[Regular Paper]

Ultra-deep Hydrodesulfurization of Kerosene for Fuel Cell System (Part 2) Regeneration of Sulfur-poisoned Nickel Catalyst in Hydrogen and Finding of Auto-regenerative Nickel Catalyst

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An idea to regenerate sulfur-poisoned Ni catalyst in flowing H_2 was tried. That is, sulfur-poisoned Ni catalyst particles are mixed with ZnO fine particles in a H_2 atmosphere at 600 K, then the each poisoned catalyst particle would release a few ppb of H_2S through the H_2 atmosphere and the released H_2S would be accepted on neighboring ZnO particles. Then, a million-fold effective improvement in the regeneration of sulfur-poisoned Ni catalyst in a flow of H_2 would be realized. After only a 90 h of trial operation, sulfur-poisoned 60% Ni/ Al_2O_3 catalyst was regenerated. Applying this idea, 12.3% Ni/ZnO was prepared and tested as a model catalyst for adsorptive ultra-deep hydrodesulfurization (UD-HDS) of kerosene in a stream of H_2 containing 25% CO_2 at 600 K. Residual sulfur in the treated kerosene was not detectable (< 0.06 wt ppm) by the ready-made sensitive sulfur analyzer even after 800 h of operation. Comparing with the conventional Ni/ Al_2O_3 catalyst, the Ni/ZnO catalyst did not produce any CH_4 . The ZnO support is regarded to serve as a kind of SMSI and to regenerate Ni catalyst automatically in the HDS. To the best of our knowledge, this is the first time that the regeneration of the sulfur-poisoned Ni catalyst in a H_2 stream was realized and the automatic regenerative Ni catalyst for adsorptive HDS was demonstrated. Other materials for the catalyst of adsorptive UD-HDS were investigated. Al_2O_3 and Fe_2O_3 were useful as sub-materials, however, Cu, Co, Mo, Pd, and Pt were not comparable to Ni and ZnO.

1. Introduction

The conventional “hydrodesulfurization” catalyst converts the organic sulfur compounds to H_2S . In a small PAFC, this H_2S must be removed in the “adsorbent.” The “adsorptive hydrodesulfurization” catalyst, which is newly defined in this paper, performs these dual functions, which is the conversion to H_2S and its adsorption, in a single catalyst. The adsorptive HDS catalyst is desirable for the small PAFC to realize a compact UD-HDS system. On the contrary, the adsorptive HDS catalyst should not be used in the main HDS process in the refinery, because the adsorbing capacity is limited and frequent changes of the catalyst become necessary. The reduced Ni catalyst, however, is sometimes used as a “guard,” or “trap” to protect the main catalyst from a trace of sulfur-poisoning¹⁾, or “finishing,” in the HDS process.

As an adsorptive catalyst for UD-HDS of kerosene, we have cited, in a previous paper²⁾, that a high concentration of Ni loaded alumina catalyst is effective, although its life is quite short. We endeavored to improve this catalyst by trying regeneration using a model of sulfur-poisoned nickel catalyst in flowing H_2 .

Bartholomew *et al.*³⁾ reported that an attempt to

regenerate sulfur-poisoned Ni catalyst in flowing H_2 at high temperature (675–725 K) was not practical. Since the binding energy of sulfur on Ni surface is much higher than that of bulk Ni, sulfur on the catalyst surface is not eluted easily. It was calculated⁴⁾ that the free energy of formation of surface Ni sulfide is $\Delta G = -112$ kJ/mole at 725 K and at 50% sulfur coverage. This value is more than twice that of bulk sulfide ($\Delta G = -52$ kJ/mole at 725 K). At 50% sulfur coverage, the equilibrium partial pressure, P_{H_2S} and P_{H_2} of Eq. (2), is expressed as follows:

