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Al(CH₃)₃-promoted Pt/MCM-41 catalysts for tetralin hydrogenation in the presence of benzothiophene and promotion mechanism of Al-promoted Pt/MCM-41 catalysts

Mingjian Luo, Qingfa Wang, Xiangwen Zhang, Li Wang, Bing Hu

1. Introduction

Reduction the aromatics in diesel fuel is an important process to increase the cetane number as well as reduce the emission of particulates, NOx and polycyclic aromatic hydrocarbons (PAH). Hydrodearomatization processes are typically used for reducing the aromatic compounds. Contrast to the hydrodesulfurization and the hydrogenation of natural aromatics, the reversible exothermic aromatic hydrogenation reaction is more favor of mild reaction temperature. Generally, the supported noble metal catalysts, which are high aromatic hydrogenation activity at mild reaction conditions, are used in the production of low aromatic diesel.

However, the activity of noble metal catalysts is dramatically suppressed by the presents of sulfur-containing and nitride-containing compounds in the feedstock.

Efforts have been paid on improving the sulfur-tolerance of noble metal of catalyst. It has been proved that the supports with suitable acidity have positive effects on the hydrodearomatization activity and sulfur-tolerance of noble-metals catalysts. These effects have been attributed to the synergic effects between acid sites and noble metal particles which leads to the formation of electron-deficient metal (M’s). The additional active sites provided by the acid sites and the hydrogen spillover between the acid sites and metal sites. For the better understand of the interaction between acid sites and noble metal particles, we have investigated the properties and the performances of AlCl₃, Al(NO₃)₃, and Al(CH₃)₃ promoted Pt/MCM-41 catalysts by post-synthesis alumination and found that: 1) For the AlCl₃ promoted catalysts, the pre-grafting AlCl₃ anchors the platinum around it and leads to the most electron-deficient Pt⁺, while grafting AlCl₃ after the support of platinum offers isolation effect which benefits the platinum dispersion as well as leads to the formation of electron-deficient Pt⁻. 2) The electron density of platinum particles decreases with the increase of AlCl₃/Pt ratio, while the scale of platinum particles decreased first and then increased. 3) Contrast to Al(NO₃)₃ and AlCl₃, the Al(CH₃)₃ has the best isolation effect and the electron-donating methyl group. Thus Al(CH₃)₃-promoted catalyst is better platinum dispersion and less electron-deficient than Al(NO₃)₃- and AlCl₃-promoted ones. And 4) the tetralin hydrogenation is in favor of high platinum dispersion and less electron-deficient Pt particles while the sulfur-tolerance prefers electron-deficient Pt⁻.
summarized.

2 Experimental

The preparation, characterization and evaluation of the catalysts were similar to the procedure described previously.\textsuperscript{15-17} 2.1 Preparation of Catalysts

MCM-41 (5 g) was shifted to a three-neck flask equipped with mechanical stirrer. Hexane (50 mL) was added to disperse the MCM-41. \text{H}_2\text{PtCl}_6\text{-ethanol} solution containing 0.05 g Pt (0.01 g Pt/g MCM-41) was added to the slurry under stirring. The slurry was maintained at 75 °C for 1 h, and then hexane was vaporized under a nitrogen stream (200 mL/min). After the support of platinum, another 50 mL hexane and required amount of Al(CH\textsubscript{3})\textsubscript{2} solution was added and maintained at 75 °C for 1 h, then the solvent was vaporized under nitrogen stream again. The obtained powder was pressed and sieved into 16~20 mesh grain. Finally, the sample was dried at 110 °C for 2 h and calcined at 400 °C for 4 h. The obtained catalysts were labeled as Pt-xAl, where x = 0, 5, 10, 15 or 20 denoted the Al/Pt mole ratio.

2.2 Characterization of catalysts

The pore structure and specific surface area of the catalysts were measured by nitrogen adsorption-desorption isotherms on a Micromeritics TriStar 3000 analyzer at -196 °C. The multi-point Brunauer-Emmett-Teller (BET) method was used in the calculation of specific surface area and the Barrett-Joyner-Halenda (BJH) model is used in the calculation of average pore size and total pore volume.

The crystal structure of the catalysts were characterized by powder XRD patterns on a Rigaku D/Max 2500 instrument with Cu Kα radiation (\(\lambda = 0.1541 \text{ nm}\)) operated at 40 kV and 200 mA. Spectra were collected in the 20 range 30°~90°. The morphology and size of platinum particles were observed on a JEM-2100F transmission electron microscope (TEM) at 200 kV.

The NH\textsubscript{3}-TPD profiles were obtained on a Quantachrome ChemBET TPR/TPD chemisorptions flow analyzer from 80 °C to 600 °C at a ramp rate 15 °C/min in He atmosphere.

