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# Active, selective, and stable Pt/Na-[Fe]ZSM5 catalyst for the dehydrogenation of light alkanes

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**Small Pt clusters in Na-[Fe]ZSM5 give high alkene selectivities, near-equilibrium alkene yields, and unprecedented stability in the catalytic dehydrogenation of light alkanes.**

Platinum-based materials are widely used in petrochemical and refining processes, such as alkane dehydrogenation.[1] Sn inhibits cracking, isomerization, and coke formation on Pt supported on $Al_2O_3$, $SiO_2$, $ZrO_2$,[2–4] $MgAl_2O_4$,[5] and K–L zeolite.[6] Sn also increases Pt dispersion and catalyst stability in Pt/γ-$Al_2O_3$,[2] but dehydrogenation rates decrease rapidly with time. Pt–Ga/$MgAl_2O_4$,[7] Pt/silicalite, and Pt–Zn/silicalite[8] also show higher selectivity and stability than Pt/γ-$Al_2O_3$. Here, we report a novel catalyst with unprecedented site activity and stability for propane and isobutane dehydrogenation. Exchanged Pt cations (0.10 wt%) in ZSM5 with $Fe^{3+}$ in framework positions and Na as balancing cations lead to high alkene selectivities, near-equilibrium alkene yields, and turnover rates and stability significantly higher than previously reported. Deactivation rate constants during $C_3H_8$ dehydrogenation are more than ten times smaller than on Pt–Sn.[2]

[Fe]ZSM5 was prepared in $NH_4^+$ form using known methods {0.44 wt% Fe, $(Si/Fe)_{at} = 200$}.[9] Al was present in trace amounts (0.03 wt%). The $NH_3$/Fe ratio during $NH_4^+$-[Fe]ZSM5 decomposition was 1.1, indicating that Fe was located at framework positions. $NH_4^+$-[Fe]ZSM5 was exchanged thrice with 0.024 M $NaNO_3$ (Fisher, 0.5 l $g^{-1}$) at 353 K for 15 h to form $Na^+$-[Fe]ZSM5. Pt cations were introduced by exchange from 0.001 M $Pt(NH_4)_4(NO_3)_2$ (Johnson-Mathey/Aesar) aqueous solutions. The Pt dispersion measured from uptakes of strongly chemisorbed hydrogen at 293 K was 0.95, indicating that Pt clusters are small ( < 1 nm). Rates and selectivities were measured in a tubular plug-flow reactor. Samples (0.03 g) were treated in 40% $H_2$/He at 773 K for 3 h before rate measurements. Rates are reported as reactant conversion or product formation rates (mol/g-atom Pt-s), which represent turnover rates because of the nearly complete dispersion of Pt clusters. Selectivities are reported on a carbon basis. Forward reaction rates ($r_f$) were obtained from measured rates ($r_{net}$) using $r_f = r_{net}/(1 - \eta)$, where the approach to equilibrium ($\eta$) depends on reaction thermodynamics and on prevalent pressures of reactants and products. Deactivation first-order rate constants ($k_d$) were determined from forward rates; mean catalyst life ($\tau$) is defined as the reciprocal of the first-order deactivation rate constant.

