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Some Principles Relating to the Regeneration of Sulfur-Poisoned Nickel Catalyst

JENS R. ROSTRUP-NIELSEN

Haldor Topsøe Research Laboratory, P. O. Box 49, 2950 Vedbaek, Denmark

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A previous study of the chemisorption of hydrogen sulfide on a nickel catalyst has been extended. It is shown that steam has no influence on the chemisorption equilibrium. Regeneration by means of desorption of hydrogen sulfide may be a slow process. Principles for the regeneration of nickel catalysts by means of oxidation and reduction have been studied. The experiments have included unpromoted and promoted catalysts and indicate great differences in their behavior.

INTRODUCTION

The chemisorption of hydrogen sulfide on a supported nickel catalyst was previously shown to be reversible, the coverage being a function of the ratio p_{H_2S}/p_{H_2} (*1*). A saturation layer was observed in the temperature range 550–645°C at ratios above $2–5 \cdot 10^{-6}$, whereas bulk sulfide (Ni_3S_2) was formed at ratios above 10^{-3} according to thermodynamic data. The saturation layer was found to contain 0.74 sulfur atoms per hydrogen atom chemisorbed at −72°C. A mean area of a hydrogen site on a randomly oriented nickel film of 8.9 Å was used as suggested by Knor and Ponec (*2*), which corresponds to 0.54 sulfur atom per nickel atom in the saturation layer or $44.2 \cdot 10^{-9}$ g-S/cm² nickel surface. The result is close to that obtained by Perdereau (*3, 4*) who used a quite different technique, the coverage of a known area being measured by the intensity of radiation of chemisorbed ^{35}S. By means of LEED studies, Perdereau has shown that the structure of the saturation layer can be regarded as a two-dimensional sulfide phase, which includes nickel atoms, the interatomic distances being close to those of bulk sulfide Ni_3S_2. This has also been discussed by McCarroll *et al.* (*5*). Hence, the well-known poisoning effect of hydrogen sulfide on many nickel catalysts may be ascribed to a blocking of the metallic surface.

This study concerns principles for regeneration of sulfur poisoned nickel catalysts implying removal of the retained sulfur. The investigated catalysts are mainly for the steam reforming of hydrocarbons, which is normally performed in the temperature range 500–850°C, but the results may be applied to nickel catalysts used for other processes in the same temperature range.

As the chemisorption is reversible, sulfur should be removed from the surface simply by decreasing the sulfur content of the feed. This may well be achieved in experiments using a high flow rate and showing no diffusion restrictions as demonstrated by Morita (*6*). However, on an industrial scale this method will normally cause a slow regeneration, even when the gas leaving the catalyst is saturated. This may follow from the example below.

It was previously shown (*1*) that the chemisorption equilibrium could be described by a Langmuir isotherm:

$$s = \frac{a \cdot (p_{H_2S}/p_{H_2})}{1 + b \cdot (p_{H_2S}/p_{H_2})} \text{ wt ppm,} \qquad (1)$$

where *s* is the sulfur coverage expressed by the sulfur content of the catalyst (wt ppm), and *a* and *b* are constants. At moderate coverages Eq. (*1*) is approximated by a linear isotherm neglecting the denominator:

$$\frac{p_{H_2S}}{p_{H_2}} = \frac{1}{a} \cdot s. \tag{2}$$

Assuming establishment of the chemisorption equilibrium in a hydrogen flow F_H (moles/hr), it follows that the ratio of sulfur leaving the catalyst as hydrogen sulfide F_S (moles/hr) to F_H is equal to the ratio p_{H_2S}/p_{H_2} determined by the isotherm (2):

$$\frac{F_S}{F_H} = \frac{p_{H_2S}}{p_{H_2}} = \frac{1}{a} \cdot s. \tag{3}$$

If x is sulfur at the catalyst (moles), where $(x = k \cdot W \cdot s)$ and $W =$ weight of catalyst, the sulfur flow leaving the catalyst becomes

$$\frac{-dx}{dt} = \frac{1}{a} \cdot F_H \cdot s \text{ moles/hr}, \tag{4}$$

$$\frac{-ds}{dt} = \frac{k}{a} \cdot W \cdot F_H \cdot s = k' \cdot s, \tag{5}$$

which yields:

$$s/s_1 = e^{-k' \cdot t}, \tag{6}$$

where s_1 is the sulfur coverage before regeneration, expressed by sulfur content of the catalyst (wt ppm), and s is the sulfur coverage after regeneration, expressed by sulfur content of the catalyst (wt ppm). Hence, the rate of sulfur removal by means of the desorption process is decreasing with time, whereas if only bulk phase reactions are involved the rate of sulfur removal will be constant, assuming as above that equilibrium is established.