The Py-FTIR and CO-FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer in transmision model with a resolution of 4 cm\textsuperscript{-1}. Self-supporting wafers of catalyst was placed into an IR cell with CaF\textsubscript{2} windows, in-situ reduced with 40 \text{ mL/min} H\textsubscript{2} at 400 °C for 2 h, then cooled to 100 °C and 30 °C before being exposed to pyridine vapor and CO, respectively. The Py-FTIR spectra were recorded after being degassed at 150 °C and 280 °C for 0.5 h. The CO-FTIR spectra were recorded after exposed to 2500 Pa CO for 30 min and evacuated at 0.01 Pa for 20 min.

2.3 Catalyst evaluation

Catalytic activity and sulfur-tolerant evaluation were performed on a continuous down-flow fixed bed reactor. Catalyst was loaded in the isothermal zone of the fixed bed reactor and in situ reduced with 120 mL/min H\textsubscript{2} at 400 °C for 4 h (ramp rate: 2 °C/min). Reaction temperature and pressure are 280 °C and 5 MPa, respectively. Tetratin (20 wt.%)-n-dodecane solution was supplied by a Series II piston pump at 0.3 mL/min (0.26 g/min, WHSV = 52 h\textsuperscript{-1}). Hydrogen flow rate is 120 mL/min. Tetratin (20 wt.%)-n-dodecane solution with 300 ppm of benzoilphenone (72 ppm of sulfur) was used for the sulfur-tolerance evaluation. The results were quantitative analyzed on an Agilent 7890A GC equipped with an HP-PONA capillary column (50 m×0.2mm×0.5μm) and an FID detector.

3 Results

3.1 Textural properties of the catalysts

Table I lists the textural properties of the catalysts. The specific surface area, pore diameter and pore volume are similar to that of the MCM-41 support.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al/Pt</th>
<th>Si/Al</th>
<th>(S_i) m\textsuperscript{2}/g</th>
<th>(D_p) nm</th>
<th>(V_p) cm\textsuperscript{3}/g</th>
<th>(d_{XRD}) mm</th>
<th>(d_{TEM}) mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>-----</td>
<td>-----</td>
<td>865.8</td>
<td>3.89</td>
<td>1.04</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pt-0Al</td>
<td>0</td>
<td></td>
<td>912</td>
<td>3.89</td>
<td>1.04</td>
<td>6.4/5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>Pt-5Al</td>
<td>5</td>
<td></td>
<td>882.9</td>
<td>3.80</td>
<td>1.03</td>
<td>6.0/3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>Pt-10Al</td>
<td>10</td>
<td></td>
<td>875.1</td>
<td>3.78</td>
<td>1.02</td>
<td>5.8/4.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Pt-15Al</td>
<td>15</td>
<td></td>
<td>858.8</td>
<td>3.85</td>
<td>1.03</td>
<td>6.4/5.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Pt-20Al</td>
<td>20</td>
<td></td>
<td>839.4</td>
<td>3.89</td>
<td>1.01</td>
<td>6.6/5.1</td>
<td>---</td>
</tr>
</tbody>
</table>

Table I. Textural properties of the reduced catalysts

\(S_i\): specific surface area; \(D_p\): pore diameter; \(V_p\): pore volume; \(d_{XRD}\): (111)/(200) face platinum particle diameter from the XRD line; \(d_{TEM}\): average diameter of platinum particle from TEM photograph.

![Fig. 1 XRD patterns of the catalysts](image)

Fig. 1 shows the XRD patterns of the catalysts in 2θ range 30.0°~90.0° range. The standard PDF card is drawn at the bottom of the figure. The face-centered cubic platinum (0) particle is indicated by the broadening of diffraction peak. The average sizes of nano-platinum particles are estimated from (111) and (200) peaks using Scherrer formula. The results are also...
listed in Table 1. The nano platinum particles can also be observed directly by TEM (Fig. 2). It can be found that size of Pt particles increase first and then decrease with the increase of Al/Pt ratio. The Pt-10Al catalyst possesses the smallest platinum particles.

![Fig. 2 TEM micrograph and platinum particle size distribution of the catalysts](image)

**3.2 Acidity of the catalyst**

The acidities of the catalysts are investigated by NH₃-TPD and Py-FTIR. Fig. 3 shows the NH₃-TPD profiles of the catalysts. The NH₃ desorption peak below 300 °C which can be observed on all catalysts and the MCM-41 support is ascribed to hydrogen-bonded NH₃ on silanol. The NH₃-TPD profile of Pt-0Al catalyst is similar to that of MCM-41, but a little more high signal above 300 °C. The difference indicates platinum and residue chlorine cause a small amount of acid site. As indicated by the signal intensity, the amount of acid site increases with the increase of Al/Pt.

