n-Hexane hydro-isomerization over promoted Pd/HZSM-5 catalysts

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Abstract
A series of Pd/HZSM-5 catalysts modified by various metallic species, including Co, Ni, Fe, Re, and Cu, was prepared by sequential impregnation. Contents of Pd and second metals in modified catalysts were 0.8 and 1.0 wt%, respectively. Physico-chemical characteristics of catalysts were investigated by nitrogen physi-sorption (BET), x-ray diffraction (XRD), transmission electron microscopy (TEM), ammonia temperature programmed desorption (NH₃-TPD), temperature programmed reduction (TPR) and hydrogen pulse chemisorption (HPC). Coke formation was studied by the method of thermogravimetric analysis (TGA). The activities of catalysts in n-hexane isomerization were studied in a micro-flow reactor under atmospheric pressure at 250 °C, and molar ratio of H₂: n-hexane of 5.92. It was found that Co, Ni, Fe, and Re additives exhibited geometric and electronic effects toward Pd/HZSM-5 catalyst, leading to an enhancement of its activity and stability. On the contrary, Cu additive caused Pd/HZSM-5 to become poorer in activity and stability.

Keywords: Pd/HZSM-5, additives, n-hexane isomerization

1. Introduction
Environmental concerns have been become a serious matter in recent times. Because of their toxicity, benzene and its derivatives are banned or gradually eliminated from the gasoline pool. According to Euro-4 and Euro-5 standards, concentrations of aromatic hydrocarbons must be reduced strongly and content of benzene in gasoline should not exceed 1 vol%. The United States and Europe specified that the limit of aromatics in gasoline should not exceed 25 vol%, and from the beginning of 2011, when the Mobile Source Air Toxics (MSAT II) standard came into effect, concentration of benzene must be limited to 0.62 vol% [1]. These factors resulted in negative effects on the anti-knocking performance of gasoline that has to be compensated by other means.

One of the effective alternatives is to increase concentration of methylated hydrocarbons which are formed through hydro-isomerization of corresponding normal paraffin. Current industrial catalyst for hydro-isomerization is based on Pt supported on halogenated alumina. Although being very active and can be operated at moderate temperature, this type of catalyst requires complicated operation, causes corrosion, and being very sensitive to impurities like sulphur compounds and water [2]. In our previous studies [3, 4], catalysts on the basis of Pt and Pd supported on HZSM-5 were developed and tested for n-hexane isomerization. The result indicated that 0.8%Pd/HZSM-5 catalyst exhibited comparable activity but less stable than 0.35%Pt/HZSM-5 one.

Compared to a mono-metallic catalyst, a bi-metallic catalyst was more stable, more selective, and showed higher activity in the conversion of hydrocarbons. A change of bond strength between chemisorbed hydrocarbons and Pt surface atoms due to electron transfer from the promoter to Pt (electronic effect) and the decrease of the Pt ensemble size thanks to a dilution of the Pt surface atoms by the second metal (geometric effect) have been proposed as reasons for beneficial effects of the promoter [5]. Yoshioka [6] also confirmed that the addition of a second metal onto a noble metal catalyst to form a bi-metallic catalyst caused a
significant increase in catalytic activity and selectivity toward branched isomers. According to Babu [7], the addition of Fe to Pd/Al2O3 caused the electronic states of Pd species to be changed, wherein reduction of PdO was hindered due to strong metal-support/ metal–metal interactions which are formed during the catalyst preparation by deposition-precipitation method.

In this study, Co, Ni, Fe, Re, and Cu were used as additives for Pd/HZSM-5 catalyst in n-hexane isomerization. The objective of this work is to study the influences of additives on properties and activity of Pd/HZSM-5 catalyst in isomerization of n-hexane.