As the chemisorption is exothermic, an improved sulfur removal should be expected when increasing the temperature. From the isotherms reported previously (*1*) the heat of adsorption is estimated roughly as being no more than 10 kcal/mole H_2S, indicating no significant temperature effect. This value is less than the value estimated by Roberts (*7*), cited by Kemball (*8*) and Duyverman (*9*). However, Roberts' estimate appears doubtful. The estimate is based on an empirical correlation of chemisorption of oxygen and hydrogen on metals and heats of formation of the corresponding bulk compounds assuming that a two dimensional compound is formed by simple stoichiometry. Thus Roberts uses data of NiS, whereas Ni_3S_2 seems more likely to be involved. Furthermore, the data of NiS are based on rhombic sulfur and not S_2, whereas the data of oxides and hydrides have been based on O_2 and H_2.

Although some effect may be achieved by increasing the temperature, this may often be difficult because of temperature restrictions of the reactor system or of sintering reactions of the catalyst. On this basis, the aim of the experimental work has been to study how the sulfur content of a poisoned catalyst is influenced by treatment with steam and steam-containing atmospheres.

METHODS

Catalysts

The experiments have included unpromoted and promoted catalysts, alkali and earth-alkaline compounds being typical promoters for reforming catalysts.

The catalysts used for the study have mainly been based on a carrier of magnesium spinel:

Catalyst A: 21 wt% Ni, 1.4 wt% K;
Catalyst B: 9 wt% Ni, 2.3 wt% K;
Catalyst C: 10 wt% Ni;
Catalyst D: 10 wt% Ni, 0.7 wt% K;
Catalyst E: 10 wt% Ni, 4.9 wt% K;
Catalyst F: 10 wt% Ni, 0.8 wt% Na;
Catalyst G: 10 wt% Ni, 1.1 wt% Ca;
Catalyst H: 10 wt% Ni, 0.8 wt% Mg.

In addition, Catalyst I based on α-alumina (7 wt% Ni) and Catalyst J based on magnesia (25 wt% Ni), were used.

Apparatus

The experiments were performed in the apparatus for hydrogen sulfide chemisorption described previously (*1*). A water pump, an evaporator, and a condenser were added for steam addition.

Analytical

Hydrogen sulfide in the exit gas and the sulfur content of the catalysts were determined as previously (*1*). The analysis of the catalysts involved a treatment with hydriodic acid prepared as described by Gustavson (*10*). This method will transform all sulfur to hydrogen sulfide. When using hydrochloric acid only sulfur in the sulfide state will be detected. In some experiments the exit gas was analyzed for sulfur dioxide and hydrogen sulfide using a method of separating the two gases mentioned by Hammar (*11*). The gas was passed through two bubble flasks containing an acidic solution of hydrogen peroxide and an acidic solution of cadmium acetate, respectively. In the former solution (0.1 ml conc. hydrogen peroxide, 1 ml 0.1 *N* sodium chloride, and 3 ml 0.1 *N* hydrochloric acid in 50 ml water) sulfur dioxide is transformed into sulfate, whereas hydrogen sulfide is passing without reaction. This solution was also added to the steam condenser following the reactor and the condensate was analyzed together with the solution in the first bubble flask.

Nickel Surface

Some experiments have included a determination of the nickel surface (sulfur capacity) by means of chemisorption of hydrogen sulfide under the following conditions:

Reduction (if sample in oxidized state):

850°C, 2 moles H_2/hr, 2 hr.

Chemisorption:

550°C, $p_{H_2S}/p_{H_2} = 11\text{–}14 \cdot 10^{-6}$,
2 moles H_2/hr, 40–45 hr.

