

Effect of supports on HDS activity of Au-Pd catalysts

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Received 10 July 2006; revised 20 March 2007

The Au-Pd catalysts have been used successfully for thiophene hydrodesulfurization (HDS). The effects of Al_2O_3 , $\text{TiO}_2\text{-Al}_2\text{O}_3$, $\text{ZrO}_2\text{-Al}_2\text{O}_3$ and $\text{CeO}_2\text{-Al}_2\text{O}_3$ supports on HDS activities of Au-Pd catalysts have been investigated. The results show that Au-Pd catalysts supported on mixed oxide exhibit much higher HDS activity and stability than that of the Au-Pd/ Al_2O_3 catalyst. $\text{TiO}_2\text{-Al}_2\text{O}_3$ is the best support among these mixed oxides. As compared with Au-Pd/ Al_2O_3 catalyst, Au-Pd/ $\text{TiO}_2\text{-Al}_2\text{O}_3$ catalyst has higher acid density and acid strength, and active surface area to absorb higher amounts of H_2 and CO.

IPC Code: Int. Cl.⁸ B01J23/44; B01J23/52; C10G25/05

Hydrodesulfurization (HDS) of petroleum feedstocks is one of the important processes in petroleum industry to produce clean fuels^{1,2}. Environmental restrictions on petroleum products to limit the sulfur level in fuels to 50 ppm or lower necessitate new generation HDS catalysts. The development of new HDS catalysts, which exhibit higher activity than commercial CoMo/ Al_2O_3 HDS catalyst, will lead to obtaining fuels with lower sulfur content in petroleum industry^{3,4}. It is known that noble metal catalysts have high catalytic performance as new HDS catalysts for petroleum^{5,6}. The nanometer gold catalysts arouse widespread interests as they exhibit good catalytic properties on CO low-temperature oxidation⁷, gas-phase epoxidation of propylene⁸, liquid phase selective oxidation⁹, photochemical degradation of azo-dye¹⁰, etc. Venzia *et al.*^{11,12} used Au-Pd catalyst in HDS of thiophene using Au-Pd bimetal catalyst supported on Al_2O_3 , SiO_2 and $\text{Al}_2\text{O}_3\text{-SiO}_2$. They discovered that the effect of supports on HDS performance of thiophene over Au-Pd catalyst is large, and the HDS activity of Au-Pd can be improved by changing support.

We report here the catalytic performance of Au-Pd supported on Al_2O_3 and mixed oxides for the HDS of thiophene.

Materials and Methods

$\text{TiO}_2\text{-Al}_2\text{O}_3$ mixed oxide was prepared by coprecipitation. 16.5057 g $\text{Al}(\text{NO}_3)_3\cdot\text{H}_2\text{O}$ was added to 22.2 mL TiCl_4 acid solution (0.989 mol/L). Then, 200 mL urea (5.5 mol/L) was slowly added to it. The

mixture was refluxed for 4 h at 368 K, filtered and washed with deionized water to remove Cl^- ions. The obtained sample was dried at 393 K overnight and calcined at 773 K for 4 h. $\text{Ce}(\text{NO}_3)_4$ (or $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$) and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ were used as $\text{CeO}_2\text{-Al}_2\text{O}_3$ (or $\text{ZrO}_2\text{-Al}_2\text{O}_3$) mixed oxide precursor, respectively. The preparation process was the same as for $\text{TiO}_2\text{-Al}_2\text{O}_3$. TiO_2 (or CeO_2 , ZrO_2) and Al_2O_3 were used in 1:1 mole ratio.

For preparing Al_2O_3 , 14.7110 g $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was dissolved in the 20 mL deionized water, heated to 368 K and stirred. $\text{Al}(\text{OH})_3$ was precipitated using 5wt% ammonia solution by continuous stirring at 368 K for 4 h. The precipitate was vacuum-filtered and washed with deionized water thoroughly. Then, it was dried at 393 K overnight, and subsequently calcined at 773 K in air atmosphere for 4 h.