$$P_{H_2S}/P_{H_2} = \exp(-\Delta G/RT) \quad (1)$$

The ratio of P_{H_2S}/P_{H_2} on the surface sulfide and on the bulk sulfide in 0.1 MPa of total pressure at 600 K, is 2.71×10^{-9} and 9.69×10^{-4} , respectively. If one gram of 3% Ni/ Al_2O_3 surface is sulfurized up to 50% sulfur coverage and regenerated under an ideal equilibrium condition in $30,000\text{ h}^{-1}$ flowing H_2 at 600 K, it will need 8.0 years for a perfect regeneration. However, it will need only 0.2 h in the case of bulk sulfide. The fact that Bartholomew *et al.* recovered only 5% of sulfur in their regeneration experiment using sulfur-saturated catalyst is understandable based on these estimations. Thus, Bartholomew *et al.* concluded that regener-

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Table 1 Equilibrium Constant of Regeneration of Sulfur-poisoned Nickel Catalyst at 600 K

Case	Reaction	ΔG (600 K, kJ/mol)	K (600 K)
1	$\text{NiS(surf.)} + \text{H}_2 + \text{ZnO} = \text{Ni} + \text{ZnS} + \text{H}_2\text{O}$	19.3	0.019
2	$\text{NiS(surf.)} + \text{Cu(bulk)} = \text{Ni} + \text{CuS}$	81.9	5.2×10^{-8}
3	$\text{NiS(bulk)} + \text{Cu(bulk)} = \text{Ni} + \text{CuS}$	19.5	0.018
4	$\text{NiS(surf.)} + \text{H}_2 + \text{CuO} = \text{Ni} + \text{CuS} + \text{H}_2\text{O}$	-21.6	84
5	$2\text{NiS(surf.)} + \text{H}_2 + \text{Ca(OH)}_2 = 2\text{Ni} + \text{CaS} + 2\text{H}_2\text{O}$	210	2.1×10^{-19}
6	$\text{NiS(surf.)} + \text{H}_2 + \text{Na}_2\text{O} = \text{Ni} + \text{Na}_2\text{S} + \text{H}_2\text{O}$	-71.4	2.2×10^6
7	$\text{NiS(surf.)} + \text{H}_2 + 2\text{NaOH} = \text{Ni} + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$	74.9	2.2×10^{-7}

ation in flowing H₂ was impractical³⁾. We did not consider the trial of Bartholomew *et al.* as impractical at all. Their concept that Ni would not be poisoned permanently by sulfur, and a trace quantity of H₂S (2.71×10^{-9} moles of H₂S) could be eluted by one mole of H₂ is not totally denied yet. To realize their attempt, an additional concept becomes necessary. However, $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ can not be changed, which is fixed from the free energy of formation of the surface sulfide. In the experiment by Bartholomew *et al.*, only 2.71×10^{-9} moles of H₂S by one mole of H₂ are eluted in one pass of H₂. We attempted to increase the efficiency of the elution of H₂S by a millionfold in this study. In case H₂ carries more H₂S molecules in one pass of H₂, the regeneration rate is expected to be accelerated.

2. Experimental Method

2.1. Theory

Equilibrium quantity of H₂S molecules is moving thermally in the H₂ atmosphere. In case a moving H₂S molecule is accepted on another material, another H₂S molecule will leave the Ni surface. At that moment even in the low H₂S equilibrium concentration, H₂S molecules diffuse through the H₂ atmosphere from the Ni surface to the acceptor rapidly. In this case, the speed of the moving H₂ atmosphere need not necessarily rapid. The total regeneration rate relates to the difference in the free energy of formation between the surface Ni sulfide and the acceptor sulfide, it also, relates to the length of diffusion path. As an acceptor, the ZnO adsorbent for H₂S may be useful. It accepts diffused H₂S as Eq. (3). As the free energy of Eq. (3) based on bulk ZnO is $\Delta G = -76.9$ kJ/mole at 600 K, the equilibrium ratio $P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{S}}$ is 7×10^6 . Combining Eq. (3) with Eq. (2), the eluted H₂S is converted to H₂O. The total regeneration reaction is shown as Eq. (4), and $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ equilibrium ratio is 1.9×10^{-2} .