Fig. 4A and 4C shows the Py-FTIR spectra of the catalysts. The bands at about 1445 and 1595 cm⁻¹ indicate the silanol or hydroxyl group; 1453, 1575 and 1619 cm⁻¹ indicate the Lewis acid site while 1542 and 1637 cm⁻¹ indicate the Brønsted acid sites. The peak at 1489 cm⁻¹ is contributed by three types of adsorption sites. The Al-free catalyst show some silanol bonded pyridine.
(1445 and 1595 cm⁻¹) and very little Lewis and Brønsted acid sites. While Al(CH₃)₃ is added, it reacts with the surface silanol and grafts onto the MCM-41. At low Al/Pt ratio (Al/Pt = 5), the Al-CH₃ bond may be hydrolysed which leads to more hydroxyl-aluminium, as indicated by the increase of peaks at 1445 and 1595 cm⁻¹. With the increase of Al/Pt ratio, the adjacent hydroxyl-aluminium dehydrates and results in the formation of Lewis and Brønsted acid. Meanwhile, the amount of hydroxyl is decreased. This is indicated by the shift of 1445 cm⁻¹ peak to 1453 cm⁻¹ and the increase of peaks at 1489, 1542, 1619 and 1637 cm⁻¹.

Fig. 4B and 4D shows the amount of acid sites. The values are calculated with the method provided by Emeis.²²

3.3 FTIR spectra of adsorbed CO

The FTIR spectra of adsorbed CO are collected to investigate the properties of nano-platinum particles (Fig. 5). Two absorbance bands can be ascribed to CO adsorbs on zero-ordered platinum atoms: the one at about 2080 cm⁻¹ is attributed to the CO linear bonding to platinum (Pt⁰-CO) and the other one between 1800 and 1900 cm⁻¹ is attributed to the CO bridged adsorbing on platinum (Pt⁰-CO-Pt⁰).¹³,²³-²⁶ The peak areas, which are related to the amount of adsorbed CO and roughly reflect the amount of accessible platinum atoms²⁷,²⁸, are listed in Table 2. Peak positions are also listed. With the increase of Al/Pt ratio, The area of linear bonded CO band increases at low Al/Pt ratio and than decreases while the Al/Pt ratio is further raised. The catalyst with an Al/Pt = 10 has the best Pt dispersion, which is consistent with XRD and TEM results. There are more defect Pt atoms (corner, edge and kink sites) in well dispersed catalyst and the defect platinum atom brings in the low vibration frequency of linear-bonded CO band (Table 3).²⁹,³⁰ Hence, the peak position shifts from 2900.69 to 2084.98 and then to 2086.73 cm⁻¹ with the
increase of Al/Pt ratio.

![Figure 5 CO FTIR spectra of the catalysts.](image)

**Fig. 5** CO FTIR spectra of the catalysts.

**Table 2. Peak position and integrated area of linear bonded CO**

<table>
<thead>
<tr>
<th>Al/Pt</th>
<th>Saturated adsorbed</th>
<th>After evacuation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance</td>
<td>Absorbance</td>
</tr>
<tr>
<td></td>
<td>Position</td>
<td>Position</td>
</tr>
<tr>
<td></td>
<td>Integrated area</td>
<td>Integrated area</td>
</tr>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>15</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>20</td>
<td>0.004</td>
<td>0.004</td>
</tr>
</tbody>
</table>

**Note:**

1. The band at 2100 cm\(^{-1}\) can be assigned to the CO bonded to electron-deficient Pt\(^{0}\) atoms. 
2. The band at 2100 cm\(^{-1}\) can be assigned to the CO bonded to electron-deficient Pt\(^{0}\) atoms. 
3. The band at 2100 cm\(^{-1}\) can be assigned to the CO bonded to electron-deficient Pt\(^{0}\) atoms. 

**4 Discussion**

Our previous studies have investigations the effects of Al-Pt interaction sequence, Al/Pt ratios of AlCl\(_3\) and aluminum promoter type on the performance of Pt-Al/MCM-41 catalyst. The promotion mechanism of aluminum promoters on the properties and performances of Pt/MCM-41 catalysts are discussed and summarized below.

**4.1 Catalytic properties**

As previously discussed, Al-promoters have anchor effect...
isolation effect, and electron-withdrawing effect which affect the formation of platinum particles. Al-promoters also provide acid sites and hydroxyl groups as well as favour the spillover hydrogen (Fig. 7).15–17

4.1.1 Isolation and anchor effects and their role on platinum dispersion. The Al-promoters can react with the silanols which are on the surface of MCM-41 and anchor onto the support.15–17 The anchored Al-promoter like a barrier which surrounds the platinum compound and confines them in definite region. Hence, the platinum is prevented from sintering and agglomerating and the platinum dispersion is improved. At the same time, the homogeneous MCM-41 surface is destructed by the anchored Al-promoter. The property of aluminum site is more similar to platinum compound than that of silicon site. Thus the platinum compound may be attracted to aluminum sites and anchored onto these sites. Contrasted to the isolation effect, the anchor effect leads to large platinum particle and slows down the platinum formation of Pt\(^{\ddagger}\).

