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Isomerization of *n*-Hexane Catalyzed by Supported Monodisperse PtRh Bimetallic Nanoparticles

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Abstract Composition and size of Pt_xRh_{1-x} bimetallic nanoparticles were varied in order to study the effects in the catalytic reforming of *n*-hexane. Hexane isomerization, an analogue to the important industrial process of hydrocarbon reforming is a reaction in which we aim to investigate the molecular level details of catalysis. It is known, that in hydrocarbon isomerization, Pt atoms act to isomerize the reactants, while small amounts of "promoter metal" atoms (such as Rh, Ir, Re and Sn) provide C–C and C–H bond breaking activity. Herein, we report on the effect of composition and size in model bimetallic Pt_xRh_{1-x} nanoparticle catalysts utilized in *n*-hexane reforming. Both nanoparticle composition and size were shown to influence catalytic turnover frequency and product selectivity. It was found, through ambient pressure X-ray photoelectron spectroscopy, that the surface of these nanoparticles is both dynamic, and Rh rich under relevant reaction conditions. The findings suggest that an ensemble effect exists, in which the highest isomer production occurs when Rh atoms are surrounded by Pt atoms on the metal surface.

Keywords Reforming · Heterogeneous catalysis · Hexane isomerization · PtRh bimetallic · Ensemble effect · Size effect

1 Introduction

The catalytic reforming of *n*-hexane, a model reaction for naptha reforming, is an industrially important multi-product reaction. The goal of studying this reaction, along with any heterogeneous catalysis reaction is to simultaneously optimize catalytic activity and selectivity [1–3]. Hydrocarbon reforming is normally accomplished through the use of a platinum catalyst, alloyed with small amounts of other "promoter" metals and supported on an acidic support [4]. The promoter metals in this catalyst, which are typically middle transition metals with high C–C bond breaking activity, act to increase the overall activity of the reaction. Through the use of colloidal synthesis, monodisperse, composition controlled nanoparticles can be synthesized, characterized, and evaluated catalytically at industrially relevant conditions, which can help elucidate the important molecular level information of this reaction.

2 Experimental

Platinum nanoparticles alloyed with rhodium were synthesized in various metal compositions through colloidal techniques. Briefly, $H_2PtCl_6 \cdot 6H_2O$ (Sigma-Adrich, 37.50 % Pt basis), $Pt(acac)_2$ (Aldrich, 97 %), and $Rh(acac)_3$ (Aldrich, 97 %) were used as metal sources in 6.5 nm particle synthesis. The ratio of Pt to Rh metals was varied, but the overall metal amount was kept at a constant 1.0×10^{-4} mol. The mole ratio of $H_2PtCl_6 \cdot 6H_2O$ to $Pt(acac)_2$ was also kept at a

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constant 4:1 for 6.5 nm. In a typical synthesis the metal salts were added to a round bottom flask, triethylene glycol (10 mL) and polyvinylpyrrolidone (28 mg, 55,000 g/mol) were added, and the solution was sonicated for 30 min to ensure dissolving of the solids. The flask was then placed under vacuum for 20 min and then repeatedly purged with argon and vacuum pumped before finally being filled with argon, to ensure an oxygen free environment. The flask was then placed in a molten salt bath held at a constant 503 K for 1 h. During this time the solution changed to dark black in color as nanoparticles were formed. Smaller sized bimetallic nanoparticles were synthesized by addition of $NaNO_3$ (7×10^{-5} mol) to a solution containing triethylene glycol, PVP and $Pt(acac)_2$ and $Rh(acac)_3$ (1.0×10^{-4} mol total metal) and following a similar reduction procedure as reported above. After synthesis, the nanoparticles were precipitated from solution by addition of acetone and subsequent centrifugation (550×9.8 m/s^2, 20 min). Nanoparticles were then supported on MCF-17 type mesoporous silica, which was synthesized by previously reported methods [5].

Catalytic measurements were made utilizing a tubular fixed catalyst bed reactor at ambient pressure. A 1/4″ diameter stainless steel reactor was mounted vertically, which allowed for a downflow operation. A 0.5 g sample of catalyst was loaded, which corresponded to a 10–12 cm bed height. The catalyst was placed in the center of the reactor tube, capped on each end with purified thermal silica filter. The remaining space in the reactor tube was filled with purified fused aluminum granulate and capped with glass wool. Prior to loading, the catalyst was pelletized and sieved to obtain 60–100 μm size granulates. To avoid misinterpretation linked with mass and heat transfers, we kept the catalyst in a kinetic region by holding the total hexane conversion below 10 %.

