Promotional Effects of Mesoporous Zeolites with Pt Nanoparticle Catalysts during Reforming of Methylcyclopentane

Kyungsu Na, Nathan Musselwhite, Xiaojun Cai, Selim Alayoglu,* and Gabor A. Somorjai*

Department of Chemistry, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Selective C−C and C−H bond activations are an important catalytic process to produce various value-added hydrocarbons via reforming processes. For producing desired product with a high yield, control of reaction pathway through the design of catalyst and fundamental understanding and clarification of reaction mechanism are prerequisite. In this work, we designed heterogeneous catalysts by combining Pt nanoparticles and two different mesoporous zeolites with microporous frameworks of BEA and MFI for the hydrogenative model reforming reaction of hydrocarbon (i.e., methylcyclopentane). Depending on the catalyst combination, the reaction pathways of (i) dehydrogenation, (ii) ring-opening with isomerization, and ring-enlargement with (iii) hydrogenation and (iv) dehydrogenation of C5-cyclic ring to C6-cyclic ring (i.e., cyclohexane and benzene) can be controlled to produce various products with high yields. Furthermore, we revealed a reaction intermediate formed at the interface of Pt and zeolite by real-time surface vibrational sum-frequency generation spectroscopic studies. This study would provide practical and fundamental insights for design of heterogeneous catalyst for controlling reaction pathways.

INTRODUCTION

Enhancement of catalytic activity and control of the reaction pathway to produce a high yield of desired product with close to 100% selectivity are of paramount interest for the development of energy-saving and eco-friendly catalytic reactions.1−4 In order to simultaneously achieve high catalytic activity with 100% product selectivity, catalytic systems should be tailored delicately. Development of synthesis strategies for metal nanoparticles (NPs) with various sizes and shapes can be one of the great contributions toward a realization of this goal.1,4 Along with this, the development of various porous inorganic supports like mesoporous (2 < diameter < 50 nm) silica materials has allowed the metal NPs to be used as a practical catalyst.5−9 Such catalytic systems (i.e., metal NPs supported on porous support) have also enabled delicate and reliable investigation of catalytic function of the metal NPs according to the alteration of various parameters such as size, shape, and composition.8−11

In addition to the mesoporous silica materials, metal NPs can also be supported on zeolites.12−14 Mesoporous transition metal oxides,15−17 carbon,18,19 and polymers.20 These supporting materials are usually in porous structure having wide surface area and large pore volume. Among them, zeolites are crystalline microporous (0 < diameter < 2 nm) aluminosilicate materials that are one of the most widespread catalytic supports in current chemical industries.12−14 Zeolites also have their own catalytic activity due to the aluminosilicate framework that can be the origin of strong acidity. Therefore, supporting a few atom metal clusters within zeolite micropores can produce a bifunctional catalyst.21−24

Conventional zeolite materials are solely microporous crystals and, accordingly, possess very low molecular diffusion efficiency. Such a system can cause quick catalytic deactivation due to a formation of a carbonaceous deposit inside the micropores.25 In addition, metal NPs can only be supported inside the micropores as a form of small clusters, which limited catalytic studies.21−24 Instead, the ordered mesoporous silica materials with higher surface area and larger size of pores in mesopore regime (2 < diameter < 50 nm) can be used for studying catalytic effects of metal NPs with various sizes, shapes, and compositions on many industrially important catalytic reactions.7−11 During the recent decades, there have been numerous attempts to synthesize hierarchically nanoporous zeolites having secondary mesopores in addition to the intrinsic micropores.25−30 The resultant materials are often called mesoporous zeolites because they are constructed with nanocrystalline zeolite particles with inter- or intracrystalline mesoporosity. The presence of mesopores can improve the molecular diffusion efficiency that can enhance catalytic lifetime.25,30 In addition, bulky reactant molecules that cannot enter the micropores can be converted over the acid sites on the mesopore wall.25,30

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Scheme 1. Five Reaction Pathways of Catalytic Reforming of MCP, Indicated by Different Numbers and Colors

First, MCP can be converted into the dehydrogenated version of MCP (1, green). Second, MCP can be ring-opened and subsequently isomerized into branched isomers as well as the linear isomer (2, pink). The C5-based cyclic ring of MCP can be further enlarged to C6-cyclic rings through hydrogenation (3, blue) or dehydrogenation (4, red) of reactive intermediate species that can be proposed as cyclohexene. The last reaction pathway is cracking (5, gray) to produce C1–C5-based hydrocarbons.

