Deep Hydrogenation of Tetralin over Pt/Pd Catalysts: Influence of Fluorine and Catalyst Preparation

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Abstract

The removal of poly-aromatics from diesel fuel has stimulated intense research because of increased stringent environmental legislation. Deep hydrogenation can greatly enhance the quality of diesel fuel. Platinum and palladium catalysts are well known as noble metals widely used in the hydrogenation reaction at low temperatures. The addition of F was found to increase sulfur tolerance for the catalysts. The condition in catalyst preparation, such as calcination temperature and the order of impregnation between metal and F-promoter has an effect on the activity and properties of the catalyst. The purpose of this work was to investigate the influence of catalyst preparation on deep hydrogenation of tetralin over Pt/Pd catalysts. A series of mono- and bi-metallic catalysts (with and without F-promoter) were prepared by incipient wetness impregnation and calcined at different temperatures (250, 300 and 350°C). The hydrogenation reaction was carried out at 275°C with a total pressure of 300 psig. The results showed that the activity of tetralin hydrogenation decreased in the order of Pt > Pd > PtPd. The addition of F increased the activity for Pd/Al_2O_3 and $PtPd/Al_2O_3$ but decreased the activity for Pt/Al_2O_3. For the order of impregnation, the catalyst prepared by adding metal before F gave a better catalytic activity than the ones prepared by adding F before metal. The suitable calcination temperature for unpromoted catalysts, F-promoted Pd, and F-promoted PtPd catalysts was 350°C while the suitable calcination temperature for F-promoted Pt catalyst was 300°C. TPR showed strong interaction between metal and support when F was added to Pd catalysts. For Pt catalysts, TPR results indicated that the metal was already reduced during the calcination of F precursor. The sulfur tolerance of the catalyst will be further investigated.

Introduction

The more stringent environmental legislation for diesel emissions in exhaust gases demands new diesel fuel specifications, including lower level of sulfur, aromatic content, and higher cetane number. High aromatic content in diesel fuel has been recognized to cause low fuel quality and formation of undesired emissions in exhaust gases. In order to reduce the harmful emission from exhaust gases, the amount of particulate matter (PM) emissions in diesel can be reduced by decreasing the sulfur and aromatic content of the fuel which raises the cetane number [1]. Because of the health hazards associated with these emissions, environmental regulations governing the composition of diesel fuel are being tightened in both Europe and the United States, leading to limitations on aromatics. As a result of these stringent environmental regulations, the technology for hydrotreating process for aromatic reduction in the middle distillates has received considerable attention in recent years.

From the previous studies, naphthalene hydrogenation has been widely used as a model reaction for evaluating hydrogenation properties. However, the hydrogenation of monoaromatics is more difficult than that of polyaromatics, so we have chosen tetralin as

the model molecule to test the catalytic performance of catalysts for the deep hydrogenation of aromatics. Tetralin hydrogenation is rarely reported, although it represents the simplest form of partly hydrogenated polyaromatics and is typically incorporated as a sequential reaction step in naphthalene hydrogenation.

In 2003, the effect of preparation method on the tetralin hydrogenation of NiW/zirconium-doped mesoporous silica catalysts was studied by Eliche-Quesada and coworkers [2]. They found that the order of impregnation affected the metal dispersion and the nature of the active phases. Recently, we [3] studied the competitive hydrogenation of polyaromatic hydrocarbons on bimetallic PtPd catalysts. We found that the addition of fluorine has a positive impact on the activity when sulfur was presented in PtPd. Since fluorine is an electronegative atom, the replacement of OH groups by fluorine made the metal electron deficient [4]. As a result, it enhanced sulfur tolerance of the catalyst. But the addition of fluorine can cause lower metal dispersion and the orders of impregnation affect metal dispersion. Besides, the addition of a second metal (e.g. Pt-Pd or Pt-Ge) was found to enhance the sulfur tolerance. This promotion has also been ascribed to a change in the electronic properties. It has been shown that the addition of germanium to platinum decreases the rate of aromatic hydrogenation, whereas the addition of palladium to platinum gives higher hydrogenation activity. It was concluded that the decrease in metal-S bond strength is not a sufficient condition to obtain high aromatic hydrogenation activity in the presence of H_2S [5]. Moreover, the effect of catalyst preparation on aromatic hydrogenation process is critical and still limited. Therefore, this present work is an attempt to elucidate the optimal parameters in catalyst preparation of platinum and palladium for tetralin hydrogenation, such as calcination temperatures and the order of impregnation between metal and F-promoter on a γ-alumina support. A series of mono- and bi-metallic catalysts (with and without F) was prepared by incipient wetness impregnation method and calcined with different temperatures at 250, 300 and 350°C. TPR and hydrogen chemisorption were used to explain the effect of preparation conditions on the reduction properties and metal dispersion of the metals. The reaction was carried out at 275°C with a total pressure of 300 psig and a H_2/aromatics molar ratio of 25. The relationship of catalyst properties to catalytic activity was also investigated.