To make short the diffusion path, a fine particle of ZnO and short distance between NiS and ZnO are needed. Table 1 shows results of some case studies of reactivities using other acceptors. Gibbs free energy calculations are based on data in the handbooks⁵⁾. CuO seems to be a suitable acceptor, but it cannot exist in an oxide form in the H₂ atmosphere. Reactivity of reduced bulk Cu is weaker than that of bulk Ni. Na₂O loses its reactivity by changing to NaOH with moisture. Ca(OH)₂ cannot be used as an acceptor. Active surface metals other than Ni, including Cu, Cr, Mo, Pt, and Pd may become useful to regenerate NiS, however, these are not considered practical, indeed. The bulk part of these metals cannot be used as sulfur acceptors, because the free energies of these bulk sulfides are about one half that of the surface Ni sulfide. Oxides of these metals cannot be used as acceptors, because they are usually reduced to metals in the H₂ atmosphere. The stable metal oxides in H₂, for example ZnO, are not useful as regenerating reagents either, because the free energies of the formation of the oxides exceed that of the metal sulfides. It is important to note that the equilibrium constant of the regeneration is improved by 7×10^6 times from 2.71×10^{-9} to 1.9×10^{-2} (from Eq. (2) to Eq. (4)) by the aid of the big negative free energy of H₂O. The regeneration of NiS will be achieved by elimination of H₂O on the right side of Eq. (4), and sulfur will be accepted as ZnS. 2.2. Materials JIS No. 1 commercial grade kerosene containing 62-70 wt ppm of sulfur, H₂, and Cat-Ni used in the experiment, were all the same as cited in the previous paper²⁾. ZnO adsorbent and support (G-72D: ZnO 82-90 wt%, ABD 1.05 g/ml, SA 50-80 m²/g) were supplied by Nissan Girdler Catalyst Co., Ltd., which was crushed and screened to provide 8-24 mesh (2.4-0.70 mm) particles. In the regeneration experiment, 150-170 mesh (0.1 mm) ZnO particles were used. γ -Alumina (SA 250 m²/g) was prepared previously in our laboratory, which was crushed and screened to provide 8-24 mesh particles. Granular CuO (0.8-2 mm) and other reagents to prepare the catalysts were supplied by Kanto Chemical Co., Inc., which are shown in section 3.3.

Table 2 Adsorptive UD-HDS of JIS No. 1 Kerosene Using Regenerated Cat-Ni

		Used catalyst	Regenerated catalyst
Sulfur	[wt ppm]	18	0.44
Catalyst age	[h]	300	2
Reaction rate constant	[h ⁻¹]	0.11	5.7
Estimated LHSV for 0.1 wt ppm sulfur	[h ⁻¹]	0.011	0.57
Volume of catalyst for 200 kW PAFC	[l]	4900	95

H₂/CO₂ = 75/25 v%, Reaction pressure: 0.50 MPaG, Reaction temperature: 325°C, LHSV: 2.00 h⁻¹, Gas/Kerosene = 300 N///, Initial sulfur: 62 wt ppm.

2. 3. Apparatus and Procedure

The same laboratory scale UD-HDS reactor and experimental procedures as cited in the previous paper²⁾ were used. BET was measured by BELSORP 28, which was provided by Bel Japan, Inc. The metal contents of the catalysts were analyzed by ICPS-200 provided from Shimadzu Corp. The regeneration experiment was carried out using the poisoned Ni/Al₂O₃ (Cat-Ni) catalyst mentioned in the previous paper²⁾.