The catalysts were prepared by deposition-precipitation method. The supports were dispersed in an aqueous solution of $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ and PdCl_2 . pH of the suspension solution was maintained at 9-10 using 0.1 M NaOH solution and stirring continued for 2 h at 343 K. After filtration, the solid was washed several times with hot distilled water to remove residual Cl^- species. The samples were dried at 393 K overnight and calcined at 573 K for 4 h. The result of inductively coupled plasma (ICP) indicated that the load of the deposit noble metals was 0.723 wt% (Au: Pd = 1.1:2.0 wt/wt).

Activity measurements of the catalysts

The hydrodesulfurization of thiophene was carried out in a pulse microreactor over 100 mg catalyst

(60 ~ 80 mesh) diluted by inert SiO₂ particles in order to limit the radial thermal gradient. The catalyst was reduced at 623 K for 2 h in H₂ (0.5 mL/s) flow, and then cooled to the reaction temperature. Pulses of 1 μL thiophene were injected into reactor. The products were analyzed on-line by gas chromatography SP-6800 with thermal conductor detector (TCD) using polyethylene glycol-20000 column. The chromatogram contained peaks corresponding to the C₄ products and unreacted thiophene. The different components of C₄ were not separated. Therefore, only the total C₄ signal was considered in activity calculations. The conversion was calculated from the ratio of the peak areas of products over the sum of the peak areas of products and thiophene. The catalytic activities of the catalysts were expressed by the rate constants K_a . The HDS of thiophene was the typical pseudo-first-order reaction¹³. According to the Bassett equation, the rate constant K_a may be determined by:

$$K_a = \frac{F_c}{RW} \frac{P_a}{P} \frac{1}{T} \ln \frac{1}{1-x} \quad \dots (1)$$

where K_a is rate constant of reaction (mol mL/KJ g s); F_c flow rate of carrier gas (mL/S); P_a atmospheric pressure (MPa); P system pressure (MPa); W weight of catalyst (g); T reaction temperature (K); X conversion (%); R gas constant (8.314 K J/mol).

According to Arrhenius equation $K_a = A \exp\left(-\frac{E_a}{RT}\right)$, apparent activation energy E_a can be calculated from slope of straight line of $\ln K_a$ versus $1/T$.

Characterization

Powder X-ray diffractometer (German Bruker-AXS Corporation D8) ($30^\circ \leq 2\theta \leq 50^\circ$; operating at 40 kV and 30 mA) was used at room temperature using Cu K α radiation combined with the nickle filter. Au_xPd_y alloy size was calculated by Scherrer formula ($d = k\lambda / B_{\frac{1}{2}} \cos\theta$).

BET surface area and porous texture were evaluated by N₂ adsorption isotherms obtained at 77 K using an ASAP2020 (micrometrics) equipment. Before each measurement, the samples were degassed at 623 K in vacuum (0.13 Pa) for 1 h. The surface area was calculated with the BET equation.

The composition of the samples was determined by ICP, American PE Corporation's Optima 5300DV.

Temperature-programmed reduction (TPR) was carried out in the in-house apparatus over 0.1 g

catalyst. The samples were heated from room temperature to 873 K in N₂ (0.67 mL/s) at a rate of 0.17 K/s in order to remove possible impurities. After cooling to room temperature in N₂, a gas mixture consisting of H₂ and N₂ (10:90 v/v) was introduced into the system and heated at a rate of 0.17 K/s for recording the TPR spectra.

TPD was carried out with the same apparatus described for TPR. Before the measurements, the samples were firstly heated from room temperature to 673 K at a rate of 0.085 K/s and kept at 673 K for 2 h in H₂. After cooling the samples to 398 K in Ar (0.67 mL/s), pyridine (or CO, H₂) was pulsed until adsorption was saturated. Then, the samples were heated to 873 K (or 673K) at a rate of 0.13 K/s for recording the pyridine-TPD (or CO-TPD, H₂-TPD) spectra.

CO chemisorption is an efficient means for determining metal surface area of catalyst. The active surface area of catalyst was calculated using Eq. (2)¹⁴.

$$S = \frac{V_0 N A_m}{W_{cat} \times 22.4 \times 10^7} \quad \dots (2)$$

where V_0 is total amount of being absorbed CO at standard conditions (mL), A_m effective covered area of CO (cm²), N Avogadro constant (6.023×10^{23}), W_{cat} weight of catalyst (g).

