

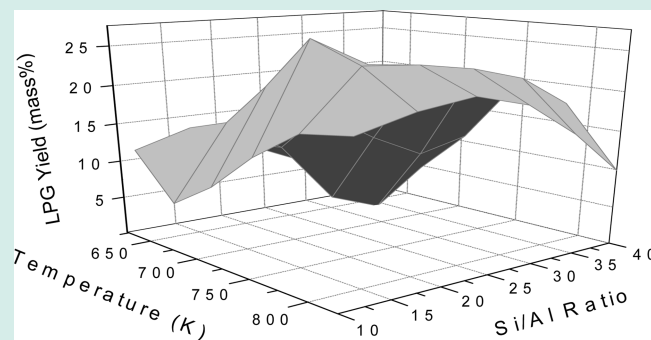
# High-Throughput Investigation of Catalysts for JP-8 Fuel Cracking to Liquefied Petroleum Gas

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**ABSTRACT:** Portable power technologies for military applications necessitate the production of fuels similar to LPG from existing feedstocks. Catalytic cracking of military jet fuel to form a mixture of C<sub>2</sub>–C<sub>4</sub> hydrocarbons was investigated using high-throughput experimentation. Cracking experiments were performed in a gas-phase, 16-sample high-throughput reactor. Zeolite ZSM-5 catalysts with low Si/Al ratios ( $\leq 25$ ) demonstrated the highest production of C<sub>2</sub>–C<sub>4</sub> hydrocarbons at moderate reaction temperatures (623–823 K). ZSM-5 catalysts were optimized for JP-8 cracking activity to LPG through varying reaction temperature and framework Si/Al ratio. The reducing atmosphere required during catalytic cracking resulted in coking of the catalyst and a commensurate decrease in conversion rate. Rare earth metal promoters for ZSM-5 catalysts were screened to reduce coking deactivation rates, while noble metal promoters reduced onset temperatures for coke burnoff regeneration.

**KEYWORDS:** high-throughput screening, JP-8, catalytic cracking, zeolite



## INTRODUCTION

The emergence of military technologies powered by liquefied petroleum gas (LPG) necessitates local fuel production at the point of use. LPG can provide distinct advantages over batteries as a mobile energy source due to its higher gravimetric energy density and longer operating times for LPG fuel cells, for example. For military applications in remote regions, logistical difficulties and harsh practical limitations make it difficult to obtain LPG through conventional distribution channels. If LPG could be derived from readily available fuels such as Jet Propellant-8 (JP-8), a kerosene-based military aviation fuel,<sup>1</sup> then supply side logistics would be greatly simplified. Developing a method for conversion of JP-8 to LPG is of critical importance to enable increased deployment of LPG powered technologies.

A high-throughput approach is applied for the discovery and optimization of catalysts for production of LPG from JP-8. Within the past two decades, the high-throughput approach has become widespread in the field of catalysis.<sup>2–4</sup> In the high-throughput approach to catalyst discovery and optimization, a large number of samples are simultaneously synthesized and then rapidly screened for their figure of merit. This typically involves the systematic investigation of a multidimensional parameter space affecting catalyst performance, including catalyst composition, preparation methods, regeneration, and operating conditions. Such an investigation would be prohibitively slow utilizing traditional one-sample-at-a-time methodologies.

This work is constrained by the design-specific needs of a practical military application. Successful catalysts are required to exceed a 5% minimum conversion of JP-8 to C<sub>2</sub>–C<sub>4</sub> hydrocarbons, the fuel cannot be desulfurized before reaching the catalyst, and no other system inputs, such as water, are possible. Any additional reactants to be cofed with the JP-8 are disallowed due to cost and logistic considerations, thereby pointing to the use of cracking as the reaction pathway in lieu of reformation techniques. Initial exploratory screening investigated supported nanoparticle catalysts on oxide supports.<sup>5</sup> It was found that oxide acidity, including Lewis acid strength, was of primary importance in determining JP-8 cracking activity. A La/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst produced LPG yields of nearly 10% on a mass basis from JP-8 cracking at reactor temperatures above 900 K.