RESULTS AND DISCUSSION

1. *Influence of Steam on the Chemisorption of Hydrogen Sulfide*

Different types of experiments were performed to study the influence of steam on the chemisorption equilibrium. In principle, one should expect two competing chemisorption reactions:

$$\mathrm{Ni} + \mathrm{H_2S} = \mathrm{Ni\text{–}S} + \mathrm{H_2} \qquad (7)$$

and

$$\mathrm{Ni} + \mathrm{H_2O} = \mathrm{Ni\text{–}O} + \mathrm{H_2}. \qquad (8)$$

The investigation was complicated by sintering effects, which may take place at temperatures above 550°C. This has been illustrated in Fig. 1. (Series 1). The catalyst pellets were divided into two parts. After sintering of one part in steam and hydrogen, the sulfur capacities (i.e., the nickel areas) of both parts of the pellets were determined at 550°C. The degree of sintering is expressed as the ratio of the sulfur capacity of the sintered catalysts (s) and that of the unsintered control (s_0). Because of this, two series of experiments were performed.

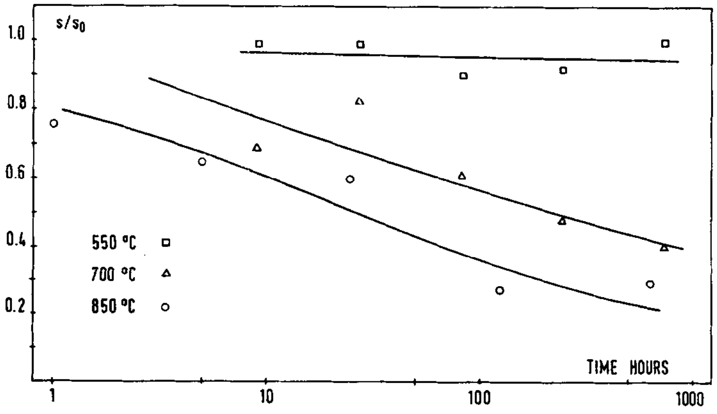

FIG. 1. Sintering of Catalyst A (Series 1). Steam flow, 3 moles/hr; hydrogen flow, 1 mole/hr. s/s_0 = sintering degree of nickel surface.

Series 2 included treatment of Catalyst C in hydrogen, steam, and hydrogen sulfide, whereas a control experiment was performed under identical conditions without steam present. Series 3 included treatment in steam and hydrogen and a similar treatment of the control in dry hydrogen, followed by a normal determination of the sulfur capacity. The ratio of sulfur uptake obtained in the experiment and the control experiment is called α.

The experimental results are shown in Fig. 2. The experiments were performed at a molar ratio H_2S/H_2 of nearly the same order ($15–20 \cdot 10^{-6}$), whereas the molar ratio H_2O/H_2 was varied between 0.1 and 10. Looked upon separately, the results from Series 2 may show that increasing H_2O/H_2 causes a decrease in sulfur uptake. This effect depends on temperature, and at 550°C no significant influence is observed. However, the results from Series 3 fit very well to the graphs obtained from Series 2 (Fig. 2). This implies that the observed effect may be explained as a sintering effect, and that steam has no influence on the chemisorption of hydrogen sulfide on nickel.

This result was tested using another experimental procedure. In Series 4, pellets were divided into two parts. The first part was treated in an atmosphere of steam, hydrogen, and hydrogen sulfide ($H_2S/H_2 = 16 \cdot 10^{-6}$; $H_2O/H_2 = 10$, 700°C) followed by treatment without steam. The second part was subjected to the treatments in the reverse order. The sulfur contents of the pellets after the experiments were very similar, indicating no influence from steam.

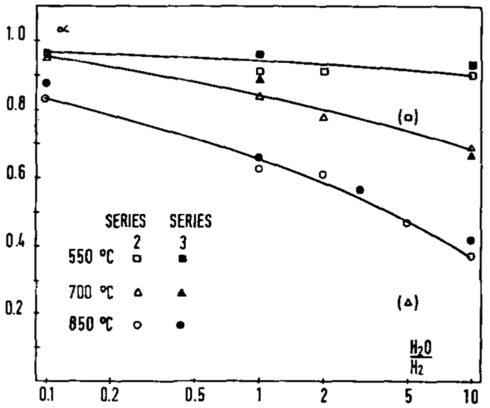

FIG. 2. Chemisorption of hydrogen sulfide in steam containing atmosphere (Series 2); sulfur capacity of samples sintered in steam containing atmosphere (Series 3). Catalyst C.

$$\alpha = \frac{\text{sulfur uptake in experiment}}{\text{sulfur uptake in dry atmosphere}}.$$

The experiments mentioned above were performed without significant change of H_2S/H_2. This ratio was changed in Series 5 performed at 700°C and using a fixed H_2O/H_2 of 5. The results are shown in Table 1. Within the accuracy of the experiments, a constant saturation layer is observed in the range of $H_2S/H_2 = 10^{-6}$–10^{-3} according to the results obtained previously in dry atmosphere (*1*). The mean is close to the corresponding value derived from Fig. 2.