H₂ chemisorption was used to measure the dispersion. Assuming atom ratio of adsorption H to Au or Pd was 1:1, the number of active atoms of noble metal per unit mass catalyst (N_a) are equal to the number of chemisorbed H atoms¹⁵. The dispersion is defined by:

$$D = N_a / N_T \quad \dots (3)$$

where N_T is the total number of noble metals atoms on per unit mass catalyst.

Results and Discussion

Effects of the supports on HDS activities of Au-Pd catalyst

To determine the structure of the catalysts in detail, the samples were investigated with XRD. The XRD patterns of the Au-Pd/Al₂O₃ and Au-Pd/TiO₂-Al₂O₃ catalysts are shown in Fig. 1. The diffraction peaks of Au_xPd_y alloy observed at $2\theta = 38.8^\circ$, 45.1° , indicated that there was interaction between Au and Pd. The peaks at $2\theta = 33.7^\circ$, 38.1° represented the diffraction peak of PdO_xCl_y and Au, separately. As compared

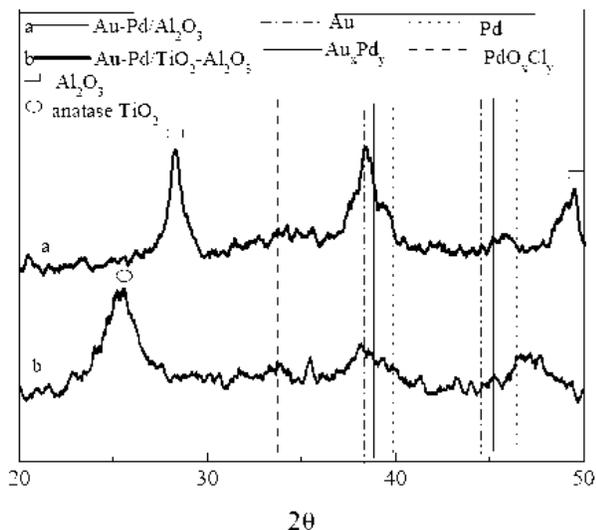


Fig. 1—XRD patterns of the catalysts

with Au-Pd/Al₂O₃, the diffraction peak area of Au over Au-Pd/TiO₂-Al₂O₃ catalyst was smaller, showing that parts of Au₂O₃ in the Au-Pd/TiO₂-Al₂O₃ catalyst were not reduced to metallic Au. The crystallite size of Au calculated with Scherrer equation in the Au-Pd/Al₂O₃ and Au-Pd/TiO₂-Al₂O₃ catalysts was 3.3 nm and 2.4 nm, respectively. The relative smaller Au crystallite showed that the TiO₂-Al₂O₃ support was advantageous to the Au dispersion. The XRD patterns also showed diffraction peak of PdO_xCl_y, which was formed during the preparation stage^{16,17}.

The activity of the catalysts is shown in Fig. 2. The catalytic activity for HDS is not dependent upon active constituents only. It has relation with support of the catalysts also. The activity of the catalyst increased gradually with the elevation of reaction temperature and Au-Pd/TiO₂-Al₂O₃ catalysts possess higher catalytic activity. The sequence of the catalytic activity was: Au-Pd/TiO₂-Al₂O₃ > Au-Pd/ZrO₂-Al₂O₃ > Au-Pd/CeO₂-Al₂O₃ > Au-Pd/Al₂O₃, which indicated that adding TiO₂ (or ZrO₂ and CeO₂) into the Al₂O₃ could improve the HDS activity of the Au-Pd/Al₂O₃ catalyst. Table 1 shows that BET surface area of Au-Pd/TiO₂-Al₂O₃ catalyst is smaller. However, its activity is higher, which shows that the BET surface area is not the primary factor for deciding the activity