2. Experimental

(NH4)2ZSM-5 zeolite (CBV3024E, SiO2/Al2O3 = 30) was distributed by Zeolyst International, USA) was calcined at 500 °C for 3 h to obtain HZSM-5. 0.8 wt%Pd/HZSM-5 catalyst was prepared by impregnation method using the procedure described in our previous work [3]. Bi-metallic catalyst was synthesized by sequential impregnations: the first impregnation with an aqueous solution of the additive metal salt, Co(NO3)2.6H2O (Merck), Ni(NO3)2.6H2O (Merck), Fe(NO3)3.9H2O (Merck), ReNO3.H2O (Aldrich), or Cu(NO3)2.3H2O (Merck), followed by the second impregnation with palladium nitrate dihydrate to give 0.8 wt% Pd + 1.0 wt% of Co, Ni, Fe, Re, or Cu catalysts. After metal loading, samples were dried at 110 °C for 2 h, 130 °C for 3 h, and then calcined at 400 °C for 2 h. Catalysts were assigned as Pd/HZSM-5, Pd–Co/HZSM-5, Pd–Ni/HZSM-5, and so on. To obtain the active catalysts, the samples were reduced in-situ under pure hydrogen flow at 400 °C for 2 h prior to the activity tests.

Physico-chemical characteristics of catalysts were investigated by various methods, including nitrogen physiosorption (BET), x-ray diffraction (XRD), transmission electron microscopy (TEM), ammonium temperature programmed desorption (NH3-TPD), temperature programmed reduction (TPR), hydrogen pulse chemisorption (HPC). Coke formation was studied by the method of thermogravimetric analysis (TGA). Catalytic activity in n-hexane isomerization was tested in a micro-flow reactor under atmospheric pressure at 250 °C, molar ratio of H2: n-hexane of 9.2 mol%; feed flow of 7.5 L h−1, and catalyst weight of 1.5 g. The reaction mixture was analyzed on the GC Agilent Technologies 6890 Plus with a FID detector, and DB 624 column with 30 m of length and 0.32 mm of outer diameter.

3. Results and discussion

3.1. Influences of additives on properties of Pd/HZSM-5 catalyst

It can be seen from figure 1 that XRD patterns of all catalysts with and without additives are similar and contain only characteristic peaks of HZSM-5 at 2θ = 7.9°, 8.8°, 23.1°, 24.1°, 29.1°. In XRD spectra of modified samples, no new peak has been found. These facts indicated that in these catalyst samples, Pd, Co, Ni, Fe, Re, or Cu species may exist in quite dispersed states.

Nitrogen physiosorption result revealed that the BET specific surface area of HZSM-5 and Pd/HZSM-5 were slightly different (353 and 298 m2 g−1, respectively). The small decrease in the BET specific area of Pd/HZSM-5 might come from the 0.8 wt% loading of palladium.

One can expect an enhancement in catalyst acidity based on the promotive effect of the second metal [8]. In fact, insertion of the second metal onto Pd/HZSM-5 catalyst resulted in an increase of acid strength and total density of medium and strong acid sites except for Co introduction. It is worth to note that there are very strong acid sites with ammonia desorption peaks at temperature higher than 500 °C for Pd–Ni/HZSM-5 and Pd–Re/HZSM-5 catalysts. From table 1 it can be seen that Pd–Co/HZSM-5 catalyst possessed the lowest density of medium and strong acid sites, while Pd–Ni/HZSM-5 exhibited the highest one. Similar result was also found in the study of Ogura [8]. According to this work, Co insertion onto Pd/HZSM-5 catalyst did not change its acidity considerably, as revealed by NH3-TPD data.

It has been shown in TEM images (figure 2) that HZSM-5 zeolite has pore diameter of about 0.6 nm. There are two types of Pd clusters existed in Pd/HZSM-5 catalyst: inside and outside the pore with the dimension of 0.57 nm and 7.36 nm, respectively (figure 2(a)). It is hard to see the geometric effect toward the metal crystallite inside the pore by TEM. However table 1 showed that addition of Co, Ni, Fe, or Re caused particle size of metals outside the pore to be smaller (∼5 nm compared to 7 nm) and the metal particle size did not change under reaction and oxidized conditions, as seen in figures 2(g) and (h).

