The controlled synthesis of metal-acid bifunctional catalysts: The effect of metal:acid ratio and metal-acid proximity in Pt silica-alumina catalysts for n-heptane isomerization

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Abstract

Several series of metal-acid bifunctional catalysts with controlled metal:acid ratios and metal site-acid site proximity were evaluated for n-heptane isomerization. Through the study of metal deposition reported in the companion paper, proximity could be achieved at four distinct scales; atomic, nano-, micro-, and millimeter scales. In the first two catalyst series, atomic and nanometer scale intimacy was obtained by depositing Pt onto acidic silica-alumina supports (Pt/Al-Si). It is demonstrated that poorly dispersed Pt/silica-alumina catalysts with nanometer-scale proximity displayed a greater degree of bifunctionality than highly dispersed catalysts with atomic-scale proximity. In the latter two series of catalysts the scale of intimacy was stretched to micrometers using physical mixtures, and to millimeters by separating layers of nonacidic Pt/silica and metal free silica-alumina. Good bifunctionality is maintained at micrometer-scale intimacy and breaks down only at the millimeter scale. The best bifunctionality is achieved at very high acid to metal site ratios; results indicated that a single metal site can supply several hundred acid sites.

Optimized bifunctional performance of Pt/silica-alumina catalysts for n-heptane isomerization requires a high acid-to-metal site ratio with nanometer to micrometer scale site proximity. The control of the numbers and proximities of metal and acid sites achieved in this work can be extended to many other metal-acid bifunctional reactions.

Keywords

Bifunctional catalysis, Platinum, silica-alumina, metal-acid ratio, metal-acid proximity, Isomerization

1 Introduction

Metal-acid bifunctional catalysts have become part and parcel of many industrially significant chemical processes for energy, environment and consumer based applications. Already established processes include, but are not limited to, selective ring opening (increase of cetane number), hydroisomerization (increase of octane number), hydrocracking of heavy oils, reforming and dewaxing [1-6]. More recently, studies on the utility of bifunctional catalysts on biomass conversion have been on the rise [7-10]. Metal-acid bifunctional catalysts have also opened interesting avenues to one step synthesis of fine chemicals and liquid fuels from syngas and biomass [7, 11, 12].

Depending on the application, controlled acidity in terms of strength and number can also be a vital parameter for optimum bifunctional performance. For example, to obtain hydrocracking products more in the middle distillate range, moderate acidity of amorphous silica-alumina is more beneficial than highly acidic zeolites [13]. Micropores in typical zeolite materials inhibits efficient molecular transport, which may result in catalyst deactivation and poor performance [14]. Weitkamp in his review paper discussed the features and importance of an “ideal” hydroconversion catalyst [15]. Constructed on a strong hydrogenating/dehydrogenating function, an “ideal” bifunctional catalyst offers flexibility in hydrocarbon conversion. On a strongly acidic monofunctional catalyst, however, distribution of products is mostly obtained in the low carbon number range due to preference for cracking which reduces the overall quality of the fuel. Introduction of metal sites could limit such cracking reactions [16]. This suggests that the balance between metal and acid function could be of great importance in bifunctional catalysis.

According to the classical mechanism of bifunctionality, proposed over 50 years ago, a close proximity between metal and acid sites was prescribed to facilitate the diffusion of reaction intermediates between the two types of sites [17]. According to this mechanism, metal (e.g., Pt) provides active sites for hydrogenation/dehydrogenation whereas isomerization/cracking takes place on the acid sites [17]. The role of each type of active sites in a bifunctional reaction has been extensively studied and the overall scheme of this reaction appears frequently in literature. Nevertheless, the degree of intimacy required between the two types of active sites for bifunctional applications has rarely been tested due to a lack of control of this parameter during synthesis of these catalysts [18-22]. Most often the closest proximity between active sites has been employed using ion exchange where metal cations exchange a fraction of the acid sites of the support. However, some reports have found that several other factors could potentially outweigh the proximity effect. Zečević et al. conducted a systematic study where controlled proximity between active sites [4]. They found that Pt nanoparticles located inside zeolite micropores and thereby maintaining closest intimacy with acid sites did not deliver optimal performance with respect to high quality diesel production. It was argued that olefinic intermediates formed on the metal sites experienced slow diffusion through zeolite micropores. This could potentially enhance the possibility for secondary undesired reactions (e.g., cracking) and diminish the quality of the fuel. A similar effect of pore size on the performance of bifunctional catalysts was reported in other studies [15, 23, 24] which prompted researchers to use materials with designed porosity, geometry and composition [25-27]. For other cases where

the classical interpretation was deemed inadequate, new hypotheses have been proposed (e.g., hydrogen spillover) [28-30]. Justifications of these new hypotheses have been reviewed in several reports [31, 32].