TABLE 1

CHEMISORPTION OF HYDROGEN SULFIDE IN STEAM-CONTAINING ATMOSPHERES[a]

Series 5

H_2S-flow[b] (mgS/hr)	$H_2S/H_2 \cdot 10^6$ (molar ratio)	α	Duration (days)
0.01	0.2	0.71	7
0.07	1.5	0.50	7
0.18	3.8	0.70	7
0.84	17.5	0.77	1
5.85	122.0	0.64	1
44.6	930.0	0.93	1
Mean		0.71	

[a] Catalyst, ca. 1.5 g-Catalyst C; hydrogen flow, 1.5 mole/hr; argon flow, 0.2 mole/hr; activation, 1 hr at 850°C; chemisorption, $H_2O/H_2 = 5$ mole/mole, 700°C.

[b] Mean of experiment and reference experiment.

On this basis, it is inferred that no competition exists between hydrogen sulfide and steam for chemisorption on the nickel surface in the investigated temperature range. This result may appear surprising, as the heat of chemisorption of oxygen is high. However, reaction (8) involves a decomposition of steam. Thus, Gonzalez and Parravano (*12*) have observed an endothermic dissociative chemisorption of steam on nickel ($\Delta H = +2.2$ kcal/mole H_2O) in the temperature range 150–300°C. A detailed analysis of the adsorption thermodynamics of the present study would be doubtful on the basis of these results.

One conclusion is that no regenerating effect is to be expected when increasing the ratio H_2O/H_2, provided that the catalyst is still in a reduced state.

2. *Regeneration Experiments*

Removal of sulfur from the nickel surface was studied in a series of experiments using poisoned catalysts. The sulfur content of these samples s_1 was not necessarily similar to their sulfur capacity of s_0. The degree of regeneration is expressed by the ratio s/s_1, where s is the sulfur content after the treatment.

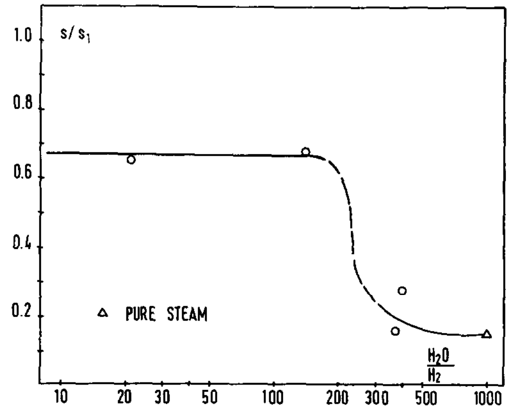

FIG. 3. Influence of H_2O/H_2 on regeneration (Series 6). Catalyst C, ($\frac{1}{2}$ g, $s_1 = 963$ wt ppm); temperature, 700°C; duration, 4 hr; steam flow, 3 moles/hr; argon flow, 1 mole/hr.

$$s/s_1 = \frac{\text{sulfur content after regeneration}}{\text{sulfur content before regeneration}}.$$

When exposed to dry hydrogen or atmospheres with $H_2O/H_2 = 2$–3 at 700°C, Catalyst C showed $s/s_1 = 0.6$ after a period of 24 hr (Series 6). Similar results were obtained with Catalysts B and J. This shows a slow regeneration rate which was to be expected from expression (6). If the H_2O/H_2 ratio was increased, no improvement was observed in accordance with the chemisorption experiments. However, at H_2O/H_2 above 200–250°C, a significant change of regeneration degree of Catalyst C was obtained as shown in Fig. 3. The increased sulfur removal is achieved at a H_2/H_2O ratio similar to the equilibrium constant for the oxidation of the catalyst:

$$\mathrm{Ni} + H_2O = \mathrm{NiO} + H_2, \qquad (9)$$

which has been calculated as 1/250 at 700°C. Other experiments involving oxidation of Catalyst C (Series 7) confirmed this result. When the gas leaving the catalyst was analyzed, sulfur dioxide and hydrogen sulfide were detected, which may indicate the following reaction pattern:

$$\mathrm{Ni\text{-}S} + H_2O = \mathrm{NiO} + H_2S \qquad (10)$$

and

$$H_2S + 2\,H_2O = SO_2 + 3\,H_2. \qquad (11)$$

This does not include the chemisorption equilibrium (1) which may be the reason of the improved regeneration.