Zeolites are known to exhibit high selectivity and activity during catalytic cracking.<sup>6</sup> Zeolite pore geometry and diffusion limitations are often the controlling factors that determine catalytic activity and selectivity.<sup>7</sup> Bimolecular and monomolecular cracking mechanisms have been identified over zeolite catalysts.<sup>8,9</sup> Bimolecular cracking involves hydride transfer between a paraffin molecule and an adsorbed carbenium ion, while monomolecular cracking involves the direct protonation of a paraffin.<sup>10</sup> Large pore zeolites favor bimolecular cracking, while medium-pore zeolites favor monomolecular cracking.<sup>10,11</sup>

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**Table 1. Selective Yields (Mass %) of JP-8 Cracking to C<sub>1</sub>–C<sub>4</sub> Hydrocarbons with Total C<sub>2</sub>–C<sub>4</sub> Target over Zeolite Catalysts with Various Si/Al Ratios at a Reactor Temperature of 823 K**

catalyst	Si/Al	CH <sub>4</sub> (%)	C <sub>2</sub> H <sub>4</sub> (%)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>3</sub> H <sub>6</sub> (%)	C <sub>3</sub> H <sub>8</sub> (%)	C <sub>4</sub> H <sub>8</sub> (%)	C <sub>4</sub> H <sub>10</sub> (%)	C <sub>2</sub> –C <sub>4</sub> (%)
ZSM-5	15	0.7	5.1	1.2	6.2	4.4	1.6	1.7	20.2 ± 1.3
ZSM-5	25	0.6	5.4	1.2	7.3	3.7	2.1	1.8	21.4 ± 1.4
ZSM-5	40	0.2	1.2	0.4	4.3	1.0	1.9	1.1	9.9
ZSM-5	100	0.1	0.5	0.2	2.6	0.5	1.3	0.7	5.7
Beta	19	0.2	0.2	0.0	1.5	0.1	1.3	0.2	3.2
Mordenite	10	0	0	0	0	0	0	0	0
Y	2.55	0.8	0.6	0.2	4.5	1.4	3.0	1.0	10.8 ± 0.5
Y	40	0.5	0.6	0.2	4.2	1.4	2.9	0.9	10.2 ± 0.5

Zeolites might therefore provide improved catalytic cracking performance for the conversion of JP-8 to LPG. In the current study, we have screened zeolites with various framework topology and Si/Al ratios for catalytic cracking of JP-8 at reaction temperatures between 573 and 923 K.

## EXPERIMENTAL PROCEDURES

**High-Throughput Reactor System.** Catalytic cracking of JP-8 was performed in a high-throughput reactor system<sup>12</sup> consisting of 16 conventional fixed bed reactors operating in parallel under similar flow, temperature, and pressure conditions. The individual reactors consisted of 1/4 in. o.d. stainless steel tubes loaded with 150 mg of powder catalyst sample. Liquid JP-8 fuel was pumped into a heated stainless steel evaporator and combined with carrier gas flowing through the evaporator. The reactant gas feed then passed through heat-traced lines to the reactor inlet, where it was split into capillaries for flow equalization before passing individually through each of the reactor tubes. Unreacted JP-8 and other hydrocarbons that would exist in the liquid phase at room temperature were removed from each reactor effluent in a 16-channel parallel heat-exchange condenser. Effluent streams from each of the individual reactors remained in separate channels throughout the analysis process to prevent mixing of reaction products. As a complement to the high-throughput experiments, a single-sample conventional fixed bed reactor (1/2 in. o.d.) was also operated to match reaction conditions for validation of high-throughput reactor performance and to perform long-time stability studies on catalysts.

**Material Synthesis and Characterization.** Zeolite catalysts with four types of framework topology were investigated, including mordenite framework inverted (ZSM-5), faujasite (USY), mordenite, and beta. Zeolites with varying Si/Al ratios ranging from 15 to 100 were obtained commercially from Alfa Aesar or synthesized in house and used as prepared. A variety of metals was loaded onto the zeolite support using either ion-exchange or wet impregnation methods.

Temperature programmed oxidation (TPO) measurements were obtained using a quadrupole mass spectrometer and a heated flow reactor using 25 mg of catalyst loaded in a quartz tube. The catalyst was pretreated in helium at 573 K for drying and removal of volatile compounds before oxidation burnoff cycles were performed. The system was heated at a ramping rate of 20 K/min in 10 sccm of flowing 10% O<sub>2</sub>/He.

**Catalytic Cracking Experiments.** JP-8 fuel (bp = 433–553 K with ~700 ppmw sulfur) was obtained directly from the US military. Lee, et al. showed that the sulfur species in JP-8 predominantly consist of benzothiophenes and dibenzothiophenes.<sup>13</sup> JP-8 fuel contains a mixture of straight chain,