It indicated that the additives showed ensemble effects to Pd/HZSM-5 catalyst. According to Gucci [9], in bi-metallic supported catalysts, the less reducible component, which strongly interacts with the support, may stabilize the second,
**Table 1.** Dimension of metal cluster observed by TEM ($d_{\text{TEM}}$), hydrogen uptake determined by HPC, temperature of maxima of NH$_3$-TPD peaks ($T_{\text{max,NH}_3\text{-TPD}}$), and acid density of catalysts.

| Catalyst            | $d_{\text{TEM}}$ (nm) | $\mu$mol H$_2$/g$_\text{cat}$ | Weak | Medium | Strong | Medium + strong |
|---------------------|------------------------|---------------------------------|------|--------|--------|-----------------|
| Pd/HZSM-5           | 7.36                   | 9.87                            | 206 °C | 273 °C | 462 °C | —               |
|                     |                        |                                 | 7.76 | 10.1   | 47.1   | 57.2            |
| Pd–Co/HZSM-5        | 4.60                   | 61.43                           | 209 °C | 283 °C | 420 °C | —               |
|                     |                        |                                 | 88.1 | 6.0    | 42.2   | 48.2            |
| Pd–Ni/HZSM-5        | 5.10                   | 2.99                            | 193 °C | 248 °C | 433 °C | 505 °C          |
|                     |                        |                                 | 96.3 | 79.1   | 79.9   | 212.6           |
| Pd–Fe/HZSM-5        | 5.17                   | 2.23                            | 204 °C | 263 °C | 467 °C | —               |
|                     |                        |                                 | 64.8 | 7.8    | 56.7   | 64.5            |
| Pd–Re/HZSM-5        | 4.93                   | 1.43                            | 215 °C | 283 °C | 446 °C | 536 °C          |
|                     |                        |                                 | 101.8 | 7.7    | 41.6   | 55.9            |
| Pd–Cu/HZSM-5        | 5–11.08                | 1.56                            | 201 °C | 290 °C | 455 °C | —               |
|                     |                        |                                 | 86.1 | 6.0    | 59.1   | 65.1            |

**Figure 2.** TEM images of different fresh and used catalysts. (a) Fresh Pd/HZSM-5, (b) fresh Pd–Co/HZSM-5, (c) fresh Pd–Ni/HZSM-5, (d) fresh Pd–Fe/HZSM-5, (e) fresh Pd–Re/HZSM-5, (f) fresh Pd–Cu/HZSM-5, (g) used Pd/HZSM-5, (h) used Pd–Co/HZSM-5.
resulted in the formation of Pd clusters. The cluster size of Pd in Pd–Cu supported on pumice (approximate 11 nm) were also seen in figure 2(f). These large clusters may come from agglomeration of Pd or Pd–Cu clusters. The cluster size of Pd in Pd–Cu supported on pumice was found to be in the range of 7–29 nm depended on the way of treatments [13]. Batista [14] confirmed that Cu insertion resulted in the formation of Pd–Cu cluster next to the Pd and Cu clusters.

The additives showed not only ensemble but also electronic effects to Pd/HZSM-5 catalyst. TPR diagram of monometallic sample Pd/HZSM-5 had only one negative peak at 80 °C (figure 3, line a), characterizing decomposition of palladium hydride formed through H-diffusion within the Pd crystallites [15].

As indicated in figure 3, Co, Cu, or Re catalysts were characterized by only one reduction peak. It can be seen from TPR diagram of the catalysts sample Co/HZSM-5 (figure 3, line f) that there is only one reduction peak at 335 °C that is characteristic of the reduction for Co3O4 [16]. The reduction peak at 450 °C of Cu/HZSM-5 sample which could be seen in figure 3 line j, is assigned to the reduction of Cu+ to Cu° [17], and the reduction peak at 370 °C of the sample Re/HZSM-5 (figure 3, line d) is attributed to the reduction of ReOx [18].

However, TPR diagrams of Ni/HZSM-5 (figure 3, line h) and Fe/HZSM-5 samples (figure 3, line b) contained double peaks, with maximum reducing temperature of 350 °C and 490 °C for the first and of 350 °C and 580 °C for the second catalysts, indicating that the reduction takes place in two stages. According to Lima [19], for the Ni/H-BEA catalyst, similar attributions may be done for the two reduction peaks on TPR diagram. The first (at 445 °C) can be attributed to the reduction of Ni2+ cations compensating framework tetrahedral anions (AlO4−) and the latter (at 555 °C) to the reduction of stable species formed by the coordination of Ni2+ cations with siloxy anions [SiO4−]. Lingaiah [11] also found that the mono-metallic Fe catalyst showed two temperature maxima at 420 °C and 620 °C which were attributed to the two-stage reduction of Fe2O3 to FeO through Fe3O4.

