n-PENTANE HYDROCONVERSION USING Pt-LOADED ZEOLITE CATALYSTS

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ABSTRACT

Pt/H-ZSM-5 and Pt/H-MOR catalysts with different Pt contents were prepared via impregnation using H₂PtCl₆·6H₂O or via exchange using Pt (NH₃)₄Cl₂, calcination in air at 530°C and reduction in H₂ at 500°C. The prepared catalysts were tested for n-pentane hydroisomerization and hydrocracking via bifunctionality at 250-500°C using micro-catalytic pulse reactor. It is found that the dispersion of Pt exchanged zeolites is higher than the corresponding Pt impregnated zeolites at all Pt contents. It is also found that the dispersion of Pt/H-ZSM-5 catalysts either exchanged or impregnated are higher than the corresponding Pt/H-MOR catalysts. TPD data showed that the impregnated catalysts possess higher acid sites number than the exchanged catalysts, while the Pt/H-ZSM-5 catalysts have higher number of acid sites than the Pt/H-MOR catalysts, whereas the latter catalysts possess higher strength of acid sites at all Pt contents. The hydroisomerization activities using Pt exchanged catalysts either supported on H-ZSM-5 or H-MOR are higher than the impregnated catalysts at almost all Pt contents. It is also concluded that the H-ZSM-5 supported catalysts either exchanged or impregnated are active than the H-MOR supported ones. Hydrocracking is higher using all H-MOR loaded catalysts.

KEY WORDS

Pentane; Hydroconversion; Hydroisomerization; Hydrocracking; H-ZSM-5; H-MOR zeolites; Platinum.

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INTRODUCTION

Environmental protection agency regulations for phasing out lead additives and oxygen-containing components like MTBE and ETBE as well as aromatics from gasoline had a significant impact on the refining industry [1]. As a result, there has been a sharp rise in the requirements for octane enhancement processes. This rise is achieved by isomerizing n-pentane and n-hexane, which are the main components of light naphtha, to the corresponding iso-pentane and mono and dibranched hexanes which have higher octane number [2-10]. Isomerization reactions generally take place over bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acid sites for skeletal isomerization via carbenium ions [11-22].

The preparation of platinum particles in zeolites [23-25] is normally carried out exchanging Na⁺ or H⁺ ions of the zeolites by positively charged platinum complexes (mostly [Pt(NH₃)₄]²⁺) [26]. It was found that a low concentration of the complex at room temperature is a good condition [27]. The catalyst acid properties, metal dispersion and, hence, its activity and selectivity are affected by the method used to load the metal [16]. In isomerization of n-butane over hybrid catalysts prepared by physically mixing H-MOR and Pd/H-MOR, the highest selectivity to iso-butane was achieved over an ion-exchanged catalyst compared to an impregnated catalyst.

The activity, selectivity and stability of acid zeolites depend on their SiO₂/Al₂O₃ structural ratio and therefore on the density of acid sites. Previous studies in n-pentane hydroisomerization depict a maximum of activity for SiO₂/Al₂O₃ ratio between 10 and 50 [28]. The second ingredient of bifunctional catalysts is the hydrogenation / dehydrogenation sites, being Pt and Pd very active in comparison with other transition metals [29, 30]. The method used in the incorporation of metal has a strong influence on metal particle size and structure.

In this communication, catalysts containing 0.15, 0.30 and 0.60 wt%Pt supported on H-ZSM-5 or H-MOR zeolites, were prepared via impregnating a Pt precursor (H₂PtCl₆) or exchanging positively charged Pt complex (Pt(NH₃)₄Cl₂), respectively to follow or discover why some authors apply this or that technique in preparing the n-paraffins isomerization catalysts without explaining why.

2. EXPERIMENTAL

2.1. Preparation of Catalysts

2.1.1. NH₄-exchanged zeolites

The parent zeolites (Na-ZSM-5 and Na-MOR) were dried overnight at 110°C then calcined in air at 530°C for 3h to remove any templating agents remaining after the zeolite synthesis. These Na-forms of the current zeolites were exchanged to the corresponding NH₄-forms using molar solution of NH₄NO₃ under reflux system at
70°C several times for 8h with fresh solutions. The NH₄-forms produced were then separated, washed several time with distilled water to remove NO₃ ions, dried at 110°C overnight then calcined at 530°C for 3h to convert them to the corresponding acid forms (H-ZSM-5 and H-MOR).