In the companion synthesis-focused work [33], Pt deposition over silica-alumina mixed oxides (Al-Si) was controlled to achieve selective adsorption of metal precursor ions over silica or alumina domains using cationic $\text{Pt}(\text{NH}_3)_4^{2+}$ (PTA) and anionic PtCl_6^{2-} (CPA) precursors respectively at appropriate pH. Due to a stronger anchoring of the PTA precursor on silica compared to the CPA precursor on alumina, two different degrees of proximity between Pt and acid sites were obtained. Pt and acid sites were in the closest proximity with highly dispersed Pt nanoparticles for samples prepared by electrostatic adsorption of $\text{Pt}(\text{NH}_3)_4^{2+}$ at high pH (atomic-scale proximity). These catalysts will be identified as “PTA-11” with 11 representing the adsorption pH. One additional set of catalysts was prepared via dry impregnation (DI) of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ over Al-Si supports without pH control. The resulting catalysts showed evidence of ion exchange [33]. These catalysts will be referred to as “PTA-DI” and presumed, based on their small particle size, to have the same level of intimacy as PTA-11. On the other hand deposition of PtCl_6^{2-} onto small alumina domains in Si-rich Al-Si led to agglomerated Pt nanoparticles after reduction. The large Pt agglomerates (~15nm) led to a catalyst series with “nanometer scale” proximity with the acid sites. This series of catalysts will be referred to as “CPA-4” with 4 representing the adsorption pH. In order to stretch the degree of proximity even further, physical mixtures of a component with only metallic function, Pt/silica and a component with only acid function e.g., amorphous aluminosilicate, were studied. For physical mixtures (referred to as “PM”), the degree of intimacy was broadly defined to be in the micrometer-scale range. In other series of catalysts, the metallic and acidic components were maintained even further apart by adding inert layers composed of quartz wool in between them (millimeter-scale intimacy). These layered catalysts were labeled as “L-#”. Schematics of these catalysts, categorized in terms of degree of intimacy have been illustrated in Figure 1.

Figure 1. Schematics of catalysts used in this study showing different degree of intimacy between active sites. Images are not drawn to scale.

In this study, we have tested these four series of catalysts with different Pt loadings in an n-heptane isomerization reaction operated at 350°C and atmospheric pressure. This reaction under such operating conditions was used more as a probe reaction to study the performance of these catalysts in light of the ratio and proximity between active sites, which can offer interesting insight into the design and synthesis of an “ideal bifunctional catalyst” for this class of reactions.

2 Materials and methods

2.1 Materials, catalyst preparation and characterization

The synthesis protocols and characteristics of the catalysts for this study have been reported in the companion paper [33]. In brief, three different silica-alumina (Al-Si) mixed oxides were used as support. Two were synthesized in-house (Al-LSi 99, Al-HSi 97) for which highly dispersed alumina domains were formed on parent nonporous silica particles. A commercial amorphous SICAL 80 (Sasol, Germany GmbH) was used as the third support. The number in the SICAL support id represents the weight % of silica in that support (SICAL 80 contains 80% silica). The total number of acid sites on these supports was from low to high: Al-LSi 99<Al-HSi 97<SICAL 80. These supports could be categorized as Si-rich Al-Si. Several catalysts were also prepared using Al-rich SICAL supports e.g., SICAL 20, SICAL 40 and SICAL 70. One nonporous, non-acidic silica (Aerosil®OX50, Evonik-Degussa, 54m²/g), named R_Si, was used to synthesize Al-LSi 99, as well as a metal-only monofunctional Pt/R_Si catalyst. Another reference catalyst Pt/R_Al1 was prepared via deposition of anionic PtCl₆²⁻ precursor on a representative alumina support at pH=4.0. This alumina was synthesized using a recipe parallel to that of Al-LSi 99 and Al-HSi 97 [33] except without silica. Instead of forming soluble polycations of Al, in this case alumina was precipitated with a fast hydrolysis of AlCl₃ solution with NaOH. The precipitates were filtered, dried and calcined at 550°C for 5h. Reduced catalysts were characterized using NH₃-TPD, XRD, pulse chemisorption and scanning transmission electron microscope (STEM) [33]. Catalysts with two target weight loadings of 0.4 wt% and 0.7 wt% Pt were prepared. As seen in Table 1, actual weight loadings varied slightly.

Table 1. Characteristics of Pt/Al-Si catalysts and results of n-C₇ transformation.

Support	Catalyst	D ^a	Total acid	n _a /n _{Pt}	conv. [mol%] ^b		multi/ mono ^c
		[%]	[μmoles/g]		initial	final	
R_Si	0.69% PTA-11	48	0	0	41	24	0.47
R_Al1	0.70% CPA-4	25	-	-	41	26	0.35
SIRAL 80	No Pt	-	290	∞	0	0	0
Al-LSi 99	0.75% PTA-11	54	<30	-	41	29	0.22
	0.46% PTA-11	61	<30	-	30	16	0.21
	0.70% PTA-DI	11	<30	-	5	2	
	0.73% CPA-4	4	<30	-	18	8.7	0.31
Al-HSi 97	0.76% PTA-11	45	199	11	36	30	0.08
	0.42% PTA-11	31	231	35	26	24	0.09
	0.70% PTA-DI	59	37.6	2	51	32	0.12
	0.40% PTA-DI	65	122	9	44	31	0.13
	0.72% CPA-4	3	143	124	10	15	0.15
	0.39% CPA-4	3	137	238	7	18	0.13
SIRAL 80	0.66% PTA-11	62	290	14	34	23	0.15
	0.32% PTA-11	100	327	20	26	16	0.13
	0.70% PTA-DI	33	344	29	48	37	0.11
	0.40% PTA-DI	41	472	56	26	26	0.09
	0.72% CPA-4	6	360	163	23	21	0.11
	0.39% CPA-4	1	307	1536	43	11	0.21
SIRAL 70	0.60% CPA-4	3	344	372	45	37	0.11

