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379

Butane Dehydrogenation Reaction on Sulfur Poisoned Group 10 Metal/SiO₂ Catalysts

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Butane cracking and dehydrogenation reactions on silica supported Ni, Pt, Pd, and S, Pb modified Ni, Pt, Pd catalysts were studied via a fixed bed reaction system. Cracking reaction path prevailed when butane reaction was catalyzed by clean Ni, Pt, Pd and sulfur poisoned Ni catalysts. The addition of sulfur into Pt and Pd catalytic systems can shift the reaction path to dehydrogenation reaction. However, the deactivation problem due to carbonaceous deposit is not improved by the addition of sulfur into the catalytic system. The origin of the sulfur effect on the change of butane reaction pathway is discussed on the basis of the concentrations of Pb and S additives, oxygen perturbation effect, metal loading, carbonaceous deposit and reaction temperatures.

INTRODUCTION

The dehydrogenation and oxidative dehydrogenation of butane over various catalysts play an important role in the petrochemical industry. They represent the most important processes for obtaining butenes and butadiene. Cr2O3-Al₂O₃ had been the major catalysts used in the butane dehydrogenation process.¹⁻³ This process required operation at a temperature of 550-650 °C and suffered a serious carbonaceous deposit problem that rapidly deactivated the catalysts. Noble metal catalysts have been used to produce isobutene from butane.4-6 Much of this work is reported in patents.7-9 Undesirable reactions such as cracking of the butane and coking of the catalysts were also the problems for metallic catalysts. Sulfur has been found to suppress the hydrocracking of organic molecules on metals catalysts.^{10,11} Swift et al. demonstrated that a trace amount of hydrogen sulphide could noticeably alter the rate of carbonaceous deposition on Ca-Ni-PO4 catalyst during the butene dehydrogenation reaction.¹² If sulfur suppresses the cracking reactivity more than its poisoning of the dehydrogenation reactivity of metallic catalysts, sulfur could be a good promoter for enhancing the dehydrogenation selectivity of metal catalysts. There are only a few reports on the effect of sulfur on dehydrogenation reaction for metal catalysts. The present work is focused on butane cracking and dehydrogenation reactions on silica supported Ni, Pt and Pd catalysts as well as catalysts influenced by sulfur, in particular for Pd catalyst. The addition of sulfur does enhance the dehydrogenation selectivity of butane reaction on Pt and Pd catalysts.

EXPERIMENTAL SECTION

The catalysts were prepared by impregnating the SiO₂ support (Cab-O-Sil M-5, 200 m²/g) with an aqueous solution of PdCl₂ (Hwang-Long Drugs, ACS grade), Ni(NO₃)₂·6H₂O (Janssen), H₂PtCl₆·6H₂O (Showa Chemicals Inc.), Cr(NO₃)·9H₂O (Janssen) and/or Pb(NO₃)₂ (Janssen). Ion-exchanged Pd/SiO2 catalyst was prepared by adding an appropriate amount of PdCl₂ solution into the SiO₂ slurry at a pH value of 9-10. The pH value of the slurry was controlled by the addition of 30% ammonia water. It was stirred at room temperature for one hour, and then filtered and washed by distilled water until the pH value of the filtrate was less than 8. Sulfur ions were generated by decomposing thioacetamide in an ammonia solution at pH = 10 and 70 °C. The sulfided catalysts were prepared by adding an appropriate amount of thioacetamide solution into the catalyst slurry at 70 °C. The pH value of the slurry was adjusted to 10 by the addition of ammonia. The slurry was then dried at 100 °C and calcined in oxygen at 250 °C for 3 h.

Catalytic activity was determined on a conventional continuous flow system with a 0.5 in. outside diameter quartz tube reactor at atmospheric pressure.¹³ A sample of 0.15 g was pretreated in situ in flowing hydrogen (30 ml/min) at 350 °C for two hours. The temperature was ramped from room temperature to the desired reduction temperature at a rate of 25 °C/min. Under the standard reaction conditions, the feed was 5 vol% butane in 95 vol% nitrogen (Sun-Fu Gas Company), the flow rate was 30 ml/min., and the reaction temperatures were ranged from 250 °C to 600

