# Development of a High-Throughput Methodology for Screening Coking Resistance of Modified Thin-Film Catalysts

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**ABSTRACT:** A high-throughput optical technique has been developed for the rapid screening of coking resistant composition-spread promoted-catalyst libraries during hydrocarbon cracking, in particular for Jet Propellant 8(JP-8) cracking. The libraries are screened by measuring changes in the catalyst's surface color due to the accumulation and burnoff of coke from the surface during JP-8 exposure and catalyst regeneration via oxygen burnoff. This rapid screening method was validated through a comparison of the coking properties of high-surface area powder cracking catalysts, and sputter deposited samples. Experiments on bimetallic (Pt–Gd) catalysts showed systematic trends consistently illustrating the superiority of Pt–Gd alloys to coking due to the presence of gadolinium.

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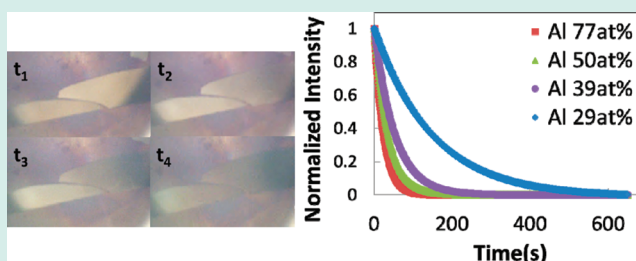


## 1. INTRODUCTION

The introduction of unmanned aerial vehicles, which utilize liquefied petroleum gas (LPG) powered fuel cells, has led to a critical need for the presence of LPG in the battlefield. Since a supply chain for LPG does not, and likely will never, exist it would be beneficial to convert the readily available JP-8, for which a supply chain already exists, directly and locally into LPG. There are four technologies typically applied to such reformation reactions: hydrothermal reformation, partial oxidative reformation, autothermal reformation, and catalytic cracking.[1−4] Catalytic cracking is the most favorable approach for this specific application, as it does not require the creation and use of purified oxygen or water. Catalytic cracking of hydrocarbons over solid acid catalysts is a well-known process.[5−14] In particular, it is well established that zeolite catalysts exhibit high selectivity and activity during catalytic cracking,[15] and we have recently demonstrated that aluminosilicate zeolite catalysts with mordenite framework inverted (MFI) structure offer high conversion of JP-8, a kerosene-based jet fuel,[16] to LPG (>20%) during catalytic cracking.[17] Unfortunately, the reducing atmosphere required for catalytic cracking induces coking of the catalyst, which will poison the active sites or block the access to them, leading to decreased conversion efficiency.

Periodic high temperature (>873 K) air regeneration of the catalysts can be used to mitigate the problem. However, high temperature regeneration can result in adverse effects such as dealumination, structural alteration, and sintering of the supported metals.[18] There has been substantial prior work done to mitigate the detrimental effects associated with catalysts regeneration.[19−24] Although these methods have met with success, the catalyst regeneration must be performed at high temperatures followed by treatments using aqueous ammonia.[19,23,24] Although in traditional fuel refineries a great amount of energy is available to be devoted to high temperature regeneration treatments; in field systems it is preferable to minimize the energy penalty by reducing the regeneration temperature. Additionally, the treating agents typically used will be difficult to transport into the field. Therefore, catalyst modifiers are needed that can increase the regeneration rate and lower the carbon burnoff temperature in presence of only air, while retaining or enhancing the LPG activity and selectivity. Further, it would also be beneficial to mitigate coking by identifying catalyst modifiers resistant to deactivation by coking during cracking. A previous study carried out in a 16-channel parallel reactor system[25] has demonstrated that platinum is a good candidate additive;[17] however, its price is detrimental to large scale production, and platinum nanoparticles tend to aggregate on zeolitic frameworks during regeneration.[26]