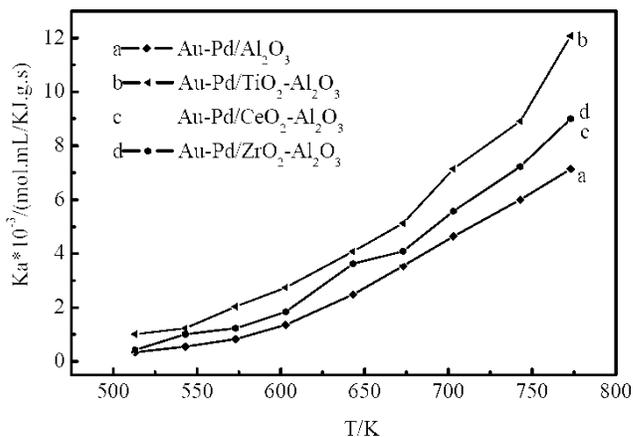


Fig. 2—Effects of supports on HDS activity of the Au-Pd catalysts.

of catalyst. Thus, catalytic activity is not correlated only with BET surface area, but also governed by the distribution of active constituent on the support and the interaction of metal-support.

Comparing with impregnation method, Au in the Au/TiO₂ catalyst prepared using deposition-precipitation method is not distributed only in the support surface. A part enters the interior support as hemispheroid¹⁸. In the Au-Pd/TiO₂-Al₂O₃ catalyst, possibly a part of Au particles are inlaid in the TiO₂-Al₂O₃ mixed oxide. The synergistic effect of Au and Pd is favorable for enhancing the affinity of Au to the sulfur compound and the activation action of Pd to hydrogen. The strong metal-support interaction of TiO₂ and Au-Pd further strengthens the coordination effect of Au and Pd, which enhances its stability making it not easy to aggregate. Therefore, at higher reaction temperature, the catalytic activity is high. The activation energy of the Au-Pd/TiO₂-Al₂O₃ catalyst for HDS reaction is smaller than Au-Pd/Al₂O₃ catalyst, as shown in Table 1. The reduction of activation energy causes the increase of catalytic activity of the Au-Pd catalysts.

Effects of supports on reduction performance of Au-Pd catalysts

The H₂-TPR can provide information concerning the reducibility of different chemical species

Table 1—The BET surface area and activation energy (E_a) of supports and catalysts

Supports	BET surface area (m ² /g)	Catalysts	BET surface area (m ² /g)	E_a (KJ/mol)
Al ₂ O ₃	261.45	Au-Pd /Al ₂ O ₃	240.76	40.55
TiO ₂ -Al ₂ O ₃	149.87	Au-Pd/TiO ₂ -Al ₂ O ₃	127.37	32.37
CeO ₂ -Al ₂ O ₃	180.02	Au-Pd/CeO ₂ -Al ₂ O ₃	177.39	38.27
ZrO ₂ - Al ₂ O ₃	239.93	Au-Pd/ZrO ₂ - Al ₂ O ₃	174.66	36.59

presented in the catalyst as well as the degree of interaction between metal-metal and metal-support. The TPR profiles of Au-Pd catalysts are shown in Fig. 3. As reported, Au_2O_3 may completely transform into metallic Au when gold catalyst is calcined¹⁹ at the 673 K. So, Au_2O_3 is completely transformed into metallic Au at 873 K. Thus, the TPR peak of Au_2O_3 in Au-Pd/ Al_2O_3 catalyst is not found. The low temperature peak appearing at 362 K in the Au-Pd/ TiO_2 - Al_2O_3 catalyst could be attributed to the reduction of Au_2O_3 . The stronger interaction between Au_2O_3 and TiO_2 results in its incomplete decomposition to metallic Au under the calcination process. No traces of any PdO phases could be found in the TPR patterns of Au-Pd samples. It might correspond to the partial reduction of PdO during the calcination process¹⁶ as well as its further reduction under the reduction atmosphere¹⁷ at ~ 303 K. The high temperature reduction peaks observed at 844 and 865 K probably correspond to the existence of PdO_xCl_y species, which were more difficult to reduce¹⁶. The high temperature reduction peak of the Au-Pd/ TiO_2 - Al_2O_3 catalyst was higher than that of the Au-Pd/ Al_2O_3 catalyst, which possibly resulted from strong metal-support interaction²¹ of Pd^{2+} in PdO_xCl_y with anatase TiO_2 . It could also be seen that the reduction peak area of the Au-Pd/ TiO_2 - Al_2O_3 catalyst was larger than that of Au-Pd/ Al_2O_3 catalyst, which could be due to the more amounts of metallic Au and Pd being reduced in the Au-Pd/ TiO_2 - Al_2O_3 catalyst. As we know, HDS of thiophene is mainly carried out over the metal sites. Obviously, more amounts of metallic Au and Pd were advantageous to catalytic reaction, which were in accordance with the results of catalytic activity.