The equilibrium constant of (11) at 700°C is $3.5 \cdot 10^{-8}$ atm, which implies that even a small amount of hydrogen will inhibit the conversion of hydrogen sulfide. Hence, sulfur removal following this reaction pattern requires a total oxidation of the catalyst. If some part of the nickel surface is still exposed to the gas, hydrogen formed by (9) will cause hydrogen sulfide to be retained at the surface.

Catalysts promoted with alkali or alkaline earth-compounds revealed great differences in the behavior of sulfur when oxidizing the catalysts with steam (Series 8). As shown in Fig. 4, a significant removal of sulfur is obtained on Catalyst C and catalysts promoted with magnesium and calcium at temperatures above 700°C, whereas the sulfur contents of the catalysts promoted with sodium and potassium remain nearly unchanged. The unpromoted Catalyst I, based on α-alumina, shows results close to those obtained with alkali-free catalysts based on spinel.

The observed trend of sulfur removal is similar to that of the free energies of reactions of sulfur dioxide with the alkali hydroxides and alkaline earth-oxides. The strong temperature dependence of the results obtained with Catalysts C, G, and H

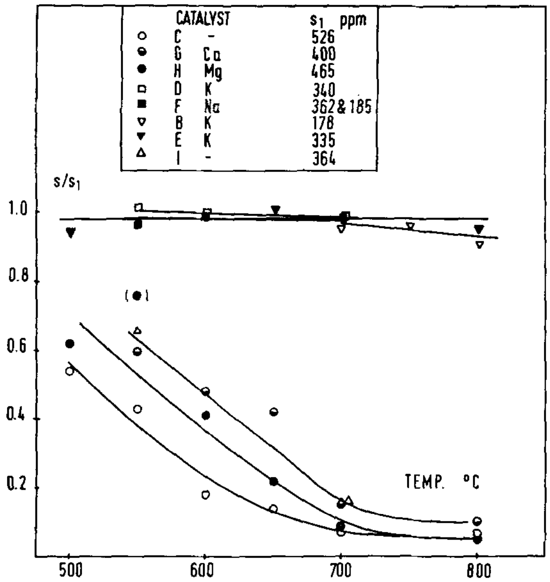

FIG. 4. Regeneration of catalysts by means of steam (Series 8). Ca. $\frac{1}{2}$ g of each catalyst; duration, 3 hrs; steam flow, 3 moles/hr; argon flow, 1 mole/hr.

$$s/s_1 = \frac{\text{sulfur content after regeneration}}{\text{sulfur content before regeneration}}.$$

may indicate a weak bonding of sulfur dioxide to the catalyst, whereas a chemical transformation into stable compounds may have caused the results obtained with the alkali-promoted Catalysts B, D, E, and F.

In principle, potassium hydroxide and sulfur dioxide will form potassium sulfate and sulfide. However, the chemisorption studies proved that hydrogen sulfide is not retained by potassium hydroxide at the low partial pressures in question. Hence, the following reaction pattern may be assumed:

$$\text{“}6\,KOH + 4\,SO_2 = 3\,K_2SO_4 + H_2S + 2\,H_2O.\text{”} \qquad (12)$$

The hydrogen sulfide formed is oxidized to sulfur dioxide by reaction (11) and in this way nearly all sulfur is retained by a multistep process. These assumptions were supported by analytical results. First, positive sulfate reactions ($BaSO_4$ precipitation) were observed on aqueous extracts from steamed catalyst. Secondly, if hydrochloric acid replaced the reducing hydriodic acid in the procedure of sulfur analysis of the catalyst, no sulfur was found, indicating no sulfur present as sulfide. However, it is also well known that minor amounts of other sulfur compounds, such as thiosulfate, and free sulfur are to be expected by reaction (12).