°C. In a typical run, the reactor was heated to the desired temperature in a flow of He. The butane/nitrogen feed stream was passed over the catalyst for 2 minutes before a sample was taken for analysis. The catalysts were regenerated by oxidation in oxygen at 250 °C for 1 h and reduction at 350 °C for 1 h between each run to avoid the perturbation from the different amounts of carbonaceous deposit affecting the activity of the catalysts. For reactions on oxygenpredosed-Pd catalysts, oxygen was dosed into the Pd catalyst system at the reaction temperature by injecting the oxygen into the flowing helium through a port located upstream of the reactor with a gas-tight Hamilton 1010 syringe. The injection port was similar to that used in gas chromatography. A Shimadzu GC-8A was used to analyze the products with a 7 feet long 0.19% picric acid on Graphpac-GC 80/100 mesh column. Product gas concentrations were determined with a Shimadzu CR-6A integrator by comparing the peak areas to those of a standard mixture. The conversion of butane is defined as (butanein - butaneout)/butanein . 100%. The dehydrogenation selectivity is defined as 100% · (all dehydrogenated products/(butanein - butaneout) on the molar basis of butane. Butanein is the concentration of butane measured before the reactant stream enters the reactor. Butaneout is the concentration of butane measured at the outlet of the reactor.

IR spectra were taken with a Digilab FTS-155 FT-IR spectrometer and were recorded with a resolution of 2 cm⁻¹ and 256 scans at temperatures described later in this manuscript. All spectra reported here have been corrected by subtracting off the adsorption of the blank catalyst disk and the ZnSe windows. The IR cell used was of a standard design that permitted the evacuation and heating of the sample under static conditions. The 20 mm diameter sample disk was made from approximately 30 mg catalyst pressed at 5000 psi, oxidized in-situ in 1 atm O₂ at 250 °C for 2 hr, reduced in 600 torr H₂ at 300 °C for 10 hr and evacuated in 3×10^{-5} torr in a glass vacuum system for 30 min at 300 °C. The H₂ gas was refreshed twice during the reduction treatment.

Powder X-ray diffraction patterns were obtained with a Diano 8536 diffractiometer using Cu K aradiation.

RESULTS AND DISCUSSION

The activity measurement for butane dehydrogenation was studied at temperatures lower than 500 °C to avoid the perturbation of the reactivity from the SiO2 support, which has activity for butane cracking and dehydrogenation reactions at temperatures higher than 520 °C. Table 1 shows results of the reaction at 450 °C. No dehydrogenation product was observed after the initial 2 minutes of flowing butane over freshly reduced Ni, Pd and Pt/SiO2 catalysts. The hydrocarbons produced were cracking products: methane, ethane and minor amount of propane with concomitant carbonaceous deposit. The catalytic activity decayed rapidly with the increase of on stream time. This is due to the blocking of the active site by the carbonaceous deposit. Carbonaceous deposit deactivation of the catalyst is a general problem for butane dehydrogenation process.^{1,5,6} An oxygen treatment at 320 °C followed by a reduction treatment can burn out the carbonaceous deposit and recover about 80% of the catalytic activity.

The carbonaceous deposit greatly influences the activity and selectivity for butane reactions on Pd and Pt catalysts. The total n-butane conversion and butene selectivity on Group 10 metals supported on SiO₂ under the influence of carbonaceous deposit at various reaction temperatures are shown in Fig. 1. The catalysts were not reactivated by an oxidation treatment between each butane pulse in this experiment. Thus the catalyst was under the effect of carbon laydown that was produced from the cracking reaction after the first butane pulse. The conversion of butane on Ni catalyst in the presence of carbonaceous deposits was much higher than those on Pt and Pd catalysts. However, the carbon laydown did not change the reaction selectivity of Ni catalyst. The major reaction pathway of butane in the pres-

Table 1. Dehydrogenation Product Distribution (in unit of ppm) of n-Butane Reaction at 450 *C on 0.15 g SiO₂ Supported Metal Catalysts with 1 wt% of Active Species

Catabyst	1-Butene	c-Butene*	t-Butene*	Butadiene	C%*	D%*
Cr-On/SiOn	27	0	53	32	10	1
Ni/SiO ₂	0	ō	0	0	100	ò
Pd/SiO ₂	0	0	0	0	100	0
Pt/SiO2	3	0	0	0	100	trace

*: c-butene denotes cis-2-butene, t-butene denotes trans-2-butene, C% denotes conversion%, D% denotes dehydrogenation selectivity%.

ence of carbonaceous deposits on Ni metal surface was still cracking.