Effects of supports on the acid property of Au-Pd catalysts

Support had the certain effect on the catalytic performances for HDS of thiophene over Au-Pd bimetal catalyst. The pyridine-TPD measurements were performed to monitor the acid strength and the acid amounts of the catalysts. The acid strength was related to the corresponding desorption temperature. The pyridine-TPD profiles of Au-Pd/ Al_2O_3 and Au-Pd/ TiO_2 - Al_2O_3 catalysts are shown in Fig. 4. The total acid amounts of Au-Pd/ Al_2O_3 and Au-Pd/ TiO_2 - Al_2O_3 catalyst were 6.475×10^{-4} mol/g and 5.918×10^{-4} mol/g, respectively. In contrast to Au-Pd/ Al_2O_3 , the total acid amounts of Au-Pd/ TiO_2 - Al_2O_3 catalyst were slightly smaller. But, the acid density of Au-Pd/ TiO_2 - Al_2O_3 catalyst was larger than Au-Pd/ Al_2O_3 , 1.7 times to the Au-Pd/ Al_2O_3 catalyst. The pyridine desorption peak

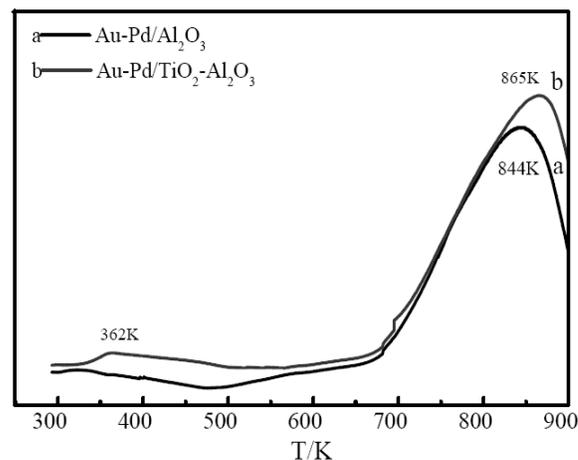


Fig. 3—TPR profiles of the catalysts.

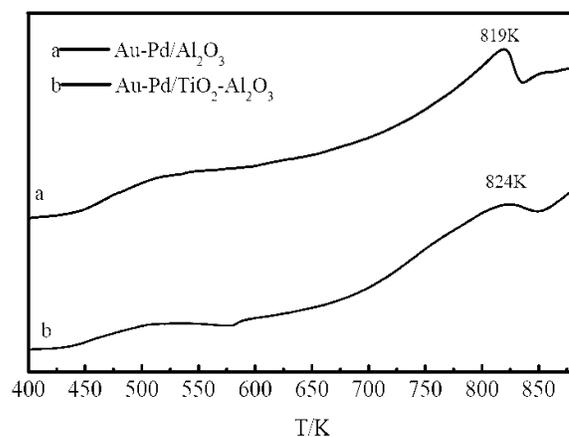


Fig. 4—Pyridine-TPD profiles of the catalysts.

temperature of Au-Pd/ TiO_2 - Al_2O_3 catalyst was higher. The acid strength increases with rise in desorption temperature. The HDS activity increased along with the increase of acid density, the activity enhancement was due to the higher acid density on surface, which was favorable for thiophene adsorption²². The higher acid strength was also advantageous to HDS reaction of thiophene²³. Brønsted acid played an important role in HDS of thiophene^{24,25}. Following a bifunctional route, both noble metal particle and Brønsted acid sites were involved for HDS reactions. Brønsted acidity of supports remarkably affected the HDS activity of the catalyst. Thiophene was adsorbed and activated on Brønsted acid sites²⁵. Acid sites did not appear in the metal but in the support. Al_2O_3 support possesses Brønsted and Lewis acid sites, while pure TiO_2 only possess Lewis acid sites. The Ti---O---Al bonds might be formed during the process of

