

Pd/HZSM-5 CATALYST FOR n-HEXANE ISOMERIZATION: PROPERTIES, ACTIVITIES, AND DEACTIVATION

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Abstract - The activity of n-hexane isomerization with 0.8 %kl Pd/HZSM-5 was studied in a micro reactor in the temperature range of 225-325°C at 0.1 Mpa with the molar ratio H_2 / hydrocarbon of 5.92, n-hexane concentration of 9.2 %mol, GHSV 2698 h⁻¹ at atmospheric pressure. The catalyst owned suitable acidity, reasonable reductivity, good metal dispersion, and appropriate balance between metallic and acidic functions. The catalyst had high activity but low stability. The cause of deactivation was examined via a comparison of physico-chemical properties between a fresh catalyst and a used one. There was no metal sintering. The mono-metallic catalyst performed high activity for n-hexane hydro-isomerization but less stable. Deactivation is mainly attributed to coke formation. Catalyst activity and stability were significantly improved with activity of 0.7 MPa compared to that of 0.1 MPa at elevated pressure. The catalyst Pd-Co/HZSM-5 is capable of resisting against coke, thereby exhibiting high stability at 0.1 MPa. The highly stable and active catalyst helped to form high quality products to result in environment-friendly gasoline.

Key words - isomerate; deactivation; coke formation

1. Introduction

Global environmental concern has led to an increasing requirement for premium gasoline blends. The limitations of aromatics and olefins have reduced the octane rating and volume of gasoline which have been compensated by isomerate, alkylate, and oxygenated compounds. Among those components, isomerate, a high octane blending component from isomerization reaction of simple paraffins [1], is a good option. Isomerate contains iso-paraffins which are environment-friendly components. Several industrial processes have been developed for light naphtha isomerization from Ipsorb Isom, Hexorb Isom (Axens) to Penex and Par-Isom (UOP). Those have provided a full list of processes that allow refiners to finish their high value gasoline products.

There are three generations of catalysts which have been developed for light naphtha isomerization: Pt/chlorinated alumina, Pt/sulfated zirconia, and Pt/zeolite [2]. Chlorinated alumina catalysts have superlative activity. However, they are water delicate, non-regenerable and require an organic chloride promoter. Carbon tetrachloride must be injected into the feed to activate the catalyst [3]. The sulfated zirconia catalysts offer higher activity than zeolitic catalysts but are still a little less active than chlorinated alumina catalysts. Sulfated zirconia catalysts do require higher hydrogen to hydrocarbon ratio and so a recycling compressor and separator are currently needed. Both sulfated zirconia and zeolitic catalysts are contaminant tolerant and regenerable. Zeolitic catalysts possess lower activity so that the reaction should be run at a higher temperature. Chlorinated alumina and sulfated zirconia are customers' choice. The platinum contents for those catalysts provided by UOP in the range of 0.12 %wt to 0.33 %wt.

Zeolitic catalysts are needed to be studied for this reaction. In comparison with the other zeolitic supports HZSM-5 is becoming better [4]. It has been found that isomerization over bi-functional catalysts is influenced by the H_2 spillover phenomenon [4]. The hydrogen migrating or spilling over from the noble metal sites onto the acidic support is responsible for the promoting effect of hydrogen. However, this effect has been observed on a limited number of catalysts. Therefore, finding out new catalyst with superior hydrogen spillover effects is evaluable for isomerization reaction. Metals such as palladium has been regarded to be good for hydrogen-dehydrogenation functions as well the hydrogen spillover effect. Hydrogen can be easily dissociated on its surface. In addition, palladium can be reduced even at temperature close to ambient [5] and from practical standpoint, palladium is less expensive and rarer than platinum.

Possessing high acidity and shape selectivity, zeolite can be deactivated by many reasons:

1. Deteriorating of the active sites;
2. Pore blockage;
3. Structure transformation;
4. Metal sintering [6].

These lead to poor performance and reduce life-time of catalysts. There is no agreement in deactivation of the n-hexane isomerization catalysts; it depends on the types of catalysts. Working with Pd/H-mordenite in C_5 - C_6 hydro isomerization, Li and research group [7] pointed out that coke accumulation is the main reason for the deactivation. Besides that Chaar and Butt [8] dealt with Pt- and Pd/SAPO11 in n-heptane conversion. They confirmed the greater extent of deactivation of the palladium-based catalyst in comparison with the Pt-based catalyst. This is because Pd/SAPO11 produced a much higher proportion of cracked products over the entire temperature range. Moreover, the palladium supported on alumina was found to be critically sintered when heated in a hydrogen medium [9]. Different from platinum catalysts, the sintering kinetics of palladium-based catalysts have not been systematically studied. Therefore, a decision has been made to investigate the relationship between the Pd/HZSM-5 deactivation during hydro-isomerization of n-hexane and the catalyst properties. This is needed to develop catalyst strategies.