In the present work, we designed heterogeneous catalysts based on the combination of Pt NPs and two different mesoporous zeolites with microporous frameworks of BEA and MFI for testing on a hydrogenative model reforming reaction of hydrocarbon (i.e., methylcyclopentane, MCP). As drawn in Scheme 1, reforming of MCP can be followed with five possible reaction pathways. First, MCP can be converted into the dehydrogenated version of MCP through reaction pathway (1, green). Second, MCP can be ring-opened and subsequently isomerized into various branched isomers as well as the linear isomer (i.e., n-hexane) through reaction pathway (2, pink). The C5-based cyclic ring of MCP can be further enlarged to C6-cyclic rings through ring-enlargement reaction pathways (black). In this reaction pathway, we are proposing that cyclohexene is a strong candidate as an intermediate state. If correct, cyclohexene can be further converted into cyclohexane via a hydrogenation pathway (3, blue) or into benzene via a dehydrogenation pathway (4, red). The last reaction pathway is cracking (5, gray) to produce C1–C5-based hydrocarbons. Among these products, cyclohexane is desired for its high octane rating among all the products, while benzene and n-hexane are unwanted for environmental concerns. In this work, these reaction pathways can be controlled by the design of heterogeneous catalysts to facilitate the formation of cyclohexane. In particular, we also studied in situ sum-frequency generation (SFG) vibrational spectroscopic studies to monitor the reaction dynamics under the real-time condition and to find an intermediate species. The present work may shed light on a fundamental understanding of the reaction mechanism and a practical idea for design of high-performance heterogeneous catalysts.

**EXPERIMENTAL SECTION**

Two mesoporous zeolites with framework types of BEA and MFI and mesoporous silica MCF-17 were synthesized by following the literature reported elsewhere.17,31,32 Poly(vinylpyrrolidone) (PVP)-capped Pt nanoparticles (NPs) with an average size of 2.5 nm were synthesized by following the literature reported elsewhere.17 The PVP-capped Pt NPs were used as the catalyst after a reductive treatment at 250 °C.

Thermal conditioning of the PVP-capped catalysts by this way gave rise to optimum activity and did not cause any measurable interference to the product distributions.8,33,34 All chemical reagents are purchased from Sigma-Aldrich and used without further purification (see Supporting Information for the details). All the prepared catalytic materials are summarized in Table S1, Supporting Information. The two mesoporous zeolites without supporting Pt NPs were simply indicated as BEA and MFI, while the Pt NPs supported versions were indicated as Pt/BEA and Pt/MFI, respectively. The pure silica MCF-17 supporting Pt NPs was indicated as Pt/SiO2. The catalytic materials prepared in this manner were characterized with X-ray diffraction (XRD), transmission electron microscope (TEM), inductively coupled plasma atomic emission spectroscopy (ICP-AES), N2 physisorption analysis, and infrared (IR) analysis.

The catalytic testing was performed using a lab-built plug-flow reactor connected to a gas chromatograph (GC) equipped with a flame ionization detector (FID). The catalytic testing was performed using a lab-built plug-flow reactor connected to a Hewlett-Packard 5890 gas chromatograph (GC). A 10% SP-2100 on 100/120 Supelco port packed column in line with a FID was used to separate and analyze the C1–C6 hydrocarbons. Mass flow controllers were carefully calibrated using a bubble flow meter and used to introduce the ultrahigh purity (99.9999% Praxair) H2 and He gases. Saturated vapor pressures of methylcyclopentane (MCP) or cyclohexene (CHE) were introduced to the reactor using a bubbler. The reactant flow was carefully calibrated at different temperatures and partial pressures of He carrier. A total flow of 40 mL/min was used. Partial pressure of reactants was calculated by using the known temperature vs saturated vapor pressure plots and was 50 Torr with 5:1 H2 excess. The 50–100 mg charges of the catalysts were diluted by quartz sand with average granular size of 0.4 mm and loaded in the reactor bed. The actual weight of catalyst used was selected to give similar total conversions in each case. The catalysts were reduced at 250 °C for 2 h under a flow of 210 Torr H2 in 550 Torr He prior to catalytic testing. The catalytic activity and selectivity were evaluated for total MCP conversions around 5%.
The SFG experiments were conducted using a mode-locked Nd:YAG dye laser (Continuum D-20) with a fundamental output at 1064 nm and a pulse width of 20 ps (see Supporting Information for the details).