branched, and cyclic hydrocarbons with carbon number from C<sub>8</sub> to C<sub>17</sub> with average molecular formula C<sub>11</sub>H<sub>21</sub> (MW = 153). Unless otherwise specified, 0.6 mL/min JP-8 was dosed using a HPLC pump (Hitachi L-2130) and combined with balance He so that the gas hourly space velocity (GHSV) in each reactor tube was constant at 40 000 (mL/h·g<sub>cat</sub>). In the single-sample reactor experiments, JP-8 was dosed at a rate of 0.125 mL/min, while the same GHSV was maintained as in the high-throughput reactor. The catalysts were activated in alternating flows of He, H<sub>2</sub>, and O<sub>2</sub> for 3 h at a temperature of 723 K prior to the introduction of JP-8. Control experiments were performed using empty reactor tubes. Because cracking is an endothermic reaction, heating was constantly supplied to the catalyst beds to maintain the reaction temperature. Catalyst regeneration treatments were performed at the reaction temperature to avoid heating and cooling cycles in either flowing air or a mixture of 20% O<sub>2</sub> in He, and in general no significant differences were detected between the two methods. Product composition was measured online using a gas chromatograph-mass spectrometer (GC-MS, Shimadzu QP-2010) equipped with a HayeSep-D capillary column (0.53 mm ID x 30 m; Agilent) using He as the carrier gas. Analysis of each injection required 35 min. Because of the limitations of the instrument, carbon species of 5 or more carbon atoms were not quantified. Product species from JP-8 cracking that were detected in measurable quantities included ethylene, ethane, propylene, propane, 1-butene, and *n*-butane. The metric for comparing catalytic activity is the percentage yield of LPG produced relative to the JP-8 feed as defined in eq 1

$$\text{LPG yield (mass \%)} = \frac{\text{mass of C}_2, \text{C}_3, \text{C}_4 \text{ hydrocarbons in cracking effluent}}{\text{mass of JP-8 feed}} \quad (1)$$

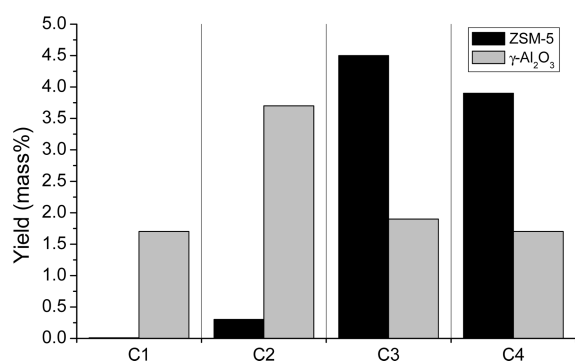
The LPG yield, as defined by eq 1, was used as the figure of merit to compare JP-8 cracking activity between the various catalysts investigated in the high-throughput approach.

## RESULTS AND DISCUSSION

**JP-8 Cracking to C<sub>2</sub>–C<sub>4</sub> Hydrocarbons.** Table 1 shows the selective mass yields of light hydrocarbons from JP-8 cracking over zeolite catalysts with four types of framework topology and varying Si/Al ratios at a reactor temperature of 823 K. These conversions were achieved without desulfurization of the fuel. The best-performing ZSM-5 catalysts exceeded 20% conversion of JP-8 to LPG on a mass basis under these conditions, with the highest production consisting of C<sub>3</sub> hydrocarbons. A lower Si/Al ratio corresponds to higher JP-8 catalytic cracking activity to LPG, but a higher Si/Al ratio

contrastingly produces a higher selectivity of C<sub>3</sub>/C<sub>2</sub> hydrocarbons. Higher Si/Al ratios shift cracking product distributions toward the gasoline fraction (consisting of C<sub>5</sub>–C<sub>12</sub> hydrocarbons), thereby reducing the gaseous yield in the C<sub>2</sub>–C<sub>4</sub> range.<sup>14</sup> High production of alkenes is observed for both the ZSM-5 and faujasite catalysts. However, a significant amount of alkanes are also produced over the lower Si/Al ratio of ZSM-5. Cracking to alkanes, especially C<sub>3</sub> and C<sub>4</sub> alkanes, is desirable because those are large components of traditional LPG fuel. For ZSM-5, the selectivity to C<sub>2</sub> increased with overall LPG yield while it decreased with Si/Al ratio. In contrast, the product distribution for zeolite Y catalysts predominantly consists of C<sub>3</sub> and C<sub>4</sub> hydrocarbons with very little C<sub>2</sub>. This is consistent with previous studies of olefin cracking, where ZSM-5 was observed to produce more ethylene than the faujasite catalyst due to the relatively small pore size of ZSM-5 resulting in larger interactions between the catalytic surface of ZSM-5 and the reactants, as well as the absence of bimolecular reactions.<sup>15</sup> Zeolite beta did not meet the desired threshold target of 5% conversion. The lack of activity of the mordenite catalysts can be attributable to their one-dimensional pore structure. The pores in mordenite have been shown to be easily blocked by coke, reducing catalyst activity, and leading to rapid deactivation.<sup>16</sup>