To identify modifiers for the catalyst with appropriate properties, a systematic investigation of a multidimensional correlation between the modifier composition, loading, pretreatment/regeneration condition, and the reaction/regeneration rate is needed. Such investigation would be prohibitively slow utilizing traditional single composition methodologies. Over the past 15 years scientists in the fields of catalysis and materials science have increasingly turned to the

utilization of high-throughput methodologies to explore large and complex phase spaces.[27−29] In the high-throughput approach to materials discovery and optimization, hundreds of samples are simultaneously synthesized and rapidly screened for the desired figure of merit. A major challenge in applying high-throughput experimentation is the development of rapid and effective parallel screening techniques. One of the most effective screening strategies involves a two-step approach implementing the combination of a primary and secondary screen.[28,30] The primary screening has to rely on fast analytical techniques, which are preferably parallelized rather than being sequential. Here, large libraries of samples are tested in a relatively imprecise manner with the intention of identifying systems with superior properties for subsequent in-depth screens. Once a potential candidate has been identified in the primary screen, a second round of screening is then undertaken under more rigorous conditions. Parallel screening techniques often are based on visually monitoring samples, either in the visual, infrared, or UV regimes. Examples of such techniques include monitoring the deflection of micromachined cantilevers due to magnetoelastic deformation or the fluorescence of an indicator during a chemical reaction.[31,32]

To successfully screen modifiers for the zeolite catalysts, a set of criteria was determined. (1) The presence of the modifier should decrease the coking rate. This will permit longer time of service between regeneration cycles, thus increasing mission readiness. (2) The modifier should decrease the temperature at which carbon burn off in air occurs. Reducing the regeneration temperature will reduce the overall amount of energy needed to perform catalyst cleaning. Such energy would be created in the field by the direct combustion of JP-8 or the liquid effluent from the catalyst bed. Thus, reducing the temperature of regeneration helps to minimize the impact of the reformer on the traditional supply chains. (3) The effects of the modifier should persist through multiple cycles. Typical issues with metals supported on zeolites include nanoparticle sintering and irreversible phase transformation (i.e., the formation of a carbide), which could result in a continuous degradation in the decoking properties during cycling. It would be preferable for units in the field to be capable of being regenerated with only air for multiple cycles to prevent the establishment of a MFI supply chain.

To identify a more economical and robust modifier for the MFI, a thin-film high-throughput optical methodology has been developed to rapidly screen new bimetallic/oxide modifiers for their ability to reduce the coking rate and the regeneration temperature. The proposed technique relies on changes in the optical properties of the catalyst surface during the accumulation and burnoff of coke to determine the relative coking rate and the onset of carbon burnoff. This technique permits the rapid screening of entire binary and ternary phase diagrams for their regenerative capabilities in a single experiment.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Sample Preparation.
Three different types of samples were prepared for this work. Unpromoted catalyst samples for validation studies were formed by pressing 150 mg $Al_2O_3$ (Catalox, Sba-200), $Nb_2O_5$ (Alfa Aesar, Product No. 11366) and $SiO_2$ (Sigma-Aldrich, Product No.236799) powder into pellets. Promoted Pt-MFI samples "used for calibration during combinatorial measurements" were prepared by standard wet impregnation methods and were subsequently pressed into pellets. Combinatorial modifier libraries were generated by

depositing ultrathin (<5 nm) composition spread samples onto pressed MFI pellets in a combinatorial ultrahigh vacuum magnetron sputtering system (with a base pressure in the range of $10^{-7}$ Pa). Samples for thickness/composition calibration were deposited onto silicon wafers and characterized by profilometry and a scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS).

### 2.2. Experiment Setup.
Catalyst coking and regeneration studies were carried out in a high-throughput screening system, which includes an in situ high-throughput optical reactor, a liquid-to-vapor dosing system, and an image recording/data analysis system. A schematic drawing for the experimental setup is presented in Figure 1.
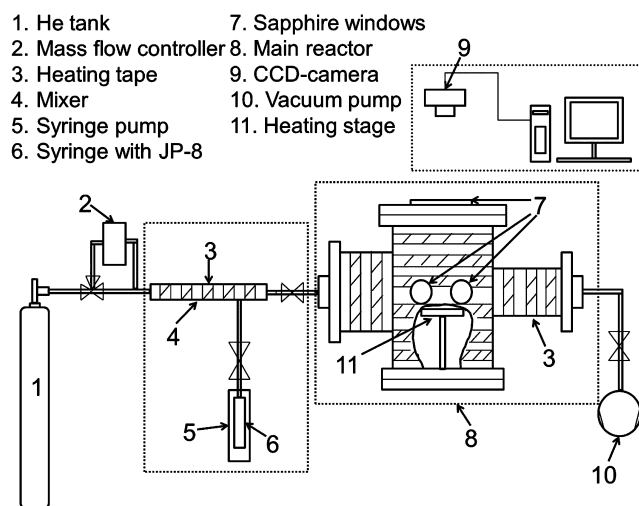