The co-precipitated Ni/ZnO catalysts were prepared in our laboratory as follows: An aqueous solution of mixture of ammonium carbonate and ammonia was added in an aqueous mixed solution of nickel nitrate and zinc nitrate. After leaving for 12 h, the precipitate was filtered and washed. The cake was dried for 12 h at 120°C and calcined for 1 h at 200°C, for 2 h at 300°C, for 1 h at 400°C, and for 16 h at 510°C, respectively. The catalyst powder was pressed and crushed into 8-24 mesh particles. The model Ni/ZnO catalyst contained 12.3 wt% Ni, and its BET area was 18 m²/g. Ni/Fe₂O₃ was prepared by the same co-precipitation method. The used reagents and properties of the catalyst are shown in section 3. 3. The impregnated Ni/ZnO catalyst was prepared as follows: The 8-24 meshed G-72D adsorbent was impregnated with the same volume of aqueous solution of nickel nitrate as the pore volume of the adsorbent. After drying for 12 h at 120°C, it was calcined in the same way as the precipitated catalyst. Ni/Al₂O₃, Mo/ZnO, Co/ZnO, Pt/ZnO, and Pd/ZnO catalysts were prepared by the same impregnation method. The reagents and supports are shown in section 3. 3. The weight percent of active metals are shown as the contents after reduction. The BET area for the Cu supported catalysts are shown as reduced catalysts because the original surface area decreased after reduction, and the BET area of other catalysts were determined based on oxide forms.

3. Results and Discussion

3. 1. A Trial Regeneration of Sulfur-poisoned Ni Catalyst

Using deactivated Cat-Ni used in the adsorptive UD-HDS, a trial regeneration was carried out. The sulfur

content of UD-HDS kerosene using Cat-Ni was 0.13 wt ppm at first, but the sulfur content became 18 wt ppm at the end of long run. Regarding the used Cat-Ni, 8.8 wt% of total Ni was assumed to be sulfurized as NiS.

In this trial regeneration, 6 ml of the used Cat-Ni was mixed with 6 ml of 150-170 mesh fine particles of the ZnO adsorbent. The mixture was returned to the reactor, and treated in 3.6 l/h of flowing H₂ at 395°C, 0.5 MPaG for 90 h. After the trial regeneration, ZnO fine particles was removed from the reactor. In the recovered ZnO particles, 2.46×10^{-3} moles of sulfur was found. The original deactivated Cat-Ni was fed 5.53×10^{-3} moles of sulfur. Therefore, 44.5% of original sulfur was removed by the regeneration. The result of the adsorptive UD-HDS experiment using the regenerated Cat-Ni is shown in Table 2. The sulfur content of treated kerosene was improved from 18 to 0.44 wt ppm.

This experiment was short for a perfect regeneration of the sulfurized Ni surface. To the best of our knowledge, however, this is the first time, that regeneration of sulfur-poisoned Ni catalyst in flowing H₂ was demonstrated.

3. 2. Finding of Auto-regenerative Ni Catalyst

The cited regeneration suggested that Ni and ZnO should coexisted in the adsorptive UD-HDS catalyst, Ni would act as a catalyst to convert the sulfur compound to NiS, and ZnO would act to regenerate the sulfurized Ni catalyst. In such a catalyst, Ni content less than that of Cat-Ni is assumed to be sufficient. Moreover, the ZnO content would be a key for determining catalyst life.

According to the above concept, we have prepared some trial catalysts. Concerning the content of Ni and ZnO and the preparing procedure, there are many variations. The typical results from a long run of adsorptive UD-HDS catalyst, which was prepared by the co-precipitation and contained 12.3 wt% of Ni, was shown in Fig. 1. Comparing with Cat-Ni, the excellent properties of the model Ni/ZnO catalyst is clear. The sulfur content of treated kerosene was less than the lower limit of detection (0.06 wt ppm) for 814 h. A ten times or hundred times sensitive analyzer is required for the effective study of UD-HDS under the practical reaction conditions, where 4,6-dimethyldiben-

LHSV: 1.00 h⁻¹, H₂/Kerosene = 300 N/l, Total pressure: 0.5 MPaG, Reaction temperature: 325°C, H₂/CO₂ = 75/25 v%, Sulfur content in the kerosene for Cat-Ni: 62 wt ppm, Sulfur content in the kerosene for 12.3 wt% Ni/ZnO: 70 wt ppm.