2.1.2. Platinum exchanged zeolite catalysts

The H-ZSM-5 and H-MOR zeolites were again exchanged with a solution containing the requisite quantities of Pt(NH₃)₄Cl₂ required to prepare H-ZSM-5 and H-MOR containing 0.15, 0.30 and 0.60wt%Pt in the finished catalysts. The exchange was carried out for 8h at 70°C with reflux. The catalysts were then dried at 110°C then calcined at 530°C for 3h.

2.1.3. Platinum impregnated zeolite catalysts

The H-zeolites were impregnated with the requisite quantities of H₂PtCl₆ in aqueous solutions with citric acid as a penetrating agent for Pt into the catalyst pores [31, 32] to obtain 0.15, 0.30 and 0.60wt%Pt. These solutions were left overnight with stirring, then dried and calcined as mentioned above. The Pt/H-ZSM-5 and Pt/H-MOR catalysts prepared were separately reduced in a flow of dry hydrogen of 20cm³min⁻¹ for 8h at 500°C before carrying out the current hydroconversion experiments.

2.2. Pulsed Micro Reactor

A micro-catalytic reactor stainless steel tube jacketed with an electrically thermostated copper block heater was installed at the injection port of a gas-chromatograph (Sigma-3B). The reactor always contained 0.20g of a catalyst whereupon H₂ carrier gas of 20cc/min passed which serves also as a reactant. The feed injected was always 0.5μl of AR n-pentane. Eluted products passed directly to a GC column of length 3.0m and internal diameter 5mm packed with 10wt% OV-101 on Chromosorb W of 60-80mesh. The column temperature was maintained isothermally at 60°C.

2.3. Temperature Programmed Desorption (TPD)

The procedure adopted by Aboul-Gheit [33, 34] to follow and measure the desorption of presorbed NH₃ on the catalysts was used. NH₃ adsorption was first carried out in a silica tube furnace after evacuation at 1.33x10⁻³Pa whilst heating at 500°C and subsequent cooling to 50°C (under vacuum). NH₃ was passed on the catalyst at a flow rate of 50 cm³ min⁻¹. TPD of the catalysts was evaluated in a DSC-30 (Differential Scanning Calorimetry) unit (Mettler TA-3000) using a gold sensor and Al crucibles. N₂ was used a purge gas at a flow rate of 50 cm³ min⁻¹. The heating rate was 10 K min⁻¹ and full-scale range was 25 mW.

2.4. Dispersion of Pt in the Zeolites

Dispersion of Pt in the current catalysts was determined by H₂ chemisorption using a pulse technique similar to that of Freel [35]. The calcined catalysts were heated in the chemisorption furnace at 500°C for 3h in a flow H₂ of 50cm³min⁻¹ then in a flow N₂ of 30cm³min⁻¹ for 2h (degassing). The furnace was shut off and the catalyst was cooled
to room temperature. H₂ was then pulsed into the N₂ carrier gas till saturation (appearance of H₂ peaks equivalent to un-chemisorbed pulses). The H₂ uptake was calculated as hydrogen atoms adsorbed per total metal atoms on the basis of 1:1 stoichiometry [36].

3. RESULTS AND DISCUSSION

3.1. Hydroisomerization of n-Pentane

3.1.1. Using exchanged and impregnated Pt/H-ZSM-5 catalysts

A series of three catalysts containing 0.15, 0.30 and 0.60wt%Pt supported on H-ZSM-5 zeolite were prepared via impregnating the H-ZSM-5 with H₂PtCl₆ solution, and another series of three respective catalysts were prepared via exchanging NH₄-ZSM-5 with a Pt complex [Pt(NH₃)₄Cl₂] solution. These catalysts were used for the hydroisomerization of n-pentane in a pulse micro-reactor in flowing H₂ stream. The activities of the Pt impregnated catalysts are found to increase as a function of Pt content, where the reaction maximum reached 36.7, 48.6 and 61.1% using the 0.15, 0.30 and 0.60wt%Pt catalysts (Fig. 1a), respectively. However, the Pt exchanged catalysts exhibited insignificantly different activities, i.e., around ~58.0% (Fig. 1b). This difference can be primarily attributed to the more ordered distribution of Pt crystallites in the exchanged catalysts, since during the exchange process, the Pt cations attach to the ordered Al in the zeolitic framework. Nevertheless, in case of impregnated catalysts, the Pt crystallites are almost randomly distributed in non-framework positions either inside or outside the channels and cavities of the zeolite. This view may be evidenced via comparing the Pt dispersion in the exchanged and impregnated catalysts (Table 1). In the exchanged catalysts Pt dispersion is higher than in the impregnated ones. In the exchanged H-ZSM-5 Pt loaded catalysts, the dispersion of Pt ranges between 88.0 and 75.0%, whereas in the Pt loaded H-MOR catalysts the dispersion ranges between 79.0 and 60.0%. These data show also that dispersion continually decreases with increasing the Pt content in the catalyst. In the exchanged H-ZSM-5 containing catalysts the difference in Pt dispersion between these three versions is not significant which may give the main reason for the insignificant difference in the hydroisomerization activities of the three Pt exchanged catalysts (Fig.1b).