1. He tank
2. Mass flow controller
3. Heating tape
4. Mixer
5. Syringe pump
6. Syringe with JP-8
7. Sapphire windows
8. Main reactor
9. CCD-camera
10. Vacuum pump
11. Heating stage

**Figure 1.** Schematic representation of the liquid fuel dosing optical reactor used in this experiment. The entire reactor is heat line traced and maintained at 500 K during dosing to prevent condensation of the JP-8 during dosing experiments. Samples are mounted on a 5.5 cm diameter heating stage during all experiments. A CCD camera mounted on top of the chamber with optical access to the heating stage is used to monitor the surface of the modified catalyst during all experiments.

The main body of the high-throughput reactor is a stainless steel chamber with optical access to the sample stage via a top-mounted optical flange. The samples are placed on a 5.5 cm diameter heating stage capable of reaching temperatures as high as 1073 K located in the center of the chamber (Blue Wave Semiconductors model SH 1.6 PVD-NR). The temperature uniformity of the heater is rated to be <2% across the entire hot zone. The heater temperature is monitored by a single type K thermocouple, which is mounted so that it is in direct contact with the back plate of the heater. The temperature is controlled to within ±1 K by an external power supply.

During dosing experiments, prior to JP-8 exposure, the combinatorial sample and a reference sample were mounted on the heating stage and affixed using stainless steel clamps. The samples were mounted in a homemade sample stage which can accommodate as many as 19 pressed pellet samples in a single experiment. The same stage can also be mounted into the deposition chamber for modifier deposition, allowing for reliable indexing of the combinatorial samples. The optical cell was then sealed and pumped to a base pressure of 20 ± 5 Pa to remove the oxygen from the reactor. The optical chamber walls were then heated to and maintained at 500 K by heating tape for the duration of the experiment to prevent

condensation of the heavier hydrocarbons. The samples were then heated to the reaction temperature, and JP-8 was introduced into the chamber.

Dosing of the liquid JP-8 was performed using a homemade liquid dosing system. A stainless steel syringe was used to feed JP-8 into a high internal surface area heated stainless steel doser kept at 500 K, which converts the liquid JP-8 into a vapor phase. A helium carrier gas then passes through the mixer and transports the JP-8 through trace-heated lines to the high-throughput reactor. About 200 sccm of reaction gas with a nominal JP-8 composition of about 30 mol % was introduced into the high-throughput reactor for each dosing. The actual JP-8 composition can vary from experiment to experiment. This does not affect the ability to compare results within a single experiment, but can be problematic when comparing different runs of a particular catalyst. Therefore, one of the 19 samples for each experiment is a Pt/MFI pressed pellet which is used as a reference.

After the initial dosing experiments either an isothermal or a temperature ramping regeneration experiment was performed to determine the compositional variation of the regeneration rate and the carbon burnoff temperature, respectively. Prior to isothermal regeneration, the substrate heater and optical chamber walls were cooled to room temperature. The substrate was then heated to, and maintained at, 723 K followed by venting the optical chamber to air. A similar preparation of the chamber was conducted during experiments to determine the regeneration temperature. The main difference was that the chamber was first vented to air, and then the substrate was heated to 873 K at 5 K/min.