SIRAL 40	0.65% PTA-11	42	420	30	44	34	0.03
	0.60% CPA-4	39	390	33	74	55	0.11
SIRAL 20	0.71% PTA-11	37	430	32	40	33	0.08
	0.72% CPA-4	40	385	26	68	43	0.21

^aDispersion by pulse chemisorption, ^bConversion at WHSV=1.0 h⁻¹, T=350°C, P=1 atm, ^cratio of multi-to-monobranched i-C₇ ratio at 22 ± 3% conv, TOS=18 h

2.2 Catalytic reaction

Transformation of n-heptane (n-C₇) was conducted in a U-shaped flow-type, fixed-bed, quartz tube reactor and operated at 350°C and atmospheric pressure. Hydroisomerization of alkanes is often conducted at higher pressures and influence of pressure on such reactions has been extensively discussed in [34]. However, study of this type of reactions at atmospheric pressure for lower molecular weight alkanes and especially for n-heptane or n-hexane is also common [1, 16, 35, 36] and in one of these studies the authors were able to successfully demonstrate the role of Pt location related to the acid sites [35]. 0.2 g of catalyst powder was supported by quartz wool. Prior to reaction, the catalyst was reduced *in situ* in flow of hydrogen (25 ml/min) at 350°C for 6 h. The reactants (n-C₇ and H₂) were introduced by flowing H₂ carrier gas through a conventional saturator (maintained at 12°C) containing n-C₇. This resulted in an H₂/n-C₇ mole ratio of 33:1. The weight hourly space velocity (WHSV) was 1.0 h⁻¹. “Initial” (time on stream, TOS=0.33 h) and “final” (TOS=18 h) activity and the extent of deactivation were measured at this WHSV. After 18 h time-on-stream, the space velocity was adjusted by changing H₂ flow rate in order to reach 22% ± 3% conversion. Product selectivity was measured at this constant conversion. Mass flow rates were regulated using Brooks controllers. Effluent gas compositions were analyzed by online gas chromatography with a flame ionization detector (FID) and a capillary column (CP-Sil PONA CB, 50 x 0.21 mm, Varian).

The reaction products were divided into four categories: (a) Aromatic (Toluene), (b) C₇ isomers (i-C₇), (c) cyclic products (Cyclic) and (d) cracking products (<C₇). Toluene was the sole aromatic compound detected. i-C₇ products were composed of monobranched e.g., methylhexane, ethylpentane and multibranched isomers e.g., dimethylpentanes. Cyclic products were composed of substituted C₅ cyclic compounds with seven carbons, e.g., dimethylcyclopentanes, ethylcyclopentane with a small fraction of methylcyclohexane and methylcyclopentane. Finally, n-C₆ to n-C₂ single chain alkanes and a few other <C₇ isomers e.g., dimethylpentane, isobutane, dimethylpropane were representatives of <C₇ products. Equations used to calculate selectivity and turnover frequency (TOF) are as follows.

$$\text{Selectivity of product i} = \frac{\text{moles of product i}}{\sum \text{moles of products with 4 or more carbon numbers}}$$

$$\text{TOF of i-C}_7 = \frac{\text{Fractional n-C}_7 \text{ conversion} \times \text{Fractional selectivity of i-C}_7 \times \text{WHSV} \left[\frac{\text{gm n-C}_7}{\text{gm cat. sec}} \right] \times \text{MW}_{\text{Pt}}}{\frac{\text{gm Pt}}{\text{gm catalyst}} \times \text{MW}_{\text{n-C}_7} \times \text{Fractional Pt dispersion}}$$

3 Results

3.1 Performance of Pt/Al-Si catalysts

The physicochemical characteristics of the Pt/Al-Si catalysts prepared using different conditions (precursor, pH) are listed in Table 1. The metal dispersion (D,%) and total number of acid sites were used to calculate the ratio of acid to active metal sites, n_a/n_{Pt} . The results of n-C₇ reactivity, specifically, initial and final conversion and the ratio of multi-to-monobranched i-C₇ products (multi/mono) are included. The product distributions at 22%±3% conversion after TOS=18 h have been plotted in Figure 2. The performances of two monofunctional catalysts, one based on only metallic function (0.69wt% Pt/R_Si prepared in PTA-11 condition) and the other based on only acidic function (SIRAL 80 Al-Si with no Pt) have been included in Table 1 and Figure 2a as references. The monofunctional Pt/R_Si catalyst showed notable activity and selectivity towards i-C₇. Also, the multi/mono ratio was found to be reasonably high (0.47) and the catalyst deactivated appreciably (Table 1). However, the Al-Si (SIRAL 80) in absence of Pt showed no activity under the studied reaction condition. Another reference catalyst, Pt/R_Al1,

showed some increased selectivity to $i\text{-C}_7$ and decreased selectivity to $<\text{C}_7$ (Table 1).

