# The Pathway to Total Isomer Selectivity: *n*-Hexane Conversion (Reforming) on Platinum Nanoparticles Supported on Aluminum Modified Mesoporous Silica (MCF-17)

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ABSTRACT: When pure mesoporous silica (MCF-17) was modified with aluminum (Al modified MCF-17), Lewis acid sites were created, but this material was inactive for the catalytic conversion (reforming) of *n*-hexane to isomers. When colloidally synthesized platinum nanoparticles were loaded onto traditional MCF-17, the catalyst showed very low activity toward isomer production. However, when Pt nanoparticles were loaded onto Al modified MCF-17, isomerization became the dominant catalytic pathway, with extremely high activity and selectivity (>90%), even at high temperatures (240−360 °C). This highly efficient catalytic chemistry was credited to the tandem effect between the acidic Al modified MCF-17 and the Pt metal.
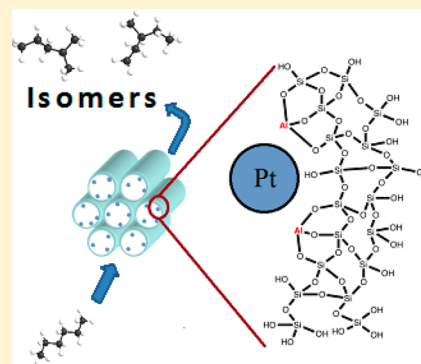
INTRODUCTION

The catalytic conversion (reforming) of linear hydrocarbons to their corresponding branched isomers is a vital reaction in the production of high octane gasoline from the naphtha feedstock of crude oil.[1] The target, like all catalytic reactions, is to optimize both the overall activity and product selectivity, simultaneously.[1−3] In naphtha reforming, branched isomers are the desired product, while cracking the hydrocarbon creates the unwanted byproducts. This chemistry is normally accomplished through the use of a platinum catalyst, alloyed with small amounts of other transition metals, and loaded onto an acidic support, such as a zeolite.[4−7] It is believed that the platinum catalyzes the dehydrogenation and hydrogenation of the hydrocarbons (promoted by the alloying of additional metals), while the isomerization occurs on the acidic support via carbocation transition species.[8,9]

The reforming of *n*-hexane provides a good model reaction in order to scientifically study the complex process of naphtha refining. Hexane can react via five major pathways: (1) cracking to shorter chain hydrocarbons; (2) isomerization to 2-methylpentane, 3-methylpentane, or multibranched isomers; (3) cyclization to methylcyclopentane or cyclohexane; (4) aromatization to benzene; (5) dehydrogenation to hexene or other unsaturated compounds. This possible reaction products for *n*-hexane reforming are displayed in Scheme 1.

In the present paper, we report on the evaluation of several catalysts in the vapor phase hydrogenation of *n*-hexane. When Al modified mesoporous silica MCF-17 loaded with Pt nanoparticles (Al modified MCF-17/Pt) was evaluated, it was found to be highly active and selective (>90%) toward isomer production, even at high temperatures. When either the Al

Scheme 1. Possible Reaction Products for *n*-Hexane Reforming
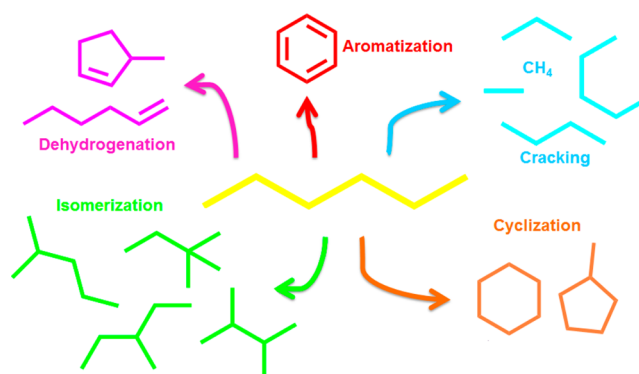
modified MCF-17 or Pt nanoparticles loaded onto unmodified MCF-17 were tested separately, it was found that both catalysts were relatively inactive. This behavior was attributed to metal−oxide interface formed between the Al modified MCF-17 and the Pt nanoparticles.

METHODS

MCF-17 type mesoporous silica was synthesized by previously reported literature methods.[10] Briefly, 1,3,5-trimethylbenzene (TMB), which was utilized as a pore swelling agent, was added to an aqueous solution of triblockcopolymer Pluoronic P123 and HCl. After stirring of this solution for 2 h at 40 °C, Tetraethylorthosilicate (TEOS) was then added and the solution was stirred for an additional

20 h. NH$_4$F was then added, and the solution was allowed to hydrothermally react at 100 °C for 24 h. The product was then calcined for 6 h at 550 °C. The pore size of the material is 30−50 nm and the surface area is ∼1000 m^2/g.