The dehydrogenation pathway of butane on Pd and Pt catalysts was enhanced by the carbonaceous deposits. The major dehydrogenation products included n-butene, cis-2-butene, trans-2-butene, butadiene and some isobutylene. The isobutylene signal partially overlapped with the butane signal in the gas chromatogram. The dehydrogenation selectivity was enhanced by the carbon laydown effect from near zero to about 40% at reaction temperatures of 350-450 °C on the Pd or Pt catalyst.

 Cr_2O_3 had been the major catalyst that was used in industry for the butane dehydrogenation reaction at temperatures around 500-600 °C with dehydrogenation selectivity of 60%. For comparison, we have also tested the activity of a Cr_2O_3/SiO_2 catalyst for the butane dehydrogenation reaction. Cr_2O_3 indeed has activity for the butane dehydrogenation reaction at temperatures higher than 500 °C, and has a dehydrogenation selectivity of 50% at 550 °C. It is interesting that the Pd and Pt catalysts affected by carbon laydown had a dehydrogenation activity comparable to Cr_2O_3 catalyst at a lower reaction temperature. Although the above study reveals that the carbonaceous deposits shift the butane reaction pathway to dehydrogenation, the carbon laydown is of little practical value for modifying the catalytic behavior of group 10 metals. This is because the amount of carbon laydown is not controllable.

Sulfur has been found to suppress the hydrocraking of organic molecules on the Pt catalyst. If the ability of sulfur to suppress the cracking reactivity is stronger than its ability to poison the dehydrogenation reactivity of metallic catalysts, sulfur could be a good promoter for enhancing the dehydrogenation selectivity of group 10 metal catalysts. The effect of sulfur on the catalytic behavior of group 10 metals for butane reaction at various temperatures is shown in Fig. 2. In this experiment the catalysts were not reactivated by an oxidation treatment between each butane pulse. The results show that the addition of sulfur into the Ni catalyst sys-



Fig. 1. Butane conversion and butene selectivity on 0.15 g of group 10 metal/SiO₂ catalysts at various temperatures.



Fig. 2. Butane conversion and butene selectivity on 0.15 g of sulfur perturbed 1 wt% group 10 metal/SiO₂ catalysts with S/metal ratio equals to 0.001.

tem does not change the reaction pathway of butane either. The major butane reaction pathway on a 1000 ppm sulfur doped Ni/SiO₂ catalyst was still cracking. The n-butane conversion and the reaction selectivity toward dehydrogenation products on sulfur doped Pd and Pt catalysts increase as compared with on undoped Pd and Pt catalysts shown in Fig. 1, suggesting that the rate of carbonaceous deposit on sulfur modified Pd and Pt catalysts are lower. However, the catalytic activity on sulfided Pd and Pt catalysts still decay rapidly with the increase of on stream time. Deactivation by carbonaceous deposit is still a problem for sulfur modified Pd and Pt catalysts. Note that the change of the butane reaction behavior shown in Fig. 2 is under the combined effects of both sulfur and carbonaceous deposits on metal surfaces. We will focus on the effect of sulfur on Pd catalysts in the following discussion.

Table 2 shows the results of total dehydrogenation reaction selectivity of butane reaction as a function of sulfur concentration on the Pd catalyst. The reaction products were analyzed after a two min pulse of butane had flowed over a freshly reduced catalyst at 450 °C to minimize the effect of carbonaceous deposit on the catalysts. A significant change in catalytic behavior was observed when sulfur was added into the Pd catalyst. The conversion of butane decreases from 100% to 29% with the dehydrogenation selectivity increasing from near zero to 31% when S/Pd ratio equals 0.05. The conversion was further depressed to 17% with the dehydrogenation selectivity increasing to 46% when the S/Pd ratio on the SiO2 surface was increased to 0.1. For the sulfur poisoned Ni catalyst, the reaction pathway was still toward cracking, even though the conversion rate was depressed to near zero by the sulfur poison.