**RESULTS AND DISCUSSION**

The Pt NPs with average size of 2.5 nm and two mesoporous zeolites with micropore frameworks of BEA and MFI were synthesized by following literature methods (see Supporting Information for synthesis details and materials characterizations). Then, the mesoporous zeolites were used as pure acid catalysts or as supporting materials for Pt NPs. As a reference catalyst, Pt NPs supported on mesoporous silica MCF-17 was tested for the same catalytic reaction. All the prepared catalysts and their physicochemical properties are summarized in Table S1, Supporting Information. Because of the nanocrystalline morphology, the mesoporous BEA and MFI zeolites exhibited much broader X-ray diffraction patterns than conventional zeolites in a bulk crystal (Figure S1 in Supporting Information). The mesoporous BEA zeolite was obtained as the nanocrystalline morphology, the mesoporous BEA and MFI were

![Figure 1](image1.png)

**Figure 1.** Product selectivity for various catalysts in hydrogenative MCP reforming. Selectivities to reaction pathways are indicated with different colors following those in Scheme 1. Pure mesoporous zeolites (BEA and MFI) without Pt NPs can do both dehydrogenation and ring-opening with isomerization. Among the two zeolites, MFI did dehydrogenation more dominantly (∼80%) whereas BEA did slightly more ring-opening with isomerization (∼55%). Pt NPs supported on mesoporous silica MCF-17 (Pt/SiO2) showed the highest selectivity toward ring-opened isomers (∼75%). Pt NPs supported on BEA (Pt/BEA) produced the largest amount of cyclohexane (∼60%), whereas Pt NPs supported on MFI (Pt/MFI) produced the largest amount of benzene (∼80%).

![Figure 2](image2.png)

**Figure 2.** Comparison of (A) mass activity and (B) product selectivity over MFI, Pt/SiO2, physical mixture of MFI and Pt/SiO2, and Pt/MFI. Selectivities to reaction pathways are indicated with different colors by following Scheme 1. MFI shows an activity of 0.21, while Pt/SiO2 shows 0.42. When these two catalysts are physically mixed, an activity value of 0.38 is obtained. However, when Pt NPs are supported on MFI (Pt/MFI), an activity is significantly enhanced to 2.65. In the case of product selectivity, the physically mixed catalyst exhibits average ranges of product selectivities to dehydrogenation (green) and ring-opened isomers (pink), whereas Pt/MFI can produce benzene (red) with ∼80% selectivity.

![Figure 3](image3.png)

**Figure 3.** In situ SFG spectra for (A) Pt/BEA and (B) Pt/MFI during the MCP reforming at 150 °C. For both spectra, a peak at ∼3035 cm⁻¹ indicates the existence of ≡CH3 peaks at 2850, 2905, and 2920 cm⁻¹ are CH symmetric stretch (sym), asymmetric stretch (asym), and Fermi resonance (FR) mode for CH3 functional group, respectively, and a peak at ∼3080 cm⁻¹ is the asymmetric stretch of the terminal olefin functional group (≡CH3). In panel A, the symmetric stretch of the terminal olefin functional group appeared, whereas no obvious asymmetric stretch of the ≡CH3 is shown in panel B. SFG spectrum for Pt/MFI (B) shows a peak at ∼3065 cm⁻¹, which can be assigned as the physisorbed benzene.

**Table 1. Activity and Product—Time—Yield Data**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>mass activitya</th>
<th>product—time—yieldb</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEA</td>
<td>0.32</td>
<td>0.14, 0.18, 0.08</td>
</tr>
<tr>
<td>MFI</td>
<td>0.21</td>
<td>0.17, 0.32, 0.11</td>
</tr>
<tr>
<td>Pt/SiO2</td>
<td>0.42</td>
<td>0.05, 0.11, 0.03</td>
</tr>
<tr>
<td>Pt/BEA</td>
<td>2.00</td>
<td>0.11, 1.17, 2.11</td>
</tr>
<tr>
<td>Pt/MFI</td>
<td>2.65</td>
<td>0.08, 0.31, 2.11</td>
</tr>
</tbody>
</table>

a In mol/h/g (×10³). Mass activity calculated from the molar amount of MCP consumed (mol) per given reaction time (h) and catalyst amount (g). b In mol/h/g (×10³). Product—time—yield calculated by multiplying overall activity with product selectivity in Figure 1. (1) Dehydrogenation. (2) Ring-opening with isomerization. (3) Ring-enlargement with hydrogenation. (4) Ring-enlargement with dehydrogenation.

**Table 2. Comparison of Benzene and Cyclohexane Selectivity According to the Reactant (i.e., MCP and CHE) for Pt/BEA and Pt/MFI Catalysts**

<table>
<thead>
<tr>
<th>reactant</th>
<th>BENa</th>
<th>CHAb</th>
<th>B/Cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCP</td>
<td>30.8%</td>
<td>58.6%</td>
<td>0.53</td>
</tr>
<tr>
<td>CHE</td>
<td>18.9%</td>
<td>39.4%</td>
<td>0.48</td>
</tr>
</tbody>
</table>

a BEN, benzene. b CHA, cyclohexane. c Product selectivity ratio of benzene (B) to cyclohexane (C). d CHE, cyclohexene. e Methylcyclopentane, MCP.

very small nanocrystals with an average diameter of 10 nm that are aggregated as having intercrystalline mesopores, and the
mesoporous MFI zeolite was obtained as thin nanosheet morphology (Figure S2 in Supporting Information). The average mesopore diameters are more than 10 nm, which is a sufficient size that can support Pt NPs with average diameter of 2.5 nm. Therefore, on these zeolite samples, Pt NPs were supported with good dispersion (Figure S2 in Supporting Information). The average loading of Pt NPs on the supporting materials used in this work is between 0.4 and 0.5 wt % that are analyzed by ICP-AES (Table S1 in Supporting Information).