When the catalysts were exposed to steam containing 1 vol% of air, a limited sulfur removal was obtained with all catalysts (Series 9). The results shown in Table 2 may indicate formation of sulfates caused by the addition of air.

In principle, it should be possible to remove sulfur retained by the promoter by means of a reduction. This presumes, first, that the promoter will not retain the hydrogen sulfide formed by the reduction, and secondly, that the reduction is to be performed under conditions where nickel oxide is reduced at a rate significantly lower than the rate of formation of hydrogen sulfide. If this is not so, hydrogen sulfide is chemisorbed at the nickel surface.

TABLE 2

REGENERATION OF CATALYSTS BY MEANS OF STEAM AND AIR[a]

Series 9

Catalyst	Promoter	s_1 wt ppm	s/s_1 550°C	650°C	700°C	750°C
C	—	526	(1.05)	(1.05)	0.71	0.73
G	Ca	525	(1.12)	0.98	0.62	1.01
H	Mg	480	0.83	0.78	0.51	0.58
I	—	364	(1.06)	—	0.97	—

[a] Catalyst, ca. 0.5 g; steam flow, 3 moles/hr; air flow, 0.3 moles/hr; duration, 3 hr.

When samples of spinel and alumina carriers impregnated with alkali and alkaline earth-compounds were exposed to the conditions for determination of the sulfur capacity (i.e., 550°C and $H_2S/H_2 = 10^{-6}$), sulfur was retained only by the calcium-containing samples, as shown in Table 3 (Series 10). This is in accordance with the well known observation that addition of lime to catalysts for cyclic reforming makes the catalysts very sensitive to sulfur poisoning, as sulfur is accumulated (*13*). If the catalyst contains magnesite, sulfur is removed before the nickel surface has been formed.

The conditions of the reduction depend on the "sulfate" formed on the catalyst and the state of nickel in the oxidized catalyst. In this connection, Catalysts A, B, D, and E promoted with potassium display unfavorable properties, as the reduction in dry hydrogen of potassium sulfate and nickel oxide in the catalyst becomes significant at about 700°C (*14*, *15*) and 350°C, respectively. However, steam is known to retard the reduction of nickel oxide (*16*), and this was used in Series 11. Catalyst B was oxidized in steam at 700°C and exposed to atmospheres with different ratios H_2O/H_2. The results of these two steps, shown in Table 4, make the existence of an optimum probable. At $H_2O/H_2 = 27$, nickel has been formed rapidly and hydrogen sulfide has been chemisorbed at the metal surface. This is confirmed by X-ray analysis and sulfide analysis. The regeneration achieved is similar to what was observed when using pure hydrogen. At $H_2O/H_2 = 52$, only traces of nickel have been formed and an improved sulfur removal achieved. The reduction rate of the sulfate is still slow. At $H_2O/H_2 = 270$, no reduction of nickel oxide can occur, but the reduction rate of the sulfate has been retarded, causing a poor regeneration.

TABLE 3

SULFUR UPTAKE OF CARRIERS IMPREGNATED WITH ALKALI AND ALKALINE EARTH NITRATES[a]

Series 10

Carrier type	Magnesium aluminium spinel s wt ppm S	α-alumina s wt ppm S
nonimpregnated	17	17
Na (1.6 wt%Na)	22	48
K (1.4 wt%K)	39	34
Ca (2.1 wt%Ca)	1760	2000
Mg (2.3 wt%Mg)	13	32

[a] Temperature, 550°C; hydrogen flow, 2 moles/hr; H_2S/H_2, $12 \cdot 10^{-6}$; duration, 24–60 hr.

TABLE 4

REGENERATION OF CATALYST PROMOTED WITH POTASSIUM[a]

Series 11

H_2O/H_2 molar ratio	Sulfur total s (wt ppm)	s/s_1	Sulfur as sulfide (wt ppm)	X-ray analysis
27	105	0.60	95	Ni
52	62	0.35	0	NiO(Ni)
270	162	0.91	0	NiO

[a] Catalyst, 0.5 g-Catalyst B sulfur content s_1 = 178 wt ppm; steam flow, 3 moles/hr; argon flow, 1 mole/hr; first period, oxidation 1 hr at 700°C; second period, hydrogen addition 23 hr at 700°C.