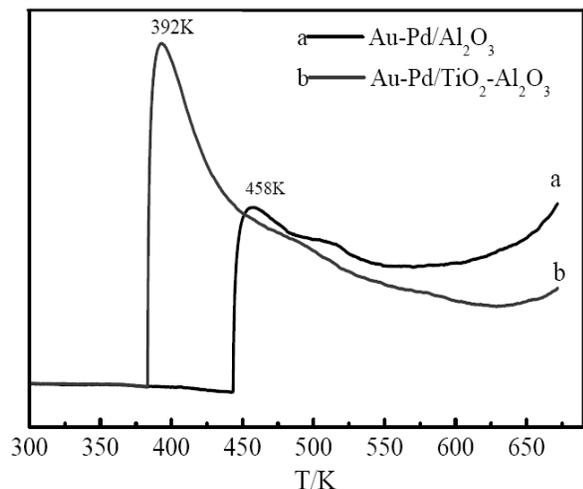


Fig. 5—CO-TPD profiles of the catalysts.

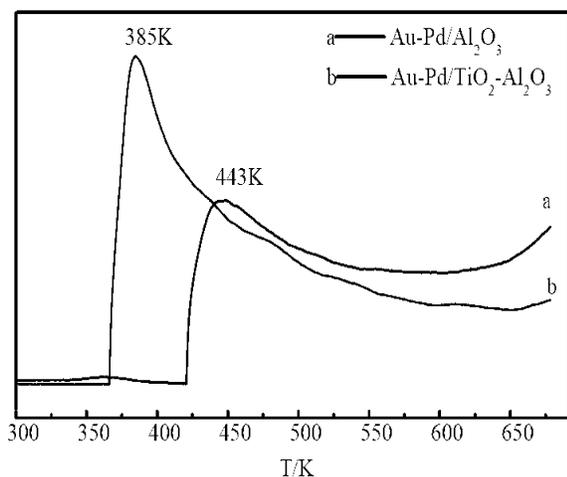


Fig. 6—H₂-TPD profiles of the catalysts.

preparing TiO₂-Al₂O₃ support. The imbalance of charges of Ti---O---Al bonds caused the formation of Ti---O (H)--- Al²⁶, which produced new Brønsted acid sites and was favorable for improving the HDS activity of thiophene.

Effects of supports on the adsorption performance of the Au-Pd catalysts

CO-TPD and H₂-TPD curves of Au-Pd/Al₂O₃ and Au-Pd/TiO₂-Al₂O₃ catalysts are shown in Figs 5 and 6, respectively. The H₂ and CO desorption peak temperature of the catalysts is similar indicating that CO and H₂ are adsorbed on the identical active sites. As compared with Au-Pd/Al₂O₃, CO and H₂ desorption temperature of Au-Pd/TiO₂-Al₂O₃ catalyst was lower and the desorption peak areas were larger.

It was reported that the CO-Pd adsorption sites were the active sites of HDS of thiophene²⁷. The HDS reaction of thiophene obeys the Langmuir-Hinshelwood model^{28,29} where adsorption-state hydrogen reacted with adsorption-state thiophene. The increase in hydrogen adsorptive amounts were propitious to improving HDS activity of thiophene.

The H₂ chemiadsorption results show that the dispersion degrees of activity sites on the Au-Pd/TiO₂-Al₂O₃ and Au-Pd/Al₂O₃ catalysts are 84% and 67%, respectively. The existence of TiO₂ could promote the dispersion of Au-Pd on the support, which is in accordance with the XRD results. The higher dispersion degree of Au-Pd shows that the catalyst has larger active surface area. Active surface area of Au-Pd/TiO₂-Al₂O₃ and Au-Pd/Al₂O₃ catalysts was 2.07 and 1.66 m²/g, respectively. Although BET surface area of Au-Pd/TiO₂-Al₂O₃ catalyst was lower than Au-Pd/Al₂O₃, the active surface was actually larger than Au-Pd/Al₂O₃. The higher dispersion degree and larger active surface area were favorable for the HDS of thiophene.

Acknowledgement

The study was supported by fund of Doctor Degree Special Scientific Research of ministry of education of P.R.China (Project 20040403001).

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