A significant finding concerning the obviously different levels of hydroisomerization of n-pentane on the impregnated catalysts could be visualized via correlating the Pt dispersion (Table 1) and acid sites density and strength in these catalysts (Table 2) with the magnitude of iso-pentane production (Fig. 1b). Although Pt dispersion and acid sites number and strength are relatively higher in the low Pt-containing catalysts than in the higher Pt-containing ones, the pentane isomers production is significantly lower. This implies that the balance between the metallic and acidic function is improper on the 0.15%Pt catalysts. This indicates that the activity of the catalyst is chiefly dependent on the magnitude of the Pt content in impregnated catalysts, which can be an important evidence that Pt in these catalysts (impregnated) is principally distributed on the external surface of the zeolite rather than being distributed in the channels and cavities of the H-ZSM-5 zeolitic support. Brito et al. [37] confirmed that
the ratio between the acid and metal function is well balanced and that the hydrogenation/dehydrogenation step on the metal function and isomerization step on acid function are not rate limiting steps, since an increase in the platinum concentration from 0.5 to 1% only increases scarcely the isopentane yield.

Furthermore, the acid sites number and strength (Table 2) in the exchanged catalysts are lower than those in the corresponding impregnated ones. This can be attributed to acquiring Al-O-Pt bonds in the exchanged catalysts in much larger numbers compared to the impregnated ones which contain much larger numbers of the Al-O-H bonding because Pt is located as isolated crystallites in non-framework sites.

3.1.2. Using exchanged and impregnated Pt/H-MOR catalysts

The other group of catalysts (Pt/H-MOR) was prepared also via the exchange and impregnation of 0.15, 0.30, and 0.60 wt% Pt. The close activity magnitudes of pentane isomerization observed in Fig.1b using the exchanged Pt/H-ZSM-5 does not occur in case of the corresponding catalysts containing exchanged Pt/H-MOR (Fig. 2a). Moreover, the activity of the 0.60wt%Pt/H-MOR catalyst is the highest, whereas that of the 0.30wt%Pt/H-MOR catalyst is lowest. However, the 0.15wt%Pt/H-MOR acquires an intermediate isomerization position. This deteriorated succession (order) of activities in these mordenite containing catalysts may be attributed to some reasons concerned with the zeolitic structure of the H-MOR zeolite; a) H-MOR has a unidirectional channel structure, where one of its three directions has very narrow channels (2.6 Å) [38] that can not permit diffusion of any molecules through them. b) The wider channels in the two other axial directions are, relatively, wide that may have caused loss ordered distribution of the Pt particles in the exchange positions in the zeolitic channels of H-MOR. This can be supported by the lower dispersion of Pt in the exchanged MOR zeolite than in the respective exchanged ZSM-5 zeolite catalysts (see Table 1).

Fig. 2 shows that the order of hydroisomerization activities of the impregnated (Fig.2a) and exchanged catalysts (Fig. 2b), correlated during the ascending limit (250-325°C), is in the following order: 0.60%Pt/H-MOR > 0.15%Pt/H-MOR > 0.30%Pt/H-MOR, irrespective of the other details on the curves. The highest activity acquired by both 0.6%Pt catalysts can be indicative of excess Pt deposition on the external surface of the H-MOR Zeolite.

3.2. Hydrocracking of n-Pentane

3.2.1. Using exchanged and impregnated Pt/H-ZSM-5 catalysts

Hydrocracking of n-pentane takes place at higher temperatures than n-pentane isomerization. Some similarity of the isomerization and hydrocracking (Figs. 2, 3) occurs, where the hydrocracking activities of the impregnated catalysts containing different Pt contents on H-ZSM-5 exhibited large differences, compared to those on the respective exchanged catalysts. The concepts of Pt dispersion and acid sites strength distribution may show compatibility with the hydrocracking data using the current catalysts. Good dispersion of platinum in the exchanged catalysts and the
relatively lower acid sites strength in the exchanged catalysts results in insignificant differences in the hydrocracking activities of the three catalysts (Fig. 3a). However, although Pt dispersion decreases with increasing Pt in the catalysts (Table 1) and also acidity decreases, it is found that (Fig. 3b) hydrocracking increases with increasing Pt. The distribution of the Pt in the external surface of the H-ZSM-5 zeolite can be the principal source for enhancing the hydrocracking activity than in the impregnated Pt/h-ZSM-5 catalysts.