Figure 2. Product distribution (at $22 \pm 3\%$ conversion) of monofunctional (a) Pt/R_Si (metal), Pt/R_Al1 and Al-Si (acidic SIRAL 80) and bifunctional (b) Al-LSi 99, (c) Al-HSi 97 and (d) SIRAL 80 supported catalysts. Product color coding: $i\text{-C}_7$ (Green), toluene (Black), cyclic (Red) and $<\text{C}_7$ (Blue). “o” with solid lines representing 0.7wt% and “x” with dashed lines representing 0.4wt% catalyst.

In the Al-LSi 99 support (Figure 2b), acid sites were introduced by Al deposition onto R_Si silica [33]. Bifunctionality becomes apparent in comparing the catalytic performance of PTA-11 on Al-LSi 99 (Figure 2b) to PTA-11 on pure silica (Pt/R_Si in Figure 2a), as $i\text{-C}_7$ selectivity improved primarily at the expense of toluene selectivity. However, in other aspects (e.g., deactivation, multi/mono) this weakly acidic catalyst was quite comparable to the monofunctional Pt/R_Si catalyst (Table 1). A relatively low number of acid sites limited ion exchange of cationic Pt in the PTA-DI catalyst synthesized on the Al-LSi 99 support [33]. Also, limited Brønsted protons might have prevented anchoring and thereby stabilizing small metal particles and as a result, Pt dispersion on the Al-LSi 99 support in the PTA-DI series was poor (11%) unlike other

more acidic Al-Si (e.g., SIRAL 80 or Al-HSi 97) supported DI catalysts. A similarly prepared (PTA-DI) 0.7wt% catalyst on R_Si silica (no acidity) support yielded even poorer dispersion (3%) which further confirms the role of Brønsted sites on metal dispersion of the final catalyst. Due to their low dispersion and acidity, these catalysts (PTA-DI over R_Si and Al-LSi 99 supports) were largely inactive (Figure 2b).

Performances of Pt catalysts supported over more acidic, Si-rich Al-Si (Al-HSi 97 and SIRAL 80) have been presented in Figure 2c and 2d. Of these, catalysts prepared by adsorption of anionic PtCl_6^{2-} (CPA-4, nanometer scale proximity) stand out with significantly higher selectivity towards i-C₇. Similar performance was observed for another 0.6wt% CPA-4 catalyst using SIRAL 70 as support (Table 1). The PTA-11 catalysts with well-dispersed Pt (atomic scale proximity) showed less preference for i-C₇ products than the CPA-4 catalysts. On the other hand, considerable differences could be observed between product selectivity of PTA-DI catalysts prepared over Al-HSi 97 and SIRAL 80 supports (Figure 2b and 2c). These results will be discussed later. With few exceptions, Pt over these more acidic supports exhibited less deactivation and lower multi/mono ratios than Pt/Si-50 and Pt/Al-LSi 99 catalysts (Table 1).

Catalytic performances of other Al-rich Al-Si supports (SIRAL 20, SIRAL 40) 0.7wt% Pt catalysts synthesized at different conditions (PTA-11 and CPA-4) have also been studied. In contrast with the Si-rich Al-Si supports, anionic PtCl_6^{2-} adsorption (CPA-4) over these Al-rich supports yielded significantly higher dispersion of Pt (Table 1). From the selectivity results plotted in Figure 3 the CPA-4 catalysts over these Al-rich Al-Si showed significantly higher selectivity towards cracking (<C₇) than the PTA-11 series.

Figure 3. Product distribution for n-C₇ conversion (at 22 ± 3% conversion) of Al-rich (a) SIRAL 40 and (b) SIRAL 20 supported 0.7wt% catalysts synthesized at different conditions.

3.3 Performance of physical mixtures and layered catalysts

Performances of PM (physical mixture) and layered catalysts (L-1 to L-3) are presented in Figure 4. Schematics of these catalysts are presented above their respective results. The two monofunctional catalysts, metal-only Pt/R₂Si and acid-only SIRAL 80, were shown as references in Figure 4.

Two different catalyst forms were used to control the proximity between active sites. In the layered setup, the active sites were the furthest apart (millimeter scale intimacy) whereas in the physical mixtures (PM) the scale of mixing was in the micrometer range. Equal mass (~0.2g) of each component was used (1:1 mass ratio). The exact mass along with the reactivity results have been summarized in Table 2 and Figure 4. In the layered setup, the components were ordered in different combinations to form L-1, L-2 and L-3 (Figure 4). According to Figure 4a, activity of the layered catalysts slightly improved from the monofunctional Pt/R₂Si although the distribution of products remained fairly identical (Figure 4b). Comparing among L-1 to L-3, no significant difference in activity or selectivity was observed (Table 2 and Figure 4) regardless of the order of components. All the layered catalysts displayed a similar degree of deactivation, apparent in Figure 4a, with a high multi/mono (Table 2) similar to that of the monofunctional Pt/R₂Si catalyst.