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. The heating rate of the pretreatment was limited to 2 K min^{-1}. After the 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, $\geq$99.0 %) was introduced using a Teledyne ISCO 500D liquid flow pump at a rate of 1.2 mL h^{-1} into the preheating reactor head which was maintained at 423 K. In the preheating zone, hexane 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). All flow lines were heated to 433 K. Quantitative analysis of flow 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 post-run processing.

3 Results and Discussion

Nanoparticles were characterized using a Jeol JEM-2100F scanning transmission electron microscope (STEM) equipped with an INCA electron dispersive spectrometer (EDS) was used in scanning mode to obtain information about the size and composition of the particles. Briefly, Pt and Rh L lines were simultaneously probed by EDS using a point-to-point e-beam size of 1.5 nm, and then overlapped on the respective high angle annular dark field (HAADF) image. STEM–EDS images are shown in Fig. 1. The larger sized bimetallic particles were found to be 6.4 ± 0.5 nm with Pt/Rh atom compositions of 80/20 and 93/7. Smaller sized $Pt_{80}Rh_{20}$ were also characterized and found to have an atom composition of 80/20 Pt/Rh and a size distribution of 2.5 ± 0.3 nm. No stray monometallic nanoparticles were observed. Nanoparticles were also characterized utilizing synchrotron based ambient pressure X-ray photoelectron spectroscopy (AP-XPS), as a means to ascertain the surface composition of the nanocatalysts under relevant reaction conditions [6]. AP-XPS samples were prepared by deposition of the particles onto a silica wafer by Langmuir–Blodgett techniques. The wafer was then loaded into the instrument for characterization. The particle surface composition was determined by investigating the Pt 4f and the Rh 3d spectra, utilizing both 380 and 650 eV excitation energies, respectively, both with probing depths of 0.8 nm. The partial pressures of the system was 100 mTorr of H_2 and 20 mTorr of hexane for the experiments. The characterization data for the nanoparticles is summarized in Table 1.

By integration of the AP-XPS spectral data, it was possible to determine the near surface composition of the bimetallic nanoparticles. The percentage of platinum atoms is plotted in Fig. 2a as a function of reaction conditions. Notably, the near surface ratio was found to always be rich in rhodium with respect to the bulk nanoparticles. Also, it was determined that the surface composition is dynamic and varies under different conditions. It was also found that nanoparticle size had little influence on the surface composition of nanoparticles, as shown in Fig. 2b, c. The final important conclusion is that under reaction conditions (5:1 H_2:hex 360 °C) the near surface was found to have an