Fig. 4a shows that the low molecular weight hydrocarbon gases (C1+C2) increase continually with reaction temperature except for the catalyst containing 0.30%Pt which acquires the highest activity gives some declination beyond 475°C. However, this C1+C2 production does not significantly exceed that occurring on the 0.15%Pt containing catalyst. This reaction is considered as undesired one and viewed to be a loss, particularly at high temperatures (500°C), where it is markedly active and exceeds 65%. The order of catalysts for production of C1+C2 is as follows: 0.30%Pt/H-ZSM-5 > 0.15%Pt/H-ZSM-5 > 0.60%Pt/H-ZSM-5. This order does not correlate with hydrogenolysis, since this reaction requires high platinum content with higher particle sizes. However, in this order the 0.60%Pt containing catalyst is the least active perhaps due to the lower Pt dispersion and lower acidity.

Fig. 4b shows that the behaviors of the 0.15 and 0.60%Pt catalysts for propane production exhibit similarity as a function of reaction temperature whereas the 0.30%Pt catalyst shows higher values of propane at temperatures ≤ 400°C. On the three current catalysts significant decline of propane takes place via increasing temperature beyond 450°C. This can be attributed to secondary hydrocracking of propane to C1+C2. Since the principal reaction of pentane hydrocracking is: C5 C2 + C3 using the noble metal catalysts; the high values of C1+C2 and C3 in Figs. 4a and 4b reach ~ 70.0 and 40.0%, respectively, take place. However, the hydrocracking of n-pentane to methane + butane is thermodynamically less possible, (Figs. 4C and 4d), hence maximum production of i-C4 is ~ 6.0% at 425°C, and maximum production of n-C4 is about 9.0-10.0% at 375-425°C. At the lower temperature region (300-400°C), i-butane production (Fig. 4c) is in the catalysts order: 0.15%Pt/H-ZSM-5 > 0.30%Pt/H-ZSM-5 > 0.60%Pt/H-ZSM-5, whereas in the high temperature region (450-500°C) the i-butane values are in the order: 0.60%Pt/H-ZSM-5 > 0.30%Pt/H-ZSM-5 > 0.15%Pt/H-ZSM-5.

In Fig. 4d, it is found that n-butane exceeds i-butane. During the low temperature region (300-350°C) the catalysts order for n-butane production is as follows: 0.15%Pt/H-ZSM-5 > 0.30%Pt/H-ZSM-5 > 0.60%Pt/H-ZSM-5. This low temperature order can be correlated with the acid sites number and strength (Table 1) as well as with the dispersion of Pt in the zeolite (Table 2). Nevertheless, in the high temperature region the 0.60%Pt/H-ZSM-5 catalyst gives the highest production of n-butane, whereas the 0.30%Pt/H-ZSM-5 catalyst gives the lowest yield of n-butane.

The distribution of Pt between the external and internal surfaces of the zeolite should significantly differ in case of impregnated catalysts than in case of the exchanged catalysts. In the former catalysts, the external surface will be more loaded with metal, which makes hydrogenolysis to be easier on the more heavily loaded catalyst. The lower dispersion of Pt on the impregnated catalysts than in the exchanged ones is evident in Fig. 5a, where C1+C2 gases are distinctly in the order: 0.60%Pt/H-ZSM-5 >
0.30%Pt/H-ZSM-5 > 0.15%Pt/H-ZSM-5. Also, data in Fig. 5b correlates reasonably well with the data in Fig. 5a.

In Figs. 5a and 5b, the hydrocracked values of C1+C2+C3 are again much higher than those of iso- and n-butane. Moreover, iso- and n-butane are to be also arranged in the order: 0.60%Pt/H-ZSM-5 > 0.30%Pt/H-ZSM-5 > 0.15%Pt/H-ZSM-5, which is not the case of the exchanged catalysts shown in Figs. 5c and 5d.