Figure 4. Conversion (a) and Product distributions at $22 \pm 3\%$ conversion (b) obtained for different two-component catalysts based on Pt/R_Si and SIRAL 80 (Al-Si). The schematic illustrates components and their proximity; yellow circles represent acidic SIRAL 80, red circles represent Pt/R_Si and the grey strip represents a layer of quartz wool. Total catalyst mass for 1:1 PM and layered catalysts was 0.4g with equal mass (~ 0.2 g) of components. Total mass of reference catalysts was ~ 0.2 g.

Table 2. n-C₇ reactivity results on physical mixture (PM) and layered catalysts (L-1 to L-3).

Type	Component Mass [g]		n-C ₇ conv. [mol%]		multi/
	Pt/R_Si	SIRAL 80	initial	final	mono
<i>Layered</i>					
L-1	0.223	0.222	53	33	0.35
L-2	0.200	0.200	58	35	0.40
L-3	0.212	0.208	53	31	0.41
<i>PM</i>					
1:2	0.154	0.080	55	38	0.13
1:1	0.100	0.100	54	41	0.06
1:1 ^a	0.209	0.203	70	57	0.11
2:1	0.080	0.150	53	45	0.10
6:1	0.034	0.174	48	40	0.12
10:1	0.018	0.181	37	32	0.18
15:1	0.013	0.188	31	28	0.21

^aused as 1:1 PM catalyst in Figure 4

The catalytic performance of the PM catalyst in Figure 4a (1:1 PM) was significantly different than that of the layered catalysts. With more intimately mixed metal and acid sites, an improvement in i-C₇ selectivity at the expense of cracking (<C₇) and cyclic products was evident. Initial activity was also significantly higher (70% versus 58% in L-2 shown in Table 2 and 41% in Pt/R_Si shown in Table 1) with significantly less deactivation and lower multi/mono ratio. In short, the performance of PM catalyst was more in line with the bifunctional Pt/Al-Si catalysts whereas the layered catalysts resembled the monofunctional Pt/R_Si catalyst.

The bifunctional nature of the PM catalysts was further assessed using different mass ratios of components. The summary of the results has been reported in Table 2 and Figure 5. A constant total mass of 0.2g was used and amounts of individual components were varied. There are obvious trends of activity (Figure 5a) and product selectivity (Figure 5b) with respect to component ratio. From left to right of Figure 5a, catalysts with a higher acid fraction experienced

less deactivation. In terms of product distribution plotted in Figure 5b, i-C₇ selectivity increased until a 10:1 acid-to-metal ratio. Toluene selectivity remained unchanged up to 1:1, then decreased. Selectivity to <C₇ decreased initially up to 1:1 ratio then increased. Finally, selectivity to cyclic products decreased with increasing ratio. High multi/mono ratio was evident at high ratios of either metallic (0.13 for 1:2 ratio) or acidic component (0.18 for 10:1, 0.21 for 15:1 ratio) seen in Table 2. At intermediate ratios (1:1–6:1), however, multi/mono ratios were significantly lower.

Figure 5. (a) Conversion and (b) product selectivity of PM catalysts with different mass ratios of Pt/R_{Si} and SIRAL 80 (Al-Si) components. Total mass of catalysts = 0.2g and selectivity data obtained for 22±3% conversion.

3.4 Stability of catalysts

From the activity data summarized in Table 1, it is evident that some Pt/Al-Si catalysts have undergone deactivation over time. More notably, the least acidic Al-LSi 99 supported catalysts suffered the greatest loss of activity. One representative catalyst from this set (0.75 wt%, PTA-11) has been analyzed using STEM before and after reaction (TOS = 18 h at 1.0 h⁻¹ WHSV). This catalyst lost 30% of its activity (Table 1). Representative STEM images presented in Figure 6, do not show any significant change in particle size in the deactivated catalyst (volume averaged particle sizes (D_v) 2.1 ± 0.4 nm before and 2.2 ± 0.6 nm post reaction. This indicates that sintering was not responsible for catalyst deactivation.

Figure 6. Representative high STEM images of 0.75% Pt/Al-LSi 99 (PTA-11) catalyst: (a) fresh catalyst, (b) after TOS=18 h. Volume (D_v), surface (D_s) and number (D_n) averaged particle sizes have been included along with histograms showing distribution of metal particle size.