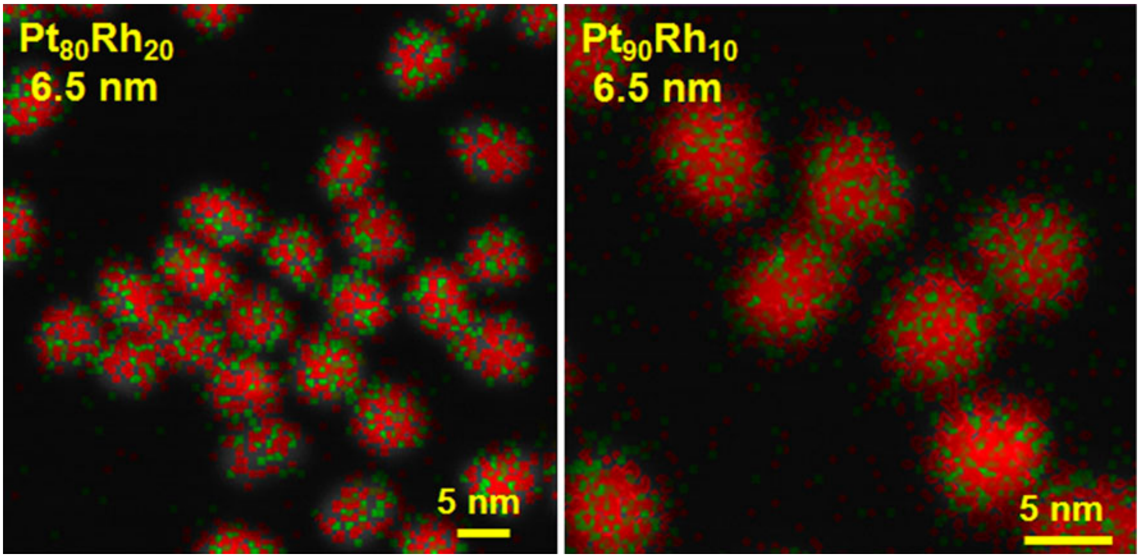

Fig. 1 Scanning transmission electron microscopy/electron-dispersive spectrometry (STEM–EDS) images of bimetallic nanoparticles. The *red points* represent the Pt L-line and the *green points* represent Rh L-line

Table 1 Characterization data of Pt_xRh_{1-x} nanoparticles

Nanoparticle (size in nm)	Pt/Rh bulk ratio[a]	Pt/Rh surface ratio[b]	Cracking selectivity (%)	Isomer selectivity (%)	Aromatic selectivity (%)	Overall TOF	Isomer TOF
Rh (6.5)	0/100	0/100	90	5	5	0.034	0.0018
Pt (6.5)	100/0	100/0	15	78	7	0.0064	0.0050
$Pt_{80}Rh_{20}$ (6.5)	80/20	70/30	48	44	8	0.013	0.0059
$Pt_{90}Rh_{10}$ (6.5)	93/7	80/20	36	55	9	0.012	0.0065
$Pt_{80}Rh_{20}$ (2.5)	80/20	70/30	57	34	8	0.019	0.0065

[a] Ratio evaluated from EDS analysis

[b] Ratio obtained in in situ condition using AP-XPS

excess of rhodium. This result was also found with the $Pt_{90}Rh_{10}$ nanoparticles.

These nanoparticles, once supported on MCF-17, were then utilized in the hydrogenative reforming of *n*-hexane. The reforming of *n*-hexane is a model reaction for the catalytic reforming of naphtha feedstock, an important reaction in oil refining. The scheme for this reaction is shown in Fig. 3. The desired pathways in this reaction are towards isomerization and cyclization products, while the cracking and aromatization product pathways are undesired.

The total *n*-hexane turnover frequency (TOF) of all tested catalysts is shown in Fig. S1. It can be seen that the monometallic rhodium catalyst had the highest activity in hexane reforming (0.034 s^{-1}), and the monometallic platinum nanoparticles had the lowest of the evaluated catalysts (0.0060 s^{-1}). The bimetallic catalysts appear to be approximately linear with respect to the monometallic particles, with the $Pt_{80}Rh_{20}$ having an overall TOF of 0.013 s^{-1} and the $Pt_{90}Rh_{10}$ having an overall TOF of 0.011 s^{-1}. The selectivity of the catalysts is shown in Fig. S2. It can be seen that monometallic rhodium nanoparticles show very low selectivity for the desired isomer products. Monometallic Pt nanoparticles were found to be about 78 % selective for desired products (cyclics and isomers). This result demonstrates that Rh, which forms a stronger metal carbon bond and subsequently has a higher C–C bond breaking ability than Pt, prefers to follow a cracking pathway, whereas Pt allows for the isomerization of hexane. The bimetallic $Pt_{80}Rh_{20}$ and $Pt_{90}Rh_{10}$ nanoparticles were found to be about 44 and 55 % selective to desired products, respectively.

By taking the product of the overall TOF and the percent selectivity of the desired isomer products it is possible to determine the turnover frequency for the isomers, or the overall production of desired products. This data is shown in Fig. 4, plotted against the AP-XPS determined near surface composition of the different catalysts. Shown in Fig. S3 is a similar plot for the TOF of the cracking product. It can be seen from the isomer plot that the TOF of desired products exhibits a volcano type behavior in which