Throughout all experiments the surface of the entire substrate heater was monitored via a CCD-based imaging system while the sample surface was illuminated using an incandescent light source. An in-house image recording/data analysis system was used for real-time monitoring of the samples. Images were obtained with a 640 × 480 pixel CCD camera (The Imaging Source DKF 21AF04) positioned above the optical chamber and were recorded at rate of 30 frames per second. Image acquisition and analysis software was developed using LabVIEW 2009. The software permits the selection of up to 30 regions of interest (ROI) with arbitrary dimensions prior to commencing dosing or regeneration. These images are used as a background and are subtracted from all subsequent images. The background subtraction removes the initial possibility of disparity in color between each sample and provides a convenient method to compare color changes across samples on an absolute grid. Within each ROI, the combination of all red, green, and blue intensity values for each pixel were summed and averaged to generate an overall intensity value for that ROI. These averages are indexed and catalogued as a function of time.

## 3. RESULTS AND DISCUSSION

The physical principle of this measurement technique is based on the change of the absorption of light from the catalyst surface during the accumulation of coke. As the coke is more absorbent than the nominally white promoted MFI, the surface of the catalyst appears to darken during coke deposition. The relationship of the reflected light to the thickness of a solid material follows an exponential function by Beer–Lambert law,[33] and the data from the CCD camera are fit to the following equation:

$$I = I_O + (I_f - I_O) \times (1 - \exp(At))$$

Where $I$ is the intensity at time $t$, $I_f$ is the stabilized intensity, $I_O$ is the intensity when JP-8 was introduced into the optical chamber, and $A$ is related to the coking rate. $A$ is not an absolute measurement of the coking rate since it will include the film thickness and its absorption coefficient, which can change slightly as the composition of the modifier, and hence the coke, is altered. However, here the change in the absorption coefficient is assumed to be a relatively small effect, and $A$ is denoted as the coking rate of a particular promoted zeolite.

It should be noted here that all information regarding product distribution, which hydrocarbon species are responsible for carbon deposition, and conversion efficiency are not accessible by this initial screening method. It is further assumed that the amount of modifier present in the catalyst is not sufficient to significantly alter the MFI activity and selectivity. It is understood that this is not necessarily the case and that the presence of platinum, for instance, can result in a modification of the product distribution.[34] Therefore, all recommended additives need to be validated by full chemiometric analysis techniques through traditional wet-impregnation catalyst preparation techniques. Additionally, the currently employed technique is not well suited for screening the coking rate of promoted dark catalysts and so must be used judiciously.

The applicability of this approach was first confirmed via JP-8 dosing experiments on unmodified $Al_2O_3$, $Nb_2O_5$, and $SiO_2$ pellets. From previous work in our group, the coking rate and activity of these three catalysts in the powder form had been ranked $Al_2O_3 > Nb_2O_5 \sim SiO_2$.[34] The samples were heated to 873 K, which had previously been determined to be their optimum cracking temperature, and then exposed to a burst of JP-8. A series of samples images were then recorded. Figure 2
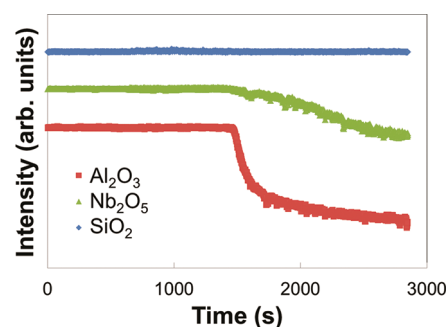


**Figure 2.** Intensity for $Al_2O_3$, $Nb_2O_5$, and $SiO_2$ as a function of time during JP-8 exposure. The curve for $Al_2O_3$ shows a rapid decrease in intensity during exposure, while the curves for $Nb_2O_5$ and $SiO_2$ over the same time period exhibit a much slower change in intensity or very little change in intensity.

shows a summary of the measured intensity of the three samples as a function of time during JP-8 exposure. The ranking of the relative coking rates by imaging experiments was found to be consistent with previous experiments. $Al_2O_3$ clearly shows a rapid decrease in intensity during exposure, while $Nb_2O_5$ over the same time period exhibits a much slower, nearly negligible, change in intensity. $SiO_2$, which was previously identified to be a poor catalyst for reformation, shows almost no change in intensity over the course of the experiment. This implies that for unpromoted catalysts parallel imaging can be used to reliably rank relative coking rates.