The mesopore surface of pure silica MCF-17 was aluminated through utilization of the grafting method.[11] The as-synthesized MCF-17 was calcined at 550 °C for 4 h in air to remove organic molecules. Then, the calcined sample was grafted with aluminum by slurring with anhydrous AlCl$_3$ in absolute ethanol, in order to give a Si/Al ratio of 10:1. The slurring solution was stirred overnight at room temperature, and then the ethanol was removed by rotary-evaporation. The precipitated Al-modified MCF-17 was dried at 130 °C for 1 h, and subsequently calcined at 550 °C for 4 h in air. For the introduction of acidic sites, the calcined Al-modified MCF-17 was slurred in 1 M of NH$_4$NO$_3$ aqueous solution for 4 h at room temperature.[12] The sample was then filtered, washed with distilled water, and dried at 130 °C for 1 h. This process was repeated three times and the final sample was calcined at 550 °C for 4 h in air to give H$^+$-Al-modified MCF-17.

Polyvinylpyrrolidone (PVP) capped Pt nanoparticles with an average particle size of 2.5 nm were synthesized and supported on mesoporous silica (MCF-17), Al modified MCF-17, and mesoporous zeolite (MFI) according to previously reported methods.[13] Briefly, H$_2$PtCl$_6$ precursor salt was dissolved in ethylene glycol in the presence of PVP, then was allowed to react at 470 K, until particles were formed and stable. The as-synthesized nanoparticles were then washed and redispersed in ethanol. To load the nanoparticles on the various support materials, a colloidal solution of PVP-capped Pt nanoparticles in ethanol was mixed with the desired support material to give a nominal metal loading of 0.5 wt %. The mixtures were then sonicated for 3 h, and the supported catalysts were then collected by centrifugation and washed with 20% ethanol in acetone.

After synthesis, the catalytic behavior of the materials was investigated in the reforming of *n*-hexane. Catalytic measurements were made utilizing a tubular fixed catalyst bed reactor at ambient pressure, which has been described in previous publications.[14−16] Briefly, a 1/4 in. diameter stainless steel reactor was loaded with 0.02−0.5 g catalyst (which was pelletized and sieved to yield 60−100 μm size granulates), then capped on each end with a purified thermal silica filter. The remaining space in the reactor tube was filled with purified fused aluminum granulate and capped with glass wool. To keep the catalysis in a kinetic region and allow for selectivity comparisons, the total hexane conversion was held between 1% and 5%.

After loading, the catalysts were first pretreated at 633 K under a gas mixture of N$_2$ (Praxair, 5.0 UHP, 10 sccm) and H$_2$ (Praxair, 5.0 UHP, 10 sccm) for 2 h, with a heating rate of 2 K min^{-1}. After pretreatment, the reactor system was cooled to 513 K, under the same gas flow. The gas flow was then changed to 16 sccm H$_2$, and *n*-hexane (Fluka, ≥ 99.0%) was introduced using a Teledyne ISCO 500D liquid flow pump at a rate of 1.2 mL h^{-1} into the heated reactor head which was maintained at 423 K. In the reactor head, hexane was evaporated and mixed with H$_2$, resulting in a two-component gas flow with a hexane:H$_2$ ratio of 1:5 entering the reactor at near ambient pressure. A Baratron type (890B, MKS Instruments) manometer was used to monitor the reactor inlet pressure. The reaction products were sampled in the vapor phase at the reactor outlet and analyzed via an in-line gas chromatograph (GC), with all flow lines heated to 433 K. Quantitative analysis of product composition was accomplished with a Hewlett-Packard (5890 Series II) GC which was equipped with an Aldrich HP-1 capillary column and a flame ionization detector (FID). A PC based GC Chemstation software (Hewlett-Packard) was utilized for automatic GC sampling, data collection and postrun processing. Postreaction characterization of the Al modified MCF-17/Pt catalyst using scanning transmission electron microscopy (STEM)/energy dispersive spectroscopy (EDS) was conducted using a Jeol 2100F TEM. Point-to-point spatial resolution of the electron probe was 1.5 nm.