Experimental

Catalyst Preparation

Commercial gamma-alumina support (γ-Al_2O_3, Saint-Gobian NorPro Corp, surface area 274 m^2/g, pore volume 1.11 ml/g and pore diameter 104 Å) was ground and sieved to 40-70 mesh to avoid internal mass transfer limitation. Pt and Pd metals were loaded on gamma-alumina using conventional incipient wetness impregnation technique (IWI) of hydrogen hexachloroplatinate hydrate (Acros) and palladium chloride (Carlo), dissolved by distilled water and concentrated hydrochloric acid, respectively. The metal weight loadings were adjusted in order to have the same total metal molar fraction in all catalysts. 1.6 wt% Pt, 0.8 wt% Pd for monometallic, and 0.4 wt% Pt - 0.6 wt% Pd co-impregnation for bimetallic catalysts on gamma-alumina with and without 3 wt% F-promoter (Unilab) were prepared by varying calcination temperatures and orders of impregnating between metal and F. After the impregnation, the catalyst was dried under an ambient temperature for 4 h, then dried in an oven at 110 ºC overnight, and finally calcined in a furnace with different calcination temperatures at 250, 300 and 350 ºC with a heating rate of 10ºC/min for 2 h. In catalyst preparation, it was observed that the different composition and the order of impregnation gave different colors. In particular, all Pt catalysts had a yellowish color, similar to the color of Pt impregnating solution. Pd/Al_2O_3 and PtPd/Al_2O_3 catalysts had an

orange color, similar to the color of the precursor solutions. By contrast, the addition of F, the Pt-F/Al$_2$O$_3$, Pd-F/Al$_2$O$_3$ and PtPd-F/Al$_2$O$_3$ became grey after calcinations. In addition, the F-Pt/Al$_2$O$_3$, F-Pd/Al$_2$O$_3$ and F-PtPd/Al$_2$O$_3$ catalysts in which F was added after metal were darker in color than the ones prepared by adding F before metals. The comparison of metal dispersion and catalytic activity for TL conversion is shown in Table 1.

Catalyst Characterization

Temperature Programmed Reduction (TPR)
      Temperature programmed reduction was carried out in a 1/4" O.D. quartz reactor. Prior to the test, 50 mg of catalyst was packed in the reactor. For Pd and PtPd catalysts, dry ice was used to cool the sample to 10°C since PdO is an easily reducible oxide, even at room temperature. The TPR profiles were obtained by passing 5.0% H$_2$/Ar through the sample and wait until the signal is stable for 20 min before heating the catalyst. The TPR runs were performed with a heating rate of 10°C/min to 700°C. The effluent gas was passed through a moisture trap to remove water and detected by thermal conductivity detector (TCD).

Hydrogen Chemisorption
      Hydrogen chemisorption was performed in the same apparatus as TPR with the pulse loop of 10μl. Prior to the experiment, 50 mg of catalyst was reduced with hydrogen at 300°C for 1.5 h, to convert metal oxide into metallic metal, and then purged by nitrogen at 300°C for 0.5 h and cooled down to room temperature, after that pulse the hydrogen gas to adsorb hydrogen on the surface of the catalyst. Volumetric hydrogen chemisorption was measured at 25°C and detected by thermal conductivity detector (TCD). The dispersion, hydrogen to metal molar ratio (H/metal), was calculated based on the mole of hydrogen chemisorbed on the catalyst.