It should be noted that in bi-metallic catalysts, the presence of Pd shifted the reduction peaks of Co, Fe, Ni, and Re to the left, but the position of Cu reduction peak remained unchanged. It was suggested that a strong interaction between Pd and Fe presumably led to the alloy formation [11], or Pd facilitated the reduction of hardly reducible metals like Co and Ni [9]. This phenomenon could be explained by the electronic interaction between Pd and Fe, Co, Ni, and Re. In general, the strongest metal-metal interaction occurs in systems between a metal with its valence band almost fully occupied and another metal with its valence band almost empty [20]. As a result, the redistribution of charge shifts d electrons from Pd into the interface region between Pd and additives. Therefore, due to the shifts of d electrons from Pd into the interface Pd–Co, Pd–Ni, Pd–Fe, and Pd–Re, the maximum reduction temperatures of Co, Ni, Fe, and Re were shifted to the lower temperature region, as seen in figure 3.

Hydrogen pulse chemisorption (HPC) results (table 1) indicate the amount of hydrogen uptake of catalysts. The number of 9.87 μmol H2/gcat of Pd/HZSM-5 corresponds to the Pd dispersion of 23% by the hydrogen dissociative adsorption model. In bi-metallic catalysts, this amount was varied depending on the metallic promoter. Pd–Co/HZSM-5 catalyst possessed high hydrogen uptake while the rest exhibited less, even less than Pd/HZSM-5. This could be understood by the TPR result (figure 3). In the catalyst reduction condition of 400 °C from the HPC procedure method, Co oxide was totally reduced to Co metal while oxides of nickel and ferrous were partially transferred to metallic nickel and ferrous, predominant part is still remained in oxide states. For the remaining two catalysts, less hydrogen uptake might come from the lower hydrogen affinity of rhenium [21] and copper [22].

Figure 3. TPR diagram of different catalysts. (a) Pd/HZSM-5; (b) Fe/HZSM-5; (c) Pd–Fe/HZSM-5; (d) Re/HZSM-5; (e) Pd–Re/HZSM-5; (f) Co/HZSM-5; (g) Pd–Co/HZSM-5; (h) Ni/HZSM-5; (i) Pd–Ni/HZSM-5; (j) Cu/HZSM-5; (k) Pd–Cu/HZSM-5.
3.2. Influences of additives on activity of Pd/HZSM-5 catalyst in n-hexane isomerization

It can be seen from table 2 that among the studied catalysts, Pd–Cu/HZSM-5 exhibited the lowest conversion and stability. It may related to the formation of Pd–Cu agglomerated cluster and the less hydrogen chemisorption of Cu, leading to the lack of metallic sites for hydrogen spill-over phenomenon, which is favourable for isomerization reaction and stability. The net electron transfer from Pd to Co, Ni, Fe, or Re caused Pd more electron affinity that enhanced adsorption of n-paraffin and hydrogen on metallic Pd sites. As a result, it should lead to an enhancement of catalytic activity and stability. The activities of catalysts promoted by Co, Ni, Fe, or Re is approximately the same and was found to be higher than that of the non-promoted catalyst.

It can be observed from table 2 that the addition of Co and Ni to the Pd/HZSM-5 led to a significant increase in its stability and its catalytic activity has not changed during 30 h on stream. This can be explained that in the promoted catalysts by Co and Ni, palladium is divided into cluster of small dimension (~5.0 nm) as TEM analysis showed and the adsorptions of n-paraffin and hydrogen on metallic Pd sites were enhanced. It can be seen from table 1 that the catalyst modified by Co is characterized by the highest hydrogen uptake and the smallest Pd particle size, which are favourable for isomerization reaction, exhibiting the highest isomerization selectivity and the most stable catalyst. At 250 °C, Pd–Co/HZSM-5 gave n-hexane conversion of ~60%, i-hexane selectivity of ~94%. All of these factors confirmed the important role of geometric and electronic effects caused by additives in bi-metallic system.