■ RESULTS AND DISCUSSION

The overall activity of all tested catalysts is shown in Figure 1. The activity is displayed as a turnover frequency, which is based
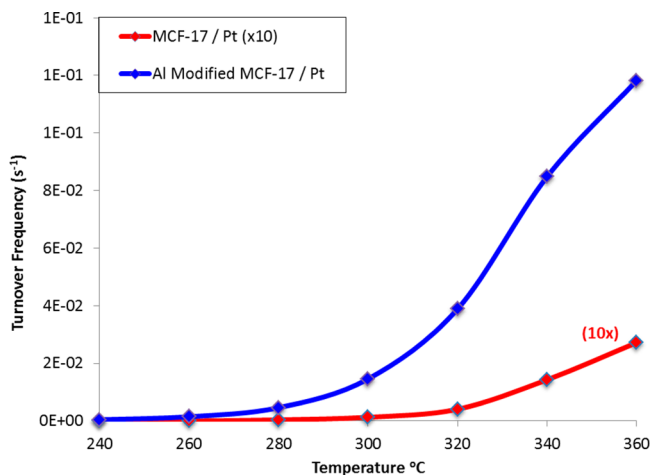

Figure 1. Overall turnover frequency (moles hexane converted mole Pt site per second) plotted against temperature for evaluated catalysts. Pt loaded on MCF-17 is shown in red for reference and is scaled by a factor of 10 to allow it to be plotted on the graph. Al modified MCF-17 is catalytically inactive, so is not plotted. Al modified MCF-17 loaded with Pt is shown in blue. The TOF for the Al modified catalyst is about 43.5× greater at the highest temperature studied (360 °C).

on the total surface area of platinum, which is calculated based on geometrical methods and TEM analysis of average nanoparticle size (2.5 nm). The reference catalyst of Pt nanoparticles loaded on mesoporous silica MCF-17 (red) displayed very low activity, and had to be scaled by a factor of 10 in order to be plotted on the same graph. The Al modified MCF-17 is not shown in the plot because it was found to be catalytically inactive at all temperatures studied. The Al modified MCF-17/Pt, which is shown in blue, displayed high activity compared to the metal free support and the unmodified MCF-17/Pt catalyst.

The overall isomer activity of the hexane reforming reaction for each catalysts is shown in Figure 2; this data is recorded at the highest temperature studied (360 °C). This data was obtained by taking the product of the overall isomer selectivity and the overall turnover frequency, in order to obtain the isomer turnover frequency (moles isomer produced per mole Pt site per second). The MCF-17/Pt catalyst (red) shows very low isomer activity (9.66×10^{-4} s^{-1}), due to the lack of acidity. The Al Modified MCF-17 (orange "x") catalyst shows no activity when Pt is not present. However, when Pt is loaded into the Al modified MCF-17 catalyst (blue), the isomer production is highly increased to 1.18×10^{-1} s^{-1}, which is about 120 times the isomer activity of the MCF-17/Pt catalyst and the Al modified MCF-17 support separately.

The specific product selectivity of the reaction is shown in Figure 3; this data is recorded at the highest temperature reactions (360 °C). The data shown is at approximately 5% total hexane conversion. Al modified MCF-17 without Pt loading showed no activity at this temperature. Isomerization is the dominant pathway on the Al modified MCF-17/Pt catalyst, with high selectivity (>90%) toward 2-methylpentane (2MP) and 3-methylpentane (3MP). The MCF-17/Pt (red) shows ∼20% selectivity toward C1−C5 cracking products, and ∼7%
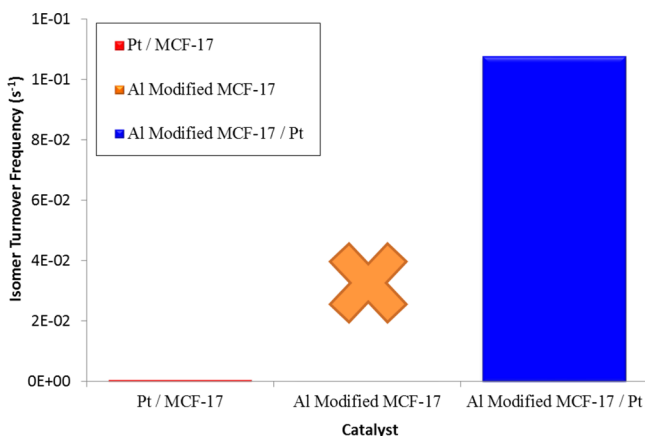
Figure 2. The product of the overall catalytic turnover and the isomer selectivity at 360 °C reaction in order to show the enhancement of adding acidity to catalysis. The MCF-17/Pt catalyst (red) shows very low activity (9.66×10^{-4} s^{-1}) without the presence of acidity. The Al Modified MCF-17 catalyst shows no activity when Pt is not present. However, when Pt is loaded into the Al modified MCF-17 catalyst (blue) the isomer production is highly increased to 1.18×10^{-1} s^{-1}, which is about 120 times the activity of the catalyst and support separately.
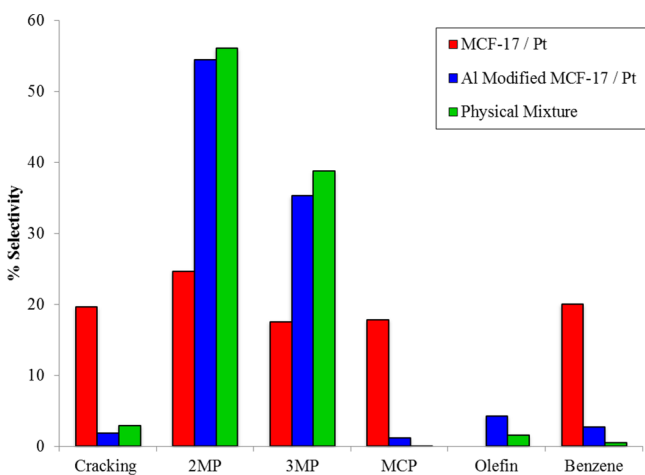