2. Experiments

(NH_4)ZSM-5 zeolite (CBV3024E, $SiO_2/Al_2O_3 = 30$ was distributed by Zeolyst International, USA) was calcined at 500°C for 3h to get HZSM-5. The palladium metal was supported on to HZSM-5 by impregnation method at the

content of 0.8 %wt as reported in our previous work [10]. Catalyst was named as follows: Pd/HZSM-5 means 0.8 %wt Pd on HZSM-5. Bi-metallic catalyst was synthesized by sequential impregnation with $\text{Co}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$, respectively. Then, samples was calcined at 500°C for 2 h, reduced in-situ under hydrogen pressure at 400°C for 2 h before being tested for the activity.

The characterization methods for catalysts were: BET- N_2 (by Micromeritics ASAP 2020 V4.01), SEM (by FE-SEM JEOL 7401), TEM (by TEM-JEOL-1400), XRD (by Bruker D8 advance $2\theta = 0.05^\circ$), TPR, hydrogen pulse chemi-sorption (by Altamira AMI 200), TPD (by AutoChemII 2920), and coke analysis. Activity of catalysts was tested in a micro reactor at the temperature range of $225 \div 325^\circ\text{C}$, atmospheric pressure, $\text{H}_2/\text{hydrocarbons}$ molar ratio of 5.92, n- C_6 concentration of 2 %mol, GHSV 2698 h^{-1} . The mixture of reaction products was analyzed on the GC Agilent Technologies 6890 Plus with a FID detector, and DB 624 column with 30 m in length and 0.32 mm in outer diameter.

The conversion can be expressed as follows:

$$X = \frac{\frac{n_{C_1}}{6} + \frac{n_{C_2}}{3} + \frac{n_{C_3}}{2} + \frac{n_{iC_4} + n_{n-C_4}}{1,5} + \frac{n_{iC_5} + n_{n-C_5}}{1,2} + n_{iC_6} + n_{i_2C_6} + n_{i_3C_6}}{\frac{n_{C_1}}{6} + \frac{n_{C_2}}{3} + \frac{n_{C_3}}{2} + \frac{n_{iC_4} + n_{n-C_4}}{1,5} + \frac{n_{iC_5} + n_{n-C_5}}{1,2} + n_{iC_6} + n_{i_2C_6} + n_{i_3C_6} + n_{n-C_6}}$$

The yield can be expressed as follows:

$$Y = \frac{n_{iC_6} + n_{i_2C_6} + n_{i_3C_6}}{\frac{n_{C_1}}{6} + \frac{n_{C_2}}{3} + \frac{n_{C_3}}{2} + \frac{n_{iC_4} + n_{n-C_4}}{1,5} + \frac{n_{iC_5} + n_{n-C_5}}{1,2} + n_{iC_6} + n_{i_2C_6} + n_{i_3C_6} + n_{n-C_6}}$$

The selectivity can be expressed as follows:

$$S = \frac{Y}{X}$$

RON of the isomer mixture can be expressed as follows:

$$RON = \sum_{i=1}^n v_i \times (RON)_i$$

Where:

- n_{C_1} , n_{C_2} , n_{C_3} , n_{iC_4} , n_{C_4} , n_{iC_5} , n_{C_5} , $n_{i_1C_6}$, $n_{i_2C_6}$, $n_{i_3C_6}$, n_{n-C_6} : moles of corresponding hydrocarbons C_1 , C_2 , C_3 , iC_4 , C_4 , iC_5 , C_5 , i_1C_6 , i_2C_6 , i_3C_6 , n- C_6 ;
- i_{1C_6} : 2,3- dimethylbutane;
- i_{2C_6} : 2- methylpentane;
- i_{3C_6} : 3- methylpentane;
- v_i : percent by volume of component (i) in mixture;
- $(RON)_i$: RON of component (i) in mixture.