$C_3H_8$ dehydrogenation rates were measured on 0.10 wt% Pt/Na-[Fe]ZSM5 at 793 K and 25 kPa $C_3H_8$. $C_3H_6$ yields were near equilibrium (Table 1; 35% *vs.* 36%) at 4.1 mol $C_3H_8$/g-atom Pt-s space velocity and the $C_3H_6$ selectivity was 97%. The net $C_3H_6$ formation turnover rate was 1.4 mol $C_3H_8$/g-atom Pt-s, which exceeds rates on 0.35 wt% Pt–Sn/γ-$Al_2O_3$ (1.1 mol $C_3H_8$/g-atom Pt-s at 31% conversion; 30 kPa, 792 K, 3.5 mol $C_3H_8$/g-atom Pt-s).[2] Net $C_3H_6$ formation rates decreased as dehydrogenation approached equilibrium with increasing residence time, but forward reaction rates did not change significantly (Table 1). $C_3H_6$ selectivities were very high (97%) and similar to those reported on 0.35 wt% Pt–Sn/γ-$Al_2O_3$ (95–98%).[2] $C_2H_4$/$C_2H_6$ ratios were above equilibrium values (*e.g.* 0.31 *vs.* 0.14, at 78.9 mol $C_3H_8$/g-atom Pt-s), indicating that $C_2H_4$ forms together with $CH_4$ in slow β-scission reactions on weak acid sites in [Fe]ZSM5, while $C_2H_6$ forms by $C_2H_4$ hydrogenation. Acid sites form during reduction of exchanged Pt cations in Na-[Fe]ZSM5. Hydrogenolysis reactions were not detected, confirming the presence of small Pt clusters.[10] Larger hydrocarbons were formed in trace amounts ( < 1% selectivity, Table 1), suggesting that Pt/Na-[Fe]ZSM5 does not effectively catalyze oligomerization-cracking cycles, which occur on H-[Al]ZSM5 and form larger alkenes and aromatics.[11]

Fig. 1 shows $C_3H_6$ formation rates and selectivities on 0.1 wt% Pt/Na-[Fe]ZSM5 at 793 K for 160 h. $C_3H_6$ selectivities initially increased sharply and then more gradually with time on stream (98.3% to 99.8%, Fig. 1), because weak acid sites responsible for β-scission deactivate during reaction. Forward $C_3H_6$ formation rates decreased from 16.7 to 3.0 moles $C_3H_8$/g-atom Pt-s during 160 h (Fig. 1). Forward reaction rates are also shown for 0.35 wt% Pt–Sn/γ-$Al_2O_3$ at 792 K and 3.5 mol $C_3H_8$/g-atom Pt-s space velocity.[2] Deactivation rates decreased with time on stream on both catalysts, apparently because concentrations of alkenes and acid sites also decreased as deactivation

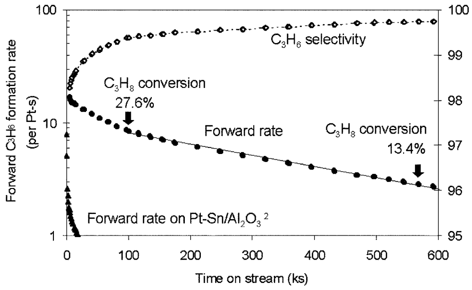

**Fig. 1** Forward $C_3H_6$ formation rates and $C_3H_6$ selectivities during $C_3H_8$ dehydrogenation reactions on 0.1 wt% Pt/Na-[Fe]ZSM5 and on 0.35 wt% Pt–Sn/γ-$Al_2O_3$.[2]

**Table 1** $C_3H_8$ dehydrogenation reactions on 0.1 wt% Pt/Na-[Fe]ZSM5[a]

| Space velocity (mol $C_3H_8$/g-atom Pt-s) | Residence time (s g-atom Pt/mol $C_3H_8$) | $C_3H_8$ Conversion (%) | Carbon selectivity (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | Others ($C_{4+}$) | $\eta$[b] | Net $C_3H_6$ formation turnover rate[c] | Forward $C_3H_6$ formation turnover rate[c] |
| 4.1 | 0.24 | 35.5 | 0.68 | 0.13 | 1.32 | 96.9 | 0.97 | 0.91 | 1.4 | 15.7 |
| 16.2 | 0.062 | 31.2 | 0.18 | 0.05 | 0.34 | 98.9 | 0.53 | 0.70 | 5.0 | 16.7 |
| 78.7 | 0.013 | 18.9 | 0.10 | 0.05 | 0.14 | 99.6 | 0.07 | 0.23 | 14.8 | 19.2 |

[a] Reaction conditions: 793 K, 25 kPa $C_3H_8$, balance He. [b] Fractional approach to equilibrium. [c] mol/g-atom Pt-s.