Figure 3. Product selectivity at high temperature reactions (360 °C). Al modified MCF-17 without Pt loading showed no activity at this temperature. Isomerization is the dominant pathway on the Al modified MCF-17/Pt catalyst, with high selectivity (>90%) to 2-methylpentane (2MP) and 3-methylpentane (3MP). The MCF-17/Pt (red) shows relatively higher (~20%) selectivity toward C1−C5 cracking products, and ~7% selectivity to olefins (the major product being hexene); the remaining products are isomerization products. A physical mixture of the MCF-17/Pt and the Al modified MCF-17 (green) showed nearly identical selectivity to the Al modified MCF-17/Pt catalyst, indicating a bifunctional mechanism may be present. However, the activity for the physically mixed catalyst was an order of magnitude lower, indicating that the close proximity of the Pt and acidic catalytic sites is necessary for the high isomer production in the Al Modified MCF-17/Pt catalyst. All data shown are at similar conversion.

selectivity to olefins (the major product being hexene); the remaining products are isomerization products. It can be seen that when the same support is previously modified with Al, the selectivity is altered to very little of these products, but greater than 90% selectivity toward the 2MP and 3MP isomers. It can be clearly ascertained that the selectivity is vastly superior after

Al modification and subsequent Pt loading of the MCF-17 support.

The STEM, TEM, and HR-TEM images of the postreaction Al modified MCF-17/Pt catalyst are shown in Figure 4, in parts a, b, and c, respectively. It can be seen from the STEM and TEM images that the particles are well dispersed throughout the catalyst, with little agglomeration of the metal. The representative STEM images and corresponding color-coded EDS spectral maps at Si K (green), Al K (blue), and Pt M (red) lines are shown in Figure 4d. It can be seen that the Al is well dispersed among the catalyst, and segregated Al domains do not exist on either the silica support or around the Pt nanoparticles. It is also important to note that no evidence of chlorine was observed in the EDS analysis, as residual Cl^{-} from the AlCl$_3$ used for support modification could have an effect on the Brønsted acidity of the catalyst.

The high temperature isomer selectivity of the Al modified MCF-17 catalyst is a remarkable finding, and most likely a direct effect of the interface between the oxide support and the Pt nanoparticles. Zeolites contain catalytically active micropores with both Lewis and Brønsted acid sites.[17] These acidic micropores are capable of catalyzing the *n*-hexane reaction without the use of any metal catalyst. Zeolite catalysis favors isomerization at low temperature, but at high temperature, cracking is the dominant pathway, even when Pt is loaded onto the zeolite.[18] The high temperature catalytic behavior of the Al modified MCF-17/Pt catalyst is strikingly different from the zeolite catalysts. From Figures 2 and 3, it can be seen that the Al modified MCF-17/Pt catalyst is highly selective for isomerization, at a temperature at which traditional zeolite catalysts perform predominantly cracking reactions. This favorable selectivity is attributed to the Al modified MCF-17 support providing acidity, without catalyzing the reaction by itself. It is well-known that aluminum modification of silica provides strong Lewis acid sites which are not present in normal silica.[19−21] These Lewis acid sites are known to stabilize carbocation transition state species, which in turn with the dehydrogenation/hydrogenation chemistry of the Pt metal, act to promote the production of isomers through a bifunctional mechanism on a traditional reforming catalyst.[22−26]