Table 1. Surface area (S_{BET}); HZSM-5 crystallite size at $7.9^\circ(d_{zeo})$; zeolite particle dimension by Scherrer equation (d); Pd cluster size by TEM (d_{TEM}), Pd cluster size by HPC (d_{Pd}), Pd dispersity by HPC (γ_{Pd}); acidity by NH_3 TPD, and metal: acid ratio ($n_{Me}: n_A$)

Catalyst	S_{BET} m^2/g	d_{zeo} nm	d nm	d_{TEM} nm	d_{Pd} nm	γ %	$n_{Me}:n_A$	Acidity (mmol $\text{NH}_3/100\text{g}$ catalyst)			
								Weak	Medium	Strong	Total
HZSM-5	353	29.6	37.7	-	-	-	-	206 $^\circ\text{C}$	-	435 $^\circ\text{C}$	-
								80.96	-	60.69	141.65
Pd/HZSM-5	298	31.5	44.7	7.19	5.0	23.3	0.022	210 $^\circ\text{C}$	-	414 $^\circ\text{C}$	-
								78.92	10.22	47.85	136.99

3. Results

3.1. Physico-chemical properties of catalyst

Figure 1 and Table 1 exhibit the properties of the Pd/HZSM-5 catalyst. The SEM image of the catalyst showed that the material was composed of platelets with dimensions ranging from 103 to 333 nm and of much smaller particles without a specific shape as shown in Figure 1a. Values of HZSM-5 crystallite size and zeolite particle dimension varied in the ranges of 29.6 – 31.5 nm and 37.7 – 44.7 nm, respectively (Table 1). Upload metal onto HZSM-5 reduced the specific area of zeolite (Table 1) which resulted from the pore blockage of HZSM-5 through palladium addition [11].

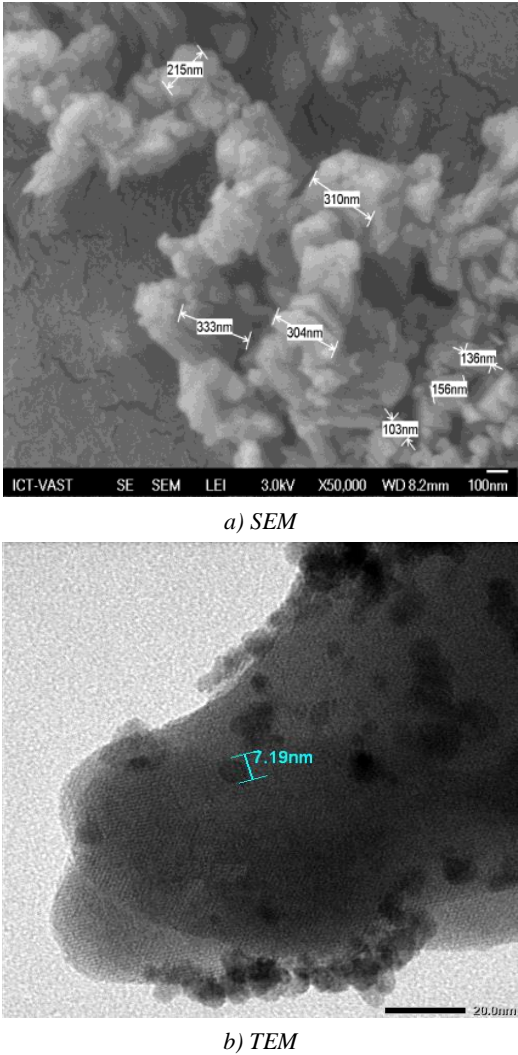


Figure 1. SEM and TEM images of Pd/HZSM-5

Figure 2 displays XRD patterns of catalysts. Two groups of peaks in the range of $2\theta = 7 - 10^\circ$ and $22 - 25^\circ$ specified the HZSM-5 zeolite [4]. The loading of Pd onto HZSM-5 did not affect the peak location but increased the height of the peaks and the crystallinity of HZSM-5 to some extent. This fact is probably due to the elimination of distorted aluminum sites [4]. The result also implied that the Pd may collaborate with structural or lattice defect sites preserving the HZSM-5 structure and making the configuration to be more ordered. One cannot see the peaks of Pd or Co presumably due to their low concentration.