Figure 1 shows the product selectivity trend versus the tested catalysts at 150 °C. All the catalytic studies in this work were performed at a low conversion level (∼5% conversion of MCP) where the catalytic deactivation was negligible and transient catalytic studies were possible. The results show a remarkable change in product selectivity depending on the catalyst. The two mesoporous zeolites evaluated without supporting Pt NPs could catalyze dehydrogenation (green) and ring-opening with isomerization (pink) more dominantly than any other reaction pathways. No other reaction pathways were observed. Among them, MFI catalyzed the dehydrogenation pathway (∼80%) more than ring-opening with isomerization (∼20%), whereas BEA catalyzed a little bit more ring-opening with isomerization (∼55%) than dehydrogenation (∼45%). From this result, we can confirm that the pure acidic zeolites without supporting Pt NPs could do both ring-opening with isomerization and dehydrogenation for MCP.

One possible reason for such different catalytic phenomenon between BEA and MFI zeolites is a difference in Brønsted acidic properties. The Brønsted acid sites by FT-IR (Figure S3A in Supporting Information), BEA has about three times more Brønsted acid sites (1.13 mmol/g) than MFI (0.36 mmol/g). The strength of Brønsted acid sites was also analyzed by monitoring desorption tendency of pyridine from zeolites with increasing the desorption temperature, showing a steeper decrease in BEA than in MFI (Figure S3B in Supporting Information). This means that the average strength of Brønsted acid sites on BEA is weaker than MFI. Since dissociation of C−H bond (∼98 kcal/mol) requires more energy than that of C−C bond (83–85 kcal/mol), MFI having stronger Brønsted acid sites could dehydrogenation via protolytic C−H bond dissociation more selectively than BEA.

Pt/SiO2 catalyst can demonstrate a sole role of Pt NPs on the MCP reforming because purely siliceous framework is catalytically inert. As shown in Figure 1, the Pt/SiO2 catalyst did the ring-opening with isomerization reaction pathway with the highest selectivity (∼75%) among the tested catalysts. This is already widespread knowledge due to the catalytic function of Pt NPs. However, the product selectivity was totally changed after supporting Pt NPs on the mesoporous zeolites (i.e., Pt/BEA and Pt/MFI). When Pt NPs were supported on both mesoporous zeolites, ring-enlargement reaction pathway was more preferable, by which cyclohexane and benzene were produced more selectively as compared to the other products. Since pure acidic zeolites and pure Pt NPs cannot produce benzene and cyclohexane under the same reaction conditions, such different product selectivities can be explained by synergistic catalysis between Pt NPs and acid sites on the zeolites. Between the two catalysts, Pt/BEA zeolite produced cyclohexane more exclusively with ∼60% selectivity, while the
selectivity for benzene was ~30%. In the case of Pt/MFI zeolite, benzene was produced with ~80% selectivity.

The combination of Pt NPs with mesoporous zeolites could also enhance the catalytic activity very significantly. As Table 1 summarizes (see also Figure 2A), after supporting Pt NPs on the mesoporous zeolites, the mass activity was enhanced from 0.32 to 2.00 for BEA and from 0.21 to 2.65 for MFI. Note that the mass activity was defined as the mole of MCP consumed (mol) during the reaction per given time (h) and catalyst weight (g). Since two catalytic functions from Pt NPs and acid sites on zeolites were combined together, we just compared the activity based on a catalyst mass. In addition, since the average loadings of Pt NPs on each catalyst are in a similar range (Table S1 in Supporting Information), it is highly reasonable for comparison of catalyst activity based on mass activity. Considering individual catalytic activities of Pt NPs and pure mesoporous zeolite, the degree of activity enhancement is dramatic.

We assumed that such a big enhancement of catalytic activity and different product selectivities might be originated from a close proximity between Pt and acid sites on zeolites that formed catalytic interfaces. Testing the same reaction with a physical mixture of Pt NPs and mesoporous zeolite could directly evidence the importance of close proximity between Pt NPs and acid sites. To prove this hypothesis, we mixed MFI and Pt/SiO$_2$ catalysts physically using a mortar and pestle, then tested them in the MCP reforming reaction. The activity for this physical mixture catalyst (shown in Figure 2A) was found to be 0.38, which was close to the average activity values of pure MFI catalyst and Pt/SiO$_2$. In addition, the physical mixture catalyst produced almost equal amounts of dehydrogenation and ring-opening with isomerization products (Figure 2B), which were very close to the average values of product selectivities from pure MFI and Pt/SiO$_2$. Most importantly, cyclohexane and benzene were not produced over the physical mixture catalyst. Through this reaction study, it can be concluded that the close proximity of the two catalytic functionalities of Pt NPs and zeolite acid sites is very important for the activity enhancement as well as selectivity control.