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**Table 2** Catalytic performances of Pt-based catalysts for propane and isobutane dehydrogenation

| | Reaction conditions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Catalyst | Reactant pressure (kPa) | *T* (K) | Space velocity[a] | Initial forward dehydrogenation rate[a] | Alkane conversion (%) | Selectivity (%) | Deactivation rate constant ($h^{-1}$) | Mean catalyst life[b] ($\tau$/h) | Ref. |
| 0.1 wt% Pt/Na-[Fe]ZSM5 | $C_3H_8$: 25 | 793 | 18.6 | 16.7 | 13–33 | 98.3–99.8 | 0.0080 | 125 | This work |
| 0.35 wt% Pt–Sn/γ-$Al_2O_3$ | $C_3H_8$: 30 | 792 | 3.5 | 7.8 | 20–31 | 95–98 | 0.11 | 9 | 2 |
| 0.5 wt% Pt–Sn/$MgAl_2O_4$ | $C_3H_8$: 39, $H_2$: 39 | 823 | 9.0 | 2.1 | 11–12 | 93–97 | 0.053 | 19 | 5 |
| 0.6 wt% Pt–Ga/$MgAl_2O_4$ | $C_3H_8$: 78, $H_2$: 23 | 878 | 0.80 | 0.47 | 30–31 | 97–98 | 0.045 | 22 | 7 |
| 0.5 wt% Pt/Zn/silicalite | $C_3H_8$: 96 | 828 | 0.70 | 0.36 | 25–27 | 99–100 | 0.010 | 100 | 8 |
| 0.1 wt% Pt/Na-[Fe]ZSM5 | i-$C_4H_{10}$: 33, $H_2$: 7 | 793 | 22.3 | 9.3 | 10–20 | 96.5–98.6 | 0.0041 | 245 | This work |
| 0.58 wt% Pt–Sn/K–L zeolite | i-$C_4H_{10}$: 33, $H_2$: 67 | 873 | 2.1 | 7.1 | 46–61 | 92–100 | 0.0078 | 130 | 6 |
| 1.0 wt% Pt–Sn/$SiO_2$ | i-$C_4H_{10}$: 8 i-$C_4H_{10}$: 8 | 773 | 22.9 | 5.4 | 15–19 | 95–96 | 0.095 | 11 | 3 |

[a] mol/g-atom Pt-s. [b] Time required for rates to decrease by $e^{-1}$.

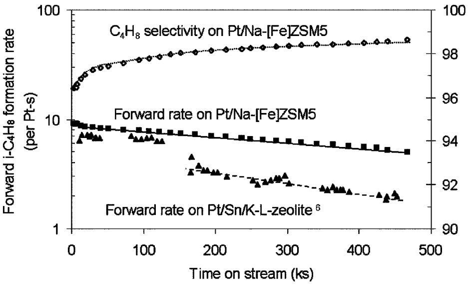

**Fig. 2** Forward i-$C_4H_8$ formation rates and $C_4H_8$ selectivities during i-$C_4H_{10}$ dehydrogenation reactions on 0.1 wt% Pt/Na-[Fe]ZSM5 and on 0.58 wt% Pt–Sn/K–L-zeolite.[6]

occurred. Deactivation rate constants then reached constant values of 0.008 $h^{-1}$ ($\tau$ = 125 h) on Pt/Na-[Fe]ZSM5 and 0.11 $h^{-1}$ ($\tau$ = 9 h) on Pt–Sn/γ-$Al_2O_3$.

Table 2 compares $C_3H_8$ dehydrogenation rate, selectivity, and stability for the best reported catalysts. Non-acidic supports and Pt–Sn clusters led to higher stability and $C_3H_6$ selectivity than Pt clusters on γ-$Al_2O_3$ or $SiO_2$ supports.[5] Pt–Ga/$MgAl_2O_4$ shows higher rates, selectivity, and stability than Pt–Sn/$MgAl_2O_4$.[8] These catalysts were more stable ($\tau$ ~ 20 h) than Pt–Sn/γ-$Al_2O_3$ ($\tau$ = 9 h) but much less stable than Pt/Na-[Fe]ZSM5 ($\tau$ = 125 h, Table 2). Pt/silicalite gave very low rates, even at temperatures much higher than for Pt/Na-[Fe]ZSM5.[9] Pt/Zn/silicalite showed very high stability ($\tau$ = 100 h), only slightly lower than Pt/Na-[Fe]ZSM5 (Table 2), suggesting that Pt clusters within protective 10-ring channels and the substantial absence of acid sites inhibit deactivation processes. Pt/Na-[Fe]ZSM5 gave substantially higher reaction rates and catalyst stability than these state-of-the-art Pt-based dehydrogenation catalysts.