With Catalyst J based on magnesia, better results were obtained on samples containing sulfur as sulfate originating from the preparation. Magnesia retards the reduction of nickel oxide (*17*) and magnesium and nickel sulfate are reduced more easily than alkali sulfates. The results in Table 5 from Series 12 show a rapid sulfur removal at 650°C even in dry hydrogen.

TABLE 5

REGENERATION OF CATALYST BASED ON MAGNESIA[a]

Series 12

H_2O/H_2 molar ratio	Sulfur content s wt ppm	s/s_1
Dry hydrogen[b]	84	0.17
1	83	0.17
10	50	0.10

[a] Catalyst, ca. 3.5 g-Catalyst J; sulfur content, s_1 = 490 ppm; temperature, 650°C; steam flow, 3 moles/hr; duration, 3 hr.

[b] 1.5 moles/hr.

CONCLUSION

Nickel catalysts poisoned by chemisorbed sulfur may show a slow rate of regeneration by means of desorption of hydrogen sulfide. Steam has been shown to have no influence on the chemisorption equilibrium. However, by steaming involving complete oxidation of the nickel, sulfur is removed easily at temperatures above 600–650°C if the catalyst is unpromoted. Similar results are obtained with catalysts promoted with magnesium and calcium. At low temperatures, sulfur dioxide may be retained by a weak bonding to the catalyst. If the catalyst is promoted with potassium or sodium, steaming of the catalyst may result in a nearly complete conversion of chemisorbed sulfur to alkali sulfate. When steam contains air, sulfates are formed on all promoted catalysts included in this investigation.

Sulfur left in the oxidized state may be removed by a reduction performed under conditions where nickel oxide is reduced at a rate lower than the rate of formation of hydrogen sulfide. Due to the high stability of alkali sulfates, regeneration of alkali-promoted catalysts becomes difficult, as the sulfates may hardly be reduced without formation of the original poisoned nickel surface. However, by adjustment of the ratio H_2O/H_2, an improved removal of sulfur may be achieved. As hydrogen sulfide formed by reduction of a poisoned calcium-promoted catalyst may be retained on the promoter, regeneration may be difficult if sulfur has been left in the oxidized state. Catalysts promoted with magnesium or based on magnesia are easily regenerated.

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REFERENCES

1. ROSTRUP-NIELSEN, J. R., *J. Catal.* **11**, 220 (1968).
2. KNOR, Z., AND PONEC, V., *Coll. Czech. Chem. Commun.* **26**, 961 (1961).
3. PERDEREAU, M., *C. R. Acad. Sci. Ser. C* **267**, 1107 (1968).
4. PERDEREAU, M., *C. R. Acad. Sci. Ser. C* **267**, 1288 (1968).
5. MCCARROLL, J. J., EDMONDS, T., AND PITKETHLY, R. C., *Nature* **223**, 1260 (1969).
6. MORITA, S., AND INOUE, T., *Int. Chem. Eng.* **5**, 180 (1965).
7. ROBERTS, M. W., *Nature* **188**, 1020 (1960).
8. SALEH, J. M., KEMBALL, C., AND ROBERTS, M. W., *Trans. Faraday Soc.* **57**, 1771 (1961).
9. DUYVERMAN, C. J., VLUGTER, J. C., AND VAN DE WEERDT, W. J., *Proc. Int. Congr. Catal. 3rd, 1964* **2**, 1416 (1965).
10. GUSTAVSON, L., *Talanta* **4**, 236 (1960).
11. HAMMAR, C. G. B., Thesis, Göteborg, 1957.
12. GONZALEZ, O. D., AND PARRAVANO, G., *J. Amer. Chem. Soc.* **78**, 4533 (1956).
13. GARLET, R., PAUL, C., AND GRANDET, L., *C. R. Congr. Ind. Gaz.* **83**, 264 (1966).
14. HEGEDÜS, A. J., AND FUKKER, K., *Z. Anorg. Allg. Chem.* **284**, 20 (1956).
15. SPITSYN, V. I., AND MEEROV, M. A., *Zhur. Obshch. Khim.* **22**, 2079 (1952); *Chem. Abstr.* **47**, 6616 (1953).
16. BANDROWSKI, J., BICKLING, C. R., YANG, K. H., AND HOUGEN, O. A., *Chem. Eng. Sci.* **17**, 379 (1962).
17. TIKKANEN, M. H., ROSSELL, B. O., AND WIBERG, Ö., *Acta Chem. Scand.* **17**, 513 (1963).