To consider a primary screen incorporating modifiers on a pressed catalyst pellet it is important to understand the differences in the relative experimental configurations. Specifically, contrary to promoted catalysts formed by wet impregnation, where uniform dispersal of the modifier is achieved throughout the catalyst, for samples deposited via physical vapor deposition techniques coverage is limited by line-of-sight. This means that only the very topmost surface of the modifier is functionally promoted. Such an approach to sample preparation would certainly not be suited for standard high-throughput chemiometric measurements, but for the optical technique considered presently this is actually beneficial. Additionally, to approximate the physical structure of a promoted catalyst (i.e., small, discrete modifier particles), it is important to ensure only partial coverage of the exposed catalyst surface by the modifier. Therefore, all modifier libraries were deposited to a maximum thickness equivalent to three to six monolayers of coverage. Discrete growth of the films was confirmed by bright field transmission electron microscopy (TEM) imaging, which show a relatively uniform dispersion of metal nanoparticles on the surface of the pressed MFI pellets (Figure 3a).

To confirm that optically monitoring the surface of a sputter surface coated MFI would provide meaningful information, a series of dosing and regeneration experiments were performed
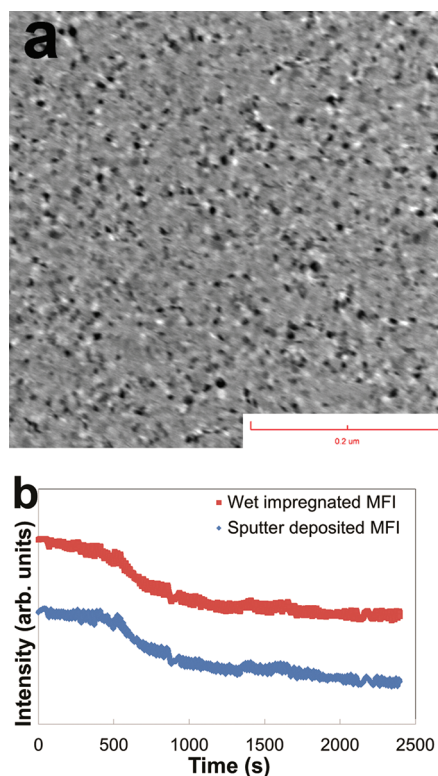


**Figure 3.** (a) Bright field TEM image of a zeolite catalyst that has had platinum sputtered on it prior to reaction with JP-8. The platinum forms discrete islands on the surface of the catalyst with an average grain size of 5.9 nm. (b) Comparison of the optical response of a platinum (Pt) sputter deposited and a wet impregnated MFI catalyst during exposure to JP-8, illustrating that the coking rates of the two samples are identical within experimental error. The $|A|$ values for the Pt promoted samples are both $0.11 \pm 0.001$, while the $|A|$ value for the pure MFI sample is $0.09 \pm 0.001$ where the error is estimated by the fit error.

comparing a platinum promoted MFI catalyst made by wet-impregnation with one prepared via sputtering. A curve comparing the dosing of the two samples is shown in Figure 3b, and illustrates that the measured coking rates are identical within the margin of error for the experiment. A combination of systematic (60 Hz) and random noise are superimposed on the data, but do not obscure the observed trends. Fits of the data reveal that both the wet impregnated and the sputter deposited Pt-modified MFI exhibit non-normalized relative coking rates of $|A| = 0.11 \pm 0.001$, while a pure unmodified MFI showed $|A| = 0.09 \pm 0.001$. Further confirmation of the effectiveness of this technique was obtained during regeneration experiments, which determined that the regeneration onset temperature for each samples was 605 K $\pm$ 3 K, which is in good agreement with the onset of carbon burnoff in temperature programmed oxidation (TPO) measurements of bulk promoted catalysts. From these measurements, it was concluded that the measurements of the reflectivity of the surface of sputtered films on pressed catalyst pellets was sufficient to determine the coking resistance and regeneration onset temperature.