Micrograph of used catalysts (figures 2(g) and (f)) showed that no evidence of metal phase agglomeration on mono- or bi-metallic catalysts could be found. This means that catalyst deactivation may not come from the sintering of Pd clusters, but may be related to coke formation on the catalyst. From table 2 it could be seen that catalyst modification by Co, Ni, Fe, and Re led to an increase in catalyst stability, while that by Cu expressed the opposite effect. It was observed that Pd–Cu/HZSM-5 was stable for only 1 h compared to 9 h for Pd–Re/HZSM-5, 16 h for Pd–Fe/HZSM-5, and over 30 h for Pd–Co/HZSM-5 and Pd–Ni/HZSM-5 samples.

There is also a connection between catalyst stability and its acidity. Pd–Re/HZSM-5 catalyst possessed high acidity and low hydrogen uptake that led to the high coke formation during short time on stream, 9 h. A similar phenomenon happened with Pd–Fe/HZSM-5, but it lasted longer, 16 h with less coke content because of its lower acidity compared to Pd–Re/HZSM-5. The highest coke content observed on Pd–Re/HZSM-5 and Pd–Ni/ZSM-5 may be due to the existence of very strong acid centres as seen in table 1.

It was observed that addition of all additives led to the increase of the coke-resistance of Pd/HZSM-5 catalyst. For mono-metallic catalyst Pd/HZSM-5, activity was reduced by 30% when only 0.16 wt% cokes was formed, but for modified catalysts deposited coke amount increased up to 0.62–3.29 wt%. However, even though the amount of formed coke on bi-metallic catalysts is more than 1 wt%, their catalytic activity remained unchanged. According to Yang [20], coke removal mechanism is as follows: hydrogen adsorbs on active sites first then reacts with the nearby coke. It can be assumed that the coke-resistance of Pd catalyst modified by Co related to their high hydrogen adsorption capacity and low acidity. But in the case of Pd–Ni/HZSM-5, coke-resistance may be related to the state of nickel oxide. TPR result indicated that in the catalyst reduction condition of 400 °C, the predominant part of nickel oxide just partially being transferred to nickel metal still remains in oxide state, which can facilitate dehydrogenation–hydrogenation reactions for palladium in order to supply and consume olefin to be fit with special high acidity of the catalyst. It is also in good connection with the hydrogen spill-over phenomenon which has been promoted by electronic and geometric effects in bi-metallic system.

Table 2. n-Hexane conversion (X_{n-C6}), isomer selectivity (S_{i-C6}), isomer yield (Y_{i-C6}), stability (τ), and coke content (C) of the catalysts at optimal temperature (250 °C).

| Catalyst | X_{n-C6} (%) | S_{i-C6} (%) | Y_{i-C6} (%) | τ (h) | C (%) |
|----------|-------------|-------------|-------------|-------|-------|
| Pd/HZSM-5 | 56.9 | 86.5 | 49.3 | 4 | 0.16 |
| Pd–Co/HZSM-5 | 59.9 | 93.6 | 56.1 | >30 | 1.02 |
| Pd–Ni/HZSM-5 | 60.3 | 90.6 | 54.3 | >30 | 1.54 |
| Pd–Fe/HZSM-5 | 65.9 | 89.1 | 58.7 | 16 | 0.97 |
| Pd–Re/HZSM-5 | 64.3 | 92.9 | 59.7 | 9 | 3.29 |
| Pd–Cu/HZSM-5 | 46.2 | 83.1 | 38.5 | 1 | 0.62 |

4. Conclusion

Co, Ni, Fe, and Re exhibited geometric and electronic effects toward Pd/HZSM-5. On these bi-metallic systems, Pd was stabilized in highly dispersed state and, on the contrary, the reduction ability of these hardly reducible additives was facilitated by Pd. Insertion of Cu onto Pd/HZSM-5 catalyst led to the formation of Pd–Cu agglomerated clusters and Pd presence did not facilitate Cu reducibility. It was found that Co, Ni, Fe, and Re were effective promoters for Pd/HZSM-5 catalyst, but Cu expressed a negative influence on its activity and stability.

Addition of additives resulted in the improvement of coke-resistance for Pd/HZSM-5 catalyst. The hydrogen spill-
over phenomenon played an important role in the mechanism of coke removal. All of the studied catalysts expressed high activity and selectivity for n-hexane isomerization at low temperature (250 °C). Catalyst 0.8% Pd/HZSM-5 promoted by 1% of Co or Ni was found to be the best catalyst for n-hexane isomerization at low temperature.

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