Fig. 1 Comparison of Model Ni/ZnO Catalyst and Ni/Al₂O₃ Catalyst in Long Run Test

zothiophene (4,6-DMDBT) or other unknown difficult-to-remove sulfur compounds persist. If a more sensitive analyzer could be developed, a slow deactivation could be observed in the low level sulfur containing products.

After the 814 h of run, this Ni/ZnO catalyst contained 0.177 moles of Ni and 0.146 moles of sulfur per 100 ml of catalyst. The high mole ratio of S/Ni 0.82 (= 0.146/0.177) may not be attained without ZnO acceptor. The activity of the catalyst was constant until 814 h of the run. The S/Ni mole ratio of the poisoned Cat-Ni was only 0.107. Comparing both catalysts, it would be confirmed that the Ni catalyst on the ZnO is regenerated automatically even in the adsorptive HDS reaction according to Eq. (4). To the best of our knowledge, this is the first time, that automatic regeneration of the adsorptive HDS Ni catalyst was demonstrated.

This experimental catalyst served to easily realize our target volume of catalyst for 200 kW PAFC (< 260 l)²⁾. This 12.3 wt% Ni/ZnO catalyst became the model catalyst for developing the industrial adsorptive

UD-HDS Ni/ZnO catalyst. Through several improvements and tests, one year catalyst life would be expected⁶⁾.

The diffusion path of the formed H₂S in this catalyst is shorter than that in previously cited regeneration experiment. The shortest path may be equal to the diameter of the ZnO particle of 0.1 mm in the trial regeneration. On the contrary, the shortest diffusion path in the Ni/ZnO catalyst may be angstrom order. This situation may lead to a high UD-HDS activity of the Ni/ZnO catalyst.

The sulfur accepting potential of bulk ZnO is much higher than that of bulk Ni. Since the free energy of Eq. (5) is $\Delta G = -43.1$ kJ/mole, almost all the regenerated sulfur is regarded to be accepted as ZnS.

In the exhaust gas, formation of CH₄ did not occur, except the formation of a small quantity of CO. The active sites for HDS, CO formation, and CH₄ formation may differ from one another. Cat-Ni has these three activities equally. Cat-Ni produced methane vigorously as shown previously²⁾. It is surprisingly good result that this experimental Ni/ZnO catalyst has highly effective HDS site, but does not have methanation active site. Ni catalyst supported on Al₂O₃, TiO₂, or SiO₂, or unsupported is well known to convert CO or CO₂ to methane. The fact that no methane is produced in the presence of CO means that ZnO acts not only as a support and as an acceptor of sulfur, but also acts as a co-catalyst which gives electronic effects to the surface Ni atoms. It might be a kind of "Strong Metal Support Interaction," which influences adversely the methanation reaction. The bulk Ni layer may neither act as a catalyst nor an acceptor, but may contribute HDS activity of the surface Ni, by transmitting the electronic effects of ZnO, Al₂O₃, and other support to the surface Ni.

Table 3 Adsorptive UD-HDS of JIS No. 1 Kerosene Using 12.3 wt% Ni/ZnO Catalyst

Catalyst age	[h]	2	406	814
Sulfur	[wt ppm]	< 0.05	< 0.05	< 0.05
Exhaust gas	[v%]			
H ₂		73.2	74.5	74.7
CO		5.8	4.7	2.8
CO ₂		19.8	20.8	22.5
CH ₄		1.3	tr	0.0
Reaction rate constant	[h ⁻¹]	> 20	> 20	> 20
Estimated LHSV for 0.1 wt ppm sulfur	[h ⁻¹]	> 2.0	> 2.0	> 2.0
Volume of catalyst for 200 kW PAFC	[l]	< 27	< 27	< 27

H₂/CO₂ = 75/25 v%, Reaction pressure: 0.50 MPaG, Reaction temperature: 325°C, LHSV: 1.00 h⁻¹, H₂/Kerosene = 300 N/l, Initial sulfur: 70 wt ppm.