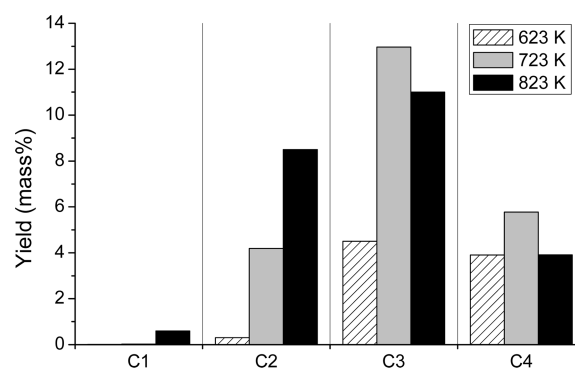
ZSM-5 also demonstrated effectiveness as a JP-8 cracking catalyst at lower temperatures. Figure 1 shows total LPG yield



**Figure 1.** Product distribution comparison from JP-8 cracking between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (light) at a reaction temperature of 923 K<sup>5</sup> and ZSM-5 (Si/Al = 25, dark) at a reaction temperature of 623 K.

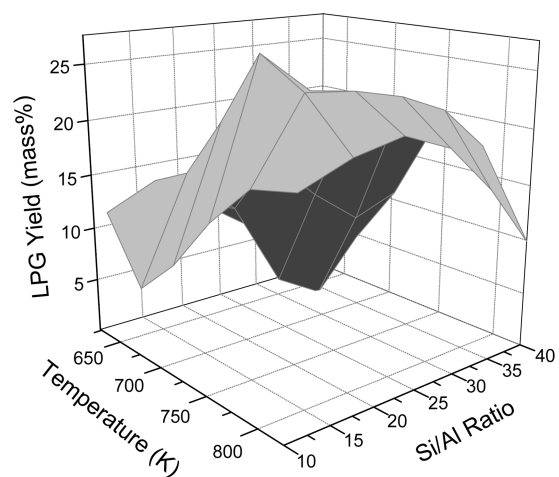
of 8.7% for ZSM-5 catalyst (Si/Al = 25) at a reactor temperature of 623 K, compared with 7.3% for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at a reactor temperature of 923 K reported previously.<sup>5</sup> For practical applications, the necessary reactor temperature greatly impacts portability, safety, and energy efficiency in nonstationary units. The product distribution for ZSM-5 consists of a higher concentration of C<sub>3</sub> and C<sub>4</sub> hydrocarbons with almost no lighter product. In contrast, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst produces a significant fraction of methane, which can be considered product loss for this application. Any remaining hydrocarbons heavier than LPG in the reactor effluent could be recycled for further cracking.

Both reaction temperature and solid acidity of the ZSM-5 catalyst were important in determining JP-8 cracking activity to LPG. The product distribution from JP-8 cracking is shown for a ZSM-5 (Si/Al = 25) catalyst for a range of reactor temperatures from 623 to 823 K in Figure 2. An increase in the cracking reaction temperature from 623 to 723 K results in increases in C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> hydrocarbon production to a total



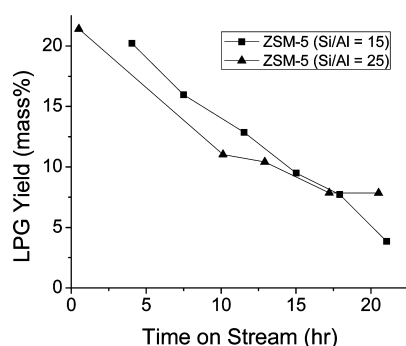
**Figure 2.** Product distribution comparison from JP-8 cracking for zeolite ZSM-5 (Si/Al = 25) at reaction temperatures of 623 K (striped), 723 K (light), and 823 K (dark).

yield of 22.9%. A further increase in temperature to 823 K shifts some of the product distribution away from C<sub>3</sub> and C<sub>4</sub> hydrocarbons toward C<sub>2</sub> hydrocarbons and trace amounts of methane. In addition, the LPG yield dips slightly at 823 K to a total of 21.4%. The combined ethylene + propylene selectivity increased, while the propylene/ethylene ratio decreased with an increase in reaction temperature, which is consistent with previous hydrocarbon catalytic cracking studies.<sup>10</sup> LPG yield from JP-8 cracking over ZSM-5 catalysts for a range of temperatures from 623 to 823 K and Si/Al ratios ranging from 11.5 to 40 are shown in Figure 3. The maximum LPG yield was observed for a Si/Al ratio of 15 and a reactor temperature of 723 K, corresponding to a C<sub>2</sub>–C<sub>4</sub> product yield of 24.5% on a mass basis.



**Figure 3.** LPG yield from JP-8 cracking over ZSM-5 zeolite catalysts for varying reactor temperatures and Si/Al ratios. A maximum is observed corresponding to a reactor temperature of 723 K and Si/Al ratio of 15:1.