3.2.2. Using exchanged and impregnated Pt/H-MOR catalysts

Fig. 6a shows that the impregnated 0.15 and 0.60%Pt/H-MOR catalysts give almost equal conversions to cracked products during a temperature range of 325-375°C, which may be attributed to a compensation effect of the higher acidity and lower magnitude of Pt sites in the 0.15%Pt/H-MOR catalyst against the lower acidity and higher Pt sites of the 0.60%Pt/H-MOR catalyst. On the other hand, the balance between the two functions of the 0.30Pt/H-MOR catalyst should be more proper than in the two other catalysts such that the hydroisomerization activity is much higher at 350-500°C (Fig. 2a) and correspondingly the hydrocracking activity is much lowest at this temperature range than using the 0.15 and 0.60%Pt/H-MOR catalysts.

Comparison of Figs. 6a and 6b show some similarity of the exchanged Pt/H-MOR and impregnated catalysts with respect to their order of hydrocracking magnitude, with some distinct difference between the 0.15 and 0.60%Pt/H-MOR catalysts. The privilege of the 0.60%Pt catalyst over the others for both isomerization and hydrocracking can be attributed to the wide pore of the H-MOR zeolite.

CONCLUSION

Comparison of the hydroconversion activities of two series of catalysts containing 0.15, 0.30 and 0.60%Pt/H-ZSM-5 and Pt/H-MOR prepared via Pt exchange or the Pt precursor impregnation. The exchange technique gave higher dispersion of platinum but somewhat lower acid sites number and strength. The exchanged catalysts properties permitted higher hydroisomerization activities in case of the H-ZSM-5 supported catalysts, whereas in case of the H-MOR supported catalysts, platinum content plays an important role, particularly through the hydrocracking of n-pentane, i.e., increases with increasing Pt in the catalysts.

REFERENCES


Table 1. Pt Dispersion in Pt/H-ZSM-5 and Pt/H-MOR catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Exchanged</th>
<th>Impregnated</th>
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<tbody>
<tr>
<td>0.15%Pt/H-ZSM-5</td>
<td>88</td>
<td>81</td>
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<tr>
<td></td>
<td>83</td>
<td>77</td>
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<tr>
<td>0.30%Pt/H-ZSM-5</td>
<td>75</td>
<td>70</td>
</tr>
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<td></td>
<td>79</td>
<td>73</td>
</tr>
<tr>
<td>0.60%Pt/H-ZSM-5</td>
<td>73</td>
<td>66</td>
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<tr>
<td></td>
<td>60</td>
<td>55</td>
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</table>

Table 2. Ammonia desorption enthalpy from the strong acid sites in H-ZSM-5 and H-MOR zeolites and their Pt loaded versions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Exchanged</th>
<th>Impregnated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_d$, J g$^{-1}$</td>
<td>Peak temp., °C</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>90.5</td>
<td>447.0</td>
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<tr>
<td>0.15%Pt/H-ZSM-5</td>
<td>86.7</td>
<td>445.6</td>
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<td>0.30%Pt/H-ZSM-5</td>
<td>81.2</td>
<td>441.1</td>
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<tr>
<td>0.60%Pt/H-ZSM-5</td>
<td>100.5</td>
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<td>H-MOR</td>
<td>80.0</td>
<td>462.0</td>
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<td>0.15%Pt/H-MOR</td>
<td>76.0</td>
<td>460.0</td>
</tr>
<tr>
<td>0.30%Pt/H-MOR</td>
<td>70.0</td>
<td>454.0</td>
</tr>
<tr>
<td>0.60%Pt/H-MOR</td>
<td></td>
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</table>
Fig. 1. Hydroisomerization of n-pentane as a function of reaction temperature using (a) impregnated Pt/H-ZSM-5 and (b) exchanged Pt/H-ZSM-5 catalysts.

Fig. 2. Hydroisomerization of n-pentane as a function of reaction temperature using (a) impregnated Pt/H-MOR and (b) exchanged Pt/H-MOR catalysts.
Fig. 3. Hydrocracking of n-pentane as a function of reaction temperature using (a) exchanged Pt/H-ZSM-5 and (b) impregnated Pt/H-ZSM-5 catalysts.
Fig. 4. Individual hydrocracked products as a function of reaction temperature using exchanged Pt/H-ZSM-5 catalysts, C₁+C₂ (a), C₃ (b), i-C₄ (c) and n-C₄ (d).
Fig. 5. Individual hydrocracked products as a function of reaction temperature using impregnated Pt/H-ZSM-5 catalysts, C₁+C₂ (a), C₃ (b), i-C₄ (c) and n-C₄ (d).
Fig. 6. Hydrocracking of n-pentane as a function of reaction temperature using (a) impregnated Pt/H-MOR and (b) exchanged Pt/H-MOR catalysts.