3. 3. Tests of the Other Components for Adsorptive UD-HDS Catalysts

It is an important matter whether or not any suitable active metals other than Ni and any supporting materials other than ZnO exist. As the components, Cu, Co, Mo, Pt, Pd, Fe₂O₃, and Al₂O₃ are especially important in the preparation of effective catalysts for the adsorptive HDS. These components were tested as materials of the adsorptive UD-HDS catalysts.

Figure 2 shows the results of adsorptive UD-HDS using Ni catalyst supported on Cu, Al₂O₃, and Fe₂O₃. These supports were compared, in the range of 7-10 wt% of Ni, as shown in **Table 4**. When high concentration of Ni is supported, catalysts show relatively active results in UD-HDS in the early catalyst stage. In this state, an aggregated Ni layer itself acts as a support and masks the properties of the supports. Cat-Ni is an example of this case. When low concentration of Ni is supported, the typical properties of the supports are made clear even in the early catalyst stage.

Ni/Cu catalyst has not been expected to act as a good acceptor from the results of the case study in **Table 1**, however, it gave a good result only in the early stage. The reason can be deduced that only a small part of Ni supported on a small surface area (0.6 m²/g) of Cu sup-

port acted as a effective UD-HDS catalyst and a thick layer consisting of the main part of Ni transmitted a good electronic effect to surface Ni. After poisoning of the small Ni surface, the catalyst that had no regenerating ability was deactivated after the 65 h of reaction.

Ni/Al₂O₃ catalyst is also clear to have no regenerating ability. The Ni surface area on the wide Al₂O₃ support may be large. Therefore, the poisoning rate of the catalyst was very low. On the other hand, inner Ni layer may be thin. Then, the electronic effects to surface Ni may be weak and UD-HDS activity is not strong. As a result, the rate of HDS is not great from the start of run, but the deactivation rate of HDS was slower than that of Ni/Cu catalyst. A great rate of UD-HDS using Ni/Al₂O₃ catalyst having a high Ni concentration, for example Cat-Ni⁽²⁾, may be attributed to the thick Ni layer.

The same tendency was observed in the Ni/Fe₂O₃ catalyst. On the contrary, the relatively narrow surface of the Ni/ZnO catalyst might form a thicker Ni layer than that on the Al₂O₃ or Fe₂O₃ support. As a result, the ZnO support acquired a stronger HDS activity than that of Al₂O₃ or Fe₂O₃ supports in a relatively low Ni content.

It became clear that Al₂O₃ or Fe₂O₃ supports are not

The same reaction conditions (initial sulfur: 70 wt ppm) as in Fig. 1.

Fig. 2 Effect of Various Supports for Ni Catalysts

The same reaction conditions as in Fig. 2.

Fig. 3 Effect of Active Metals on ZnO Support

Table 4 Properties of Metal Supported Catalysts

Catalyst	Active metal [wt%]	BET [m ² /g]	Reagent	Support
Ni/ZnO	8.1	15	Ni(NO ₃) ₂ ·6H ₂ O	G-72D
Ni/Cu	6.8	0.6	Ni(NO ₃) ₂ ·6H ₂ O	CuO granular
Ni/Al ₂ O ₃	9.9	210	Ni(NO ₃) ₂ ·6H ₂ O	γ-Al ₂ O ₃
Ni/Fe ₂ O ₃	8.6	110	Ni(NO ₃) ₂ ·6H ₂ O	Fe(NO ₃) ₃ ·9H ₂ O
Co/ZnO	7.3	14	Co(NO ₃) ₂ ·6H ₂ O	G-72D
Mo/ZnO	6.8	17	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	G-72D
Pd/ZnO	2.0	21	PdCl ₂ + HCl	G-72D
Pt/ZnO	0.76	29	H ₂ PtCl ₆ ·6H ₂ O	G-72D
Co/Cu	6.3	0.6	Co(NO ₃) ₂ ·6H ₂ O	CuO granular

The same reaction conditions as in Fig. 2.