Catalytic Activity Testing

      The catalytic activity measurements were carried out in a continuous fixed bed stainless steel 3/4" O.D. reactor equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The catalytic activity was measured at the temperature of 275˚C with a total pressure of 300 psig and H$_2$/HC molar ratio of 25. 30 mg of catalyst was used in each test. The catalyst was first reduced under flowing of H$_2$ at 300 psig for 2 h. After the pretreatment, the reactor was cooled down in H$_2$ to 275˚C. Then, liquid feed was introduced to the reactor using a high-pressure pump. 1,2,3,4-Tetrahydronaphthalene (tetralin, TL, Across, 97+%) was used in this work. The products were online analyzed by a HP6890 gas chromatograph with FID using HP-5 column.

Results and Discussion

Characterization of Catalysts

Temperature Programmed Reduction (TPR)
      The TPR was utilized to study the interaction of the metal on catalyst surface by the measurement of the hydrogen consumption during the reduction of the oxides at a constant heating rate. The temperature at which reduction occurs and the number of reduction peaks depend on: oxidation state of the metals, interaction of the oxides among them, interaction of the oxides to catalyst, and catalytic action of neighbor metal present or generated during reduction [6]. From the TPR profile, it was seen that each metal exhibited

different reduction temperatures. From Fig. 1, TPR profiles of Pt/Al$_2$O$_3$, the presence of three reduction peaks in the TPR curves was observed. The low-temperature peak corresponds to the reduction of PtO$_2$ species [7]. The middle temperature peak, a maximum temperature peak at about 250°C, arises from the reduction of oxy- or hydroxychlorinated Pt species in the three-dimensional bulk phase [1]. At high temperatures, the hydrogen consumption peak is the reduction of oxychlorinated species in two-dimensional dispersive phase, with a strong interaction with alumina [8]. In comparison, as the calcination temperature increased, the chlorinated Pt was converted to PtO$_2$ and the Pt species were strongly interacted with the alumina support due to the higher reduction temperature of the first peak. However, the part of chlorine present in Pt/Al$_2$O$_3$ catalyst formed oxychlorinated species, which would be more difficult to reduce.
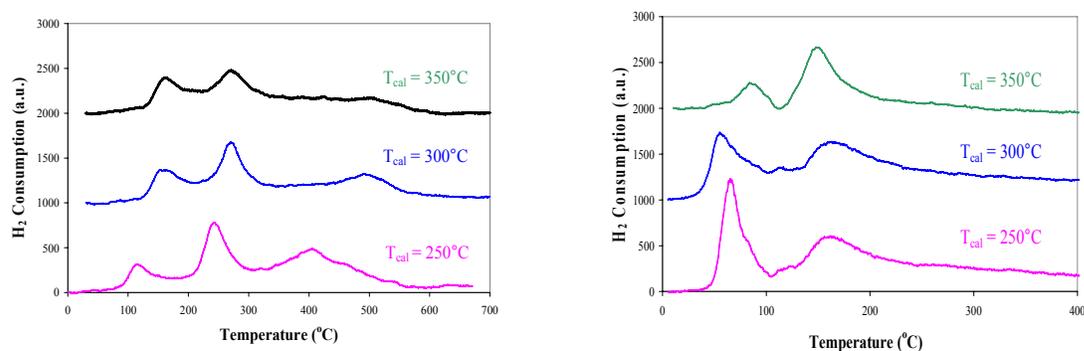

Figure 1 Temperature Programmed Reduction of Pt and Pd/Al$_2$O$_3$.

The TPR profiles of the Pd sample showed a positive peak at 60°C which corresponded to the reduction of PdO species and a little negative peak at 100°C could be due to the decomposition of Pd hydride, which was formed through H-diffusion into the Pd crystallites [1]. In addition, the TPR profile of Pd sample showed a broad reduction peak at 170°C, suggesting the presence of several Pd species. TPR profile showed high hydrogen consumption for catalyst calcined at low calcination temperature (250°C).