To determine the type of mechanism present in this system, a catalytic experiment using a physical mixture of Pt supported on unmodified MCF-17 and Pt free Al modified MCF-17 was run. If a bifunctional promotion of isomerization between the Pt nanoparticles and the Al modified MCF-17 support exists, the catalytic results should be identical to the results obtained from the Al modified MCF-17/Pt catalyst. It was found that the selectivity for this reaction is similar to that for the Al modified MCF-17 with Pt loaded (selectivity data shown in Figure 3). However, the activity of the mixed catalysts was an order of magnitude lower than that of the Al modified MCF-17 catalyst (1.08×10^{-2} s^{-1}). This could be explained by the fact that a bifunctional mechanism may be occurring; however, it appears that a majority of isomer products formed from the Al modified MCF-17/Pt catalyst require the direct contact of the Al modified support and the Pt metal. This result suggests that the primary active sites in this reaction, the Pt metal surface and the acidic Al sites, must be in a very close proximity to each other (nanometers not microns) in order to produce the high isomerization activity.

Infrared spectroscopy was utilized to investigate the amount of acid sites in the Al modified MCF-17 support, and the resulting spectrum is shown in Figure 5. When we utilize the
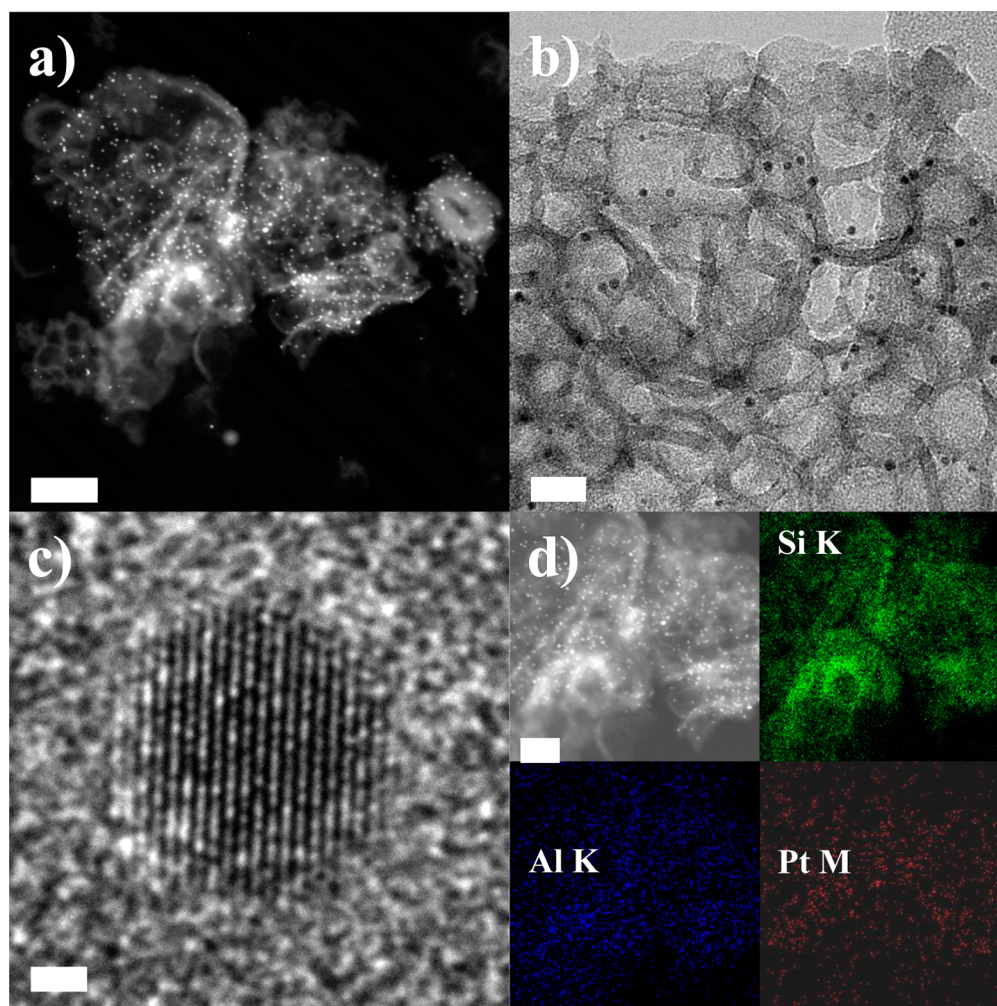
Figure 4. (a) STEM, (b) TEM, and (c) HR-TEM images of the post-reaction 2.5 nm Pt NPs supported on Al-modified MCF-17. (d) Representative STEM image and corresponding color-coded EDS spectral maps at Si K (green), Al K (blue), and Pt M (red) lines. The scale bars in the images correspond to (a) 50, (b) 20, (c) 1, and (d) 50 nm.
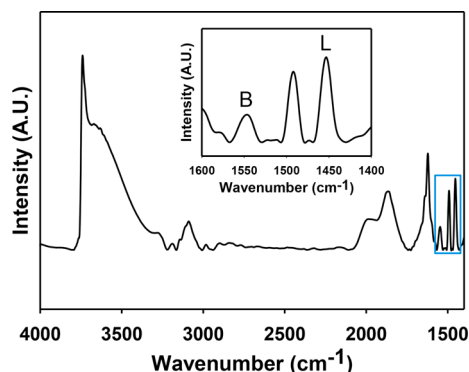