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Contrast the catalysts in similar platinum dispersion, it can be found that: (1) the Al(CH\(_3\))\(_3\)-promoted catalysts have much better catalytic activity than the AlCl\(_3\)-promoted ones; (2) the AlCl\(_3\)-promoted ones is better than Al(NO\(_3\))\(_3\)-promoted one; and (3) the Al-free catalyst is better than Al(NO\(_3\))\(_3\)-promoted one. Combine with the above discussed electron-withdrawing effect of Al-promoters, it can be concluded that the tetralin hydrogenation is in favour of less electron deficient platinum particles.40, 41 Additionally, the acid sites and hydroxyls provide additionally active sites and favour spillover hydrogen which may also contribute to hydrogenation activity.40, 41
The catalyst is mainly caused by the competitive adsorption of benzothiophene which hinders the adsorption and hydrogenation of tetralin. Therefore, good sulfur-tolerance can be achieved if the hydrogen desulfurization activity is improved. In other words, the low residual benzothiophene concentration in the product implies the catalyst probable have good sulfur-resistance. The residual benzothiophene concentration at stable condition are listed in Table 4.

The primary factor that determines the sulfur-tolerance of the catalyst is also the platinum dispersion. As it is observed in Fig. 8B, the pseudo-first-order rate constant keeps a increase intendency with the increase of platinum dispersion under sulfur-containing condition. The reason is that high platinum dispersion also provides more activity sites for both the tetralin hydrogenation and benzothiophene hydrogenation. As it is showed in Table 4, the residual benzothiophene concentration is 8.7 at Al/ Pt =2 and 12.8 at Al/ Pt =10 for AlCl3- and Al(CH3)3-promoted catalysts, respectively. These two catalysts are also the highest platinum dispersion catalysts for the AlCl3- and Al(CH3)3-promoted catalysts, respectively.

The electron density of platinum particle also affects the sulfur-tolerance of the catalyst. As it is observed in Fig. 8, the Al(NO3)3-promoted catalyst and high Al/Pt ratio AlCl3-promoted catalysts, though low or similar pseudo-first-order rate constant as the Al-free catalyst under sulfur-free condition, has a high pseudo-first-order rate constant than the Al-free catalyst under sulfur-containing condition. Table 3 also shows that the relative rate constants of all Al-containing catalysts under sulfur-containing condition (k1 ’) and after the sulfur-containing condition (k1 ’) are much higher than under sulfur-free condition (k1 ). The reasons are that (1) the platinum particles in Al-containing catalyst are more electron-deficient than those in the Al-free one; (2) the electron-deficient Pt8+ strengthens the adsorption of electronnegative benzothiophene; and (3) the Pt8+ pulls the electrons of benzenic ring and thiophenic ring, and thereby destabilizes the rings which promotes the hydrogenation of thiophenic ring and the scission of S–C bond. As a result, high benzothiophene hydrogenation activity is achieved on electron-deficient Pt8+ catalyst. This point is verified by the residual benzothiophene concentration listed in Table 4. All Al-containing catalysts have much lower residual benzothiophene concentration than the Al-free one. When benzothiophene concentration brought down, the tetralin hydrogenation activity is improved. In summary, the sulfur-tolerance of the catalyst is in favour of the electron-deficient Pt8+.

Additionally, similar to tetralin hydrogenation, benzothiophene can be adsorbed onto the acid sites and hydroxyl sites, and then be hydrogenated by the spillover hydrogen. Therefore, acid sites might also contribute to the sulfur-tolerance of the catalysts. 

5. Conclusions

The Al(CH3)3 promoter affects the platinum dispersion, decreases the electron density platinum particles, provides additional acid sites and favors the hydrogen spillover which benefit the tetralin hydrogenation activity and sulfur-tolerance of Pt/MCM-41 catalysts. The pseudo-first-order rate constants of the catalyst with a Al/Pt = 10 are 5.57 and 14.27 times as high as that of the Al-free under sulfur-free and sulfur-containing conditions, respectively. The improvement in platinum dispersion, which is mainly attributed to the isolation and anchor effects of Al promoters, is the primary factor that benefits both tetralin hydrogenation performance and sulfur-tolerance of Al-promoted catalysts. The formation of electron deficient Pt8+, which
caused to the electron-withdrawing effects of Al-promoters, enhances the sulfur-tolerance while reduces the tetralin hydrogenation activity to some extent.

Acknowledgements

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References