A sulfur poison may alter the catalytic behavior of metallic catalysts through several ways. The sulfur may block an active site, induce a surface reconstruction and surface charge redistribution, change the oxidation states of the metal, and induce a sintering process. All these factors could contribute to the variation in reaction selectivity between cracking and dehydrogenation. However, evidence (see dis-

Adsorption of sulfur generally accelerates metal agglomeration and thereby increase the particle size of the supported metal.^{14,15} Table 3 shows the product distribution of butane reaction on Pd catalysts with various Pd loading and different method of preparation. Metal catalysts usually have larger metal particle sizes when the amount of metal loading on the support is higher. Metal catalysts prepared by the impregnation method would also have a larger metal particle size as compared with the particle size of metal catalysts prepared by the ion exchange method. However, the correlation between reaction selectivity and the amount of Pd loading for butane reaction on Pd catalysts that are prepared by the ion exchange method and by the impregnation method is similar. Moreover, the dehydrogenation selectivity is even lower when butane reaction is catalyzed by Pd catalysts with a higher Pd loading, suggesting that the increase in dehydrogenation selectivity is not correlated to the increase in metallic particle size. So the increase in dehydrogenation selectivity on sulfided Pd catalysts should not be due to metal agglomeration.

The increase in dehydrogenation selectivity of the butane reaction on low Pd loading catalysts is interesting. The particle size of a 1% Pd/SiO₂ catalyst prepared by the impregnating method is around 47 Å. The particle size of the metal with a Pd loading lower than 1% would be expected to be smaller than 47 Å. It has been reported that the electron binding energy of metal increases gradually with the decrease in metallic particle size when the diameter of the metal particle is smaller than 30 Å.¹⁶ The increase in electron binding energy suggests that the surface charge distribution of the metal with a smaller particle size has been altered by a change in the electron withdrawing potential of the nuclei. The increase in dehydrogenation selectivity of the butane reaction on a low Pd loading catalyst could be the result of the combined effects of the surface charge redistribution of met-

Table 2. Dehydrogenation Product Distribution (in unit of ppm) of n-Butane Reaction at 450 *C on 0.15 g Sulfur Perturbed 1 wt% Pd/SiO₂ Catalysts

S/Pd	1-Butene	c-Butene	t-Butene*	Butadiene*	C%*	D%*
0.005	7	22	27	0	99	trace
0.05	990	2400	3100	310	29	31
0.1	770	2000	2700	470	17	46

*: c-butene denotes cis-2-butene, t-butene denotes trans-2-butene, C% denotes conversion%, D% denotes dehydrogenation selectivity%.

Pd% (size) ^a	1-Butene	c-Butene ^b	t-Butene ^b	Butadiene	С% ^ь	D%b
1(47) ^c	0	0	0	0	100	0
0.1() ^c	220	620	770	30	64	3
0.01() ^c	320	800	1100	11	24	12
1() ^d	0	0	0	0	100	0
0.1() ^d	4	10	11	0	100	trace
0.01() ^d	230	670	770	13	24	9

Table 3. Dehydrogenation Product Distribution (in unit of ppm) of n-Butane Reaction at 450 *C on 0.15 g Pd Catalyst with Different Particle Sizes

^a (size) denotes the particle size (in unit of Å) of the SiO₂ supported Pd.

^b c-butene denotes cis-2-butene, t-butene denotes trans-2-butene, C% denotes conversion%, D% denotes dehydrogenation selectivity%.

^c Catalysts prepared by impregnating method.

^d Catalysts prepared by ion exchange method.

--: The X-ray diffraction pattern of Pd crystal was too weak to be used to estimate the particle size.

al and the low conversion of butane. It is well known that the surface charge distribution of metal can be modified by the addition of sulfur. The modification of the butane reaction selectivity by the addition of sulfur may also be the result of surface charge distribution.

Sulfur adsorption on a metal surface can block the active sites of metal and make them inaccessible to other molecules. In heterogeneous catalysis, the chemisorption of reagents is a preliminary step of a surface reaction. The reaction of sulfur with metal would also change the oxidation states of metal catalysts. However, the site blocking effect and the changing of the oxidation states of sulfided Pd/SiO₂ catalysts contribute little to the shift of butane reaction pathway. The site blocking effect of sulfur on the catalytic behavior of Pd catalysts can be simulated by putting other kinds of species onto the Pd surface where the species can strongly interact with the Pd metal. Infrared (IR) spectra of CO adsorption on Pd surface shown in Fig. 3 indicate that presorbed oxygen can block some of the Pd active sites and induce a change of the Pd oxidation state. CO adsorption on oxygen calcined Pd/SiO₂ shows IR bands at 2162 cm⁻¹ and a small hump centered at 2110 cm⁻¹ (Fig. 3a). CO adsorption on reduced Pd/SiO2 shows IR bands at 2083, 1980 and 1933 cm⁻¹ (Fig. 3b). CO adsorption on oxygen predosed Pd/SiO₂ shows IR bands at 2152, 2106, 1975 and 1952 cm⁻¹ (Fig. 3c). The appearance of the IR bands at frequencies higher than 2100 cm⁻¹ in Fig. 3c confirms that some of the surface Pd atoms were oxidized by the predosed oxygen. The intensities of IR bands at frequencies lower than 2100 cm⁻¹ in Fig. 3c are weaker than those in Fig. 3b, indicating that some Pd active sites on the reduced Pd catalyst are covered by the presorbed oxygen atom.