However, it was still unclear to explain the remarkable change in product selectivity. The two mesoporous zeolites supporting Pt NPs (i.e., Pt/BEA and Pt/MFI) can commonly produce C$_6$-cyclic ring products (i.e., cyclohexane and benzene) most dominantly through the ring-enlargement of the C$_5$-cyclic ring of MCP. The product selectivity toward C$_6$-cyclic ring products over both catalysts is more than 90%. We believed that a specific intermediate state must be formed, which can further be converted to C$_6$-cyclic ring products with high product selectivity. If this is correct, it is highly probable that there is a specific and reactive intermediate state. For such a bifunctional catalytic process due to the Pt NPs and acid sites on the zeolites, the rate-determining step is assumed to the skeletal rearrangement of carbenium ion with or without beta-scission on the acid sites while the Pt NPs establishes only a rapid equilibrium between paraffin and olefin. Therefore, the product distribution should be strongly influenced by the intermediate species of high reactivity. On the basis of this phenomenon, in order to detect such an intermediate species, we did reaction studies using an in situ SFG spectroscopic tool under the reaction conditions. SFG spectroscopy is a surface/interface specific nonlinear technique that can provide molecular vibrational information under reaction conditions.$^{40,41}$

Figure 3 shows the in situ SFG spectra obtained at the interface of Pt/BEA (Figure 3A) and Pt/MFI (Figure 3B) during the MCP reforming reaction at 150 °C. The appearance of a peak at ~3035 cm$^{-1}$ in both spectra demonstrates the existence of ==CH.$^{32-48}$ Broad peaks between 2850 and 2920 cm$^{-1}$ in Figure 3A can be deconvoluted into three peaks with 2850, 2905, and 2920 cm$^{-1}$, which corresponds to symmetric (sym), asymmetric (asym), and Fermi resonance (FR) of CH$_2$, respectively. These peaks are also present in Figure 3B, but only a peak corresponding to FR of CH$_2$ is significant, indicating that either the molecules with CH$_2$ are ordered or the concentration of the CH$_2$ on the surface is high, or both. Since no cracking was observed at this reaction condition, these peaks can be attributed to the C$_6$-based unsaturated hydrocarbon species such as cyclohexene or cyclohexadiene.

A peak at ~3095 cm$^{-1}$ can be assigned as an asymmetric stretch of the terminal olefin functional group (i.e., ==CH$_2$), and its symmetric stretch is shown at 2995 cm$^{-1}$ in Figure 3A, which indicates the presence of the ring-opened olefin intermediate such as 1-hexene. No obvious symmetric stretch mode for ==CH$_2$ was observed in Figure 3B. However, Pt/MFI sample shows a much broader peak at ~3065 cm$^{-1}$ that is originated from a physisorbed benzene species (Figure 3B).$^{46}$

As already evidenced above, Pt/MFI produced more benzene than Pt/BEA, which is confirmed again by SFG. There is a shoulder peak at ~2780 cm$^{-1}$, which can be assigned by the CH$_2$ stretch in unsaturated C$_6$-based cyclic intermediates.$^{47}$

According to the SFG study data, the strongest possible candidate for an intermediate species can be unsaturated hydrocarbon with C==C double bond. Considering the general catalytic functions of Pt NPs and acid sites of zeolite, we could suggest cyclohexene (CHE) as a strong candidate for an intermediate species. If this is true, CHE can be further hydrogenated to cyclohexane (reaction pathway (3)) or dehydrogenated to benzene (reaction pathway (4)) depending on the zeolite types. As the product selectivity data shows, Pt/BEA produced more cyclohexane, whereas Pt/MFI yielded much more benzene. This means that Pt/MFI did more dehydrogenation on the assumption that cyclohexene was the intermediate state. This tendency was also highly consistent with the fact that the pure MFI zeolite without supporting Pt NPs did dehydrogenation much more predominantly than BEA did (Figure 1).