Figure 5. FT-IR spectrum of Al-modified MCF-17. Due to the large density of silanol on the mesopore wall, an intense peak is observed at 3720 cm^{-1}, which indicates a stretching band of the Si—OH bond. After pyridine adsorption, both Brønsted and Lewis acid sites are distinguishable at 1550 and 1450 cm^{-1}, respectively (see inset spectrum for magnification). When we utilize the adsorption coefficients of Brønsted and Lewis acid sites (1.13 and 1.28 cm/μmol, respectively),[23] the amount of Brønsted and Lewis acid sites can be quantified to 0.4 and 1.3 mmol/g, respectively.

adsorption coefficients for both Lewis and Brønsted acid sites (1.13 and 1.28 cm/umol, respectively),[27] it is possible to

quantify the amount of each type of acid site in the support to 0.4 and 1.3 mmol/g, respectively. To put this into relation with the amount of metal sites, the number of surface Pt atoms was calculated based on spherical TEM projected surface areas and metal loading (as determined by elemental analysis). The concentration of surface Pt atoms per gram catalyst was found to be 0.011 mmol/g, giving an acid site to metal site ratio of about 40:1 for Brønsted sites and about 120:1 for Lewis sites. It appears that when Pt nanoparticles are added to the catalytically inactive modified silica support, the Pt metal accomplishes the necessary dehydrogenation/hydrogenation reactions to the hydrocarbon, while the Lewis acidity of the support promotes isomerization through an enhanced formation of carbocation intermediates.

It was found that neither the Pt nanoparticle size nor the concentration of Al added to the mesoporous silica altered either the catalytic activity or selectivity. No changes in Pt nanoparticle stability were found between the modified and unmodified MCF-17 catalysts (based on catalytic deactivation rates and post reaction TEM images). The Al modified MCF-17/Pt catalyst also shows only a 20% deactivation after a second cycle. It is well-known that Pt dissociates molecular hydrogen, which can spill over onto the support and prevent coke formation, which is the primary reason for catalytic

deactivation in zeolites.[28,29] The catalyst studied in this work is less susceptible to this type of catalytic deactivation.

CONCLUSIONS

In summary, three model catalysts were studied for the isomerization of *n*-hexane. The catalysts were colloidally synthesized Pt nanoparticles (2.5 nm) loaded onto mesoporous silica (MCF-17), MCF-17 which had been modified with Al, and the third catalyst was Al modified MCF-17 mesoporous silica loaded with Pt nanoparticles (2.5 nm). It was found that the unmodified MCF-17/Pt catalyst was selective toward the undesired cracking products, and showed low overall activity for *n*-hexane reforming, indicating that the Pt metal alone was not a major contributor to the chemistry. The Al modified MCF-17 catalyst without Pt was found to be catalytically inactive at all studied temperatures, indicating the acidity alone could not accomplish the isomerization chemistry. However, when Pt nanoparticles were loaded onto this Al modified MCF-17 support, the catalyst was found to be remarkably active and selective for the isomerization of *n*-hexane. This remarkable selectivity was attributed to the close proximity between the acidic sites in the catalytically inactive oxide support and the Pt metal, which act in tandem to significantly promote the isomerization of the hydrocarbon.

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Notes
The authors declare no competing financial interest.

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