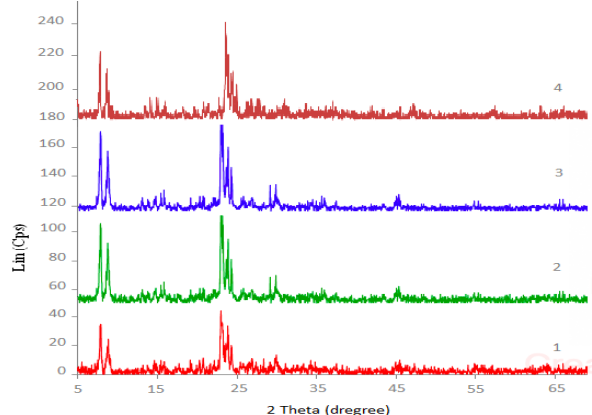


Figure 2. XRD pattern of HZSM-5 (1) and catalysts: fresh Pd/HZSM-5 (2); Pd-Co/HZSM-5 (3); used Pd/HZSM-5 (4)

Pd had a dispersity of 23.3% and a crystallite size of 5nm. The Pd cluster size (d_{Pd}) calculated by HPC and measured by TEM are relatively closed: 5 nm by HPC (Table 1) and 7.19nm by TEM (Figure 1). It has been confirmed by Occhiuzzi that 0.88 %wt Pd/ZrO₂-WO₃ catalyst has the values of 29.3nm for the Pd cluster size (d_{Pd}) and 3.8% for metal dispersity (γ_{Pd}) [12]. Another work on 2.0 %wt Pd/HZSM-5 by Thomson specified the Pd cluster size in the range of 12.5 nm with metal dispersion of 9.4% [13]. The difference between metal dispersion in this work and those in the others appeared because of the fact that the surface area of our catalyst (353 m²/g) is much higher than that of ZrO₂-WO₃ (36 m²/g) and the metal: the acid ratio in our catalyst (0.022 %wt, Table 1) is more reasonable than that in Thomson's study (2.0 %wt). A relatively small metal cluster size in this work is good for isomerization reaction [14].

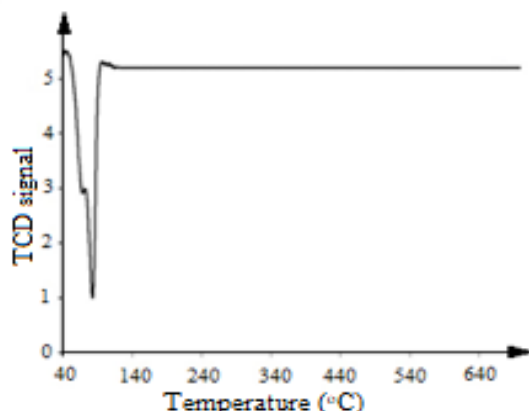


Figure 3. TPR spectra of Pd/HZSM-5 catalyst

The Pd supported on HZSM-5 is characterized by the peak at 75°C (Figure 3). The negative peak 75°C is attributed to H₂-desorption from the decomposition of a bulk palladium hydride formed through H-diffusion within the Pd crystallites [15]. The relatively low reduction peak of palladium is favourable for the catalyst in terms of pretreatment.

Table 1 shows that upload palladium onto HZSM-5 led to the reduction of acidity. This matter was declared by Ho Si Thoang [14] and Villegas [16]. This could be due to the fact that palladium did substitute for proton H⁺ of silanol group in HZSM-5 [17, 18].

It has been known that activity of a bifunctional catalyst in n-hexane isomerization is regulated by the metal-acid balance. This equivalence can be identified by the proportion of the number of metal sites n_{Me} to the number of acid sites n_A associated in the reactions. Table 1 represents that $n_{Me}: n_A$ ratio is about 0.022 for the studied catalyst Pd/HZSM-5. Alvarez and co-workers [19] claimed that an excellent $n_{Me}: n_A$ equivalence in isomerization of n-heptane over Pt/HZSM-5 should be around the number of 0.025. It has been observed that by this ratio, olefinic transitional species which were dehydrogenated by metal sites are sufficient to be provided to the number of acid sites, and that the thorough activity is regulated by the catalyst acidity. As showed in Table 1, the value of $n_{Me}: n_A$ ratio in palladium supported on HZSM-5 in this work is well correlated with the ideal number.