Table 4 shows the butane reaction products distribu-

tion on oxygen perturbed Pd catalysts. A fully oxidized Pd catalyst (oxygen calcined Pd without reduction pretreatment) did not have any catalytic activity for the butane dehydrogenation reaction. The selectivity toward dehydrogenation for butane reaction on fully reduced Pd and on oxygen predosed Pd catalysts are similar. Two aspects of the data shown in Table 4 suggest that the oxidation states of Pd catalysts and the blocking of Pd active sites play a minor role in changes in the butane reaction selectivity. First, the butane reaction selectivities on reduced Pd and oxygen perturbed Pd are similar, suggesting that the variation of the Pd oxidation states would not induce any significant difference in the



Fig. 3. IR spectra of 2.5 torr CO adsorption on (a) oxidized Pd/SiO₂, (b) reduced Pd/SiO₂, (c) reduced Pd/SiO₂ predosed with 0.3 torr of oxygen for 30 second at room temperature.

	0 .0				
1-Butene	c-Butene ^a	t-Butene ^a	Butadiene	C%ª	D%ª
trace	0	80	0	10	trace
110	330	370	0	80	1
trace	0	60	0	18	trace
110	300	360	0	80	1
	1-Butene trace 110 trace 110	1-Butene c-Butene ^a trace 0 110 330 trace 0 110 300	1-Butene c-Butene ^a t-Butene ^a trace 0 80 110 330 370 trace 0 60 110 300 360	1-Butene c-Butene ^a t-Butene ^a Butadiene trace 0 80 0 110 330 370 0 trace 0 60 0 110 300 360 0	1-Butene c-Butene ^a t-Butene ^a Butadiene C% ^a trace 0 80 0 10 110 330 370 0 80 trace 0 60 0 18 110 300 360 0 80

Table 4. Dehydrogenation Product Distribution (in unit of ppm) of Butane Reaction at 350 and 450 °C on 0.15 g Oxygen Perturbed 0.1 wt% Pd/SiO₂ Catalysts

^a c-butene denotes cis-2-butene, t-butene denotes trans-2-butene, C% denotes n-butane conversion%, D% denotes dehydrogenation selectivity%.

^b Catalyzed by fully reduced Pd.

^c Catalyzed by catalysts b but predosed the surface with 10 cc of oxygen at 350 °C.

butane reaction selectivity. Second, the partial blocking of the Pd active sites by oxygen did not induce any noticeable change in the butane reaction selectivity, suggesting that site blocking contributes little to the shift in the butane reaction pathway.

The results of butane reaction on Pb perturbed Pd catalysts further support that the variations in the butane reaction selectivity is not directly correlated to site blocking by sulfur on Pd catalysts. Table 5 shows the product distributions of the butane reaction on Pb perturbed Pd catalysts. The addition of Pb into the Pd catalysts did not change the catalytic behavior for the butane reaction when the Pb/Pd ratio is lower than 0.1. This is similar to the butane reaction on sulfided Ni catalyst systems. This result suggests that site blocking would not change the catalytic characteristics of Pd for butane reaction. However, the total conversion rate of butane reactions (including cracking and dehydrogenation reaction) dropped to 9% while the dehydrogenation selectivity increased to 22% when Pb/Pd ratio rose to 1.

The decrease of Pb/Pd/SiO₂ catalytic activity for the butane reaction is due, at least partially, to the blocking of the activity sites of Pd by Pb. The increase of reaction selectivity toward dehydrogenation products may, however, be due to the influence of several factors. A sequential reaction pathway has been suggested to explain the alkane cracking reaction mechanism.¹ The dehydrogenation products are proposed to be the reaction intermediates for the cracking products of the alkane reaction. For a sequential reaction, the selectivity toward intermediates should increase when reaction conversion decreases.¹⁷ The increase of reaction selectivity toward dehydrogenation products therefore could be a result of the lower total conversion on high Pb content Pd catalyst.