**Time-on-Stream Deactivation.** Despite the relatively high LPG yields observed for ZSM-5 catalysts, time-on-stream (TOS) performance is also important in regards to a practical application. The reducing atmosphere required during catalytic cracking results in coking of the catalyst and a commensurate decrease in catalyst activity. LPG yields from JP-8 cracking for increasing TOS are shown for ZSM-5 (Si/Al = 15 and 25) at a reactor temperature of 823 K in Figure 4. When sampling strategy permitted, multiple measurements were collected consecutively to provide an estimate of the standard error in



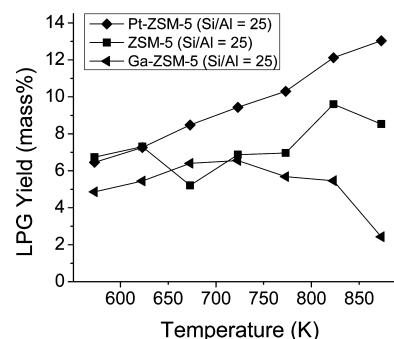
**Figure 4.** LPG yield from JP-8 cracking ZSM-5 (Si/Al  $\leq$  25) catalysts for up to  $\sim$ 20 h of time on stream at a reactor temperature of 823 K.

LPG yield, which ranged from  $\pm 0.21\%$  to  $\pm 0.52\%$ . Initial JP-8 conversion to LPG exceeding 20% on a mass basis was observed for both catalysts, with longer term conversions above 10% after 10 h TOS. Deactivation is attributed to carbon coke formation on the catalyst and continues steadily up to  $\sim$ 20 h TOS, at which time the Si/Al = 15 catalyst no longer exceeds the 5% target threshold for conversion. Over the duration of the 20 h period, the ZSM-5 (Si/Al = 15) catalyst produces a total of  $\sim$ 39.1 g of LPG per gram of catalyst. For the Si/Al = 15 catalyst, the fraction of product that is propylene increases steadily from  $\sim$ 31% after 4 h on stream up to  $\sim$ 47% after 21 h on stream. In contrast, the ZSM-5 (Si/Al = 25) catalyst exhibited LPG yields in excess of 7.5% after 20 h TOS, maintaining a greater resistance to deactivation than the Si/Al = 15 catalyst.

LPG yields from JP-8 cracking for three promoted ZSM-5 catalysts prepared through ion-exchange are compared to the base zeolite in Table 2. The incorporation of La into the zeolite provided the greatest boost to initial activity at 350  $^{\circ}$ C, followed by Cu. The higher activity of the La-ZSM-5 catalyst could be explained through increasing solid acidity because of the formation of hydroxyl groups via the Hirschler–Plank mechanism on the multivalent La atoms.<sup>17</sup> Differences also emerge between the Cu and Pt containing catalysts. The Cu-ZSM-5 product distribution is most similar to that of the base catalyst, especially with regards to alkane yield. The addition of Pt to ZSM-5 did not show an increase in activity at 623 K as compared to the base catalyst. AAS analysis determined a Cu loading of 1.39% on the Cu-ZSM-5 catalyst, while 2.22% of Pt loading was measured on the Pt-ZSM-5 catalyst. The dehydrogenation function of Pt<sup>7</sup> explains the higher alkene yields and lower alkane yields as compared to the base catalyst.

Although the La and Cu ion-exchanged ZSM-5 catalysts showed high initial activity at 623 K, only Pt and Ga ion-exchanged ZSM-5 catalysts demonstrated long-term sustained activity above the 5% conversion target. Catalyst performance after successive reaction and coke burnoff treatments was investigated in increasing temperature increments of 50 K. The

catalysts were exposed to JP-8 for  $\sim$ 12 h at each reaction temperature. In an attempt to mitigate the effects of coking deactivation observed during JP-8 cracking, the catalysts were exposed to a mixture of 20% O<sub>2</sub> in He for 1 h prior to introduction of the JP-8 feed at each reaction temperature. The cyclic treatments served to test catalyst performance at varying temperatures following coke burnoff. The duration of coke burnoff was chosen to simulate a reasonably brief amount of time for a prototype fuel processing system. Figure 5 shows a



**Figure 5.** LPG yield from JP-8 cracking over ion-exchanged ZSM-5 catalysts as compared to the base zeolite for increasing reaction temperatures from 573 to 873 K. One hour of oxygen regeneration was performed prior to initiating JP-8 cracking at each respective reaction temperature.