Fig. 2 shows isobutane dehydrogenation rates and selectivities (793 K, 33 kPa i-$C_4H_{10}$, 7 kPa $H_2$, 22 mol i-$C_4H_{10}$/g-atom Pt-s) on 0.1 wt% Pt/Na-[Fe]ZSM5 for 130 h. $H_2$ was used to inhibit deactivation near the bed inlet, as also used in previous studies.[3,6] Initial $C_4H_8$ selectivities were 96.5% and increased gradually with time to 98.6% (Fig. 2). i-$C_4H_8$ selectivities within $C_4$ alkene products also increased (94% to 96%), because of deactivation of acid sites responsible for β-scission and isomerization. Initial forward i-$C_4H_8$ formation rates were 9.3 mol i-$C_4H_8$/g-atom Pt-s at 20% conversion (46% equilibrium conversion). The deactivation constant was 0.004 $h^{-1}$ between 20 and 470 ks ($\tau$ = 250 h). Similar data on (0.58 wt%) Pt–Sn/K–L zeolite,[6] which exhibits the best previously reported activity, selectivity, and stability in i-$C_4H_8$ dehydrogenation, are shown in Fig. 2 at 873 K, 33 kPa i-$C_4H_{10}$, 67 kPa $H_2$ pressure, and 2.1 mol i-$C_4H_{10}$/g-atom Pt-s space velocity,[6] conditions leading to equilibrium conversions of 58%. Initial forward rates on Pt/Na-[Fe]ZSM5 at 793 K were higher than on Pt–Sn/K–L at 873 K (7 mol i-$C_4H_8$/g-atom Pt-s). Deactivation constants were lower on Pt/Na-[Fe]ZSM5 (0.004 $h^{-1}$) than on Pt–Sn/K–L (0.008 $h^{-1}$) even at the lower $H_2$ pressures (7 kPa *vs.* 67 kPa) on Pt/Na-[Fe]ZSM5. Pt/Na-[Fe]ZSM5 gave higher rates at 80 K lower temperature, as well as better stability with much lower $H_2$ addition requirements.

Pt/Na-[Fe]ZSM5 used previously in $C_3H_8$ (Fig. 1) and i-$C_4H_{10}$ reactions (Fig. 2) were treated in 1% $O_2$/He at 723 K for 2 h. Then, dehydrogenation was carried out on each catalyst for 50 h. These treatments restored initial rates (16.1 *vs.* 16.7 mol $C_3H_8$/g-atom Pt-s, 8.8 *vs.* 9.3 mol i-$C_4H_{10}$/g-atom Pt-s) and selectivities (98.7% *vs.* 98.3% $C_3H_6$, 97.0% *vs.* 96.5% $C_4H_8$). Mean catalyst lives for regenerated catalysts were also similar to those of fresh catalysts (112 h *vs.* 125 h for $C_3H_8$, 220 h *vs.* 250 h for i-$C_4H_{10}$).

We conclude that replacing $Al^{3+}$ with $Fe^{3+}$ in the ZSM-5 framework retains exchange sites required for anchoring of Pt precursors. This leads to well-dispersed Pt clusters, which can be accommodated within the protected environment of 10-ring zeolite channels in ZSM5. The weaker acidity of {Fe–OH–Si} compared with {Al–OH–Si} leads in turn to higher alkene selectivity and catalytic stability. These weaker acid sites give lower rates of acid-catalyzed alkene oligomerization and cyclization reactions, and consequently lower yields of aromatics and unreactive organic residues, as recently reported for H-[Fe]ZSM5.[12] We achieve these improvements without relying on bimetallic clusters, which can unmix during oxidative regenerations, and without significant $H_2$ partial pressures in alkane reactant streams. These novel materials can be fully regenerated using mild-oxidative treaments without a detectable decrease in Pt dispersion, zeolite crystallinity, or catalytic selectivities and to lower rates of undesired side reactions.

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