The TPR profile of the bimetallic PtPd catalyst could not be explained by the simple addition of the individual contribution of the two metals as shown in Fig. 2. The bimetallic PtPd catalyst showed the broad reduction peak which merges between Pt and Pd catalyst, indicating a strong interaction between the two metals which could be alloy formation [9].
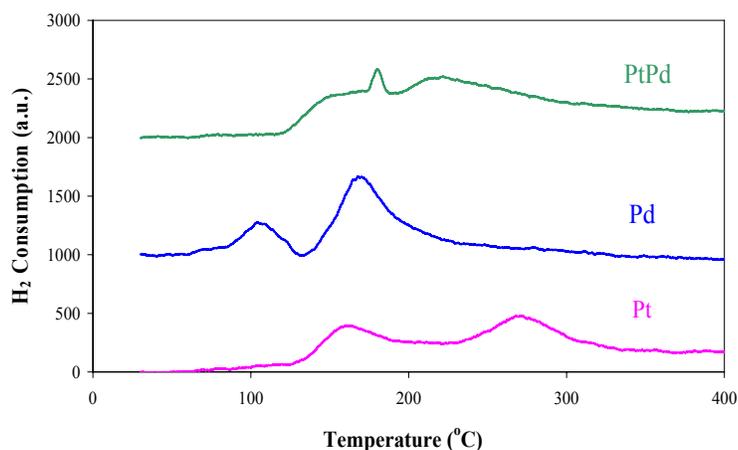

Figure 2 Temperature Programmed Reduction of Pt, Pd, and PtPd/Al$_2$O$_3$ Catalysts.

TPR profiles of F-promoted catalysts prepared with different orders of impregnation between Pt and F are shown in Fig 3. The disappearance of hydrogen consumption when the F is added, especially then one prepared by adding metal before F, is due to the auto-reduction of platinum during the calcination of F-precursor, NH_5F_2.
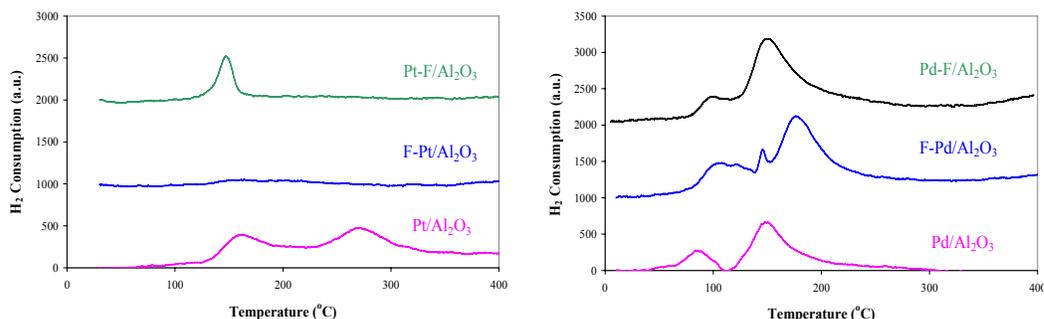

Figure 3 Temperature Programmed Reduction of order of impregnation between metal and F-promoter at 350°C calcination temperatures.

In contrast, the addition of F did not exhibit the auto-reduction during the calcination. As shown in Fig 3. The addition of F after Pd resulted in stronger interaction with the surface than the addition of F before Pd since its peaks was shifted to higher temperature. The TPR profiles of PtPd with and without F-promoter are shown in Fig. 4. The catalysts with F exhibited lower hydrogen consumption than the unpromoted catalyst. This may be due to the partial reduction of Pt during calcination of F precursor.
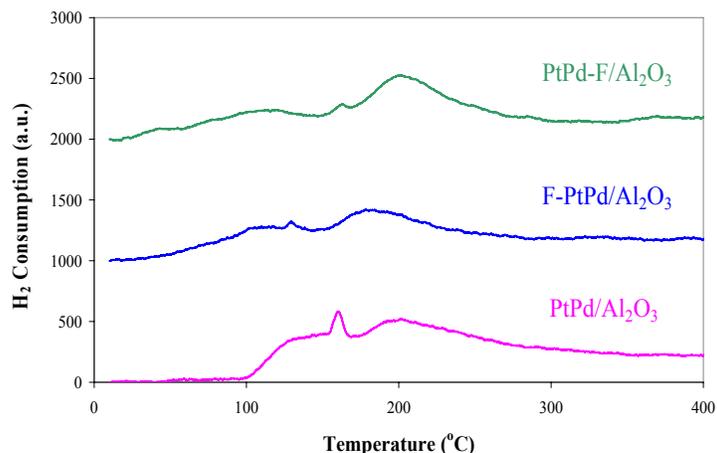

Figure 4 Temperature Programmed Reduction of order of impregnation between metal and F-promoter of PtPd/Al_2O_3 catalysts at 350°C calcination temperatures.