The change in the butane reaction selectivity may also be caused by the surface reconstruction of Pd induced by the addition of Pb. The X-ray diffraction patterns shown in Fig. 4 indicate that a new Pb/Pd microstructure appeared when the Pb/Pd ratio equals 1. Two new X-ray diffraction peaks appear at 38.8 and 45° when Pb/Pd ratio is increased to 1. These peaks cannot be unambiguously assigned to any species because the other X-ray diffraction peaks are too weak to be distinguished from the noise level. The species that produces the X-ray diffraction peaks at 38.8 and 45° is tentatively assigned to PbPd₃ since PbPd₃ crystals give X-ray diffraction peaks at 31.5, 38.8, 45, 50.7 and 55.9° (between the 20 range of 30-60°) with relative intensities of 20, 100, 80, 20 and 20.

According to numerous studies, sulfur adsorption is also able to induce surface reconstruction.^{18,19} The surface charge density distribution on sulfur modifed Pd surface can be altered by the surface reconstruction.^{20,21} It is known that the activity and selectivity of hydrogenolysis and isomeriza-

Table 5. Dehydrogenation Product Distribution (in unit of ppm) of Butane Reaction at 450 'C on 0.15 g Pb Perturbed 1 wt% Pd/SiO₂ Catalysts

Pb/Pd	1-Butene	c-Butene*	t-Butene*	Butadiene	C%*	D%*
0.01	0	0	0	0	100	0
0.1	17	0	61	0	80	trace
1	170	540	550	240	9	22

*: c-butene denotes cis-2-butene, t-butene denotes trans-2-butene, C% denotes conversion%, D% denotes dehydrogenation selectivity%.

tion of butane are sensitive to the change of supported metal morphology.²² The change in selectivity of butane on sulfided Pd catalysts, just like in the case of the butane reaction on Pb modified Pd catalysts, can be a consequence of a surface reconstruction and surface charge redistribution created by sulfur adsorption. Although the change in selectivity can also be a consequence of the decrease in conversion rate on sulfur poisoned Pd catalysts, the change in selectivity caused by the decrease in conversion rate can be distinguished from the factors that come from the sulfur modifica-



Fig. 4. X-ray diffraction pattern of Pb perturbed 1 wt% Pd/SiO₂ catalysts. The Pb/Pd ratio are (a) 0 (b) 0.01 (c) 0.1 (d) 1.



Fig. 5. Plot of the dehydrogenation selectivity vs. the nbutane conversion% on Pd and sulfur perturbed Pd catalysts.

tion effects. A comparison of the selectivity vs. conversion rate of butane reaction on Pd and sulfur modified Pd catalysts would reveal the contribution of sulfur effects on the selectivity variation. Fig. 5 is a plot of the selectivity vs. conversion of the butane reaction on Pd and sulfur modified Pd catalysts. The selectivity toward dehydrogenation products for the butane reaction with various conversion on sulfided Pd is about 4 times higher than those on the Pd catalyst. The promotion of dehydrogenation selectivity on sulfided Pd catalysts is apparently not simply due to the decrease in the butane reaction conversion rate.

CONCLUSIONS

From the dependence of the n-butane conversion and the dehydrogenation selectivity of butane reaction on the metal loading, the oxidation state, and the Pb, S modification of Ni, Pt and Pd catalysts, we draw the following conclusions:

1. The reaction pathway of butane on Ni, Pt and Pd catalysts is cracking. The addition of sulfur into the Pt and Pd catalytic systems can shift the reaction pathway to dehydrogenation while the reaction pathway of butane on Ni is not changed by the addition of sulfur.

2. The sulfur modified Pd catalysts could have a dehydrogenation activity that is comparable to that of the Cr_2O_3 catalyst, a commonly used commercial catalyst for butane dehydrogenation but at a much lower reaction temperature.

3. The low loading of Pd and the high loading of Pb can reduce Pd's catalytic activity toward cracking and increase its dehydrogenation activity. The effects of Pd surface reconstruction and surface charge redistribution may be applied to interpreting the change of reaction selectivity on Pd catalysts.

4. The factors induced by the addition of sulfur in Pd catalytic systems, such as the blocking of active sites, the changing of the chemical states, and metal agglomeration, contribute little to the enhancement of dehydrogenation activity for the butane reaction on sulfur modified Pd catalysts.

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Key Words

Butane; Dehydrogenation; Pd; Pt; Ni; Sulfur.

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