3.2. Catalyst activity

Catalytic activity, stability of catalyst, and calculated RON of isomers mixture at 250°C and 0.1 MPa are displayed in Table 2. Conversion, selectivity, and yield reached 56.9%, 86.5%, and 49.3%, respectively. The resulting isomer mixture has RON of 49.5 (Table 2). Comelli and co-workers represented conversion, selectivity, and yield of Pt/WO_x-ZrO₂ calcined at 700°C for n-hexane isomerization at 200°C, 240 min of 42%, 99%, and 41.58%, respectively [20]. This result is relatively comparable to the result of our work. The conversion in their work is a bit lower and the selectivity is a bit higher due to the relatively low operating temperature (200°C vs 250°C). This fact may come from the higher acidity of their catalyst in comparison with our catalyst.

Table 2. Catalytic activity, RON of isomer mixture, stability of catalysts at 250°C

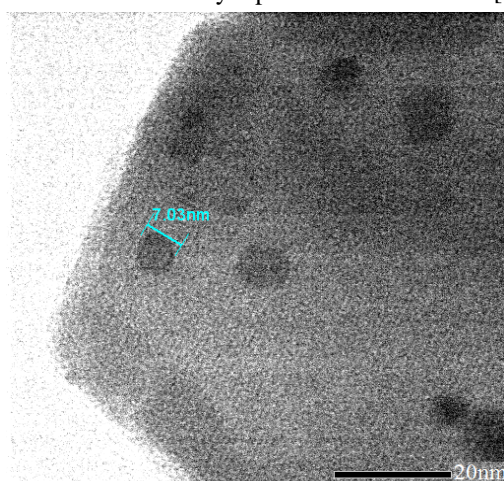
Catalyst	P (Mpa)	X (%)	S (%)	Y (%)	RON	T (h)
Pd/HZSM-5	0.1	56.9	86.5	49.3	49.5	4
	0.7	76	99	75	63	> 30
Pd-Co/HZSM-5	0.1	59.9	93.6	56.1	52	> 30

3.3. Study the cause of catalyst deactivation

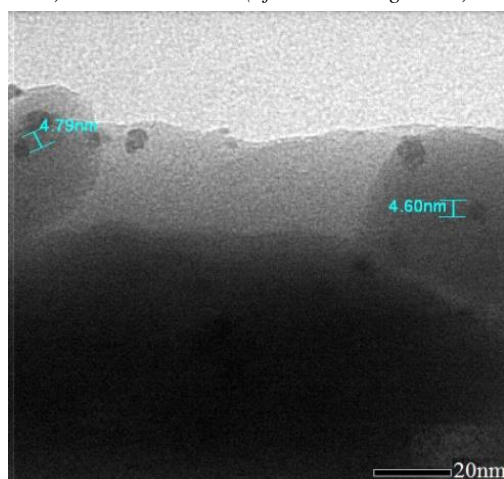
In order to replace platinum in the n-hexane isomerization catalyst, the palladium-based catalyst should not only have a high surface area, high dispersion, good reducibility, and high activity but also have reasonable stability. Four hours does not show ideal stability for a promising catalyst (Table 2).

As mentioned earlier, there are many causes of catalyst deactivation. The XRD pattern of the used Pd/HZSM-5

catalyst proved that the structure of carrier was not affected under reaction condition (Figure 2). Palladium seems to be strange in terms of hydrogen behavior. The palladium readily adsorbs hydrogen at room temperature to form palladium hydride as shown in Figure 3. However, the correlation of two TEM images of Pd/HZSM-5 catalyst did not confirm that metal sintering was the cause of catalyst deactivation. Palladium clusters in fresh Pd/HZSM-5 catalyst in the range of 7.19nm (Figure 1b) remained unchanged in used Pd/HZSM-5 catalyst (7.03nm) (Figure 4a). Catalyst deactivation is not related to the metal sintering but the coke formation. Coke content built up to 0.16% after 4 working hours, leading to 30% reduction of activity (Table 3). Li and co-workers also found coke inside mordenite pore openings while working on C₅/C₆ hydro-isomerization [7]. They confirmed that coke amount of the catalyst discharged from the top section of the reactor was 3.0 %wt and its carbon to hydrogen ratio was 0.89 that corresponds to a formula C₁H_{1.12}. While working on platinum HY catalysts over n-hexane isomerization Ribeiro and co-workers also found that both the acid and hydrogenating sites are poisoned by coke [21]. The deactivated PtHY (6%) had a coke content of about 4.0 %wt. The mechanism of coke formation in catalysts and its nature have been widely reported in the literature [7].