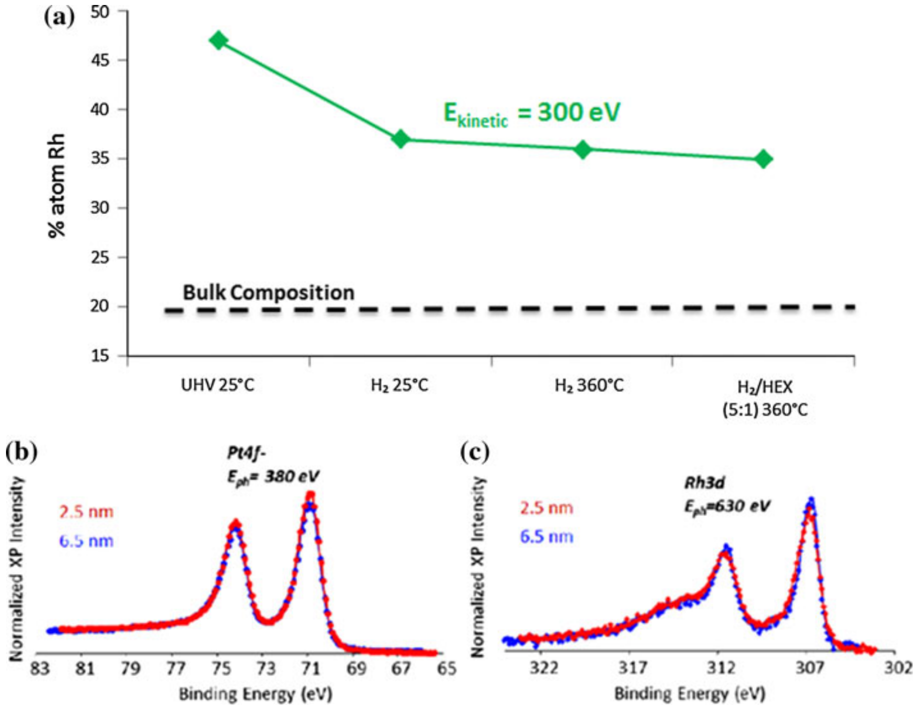

Fig. 2 **a** Composition of near surface atoms in bimetallic 6.5 nm $Pt_{80}Rh_{20}$ nanoparticles. The *green line* represents the near surface composition of the nanoparticles as obtained via integration and normalization of the 380 and 630 eV AP-XPS spectra. The *dashed line* represents the bulk composition of the nanoparticles. **b** The Pt 4f and **c** Rh 3d spectra (380 and 630 eV, respectively) shown for the 2.5 nm $Pt_{80}Rh_{20}$ nanoparticles in *red* and the 6.5 nm $Pt_{80}Rh_{20}$ in *blue*. The spectra show there is no difference in surface composition between the two different sized particles

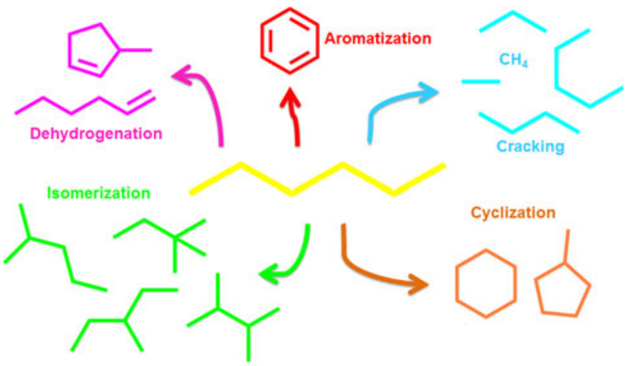

Fig. 3 Reaction scheme for *n*-hexane reforming. Desired products are isomerization and cyclization products shown in *green* and *orange*, respectively. Undesired products are cracking and aromatization products, shown in *blue* and *red*, respectively

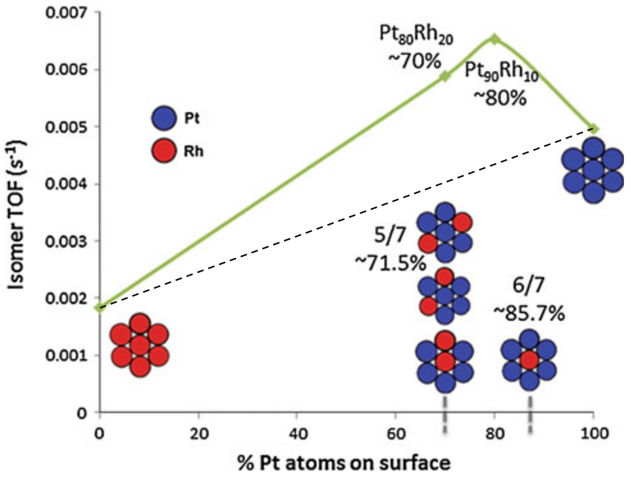

Fig. 4 Isomer TOF plotted against the near surface composition of the 6.5 nm NPs using AP-XPS. The maximum rate occurs on the bimetallic nanoparticles, where the surface ratio is 80:20 Pt:Rh. The *dotted line* represents what would be expected if a linear relationship existed with atomic composition. The actual data exhibits about a 60 % increase in isomer TOF. This type of behavior can be attributed to an ensemble effect between the surface Pt and Rh atoms. The images shown are models for 111 fcc crystal faces