Fig. 4 Effect of Noble Metals on ZnO Support

The same reaction conditions as in Fig. 2.

Fig. 5 HDS Activity of Ni and Co on Cu Support

suitable as accepting materials of H_2S . They were, however, expected to be suitable as sub-materials that have an ability to distribute Ni widely and bring a long life and high activity in the industrial adsorptive UD-HDS catalysts.

As active components other than Ni for the UD-HDS catalyst, Mo and Co were tested by supporting on ZnO. **Figure 3** shows that, these components are active only in the early stage, and they are not comparable to Ni under these reaction conditions.

It seems that Co has comparable HDS ability with Ni on Cu support as shown in **Fig. 5**. However as shown in **Fig. 3**, Co was not regenerated as rapidly as Ni on ZnO. The reason that Co can not be regenerated on ZnO is understandable, if the free energy of the surface Co sulfide is greater than that of Ni. The similar tendency was shown in the Mo/ZnO catalyst. To regenerate Co or Mo, powerful acceptor Na_2O will be useful as shown in **Table 1**.

Pt and Pd were tested in the usual low concentrations. These noble metals are relatively active in spite of low concentrations. However these did not act as

sufficient UD-HDS catalysts in wide temperature range as shown in **Fig. 4**.

Consequently, the Ni/ZnO catalyst was made clear to be the best for the adsorptive UD-HDS.

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要 旨

燃料電池システム用の灯油超深度脱硫（第2報）硫黄被毒 Ni 触媒の
水素による再生と自動再生型 Ni 触媒の発見

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硫黄で被毒した Ni 触媒を水素気流中で再生させる一つのアイデアを試みた。それは、硫黄被毒した Ni 触媒粒子に ZnO 微粒子を混合して H₂ 雰囲気中で 600 K にすると、それぞれの被毒 Ni 粒子は硫黄を数 ppb の H₂S として水素中に放出し近隣の ZnO 粒子に受容される。それによって、一通過の H₂ による硫黄被毒 Ni 触媒の再生効率が百万倍も改善されるであろう。硫黄被毒した 60% Ni/Al₂O₃ 触媒がたった 90 時間の試行で再生された。このアイデアを応用して、12.3% Ni/ZnO 触媒を調製し、25% CO₂ を含む水素中 600 K での灯油吸着型超深度脱硫 (UD-HDS) モデル触媒としてテストした。生成油中の硫黄は既成の

高感度硫黄分析計では検出できない状態 (< 0.06 wt ppm) が 800 時間以上継続した。Ni/Al₂O₃ 触媒に比較して Ni/ZnO 触媒は CH₄ を全く生成しなかった。ZnO 担体は一種の SMSI 効果を発揮し、かつ水素化脱硫中に Ni 触媒を自動再生することがわかった。筆者らの知り得る限りでは、水素流中での硫黄被毒 Ni 触媒の再生と、吸着型水素化脱硫 Ni 触媒の自動再生は、これが最初のデモンストレーションである。その他の吸着 UD-HDS 触媒素材を探索した結果、Al₂O₃ と Fe₂O₃ は副資材として有望であるが、Cu, Co, Mo, Pd, Pt は Ni および ZnO に匹敵するものでないことがわかった。

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Keywords

Adsorptive ultra-deep hydrodesulfurization, Desulfurization, Kerosene, Fuel cell, Regeneration, Nickel zinc oxide catalyst