Hydrogen Chemisorption

Hydrogen chemisorption is a technique for determining the metal dispersion of the catalysts. The dispersion, in terms of hydrogen to metal molar ratio (H/metal), was calculated based on the mole of hydrogen chemisorbed on the metal in the catalyst. From the experiments, the addition of F gave lower metal dispersion than un-promoted in which F was added before metal in both mono- and bi-metallic catalyst but gave higher metal dispersion in which metal was added before F in both mono- and bi-metallic catalyst, at higher calcination temperature. Since, fluorinated aluminas are more hydrophobic and tend to lose surface area more easily than the parent alumina supports. These changes seem to

be adversely affecting the metal dispersion during the calcinations [5]. So, the order of impregnation of metal before F can enhance the metal dispersion which may provide strong interaction with the surface and the higher calcination temperature, the higher metal dispersion.

Table 1 Comparison of metal dispersion and catalytic activity for TL conversion

Catalyst	Order of impregnation	H_2 Chemisorption (H/M)			TL Conversion (%)		
		Calcination temperature (°C)			Calcination temperature (°C)		
		250	300	350	250	300	350
Pt/Al_2O_3	Pt	0.46	0.52	0.54	75.91	73.00	78.64
$Pt-F/Al_2O_3$	F, Pt	0.33	0.43	0.30	36.75	38.82	30.38
$F-Pt/Al_2O_3$	Pt, F	0.49	0.58	0.44	58.23	46.98	35.68
Pd/Al_2O_3	Pd	0.32	0.47	0.48	28.93	42.42	45.77
$Pd-F/Al_2O_3$	F, Pd	0.3	0.32	0.35	13.00	32.19	51.04
$F-Pd/Al_2O_3$	Pd, F	0.42	0.44	0.61	33.63	38.06	54.72
$PtPd/Al_2O_3$	PtPd	0.34	0.36	0.41	15.36	26.64	34.21
$PtPd-F/Al_2O_3$	F, PtPd	0.14	0.14	0.17	21.47	26.95	39.42
$F-PtPd/Al_2O_3$	PtPd, F	0.18	0.38	0.43	13.70	31.48	46.96

Catalytic activity measurement

From Table 1, it was seen that Pt had the highest tetralin conversion while Pt with F-promoter had the lowest tetralin conversion corresponding with the metal dispersion of Pt. It was observed that the addition of F reduced the metal dispersion for Pt catalysts. However, in the case of Pd and bimetallic PtPd catalyst, the addition of F enhanced the catalytic activity, especially the ones prepared by impregnation of metal before F, which also corresponded to the degree of metal dispersion. In most of the cases, when the calcination temperature was increased, the metal dispersion was increased, thus the catalytic activity was enhanced.

Conclusions

In this work, the investigation on the influence of fluorine and catalyst preparation by performing sequences of TPR and hydrogen chemisorption showed that the activity depended on the degree of metal dispersion. For unpromoted catalysts, the activity of tetralin hydrogenation decreased in the order of Pt > Pd > PtPd. The addition of F increased the activity for Pd/Al_2O_3 and $PtPd/Al_2O_3$ but decreased the activity for Pt/Al_2O_3. This was due to the decrease in Pt dispersion when F was added. For the order of impregnation, the catalyst prepared by adding metal before F gave a better catalytic activity than the ones prepared by adding F before metal. The suitable calcination temperature for unpromoted catalysts, F-promoted Pd, and F-promoted PtPd catalysts was 350°C while the suitable calcination temperature for F-promoted Pt catalyst was 300°C. Moreover, TPR results indicated the possibility of alloy formation of the bimetallic Pt-Pd catalyst. From the

results of this study, it was shown that the catalyst preparation is an important role for the product distribution.

Acknowledgements

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