For the justification of our hypothesis as well as supporting the SFG data, we tested the reaction under identical conditions with CHE instead of MCP. Figure S4, Supporting Information, shows the GC FID signal data obtained from the CHE hydrogenation over four catalysts, i.e., BEA, MFI, Pt/BEA, and Pt/MFI from bottom to top. In this signal data, the peaks of benzene and cyclohexane were highlighted with pink and blue colors, respectively. As summarized in Table 2, the selectivity ratio for benzene to cyclohexane (i.e., B/C ratio) from CHE hydrogenation over Pt/BEA was 0.48, which was a very close value to the B/C ratio from MCP reforming over the same catalyst (0.53 in Table 2). In addition, the B/C ratio from CHE reforming over Pt/MFI was 6.41, which was also similar to the value from MCP reforming (6.73 in Table 2). It is also noteworthy that CHE hydrogenation yielded >80% conversion over the Pt/zeolite catalysts due to the higher reactivity of CHE than MCP. From the comparison reaction results, it can be concluded that CHE is the strongest candidate as an intermediate state. This intermediate state with high reaction probability was formed at the catalytic interface between Pt...
NP\-s and acid sites on zeolites, which can migrate between two catalytic sites to be converted further into cyclohexane or benzene. As proved above, the distance between Pt NPs and acid sites should be sufficiently close for migration of CHE intermediate before its extinction.

From the controlled experiments with CHE and SFG studies with MCP, we proposed a reaction mechanism of MCP reforming to produce cyclohexane or benzene selectively (Scheme 2). The MCP was first dehydrogenated on the surface of Pt NPs and subsequently migrated to the acidic sites on the zeolite to produce a ring\-opened unsaturated carbocation. This short\-lived reactive intermediate species could be converted further to form cyclohexene by ring\-closure. Depending on the acidic properties of zeolite, the cyclohexene can be further hydrogenated to cyclohexane or dehydrogenated to benzene.

Effect of reaction temperature was also investigated. As the temperature increased from 150 to 250 °C, the overall activity of all the catalysts increased as expected (Figure S5, Supporting Information). However, the increasing tendency was quite different. The overall activity of Pt/SiO\(_2\) catalyst was not so significantly enhanced, whereas other zeolite\-based catalysts exhibited huge enhancement of catalytic activity. This is because the catalytic contribution of zeolite becomes much more significant than that of Pt NPs as the temperature increases. However, the dominant products were C\(_1\)−C\(_5\) cracked hydrocarbons as the reaction temperature increased due to the enhancement of cracking tendency by acidic sites on zeolites.

## CONCLUSIONS

In conclusion, we discovered highly active and selective, toward the ring\-enlargement of MCP molecule, catalytic interfaces formed when colloidal Pt NPs were supported on mesoporous zeolites of BEA- and MFI\-type. We also identified CHE molecule as a reactive intermediate within the time scale of reaction turnovers and as playing an important role for the control of reaction pathways. This CHE was converted to cyclohexene and/or benzene depending on the specific zeolite type. Furthermore, the CHE reaction intermediate formed at the interface of Pt and zeolite was also revealed by real\-time SFG spectroscopic study. In a practical point of view, the present work would provide how to control the reaction pathway via the rational design of heterogeneous catalyst based on mesoporous zeolites. In the case of scientific viewpoint, fundamental understanding of a catalytic reaction with clarification of the intermediate state would be given for selective C−C and C−H bond activations and their subsequent reassembly. Further works on the effects of acidic properties, size, and composition of metal NPs on MCP reforming and also SFG studies on Pt/BEA and Pt/MFI are underway.

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The authors declare no competing financial interest.


Supporting Information

Promotional Effects of Mesoporous Zeolites with Pt Nanoparticle Catalysts during Reforming of Methylcyclopentane

Kyungsu Na, Nathan Musselwhite, Xiaojun Cai, Selim Alayoglu* and Gabor A. Somorjai*

Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Synthesis of catalytic materials

Two mesoporous zeolites with framework types of BEA and MFI, and mesoporous silica MCF-17 were synthesized by following the literatures reported elsewhere.[1-3] All chemical reagents are purchased from Sigma-Aldrich and used without further purification.

For mesoporous BEA zeolite, a cyclic diammonium-type organic molecule was used as the zeolite structure-directing agent (SDA), which was prepared by organic reaction following the literature.[1] In a typical zeolite synthesis, sodium-silicate was used as the silica source and Al₂(SO₄)₃·18H₂O was used as the alumina source. The silica and the alumina sources were dissolved in water with NaOH and organic SDA to give molar composition of 30Na₂O / 5Al₂O₃ / 100SiO₂ / 10SDA / 15H₂SO₄ / 6000H₂O. After aging for 1 h at room temperature, the mixture was transferred to a Teflon-coated stainless-steel autoclave and heated at 170°C for 1 d in an oil bath on the magnetic stirrer equipped with heating system.

For mesoporous MFI zeolite, a diquaterrainary ammonium-containing organic surfactant was used as the zeolite SDA, which was prepared by organic reaction following the literature.[2] In a typical zeolite synthesis, sodium-silicate, Al₂(SO₄)₃·18H₂O, NaOH, SDA, H₂SO₄ and distilled water were mixed to obtain a gel composition of 30Na₂O / 1Al₂O₃ / 100SiO₂ / 10SDA / 24H₂SO₄ / 4000H₂O. The gel mixture was immediately shaken by hand very vigorously for 5 min to obtain as homogeneous a gel as possible. After further aging for 6 h under magnetic stirring in an oven at 60°C, the gel was hydrothermally treated at 150°C for 4 d in an oil bath on the magnetic stirrer equipped with heating system.

