also decreases equilibrium conversion levels. We compensated for these thermodynamic effects by slightly increasing reaction temperatures (from 673 to 723 K). Deactivation rate constants were slightly smaller (0.003 h^{-1}) with 7 kPa H_2 at 723 K than without adding H_2 at 673 K (0.004 h^{-1}) (Fig. 2). These deactivation rate constants resemble those reported on Pt–Sn/Al_2O_3–Cl–Li (0.003 h^{-1}); these latter values required, however, much higher H_2 pressures

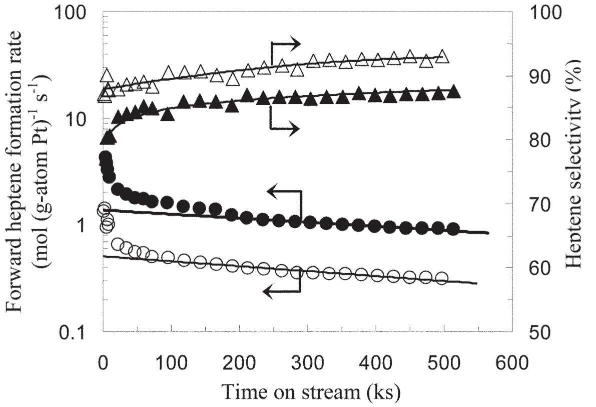

Fig. 2 Forward formation rates and selectivities for heptene isomers during *n*-heptane dehydrogenation on Cs–Pt/Na–[Fe]ZSM-5; open symbols (○,△) 673 K in the absence of H_2 and solid symbols (●,▲) 723 K in the presence of 7 kPa H_2. *n*-Heptane partial pressure: 25 kPa; space velocity: 12 mol (g-atom-Pt)$^{-1}$ s^{-1}.

Table 2 Catalytic performance of Pt-based catalysts for *n*-heptane dehydrogenation

Catalyst	Reaction conditions Reactant pressure/kPa	*T*/K	Space velocity[a]	*n*-Heptane conversion (%)	Net heptene formation rate[a]	*n*-Heptenes selectivity (%)	Deactivation rate/h^{-1}	Ref.
Cs–Pt/Na–[Fe]ZSM-5	*n*-Heptane: 25 H_2: 7	723	12	13	1.6	85[b]	0.003	This work
Pt–Sn/Al_2O_3–Cl–Li	*n*-Heptane: 31 H_2: 220	743	1.7	8	0.14	90	0.003	12

[a] mol (g-atom Pt)$^{-1}$ s^{-1}. [b] Fraction of *n*-heptene isomers: 10% 1-heptene, 29% *trans*-2-heptene, 28% *trans*-3-heptene, 16% *cis*-2-heptene, 17% *cis*-3-heptene.

(220 kPa)[12] (Table 2). Heptene formation rates (compared per Pt, because dispersion were not reported in the earlier study[12]) on Cs–Pt/Na–[Fe]ZSM-5 were almost ten-fold higher than on Pt–Sn/Al_2O_3–Cl–Li catalysts[12] at similar conditions (Table 2). This latter catalyst is the only practical dehydrogenation catalyst reported for the synthesis of linear alkenes from larger *n*-alkanes. No branched heptenes were detected during *n*-heptane reactions and linear heptene isomers were in equilibrium with each other on the catalysts reported here at all reaction conditions (Table 2).

In summary, we provide evidence here for the unique catalytic properties of Pt/Na–[Fe]ZSM-5 with residual acid sites titrated by Cs after reduction of exchanged Pt cations for the dehydrogenation of *n*-pentane and *n*-heptane. These materials catalyze dehydrogenation of larger *n*-alkanes with unprecedented rates and with very high selectivity to *n*-alkenes. The catalyst stability is excellent in comparison with catalytic materials in previous reports, which required much higher H_2 pressures for stable operation. These catalysts provide effective routes for the synthesis of useful linear alkenes using the corresponding *n*-alkanes as feedstocks. Our study extends the applicability of these materials beyond their initial disclosure for dehydrogenation of C_2–C_4 alkanes. It also provides compelling evidence that Brønsted acid sites must be rigorously excluded to preserve the desired linear nature of the alkenes formed in dehydrogenation turnovers.

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$$n\text{-Alkane} \rightleftharpoons \text{Alkene}\ (i) + \text{H}_2$$

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

Forward rates are given by:

$$r_{\text{f},i} = r_{\text{net},i}/(1 - \eta_i).$$

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