4 Discussion

4.1 Effect of metal-acid site balance

In his review, Guisnet described an “ideal” bifunctional catalyst in light of the balance between metal and acid sites [34]. The performance of catalysts studied here can be similarly interpreted. To quantify the balance between active sites, the ratio of acid to active metal sites, labeled as n_a/n_{Pt} , was calculated. Such a metric has not been used often in literature [20, 21, 35]. The Pt/Al-Si, PM and layered catalysts with varying degree of acidity and metal dispersion constitute a wide variation of acid to metal site ratio. For the Pt/Al-Si catalysts, in particular, the resulting n_a/n_{Pt} ratios are included in Table 1. On the other hand, for the PM and layered catalysts, n_a/n_{Pt} values were determined by combining values for individual component at the respective mass ratios. The performance of the monofunctional catalysts can be used as a reference. An acidic support (SIRAL 80) in the absence of metal was completely inactive to n-C₇ conversion (Table 1). A much more acidic zeolite support, metal-free, would promote cracking at these conditions [16]. On the contrary, metallic Pt/R₂Si catalyst in the absence of acid sites ($n_a/n_{Pt} \sim 0$) showed significant activity and selectivity towards all four types of products. Although isomerization is largely regarded to take place at the acid sites, formation of isomerized products on a monofunctional Pt/silica catalyst has been reported [36-38]. At similar conditions, monofunctional Pt catalysts can favor dehydrocyclization of long chain alkanes. During C₇ transformation, the C₅ and C₆ substituted cyclic intermediates (e.g., 1,2-dimethylcyclopentane and ethylcyclopentane) that form via dehydrocyclization on the metal sites could undergo nonselective hydrogenolysis and produce some specific i-C₇ products (e.g., 3-methylhexane, 2,3-dimethylpentane). In agreement with this, these two i-C₇ products constituted the majority (87%) of the i-C₇ products from the Pt/R₂Si catalyst.

For the PM catalysts, product selectivity was quite sensitive to the metal-to-acid ratio (Figure 5b). This offers the first glimpse on the influence of active site ratio on bifunctional performance. Product selectivity of all the catalysts have been plotted with respect to n_a/n_{Pt} in Figure 7 where all but the cracking product ($<C_7$) selectivity (Figure 7d) showed obvious trends regardless of Pt dispersion, nature of acid sites and proximity between metal and acid sites.

Figure 7. Product selectivity of all catalysts as functions of acid to metal ratio toward (a) toluene, (b) i -C₇, (c) cyclic and (d) $<C_7$. The legend in (a) is common to all.

As seen from Figure 7a and 7c, both toluene and cyclic product selectivity decreased with n_a/n_{Pt} . A higher metallic fraction could boost toluene and cyclic product selectivity as they form predominantly at the metal sites via dehydrocyclization [38]. On the contrary, selectivity towards i -C₇ increased with n_a/n_{Pt} (Figure 7b). At high n_a/n_{Pt} , the catalysts would favor the bifunctional

pathway and hence exhibit higher selectivity towards *i*-C₇. The selectivity of these three products approached that of monofunctional Pt/R₂Si catalysts (seen on the vertical axes) as n_a/n_{Pt} decreased. The trend in <C₇ product selectivity was not as straightforward (Figure 7d). At $n_a/n_{Pt} > 100$, <C₇ selectivity increased particularly for the Pt/SIRAL 80 and PM (SIRAL 80 used as acidic component) series which was accompanied by high multi/mono ratios seen in Table 1 and 2. It is speculated that at such high n_a/n_{Pt} ratios the number of acid sites that each olefinic intermediate has to traverse during its diffusion from one metal site to another is greatly enhanced. This increases the possibility of secondary branching and cracking reactions occurring. The Al-rich SIRAL (SIRAL 40, SIRAL 20) supported CPA-4 catalysts (labeled “Al-rich SIRAL (CPA)” in Figure 7, filled red triangles) stand out in Figures 7b and d. The effect of residual chloride in these samples will be discussed later.

Using these n_a/n_{Pt} correlations, reaction performance of the Pt/Al-Si catalysts in Figure 2 can be explained. Poorly dispersed CPA-4 catalysts prepared on acidic Si-rich supports e.g., Al-HSi 97, SIRAL 80 had very high n_a/n_{Pt} ratio that ultimately enhanced their bifunctional nature leading to high selectivity towards *i*-C₇. In the PTA-11 catalysts, Pt was brought even closer to the acid sites (atomic-scale intimacy) on the same supports by maintaining high Pt dispersion (Table 1). Thus, due to high dispersion, the n_a/n_{Pt} ratio became too low to exhibit the same level of bifunctionality as the CPA-4 catalysts. Moreover, comparing between the PTA-DI catalysts, Pt was better dispersed over Al-HSi 97 than over SIRAL 80 support with the former containing significantly less acid sites than the other (Table 1). This resulted in a much smaller n_a/n_{Pt} ratio in the Al-HSi 97 catalysts. Hence, PTA-DI catalysts over Al-HSi 97 acted more like the monofunctional metallic catalyst whereas SIRAL 80 supported DI catalysts were more bifunctional.