comparison of the initial activity following the coke burnoff treatment at each temperature for base ZSM-5 (Si/Al = 25) catalyst with promoted catalysts consisting of a noble metal loading (Pt) and a non-noble metal loading (Ga) prepared via ion-exchange over a reactor temperature range increasing from 573 to 873 K. Multiple measurements were collected at a single data point to provide an estimate of the standard error in LPG yield, which was determined to be  $\pm 0.58\%$ . The Pt-ZSM-5 catalyst was most able to mitigate the effects of coking deactivation via the O<sub>2</sub> treatments at low reactor temperatures, exhibiting steady increases in cracking activity with increasing reaction temperature. In contrast, the base ZSM-5 catalyst and the Ga-ZSM-5 catalyst exhibit variable activity over this temperature range. The Pt-ZSM-5 catalyst performed best at higher reactor temperatures, even in comparison to the base ZSM-5 catalyst, while the Ga-ZSM-5 catalyst performed worse. The sharp reduction in JP-8 cracking activity for the Ga-ZSM-5 catalyst at a reactor temperature of 873 K is attributed to poor coke burnoff ability and a lack of stability through multiple reaction and regeneration cycles. The Pt-ZSM-5 catalyst demonstrated excellent long-range stability, with JP-8 cracking activity to LPG exceeding 13% on a mass basis at the 873 K reactor temperature, which also corresponded to the longest amount of TOS in the reactor. The increasing LPG yield observed for the Pt-ZSM-5 catalyst with increasing reactor temperature primarily manifests through greater propylene

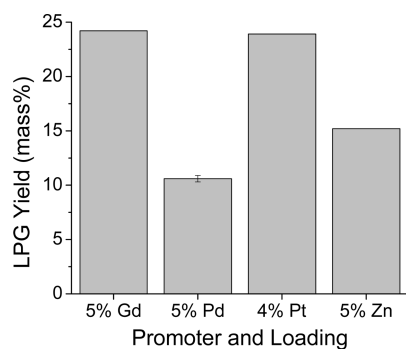
**Table 2.** Selective Yields (Mass %) of JP-8 Cracking to C<sub>2</sub>–C<sub>4</sub> Hydrocarbons at a Reactor Temperature of 623 K for Promoted ZSM-5 Catalysts Prepared via Ion Exchange

catalyst	Si/Al	C <sub>2</sub> H <sub>4</sub> (%)	C <sub>2</sub> H <sub>6</sub> (%)	C <sub>3</sub> H <sub>6</sub> (%)	C <sub>3</sub> H <sub>8</sub> (%)	C <sub>4</sub> H <sub>8</sub> (%)	C <sub>4</sub> H <sub>10</sub> (%)	C <sub>2</sub> –C <sub>4</sub> (%)
Cu-ZSM-5	25	0.3	0.0	2.4	2.9	2.1	1.9	9.7
La-ZSM-5	25	0.4	0.1	4.1	1.7	3.4	1.2	10.9
Pt-ZSM-5	25	0.1	0.0	2.6	1.4	3.0	1.3	8.5
ZSM-5	25	0.3	0.0	2.0	2.7	1.7	1.9	8.6 $\pm$ 0.2



yields. In addition to the dehydrogenation function of Pt, this is expected because ZSM-5 catalysts have been shown to be effective for producing propylene.<sup>18</sup>

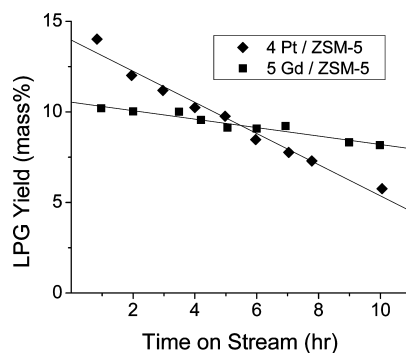
High-throughput optical screening was performed previously to identify potential ZSM-5 promoters for JP-8 cracking.<sup>19</sup> On the basis of the results from these studies, monometallic catalysts containing 5% Gd, 5% Zn, 5% Pd, and 4% Pt were prepared through wet impregnation into ZSM-5 (Si/Al = 25). JP-8 cracking activity to LPG for these four catalysts is shown in Figure 6 following ~30 h TOS and a subsequent air



**Figure 6.** LPG yield from JP-8 cracking at a reactor temperature of 873 K after first regeneration treatment following 30 h TOS for promoted ZSM-5 catalysts identified through high-throughput optical screening.<sup>19</sup>

regeneration treatment all at a reactor temperature of 873 K. The reported activity therefore describes both the regenerability and stability of the catalysts. Each of the catalysts exceeded the 5% threshold target at this temperature, but strong discrepancies emerged between them. The Gd-promoted ZSM-5 catalyst demonstrated the highest LPG yield under these conditions, with the activity comparison ranking in the order of Gd  $\approx$  Pt > Zn > Pd. An important result is that the Gd-promoted ZSM-5 catalyst matches the performance of the Pt catalyst, offering the potential to replace the precious metal loading with a cheaper alternative.