A further proof of principle study was undertaken to illustrate the sensitivity of this approach to small changes in the composition of the modifier. In this portion of the study, gadolinium was alloyed with platinum via combinatorial codeposition on pressed MFI pellets. For this series a maximum concentration of 30 at % gadolinium was deposited. Gadolinium was chosen because of its ease of oxidation and the tendency of rare earth oxides to exhibit high oxygen mobility at relatively low temperatures.[35] The composition-spread samples were evaluated simultaneously with a wet-impregnated Pt-MFI pellet in the same reactor, and the coking rates of the different composition were normalized to that of the Pt-MFI sample. Normalization permits a direct comparison of the effectiveness of the alloyed modifier to improve the coking and regeneration properties of platinum.

Figure 4a shows the carbon burnoff temperature as a function of platinum content for the Pt−Gd samples. Clear differences between samples with compositional differences of ~3 at % are readily discernible and a clear trend is observed. Moreover, the regeneration temperature is shown to monotonically increase as gadolinium is added to the platinum, and appears to be approaching saturation at about 760 K. This result is counter intuitive as the gadolinium likely oxidizes during regeneration and thus could have served as a source of oxygen for oxidation of the coke at the interface with the metal.[36] A possible explanation could be that the as-deposited films result in the formation of an alloy of platinum and gadolinium, with the presence of platinum effectively blocking the oxidation of gadolinium.

The relative coking rates of the Pt−Gd composition spread are plotted in Figure 4b. Here a monotonic decrease in the coking rate is observed as gadolinium is mixed with the platinum, indicating that gadolinium could be an effective anticoking additive in combination with platinum.

On the basis of the results of the thin-film, primary screen monometallic and mixed Gd−Pt impregnated zeolite samples were prepared using normal bulk catalyst synthesis techniques. From these results, the details of which will appear in a future publication, it was confirmed that gadolinium does effectively reduce the overall coking rate both as a monometallic and as a bimetallic additive to the zeolite. Additionally, bulk temperature programmed desorption (TPO) measurements confirm that coke oxidation occurs at much higher temperatures for pure
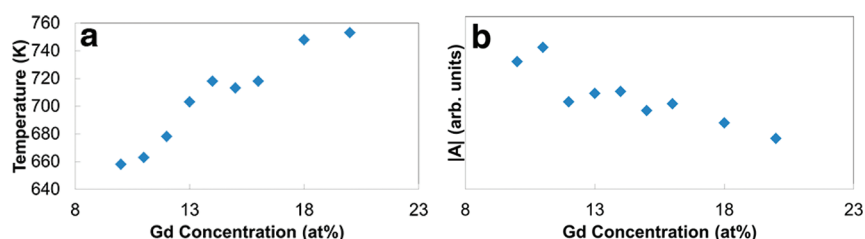
**Figure 4.** (a) Carbon burnoff temperature as a function of platinum content for the Pt−Gd samples. The regeneration temperature monotonically increases with the increasing gadolinium content. (b) The relative coking rates of the Pt−Gd composition spread. Here a monotonic decrease in the coking rate is observed with the increase of gadolinium.

gadolinium (723 K) than for pure platinum (603 K). Finally, the product distribution, although altered from pure Pt/zeolite, was still above 20 wt % in the range of LPG.

## 4. CONCLUSIONS

A thin-film high-throughput optical methodology for the rapid screening of composition-spread promoted-catalyst libraries for their anticoking properties during catalytic cracking of JP-8 was developed. This method was used to characterize the samples cycling ability and the temperature for carbon burn off. Both platinum promoted catalyst and bimetallic (Pt−Gd) catalysts were studied by using this screening technology. From this work it was found that alloying platinum with gadolinium could decrease the coking rate of the catalysts, while slightly increasing the regeneration temperature (~120 K), thus providing longer time of service in the field. These results were confirmed via traditional wet impregnation methods, further illustrating the power of this technique to discover new additives for cracking reactions. This measurement technique is insensitive to feed stocks and can be readily expanded to any anticoking modifier study including diesel and biodiesel cracking studies. It can also be useful in select redox reactions where the catalyst switches oxidation states or even switches from an oxidized to a metallic state. Although only limited data are presented here, this technique can be readily applied to the systematic screening of larger libraries with improved throughput.

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### Notes
The authors declare no competing financial interest.

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