Of the four different types of products, *i*-C₇ is the one that primarily forms via a bifunctional pathway and is deemed the best metric for bifunctionality. TOFs of *i*-C₇ products per active metal site have been calculated for all the catalysts and are presented in Figure 8. These TOFs were based on the number of Pt sites from chemisorption (Table 1). At $n_a/n_{Pt} < 10$, TOFs toward *i*-C₇ products of all the bifunctional catalysts were more or less similar to that of monofunctional Pt/R₂Si catalyst. At $n_a/n_{Pt} > 10$, TOFs of *i*-C₇ increased thereby showing evidence of bifunctionality. Alvarez et al. used Pt/zeolite catalysts with various platinum loadings and showed that up to a specific metal-to-acid site ratio (0.03), activity of *n*-decane transformation increased linearly [21]. This means that the metallic sites act as the rate limiting sites up to this ratio which in equivalent n_a/n_{Pt} would be 33. Beyond this ratio, activity reached a plateau meaning the reactions occurring at the acid sites have become rate limiting and ideal bifunctionality conditions have been met. This trend was later confirmed as Batalha et al. expressed the activity in terms of TOF per acid site and correlated it with metal-to-acid site ratio [19]. However, for Pt/amorphous Al-Si, Regali et al [35] found that with increasing metal to acid ratio the rate of bifunctional hydrocracking of *n*-hexadecane remain almost unchanged and only the monofunctional hydrogenolysis reaction rate increases. However, in contrast to the present work, either a lower temperature [21] or a higher pressure [35] was used in those studies. It is widely reported that the dehydrocyclization mechanism is favored at low pressures and/or high temperatures. Hence, such dehydrocyclization mechanism probably played no significant role in any one of these studies.

It can be summarized that under the reaction conditions explored here, bifunctional Pt/Al-Si catalysts act monofunctionally below a certain n_a/n_{Pt} . Musselwhite et al. reported similar observations using a high Pt loading on mesoporous aluminosilicates [16]. They hypothesized that there were simply too few acid sites within an “effective radius” between two Pt nanoparticles for the catalyst to be bifunctional. A minimum number of acid sites per metal site would therefore be required to fully suppress the monofunctional pathway. At the other end of the spectrum, samples with very high n_a/n_{Pt} ratios (>200) mostly corresponded to samples where Pt is very poorly dispersed ($<10\%$). Increasing the n_a/n_{Pt} ratio clearly leads to a significant increase in TOF of i-C₇. Also according to Figure 8, each metal site appears to be capable of feeding hundreds of acid sites without affecting the reaction rate. This confirms the high hydrogenating/dehydrogenating activity of Pt particles and is consistent with the work of Batalha et al. who found that each metal site can feed ~250 acid sites without significantly affecting bifunctional activity [19]. The fact that this limit is higher in the present work might be due to an over-estimation of the number of relevant acid sites (some of the acid sites of the Al-Si determined by NH₃-TPD might be too weak to play any significant role).

Figure 8. TOF (per active metal site) of i-C₇ products with respect to acid-to-metal ratio. TOF determined using conversion and selectivity of i-C₇ at 1.0 h⁻¹ space velocity, TOS=18 h, H₂/n-C₇ = 33. Both axes are logarithmic.

4.2 Cause of deactivation

Traditionally, catalytic naptha reforming exhibits complicated nature of deactivation. Coking and sintering are two of the major sources of deactivation in these catalysts [39]. With high resolution TEM imaging in Figure 6, it was shown that sintering of Pt nanoparticle could not be a responsible for the deactivation of the catalysts. On the other hand, carbonaceous deposits on

metal and/or acid sites can cause coking [40]. The catalysts with low (Pt/Al-LSi 99) or no (Pt/R_Si) acid sites in this study underwent maximum deactivation. Also the PM catalysts in Figure 5 exhibited less deactivation with increasing proportion of the acidic component. Same trend was evident on other Pt/Al-Si catalysts as evident from Figure 9a where the extent of deactivation of all the $\text{Pt}(\text{NH}_3)_4^{2+}$ derived catalysts used in this study are presented with respect to acid-to-metal site ratio i.e., n_a/n_{Pt} . This suggests that the metallic sites tend to undergo deactivation more than the acid sites. Cyclic products formed via dehydrocyclization mechanism on metal sites can facilitate coking and subsequent deactivation of catalyst [38, 40]. In Figure 9b, the extent of deactivation of all the $\text{Pt}(\text{NH}_3)_4^{2+}$ derived catalysts has been correlated with the selectivity of cyclic products. In this figure, some correlations could be observed with some discrepancies. In general, from the monofunctional Pt/R_Si to the bifunctional Pt/Al-Si, the catalysts forming more cyclic products underwent deactivation more.

Figure 9. $\text{Pt}(\text{NH}_3)_4^{2+}$ derived catalyst deactivation as a function of (a) n_a/n_{Pt} and (b) selectivity of cyclic products.

4.2 Role of proximity

From Weisz's pioneering work on the intimacy criterion in bifunctional catalysts, it is often taken *a priori* that proximity between active sites in a bifunctional catalyst needs to be as close as possible for greatest bifunctionality [17]. However, recent results suggest that closest proximity between active sites may not always be the most beneficial; as noted above, Zečević et al. even found it to be deleterious [4]. Similarly, in this study, the i-C₇ selectivity trend in Figures 7b and 8 suggests that the CPA-4 catalyst series with nanometer scale proximity (filled blue rectangles and filled black triangles in Figures 7b and 8) are more bifunctional than the other series (PTA-11 or DI) with atomic scale proximity. The physically mixed samples at micrometer-scale intimacy (open green rectangles in Figures 7b and 8) also exhibit greater bifunctionality than the atomically intimate catalysts (red open and filled and black open triangles, open blue squares).