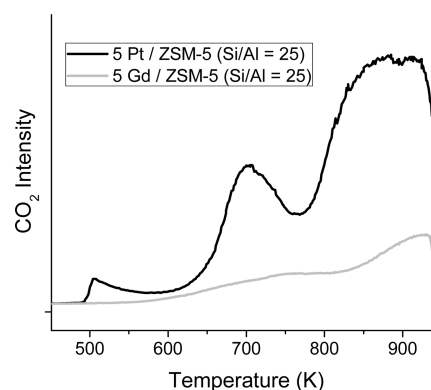
The performance of the ZSM-5 catalysts promoted with Gd and Pt was evaluated at a more moderate reaction temperature of 723 K in the single-sample reactor, and the observed TOS deactivation for the two catalysts is shown in Figure 7. The Pt catalyst provides higher initial activity than the Gd catalyst, but the deactivation rates differ significantly. Crossover occurs between 5 and 6 h TOS so that, after 10 h TOS, the Gd catalyst



**Figure 7.** Time on stream deactivation at a reactor temperature of 723 K for catalysts consisting of metals impregnated on zeolite ZSM-5 (Si/Al = 25).

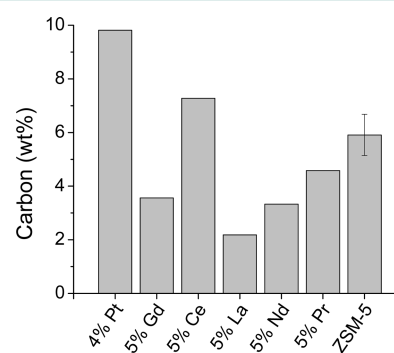
significantly outperforms the Pt catalyst. As a result, strong differences emerge depending on the promoter used for the ZSM-5 catalyst. The Gd-promoted ZSM-5 catalyst offers much longer operating times exceeding the target threshold before regeneration is required in comparison to the Pt-promoted catalyst. However, the Gd-promoted ZSM-5 catalyst proved ineffective for coke burnoff regeneration at 723 K reactor temperature.

**Catalyst Regeneration.** Figure 8 shows a comparison of carbon burnoff during TPO between ZSM-5 (Si/Al = 25)



**Figure 8.** Temperature programmed oxidation spectra for postreaction Pt (dark) and Gd (light) promoted ZSM-5 (Si/Al = 25) catalysts.

catalysts containing Pt and Gd. Three distinct carbon burnoff positions are shown in the spectra of the Pt catalyst, corresponding to ~500, 650–700, and >800 K. In contrast to the distinct peaks visible in the spectrum for the Pt catalyst, carbon burnoff from the Gd catalyst shows a gradual increase in carbon dioxide formation until a shoulder is reached near ~773 K. In both cases, the final peak has an onset temperature near 823 K, above which temperature the rate of coke burnoff significantly increases. The TPO spectra lend insight to the effectiveness of the Pt catalyst for regeneration at 723 K, in contrast to the Gd catalyst. This result is supported by CH elemental analysis of postreaction catalysts, as shown in Figure 9. The amount of carbon coke formed on the Pt catalyst (9.8%) after 10 h TOS greatly exceeds that of the Gd catalyst (3.6%), which is in good agreement with what would be expected from the relative deactivation rates. In addition, while significantly more carbon coke is formed on the Pt catalyst than the base zeolite ( $5.9 \pm 0.8\%$ ), the Gd catalyst forms less coke than both

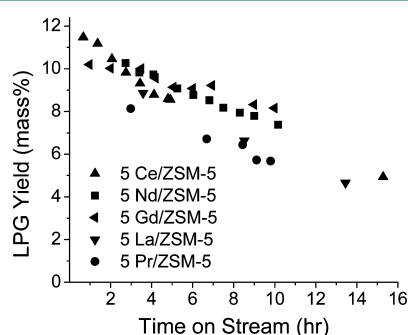


**Figure 9.** Carbon content as determined by CH elemental analysis on postreaction catalysts after JP-8 cracking for 10 h TOS at a reactor temperature of 723 K.

the Pt catalyst and the base zeolite. This result is attributable to modification of the catalyst's solid basicity, where the presence of Gd inhibits the adsorption of coke precursors and thereby reduces the coke load that forms during cracking.<sup>20,21</sup>

Comparison of the various aspects of performance for the Pt- and Gd-containing catalysts yields some striking differences. The Pt catalyst exhibits higher initial activity at moderate reaction temperatures and the potential for lower temperature regeneration via carbon burnoff. In contrast, the Gd catalyst reduces the amount of coking that forms on the catalyst and thereby decreases the deactivation rate of the ZSM-5 catalyst. As a result, both promoters provide different function that can be tuned to the needs of a practical application.