the maximum occurs not on the monometallic nanoparticles, but on the $Pt_{90}Rh_{10}$ bimetallic catalyst. By utilizing the AP-XPS measured near surface compositions for these particles, the ratio of Pt to Rh atoms in an ideal FCC (111) face is 1:5, which corresponds to one Rh atom surrounded by five Pt atoms. Which means the maximum isomer production occurs when one Rh atom is encircled by Pt atoms.

This type of behavior can be attributed to the ensemble effect, a well-known phenomenon in surface science. In the ensemble effect a different catalytic turnover can occur due to the surface ensemble of bimetallic catalysts. This effect has previously been shown to be present in *n*-hexane reforming catalyzed by Pt–Au alloys [7, 8]. It has found that when catalytically inert Au is diluted on a Pt (111) single crystal it acts to block high coordination threefold sites. This acts to decrease aromatization chemistry, thus promoting isomerization. In this work the Pt surface is diluted with a more active Rh atom, this Rh atom acts to promote C–H bond activation, and when surrounded by Pt atoms allows for higher isomer formation.

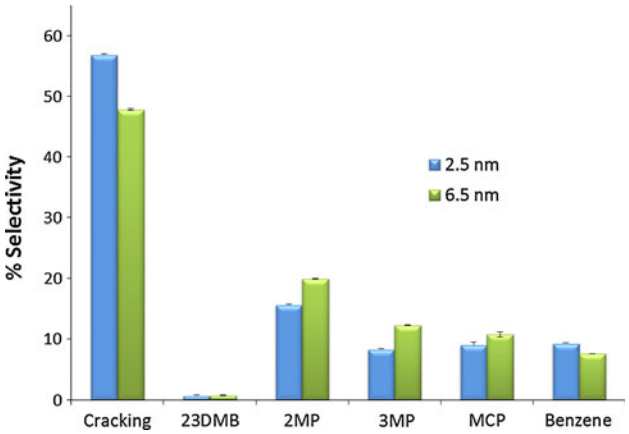

Fig. 5 Impact of size on the selectivity of *n*-hexane hydrogenation for $Pt_{80}Rh_{20}$ catalysts: smaller sizes show more selective towards the cracking product, while larger sized nanoparticles produce more isomers (*23DMB* 2,3-dimethylbutane, *2MP* 2-methylpentane, *3MP* 3-methylpentane, *MCP* methylcyclopentane)

The size effect of the particles is shown in Fig. 5. It can be seen that on the 2.5 nm $Pt_{80}Rh_{20}$ particles the cracking and aromatization products increased at the expense of the desired isomer products. It should also be noted the activity of the smaller sized catalysts is higher than the larger catalysts. It was found, via APXPS, that the surface compositions of these two catalysts is similar (around 70/30 Pt/Rh), so therefore the differences in selectivity and activity are purely due to particle size and the corresponding position of surface atoms, i.e. corner, terrace, and edge sites. It may be possible that Rh atoms preferentially occupy corner and edge sites, which would have high catalytic activity, while Pt rich terraces would have intrinsically lower activity. In the smaller sized particles the ratio of corner and edge sites is much higher, so therefore it would follow that the cracking activity would be higher in these particles.

In summary, on monometallic surfaces, Rh acts to activate the hexane, but then cracks the molecule with high TOF. On monometallic Pt surfaces, selectivity toward desired products is much higher, but activity is very low due to the inability of Pt to activate the C–H bond as well as Rh. However, when Rh is diluted on a surface of Pt, the Rh acts to activate the C–H bond, and the surrounding Pt atoms allow for the formation of desired isomer products. The bimetallic nanoparticles were shown to be rhodium rich under reaction conditions, with the optimum surface composition for isomer production occurring on the $Pt_{90}Rh_{10}$ nanoparticles (93/7 Pt/Rh surface composition). The size of the bimetallic nanoparticles was shown to effect product selectivity by increasing isomer production at the expense of cracking on larger sized particles.

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