MCF-17 type mesoporous silica was synthesized by previously reported literature methods.[3] 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. NH₄F 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 resultant zeolite precipitates and the mesoporous silica MCF-17 obtained after designated hydrothermal treatment times were collected by filtration, washed with distilled water, dried at 130°C, and calcined at 550°C for 4 h in air to remove organic species. Among the resultant materials, two mesoporous zeolites were further ion-exchanged to H⁺-form to introduce acidic function on the aluminosilicate
framework. In a typical ion-exchange process, the calcined zeolite samples were first ion-exchanged to NH$_4^+$-form with a 1 M NH$_4$NO$_3$ aqueous solution three separate times (NH$_4$NO$_3$/Al = 10), and then, subsequently converted to the H$^+$ form through calcination in air at 550°C for 4 h.

Poly(vinylpyrrolidone) (PVP)-capped Pt nanoparticles (NPs) with an average size of 2.5 nm were synthesized by following the literature reported elsewhere.[4] In a typical synthesis, H$_2$PtCl$_6$ was used as Pt precursor, which was dissolved in ethylene glycol in the presence of PVP. This solution was reacted at boiling solvent temperatures, and the as-synthesized PVP-capped Pt NPs were washed and re-dispersed in ethanol to give colloidal solution of Pt NPs with the concentration of 1 mg/mL. For supporting Pt NPs on porous supports, this colloidal solution of Pt NPs was added to the supporting materials to give desired loading of Pt (0.3 ~ 0.5 wt%). The colloidal suspension was sonicated for 5 h at room temperature using a commercial ultrasonic cleaner (Branson, 1510R-MT, 70W, 42 kHz). The brown precipitates were separated by centrifugation (4000 rpm, 10 min), washed with ethanol for four times, and dried in an oven at 60°C overnight.

All the prepared catalytic materials are summarized in Table S1. The two mesoporous zeolites without supporting Pt NPs were simply indicated as BEA and MFI, while the Pt NPs supported versions were indicated as Pt/BEA and Pt/MFI, respectively. The pure silica MCF-17 supporting Pt NPs was indicated as Pt/SiO2.

**Characterization**

X-ray diffraction (XRD) patterns were taken with a Bruker D8 Venture diffractometer equipped with Cu tube operated at 40 W (40 kV, 1 mA). Transmission electron microscope (TEM) images were taken with a Hitachi H-7650 TEM operated at 120 kV. Elemental analyses by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using a PerkinElmer optical emission spectrometer (Optima 7000 DV). N$_2$ physisorption analysis for determination of surface area and mesopore size was carried out using Micromeritics ASAP2020 volumetric analyzer at the liquid nitrogen temperature (77 K). The surface area was calculated by Brunauer-Emmet-Teller (BET) equation from the adsorption data obtained at P/P0 values between 0.05 and 0.2. The average mesopore size was determined from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm.

For IR measurement of mesoporous BEA and MFI zeolites, the H$^+$-form of zeolite samples were pressed to produce self-supporting wafers (ca. 12 mg/cm$^2$) without binding agents.[5] The samples were subsequently degassed at 500°C for 2 h in a lab-made in-situ IR cell. After cooling down to room temperature, a organic base, pyridine was used as a probe molecule, and pyridine was adsorbed on the acidic sites of degassed samples at room temperature for 1 h. The physisorbed and weakly bound species were then desorbed for 1 h under vacuum at 150°C. After cooling down to room temperature, IR spectra were collected using an FT-IR spectrometer (Nicolex Nexus-670) equipped with Mercury-Cadmium-Telluride (MCT) detector at room temperature with 80 scans and 2 cm$^{-1}$ resolution for each spectrum. The concentration of Brønsted acid site was determined using a molar extinction coefficient (5.98 cm/mmol) of pyridine IR band at the wavenumber of 1550 cm$^{-1}$.[6] The strength of Brønsted acid site in BEA and MFI zeolites was analyzed by monitoring the desorption tendency of pyridine molecule according to the increase of desorption temperature from 150 to 350°C with an interval of 50°C. For this experiment, the
zeolite sample after the adsorption of pyridine was heated to the desired desorption temperature and maintained for 1 h. Then, the IR spectra were collected to quantify the amount of Brønsted acid sites. The desorption tendency was graphitized versus the desorption temperature.