a) Used Pd/HZSM-5 (after 4 working hours)



b) Fresh Pd-Co/HZSM-5

Figure 4. TEM images of catalysts

Table 3. Coke content and adsorbed hydrogen of catalysts

Catalyst	Coke content, %	Adsorbed hydrogen, $\mu\text{mH}_2/\text{g}_{\text{cat}}$
Pd/HZSM-5	0.16	8.8
Pd-Co/HZSM-5	1.02	22.7

It has been proved that hydrogen has affirmative effectiveness to n-hexane isomerization. It plays a vital role in diminishing hydrocracking and eliminating coke precursors [1]. Our work also confirmed that the hydrogen pressure has a positive order. Therefore the effect of hydrogen is not only to accelerate the reaction rate but also inhibit catalyst deactivation. The catalyst life time was remarkably increased when total pressure increased from 0.1 MPa to 0.7 MPa (Table 2). At low hydrogen partial pressure, there is less hydride transfer phenomena leading to a longer lifetime of surface intermediate. In this scene, cracking and oligomerization will prevail at short residence time; polymerization and coke formation will prevail at long residence time resulting in the failure of catalyst lifetime.

Beside changing in reaction condition, catalyst modification is another option to improve catalyst lifetime. The amount of coke in the catalyst examined in this work is not as high as in Pd/HM [7] but can slow down the catalytic activity within four hours. This is probably due to the weak coke resistance ability of the Pd/HZSM-5 catalyst. The bi-metallic catalyst was found to be effective in terms of stability improvement. In this work, Pd/HZSM-5 was modified by the second metal. The bi-metallic catalyst activity remained unchanged more than 30 hours under the same reaction condition of a mono-metallic catalyst. This is thanks to the two effects: geometric and electronic ones. The addition of a cobalt metal into the Pd/HZSM-5 catalyst reduced the metal cluster size which was clearly seen in TEM images. The metal cluster size in the mono-metallic catalyst of 7.19 nm (Figure 1b) was reduced to 4.60 - 4.79 nm in the bi-metallic catalyst (Figure 4b). Smaller palladium clusters are favourable for the hydrogen spill over phenomena [5]. The interaction between palladium and cobalt made these metals become more attractive to hydrogen. It can be clearly seen from Table 3 that adsorbed hydrogen by the mono-metallic Pd/HZSM-5 catalyst of 8.8 $\mu\text{mH}_2/\text{g}_{\text{cat}}$ was remarkably increased to 22.7 $\mu\text{mH}_2/\text{g}_{\text{cat}}$ by the bi-metallic catalyst. Hydrogen has a positive effect on both catalyst activity and coke resistance ability. Hydrogen did not only retain catalyst activity by diminishing hydrocracking and eliminating coke precursors but also promoting hydride transfer step in the bi-functional and bi-molecular mechanism. Indeed, coke content in Pd-Co/HZSM-5 built up to 1.02% which is much higher than in the ono-metallic catalyst Pd/HZSM-5 but the activity of the bi-metallic acid still remained (Table 2 and 3).

4. Conclusions

The catalyst Pd/HZSM-5 under study owned suitable acidity, reasonable reductivity, good metal dispersion, and appropriate balance between metallic and acidic

functions. Catalyst exhibited great achievement at atmospheric pressure.

Coke formation and weak coke resistance ability at atmospheric pressure of the mono-metallic catalyst are the main reasons for catalyst deactivation. Total pressure was favourable in terms of reaction conversion, reaction selectivity, and catalyst lifetime. At 0.7 MPa, The Pd supported catalyst produced the 63 RON mixture containing environment-friendly iso-paraffins and lasted for more than 30 hours. These iso-paraffin components are a good blending stock for premium gasoline. Adding the second metal (Co) with appropriate content into a mono-metallic catalyst enhanced coke the resistance ability of the Pd/HZSM-5 catalyst. The Pd-Co/HZSM-5 was believed to be stable for more than 30 hours.

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