To gain more insight into this issue and to address the effect of residual chloride on alumina, in Figure 10 the selectivities of the $i\text{-C}_7$ and $<\text{C}_7$ products as well as Pt dispersion have been plotted against alumina content. The results from chloride-containing CPA-4 preparations are given in Figure 10a and include the 100% alumina Pt/R_Al catalyst, and results for the PTA-11 derived catalysts are given in Figure 10b with the Pt/R_Si catalyst at 0% alumina. Both series show that $i\text{-C}_7$ selectivity diminishes and $<\text{C}_7$ selectivity increases with Pt dispersion. This once again suggests that the catalysts with the closest (atomic scale) proximity between metal and acid sites are not the most bifunctional.

On the other hand, it can be argued that residual chloride may induce bifunctionality, at atomic scale intimacy, by the acid sites on alumina it creates. Unfortunately the amount of residual Cl^- on these samples was too low to be detected by XPS. In the companion paper [33], evidence of increased acidity in the form of a higher temperature desorption peak is seen in comparing the NH_3 -TPD profiles of the Pt-free Al-Si supports in DI water (near pH 4) with the CPA-4 catalysts (prepared at pH 4). Several conclusions can be offered by comparing the sets of catalysts in Figures 10a and 10b.

A first comparison can be made between the CPA-derived alumina-only catalyst (100% alumina in Figure 10a) and the PTA-derived silica only catalyst (0% alumina in Figure 10b). As discussed earlier the nonacidic Pt/silica catalyst itself shows some $i\text{-C}_7$ selectivity by virtue of a pathway over the metal surface. The Pt/alumina catalyst shows a boost in $i\text{-C}_7$ selectivity from 22 to 28% which may be attributed to small amounts of residual chloride. This increase in selectivity may be larger than it appears, since the number of metal sites is lower on the alumina-only catalyst by a factor of two (dispersion 25% as opposed to 48%). However, the difference in $i\text{-C}_7$ selectivity between the alumina-only catalyst and the highest selectivities obtained – about 80% in Figures 2 and 10a – is large and argues that the role of residual chloride is relatively small in comparison with the intimacy effect.

A second comparison can be made in Figure 10 between the CPA-4 and PTA-11 catalysts at 60 and 80% alumina. The particle size is nearly the same for all four samples with dispersions about 40%, or 2.5 nm. In the catalysts of Figure 10a, the Pt particles are on alumina patches and thus atomically close to residual chloride acid sites, while the Pt particles in Figure 10b are on silica. The Pt sites intimately contacted with residual chloride (Figure 10a) actually show less $i\text{-C}_7$ and more cracking than the corresponding catalysts in Figure 10b. Residual chloride explains the previously noted anomalous performance of CPA-4 catalysts on these Al-rich SIRALs in Figure 7 (filled red triangles). Chlorinated alumina has been shown to display strong Brønsted acidity which can contribute to cracking reactions [41, 42], and several papers have noted that increased chloride levels on alumina causes increased cracking at the expense of heptane isomerization [42,43]. It can be suggested that residual chloride on the alumina phase of these composite catalysts also gives rise to acid sites leading to stronger adsorption of isomerized alkylcarbenium ions and so promotes cracking versus isomerization. However, this is difficult to ascertain definitively from the current data, given the independence of metal/acid ratio and site proximity as well as the difficulty in measuring residual chloride. A study in which residual Cl^- is

carefully measured and isolated from the proximity effect is needed and will be the subject of future work.

Figure 10. Product ($i-C_7$ and $<C_7$) selectivity and Pt dispersion of supported (a) CPA-4 and (b) PTA-11 catalysts with 0.7wt% Pt.

Significant loss in bifunctionality was observed only for the layered catalysts with millimeter-scale proximity. At this point, they essentially acted as monofunctional (metallic) catalysts. However, the bifunctional reactivity of the PM catalysts, with micrometer scale metal-acid site proximity, remained intact. According to Figures 7 and 8, the product distribution and TOFs from even the micrometer intimate PM catalysts were comparable to Pt/Al-Si catalysts with similar n_a/n_{Pt} ratio. Kim et al. used zeolites crystals with different thickness (from bulk crystals to nanosheets) and showed that selectivity of $n-C_7$ conversion remained nearly unchanged up to 300nm distance between metal and acid sites [44].

5 Conclusions

A series of bifunctional metal (platinum)-acid (silica-alumina) catalysts with wide ranges of acid:metal ratios and proximity between metal and acid sites was studied for n -heptane conversion. Catalysts which exhibited the greatest degree of bifunctionality has the highest ratio of acid to metal sites as well as a nanoscale or even micrometer scale of intimacy between the metal and acid sites, and not atomic-scale intimacy. Results from this study can be extended to designing bifunctional catalysts for numerous other applications.

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