Catalytic reaction studies
The catalytic testing was performed using lab-built plug-flow reactor connected to a Hewlett Packard 5890 gas chromatograph (GC). A 10% SP-2100 on 100/120 Supelco port packed column in line with a FID detector was used to separate and analyze the C1 – C6 hydrocarbons. Mass flow controllers were carefully calibrated using a bubble flow meter and used to introduce the ultra-high purity (99.9999 % Praxair) H₂ and He gases. Saturated vapor pressures of methylcyclopentane (MCP) or cyclohexene (CHE) were introduced to the reactor using a bubbler. The reactant flow was carefully calibrated at different temperatures and partial pressures of He carrier. A total flow of 40 ml/min was used. Partial pressure of reactants was calculated by using the known temperature vs. saturated vapor pressure plots and was 50 Torr with 5:1 H₂ excess. 50-100 mg charges of the catalysts were diluted by quartz sand with average granular size of 0.4 mm and loaded in the reactor bed. The actual weight of catalyst used was selected to give similar total conversions in each case. The catalysts were reduced at 250°C for 2 h under a flow of 210 Torr H₂ in 550 Torr He prior to catalytic testing. The catalytic activity and selectivity were evaluated for total MCP conversions around 5%.

Sum Frequency Generation (SFG) spectroscopic studies
SFG experiments were conducted using a mode-locked Nd:YAG dye laser (Continuum D-20) with a fundamental output at 1064 nm and a pulse width of 20 ps. The repetition rate is 20 Hz. A frequency doubling crystal was used to generate the 532 nm beam, the visible beam. The tunable IR beam was generated using a homemade optical parametric generator (OPG) and optical parametric amplifier (OPA). A copropagating reflection geometry was used for the SFG setup with incident angles of 63° and 48° with respect to the surface normal for the visible beam and IR beam, respectively. The visible beam and IR beam overlaps both spatially and temporarily on the sample surface and generates the SF signal. SF photons were detected by a photomultiplier tube (Hamamatsu, R928) with a SRS Gated Integrator & Boxcar Averager and a SR 245 Computer Interface (Stanford Research System). Total internal reflection (TIR) geometry with an equilateral (60°) fused silica prism was adopted. The exponential decay of the evanescence wave, which breaks the symmetry of the nanoparticles, allows the detection of molecules on the symmetric nanoparticle surfaces. The near critical angle incidence of the IR beam significantly enhances the SF signal. All the SFG experiments were performed in ppp polarization combination.

The intensity of the SF signal is given by the following equation,

\[ I_{SF} = \left| \chi_{NR}^{(2)} + \chi_{R}^{(2)} \right|^2 I_{IR}I_{VIS} = \left| \chi_{NR}^{(2)} + \sum \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \right|^2 \]

Where \( I_{SF} \) represents the intensity of the SF signal, \( \chi_{NR}^{(2)} \) is nonresonant second order susceptibility, \( \chi_{R}^{(2)} \) is resonant second order susceptibility, \( I_{IR} \) and \( I_{VIS} \) stand for
the intensity of IR beam and visible beam, respectively. \( A_q \), \( \omega_{\text{IR}} \), \( \omega_q \), and \( \Gamma_q \) are the amplitude, the scanning IR frequency, the \( q \)-th resonant vibrational frequency of the adsorbates, and the line width, respectively.

**References**

Figure S1. X-ray diffraction (XRD) data of mesoporous BEA (A) and MFI (B) zeolites. In comparison, conventional zeolite counterparts are also added with blue colors. The mesoporous zeolites exhibited much broader XRD patterns (pink) than conventional zeolite due to the nanocrystalline morphologies.

Figure S2. Transmission electron microscope images of mesoporous BEA and MFI zeolites (top row) and Pt NPs supported BEA and MFI (bottom row).
Figure S3. FT-IR spectra of mesoporous BEA (red) and MFI (blue) zeolites obtained after the adsorption of pyridine molecule and subsequent desorption of physisorbed pyridine at 150°C (A), and amount of Brønsted acid site as a function of desorption temperature between 150 and 350°C (B). B and L in the IR spectra indicate the Brønsted and Lewis acid sites, respectively. The IR spectra in (A) are normalized with the band between 2100 and 1750 cm⁻¹, which is originated from Si-O-Si stretching band.
Figure S5. GC FID signal data of cyclohexene reforming over BEA, MFI, Pt/BEA and Pt/MFI from bottom to top. The highlight region in red and blue indicate peaks from benzene and cyclohexane, respectively.

Figure S6. Activity increase phenomenon of catalysts versus the reaction temperature of 150, 200 and 250°C.
Table S1. Physicochemical properties of catalysts tested in this work.

<table>
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<tr>
<th>Catalyst</th>
<th>Si/Al ratio</th>
<th>Pt loading (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Mesopore size (nm)</th>
<th>Brønsted acidity (mmol/g)</th>
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