**Effect of Rare Earth Promoters on ZSM-5 Deactivation.** The demonstrated benefits of using Gd as a promoter for ZSM-5 catalysts for JP-8 cracking to LPG motivated investigation of other rare earth metals as promoters, which were evaluated in the single-sample reactor. Figure 10 shows



**Figure 10.** Time on stream deactivation at a reactor temperature of 723 K for rare earth impregnated ZSM-5 (Si/Al = 25) catalysts.

the LPG yield from JP-8 cracking for rare earth-promoted ZSM-5 (Si/Al = 25) catalysts with increasing TOS at a reactor temperature of 723 K. Data points were collected for each catalyst as frequently as sampling strategy allowed. Extrapolating back to the point of initial TOS, the initial activity ranks in the order Ce > Nd > Gd ≈ La > Pr, as shown in Table 3.

**Table 3. Predicted LPG Yield at Initial TOS and Duration Catalyst Exceeds the 5% (Mass Basis) Threshold Target for LPG Yield from JP-8 for Rare Earth-Promoted ZSM-5 (Si/Al = 25) Catalysts with 5% Nominal Metal Loading Prepared via Wet Impregnation**

promoter	LPG yield at initial TOS (%)	TOS exceeding 5% threshold (h)
Gd	10.5	22.9
Nd	11.2	16.0
Ce	12.1	15.2
La	10.4	12.6
Pr	9.2	11.7

Compared to the other promoters, the Ce catalyst exhibits a higher initial rate of deactivation at low TOS (<4 h) before the rate slows significantly. The best catalysts for long-range deactivation rates correspond to Gd > Ce ≈ Pr > Nd > La. However, as a fraction of the initial activity, the deactivation rate of Pr exceeds that of Nd. The Nd catalyst consistently provides the highest LPG yield on a mass basis over the range from 3 to 5 h TOS, along with the Gd catalyst, while the Ce catalyst provides the highest initial activity. For long-range

performance in excess of 6 h TOS, the Gd catalyst exhibits the highest activity. The Pr catalyst is the worst performing catalyst of the group for periods up to 10 h TOS and beyond.

Threshold TOS values were predicted corresponding to the time at which catalyst activity would decrease below the 5% conversion target. These results are included in Table 3 and show good agreement with the results already discussed. Gd greatly extends the operating time of the catalyst in excess of the 5% threshold target beyond 20 h TOS. Of the remaining catalysts, the Nd and Ce promoted catalysts are the best performing, lasting beyond 15 h of time on stream, while the La and Pr promoted catalysts are laggards, falling below 13 h TOS. In lieu of regeneration efforts, the threshold time on stream would have an impact on the cost and logistics of changing catalysts in a prototype unit.

CH elemental analysis was used to measure the amount of carbon coke formed on promoted ZSM-5 (Si/Al = 25) catalysts after JP-8 cracking for 10 h at a reaction temperature of 723 K, as shown in Figure 9. A control test with fresh ZSM-5 revealed only negligible amounts of carbon. The sample promoted with only Pt shows the highest carbon formation, followed by the Ce catalyst. This is consistent with the TPO results showing high rates of carbon burnoff for the Pt catalyst. The other promoted catalysts show reduced carbon content from the base ZSM-5 catalyst. The H/C molar ratio of the spent catalyst provides a measure of the hardness of the coke that is formed, with lower values indicating "harder" coke. The Pt catalyst exhibits the lowest H/C ratio (0.94), while the H/C ratio for the Gd catalyst (1.51) is above that of the base ZSM-5 catalyst ( $1.30 \pm 0.05$ ). This provides further evidence for the benefits of coking reduction provided by the Gd catalyst.

## CONCLUSIONS

Using a high-throughput approach, we carried out the catalytic cracking of JP-8 over aluminosilicate zeolite materials with various Si/Al ratios at 573–873 K. Si/Al ratio and shape-selectivity of the zeolite pore structure contributed to high JP-8 cracking activity. The highest C<sub>2</sub>–C<sub>4</sub> hydrocarbon yield obtained in this study was 24.5% over ZSM-5 (Si/Al = 15) at 723 K. However, the reducing atmosphere required during catalytic cracking resulted in coking of the catalyst and a commensurate decrease in conversion rates. Metal promoters for ZSM-5 catalysts were explored to reduce deactivation and improve coke burnoff regeneration. It was found that rare earth metals reduced the deactivation rate, and elemental analysis showed less carbon due to coking compared to the base catalyst. Temperature programmed oxidation experiments showed that noble metals reduced onset temperatures for coke burnoff regeneration.

The overall goal of this research work was to demonstrate the utility of a high-throughput approach for systematically accelerating the process of catalyst discovery and optimization. This approach proved highly effective for developing successful catalysts to meet the needs of a fuel processing system for JP-8 cracking to LPG. This work has developed a research framework for investigating complex catalytic processes on a rapid time scale, and the results can be extended to other hydrocarbon-based catalytic cracking systems to create effective energy solutions.

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## Notes

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## ABBREVIATIONS

Si/Al = silicon-to-aluminum ratio

TOS = time-on-stream

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