

NOTE

TPSR(TEMPERATURE-PROGRAMMED SURFACE REACTION) STUDY OF SULFUR-POISONED NICKEL CATALYST

Heung Yong HA, Taehoon LIM, Jong Shik CHUNG* and Sang Heup MOON**

Reaction Engineering Laboratory, Korea Institute of Science & Technology,
Cheongryang P.O. Box 131, Seoul 136-791, Korea

*Dept. of Chemical Engineering, Pohang Institute of Science & Technology,
P.O. Box 125, Pohang 790-600, Korea

**Dept. of Chemical Engineering, Seoul National University, Shinlim-dong
san 56-1, Kwanak-ku, Seoul 151-742, Korea

(Received 25 October 1989 • accepted 27 December 1989)

INTRODUCTION

Nickel is easily poisoned by sulfur even when the ambient stream contains very low levels of sulfur. For example, a study [1] shows that the hydrogen stream containing only 1 ppb of H_2S readily forms a monolayer of nickel sulfide on the surface at $390^\circ C$. Many studies therefore have been made of the sulfur effects on the catalytic properties of nickel [2,3] and of the methods to protect nickel from sulfur poisoning [4].

The sulfur-poisoned nickel, however, is very difficult to regenerate. Thus, few works have been reported on the catalyst regeneration at least in the open literature. A common method to regenerate poisoned metal catalysts is to treat them in reactive gas streams such as H_2 [5] and O_2 [6]. But, this method has not been efficient in regenerating the sulfur-poisoned nickel.

Regeneration in H_2 has been unsuccessful because the surface nickel sulfides are relatively stable under the reducing atmosphere. McCarty and Wise [7] have indicated that the H_2 stream in equilibrium with the sulfur-covered nickel surface, at 89% saturation coverage, contains only 4.4 ppb of H_2S at $350^\circ C$. This means that regeneration of poisoned nickel even with extremely pure H_2 would take a very long time, and therefore the regeneration method is impractical.

Regeneration in O_2 is acceptable only when care is taken of the reaction conditions. That is, the O_2 partial pressure in the gas stream is maintained extremely

low, e.g., between 1.4×10^{-8} and 7×10^{-6} Torr [6]. The reason for using such low O_2 pressures is explained as follows [8].

During the O_2 treatment, two competing reactions occur on the catalyst surface: oxidation of sulfur to SO_2 and nickel to nickel oxide. At low O_2 pressures, the nickel oxidation is relatively slow and sulfur is oxidized to SO_2 to be removed from the surface at comparable rates. At high O_2 pressures, however, nickel oxide formation is very fast and the catalyst surface is almost completely covered with the nickel oxide layers. The surface sulfur is then buried below the nickel oxide layers becoming inaccessible to the regenerative O_2 stream. In fact, it has been observed that the competition between sulfur removal and nickel oxide formation depends on the O_2 partial pressure and the reaction temperature [1].

This communication is to report the results of our TPSR (Temperature-Programmed Surface Reaction) study of the sulfur-poisoned nickel catalyst, which seem to support the above observations by previous workers.

EXPERIMENTAL

The sample, sulfur-poisoned nickel catalyst has been obtained from the benzene hydrogenation unit of Yukong, Ltd. The catalyst, which is supported on alumina, contains 23.8 wt% of nickel and 0.52 wt% of sulfur according to analyses by atomic absorption.

Shimadzu GC-8APFP has been modified for the TPSR experiments so that the separation column in the GC oven is replaced by a micro-reactor. The sulfur compounds liberated by the TPSR have been detected

*To whom all correspondence should be addressed.

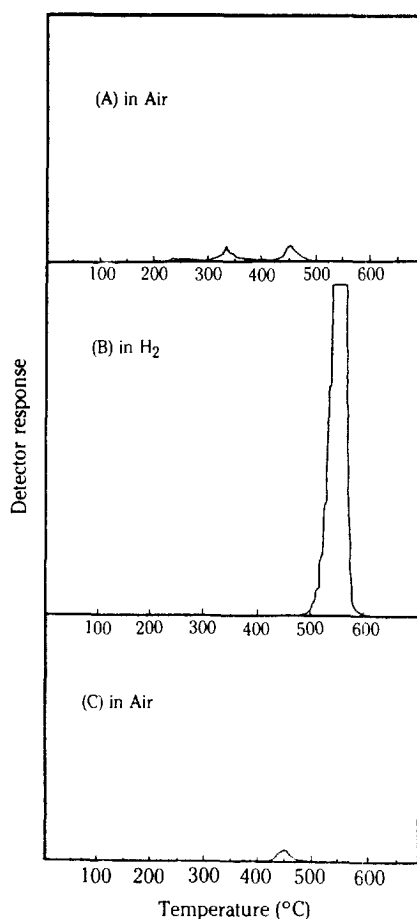


Fig. 1. TPSR spectra obtained by treating sulfur-poisoned Ni/Al₂O₃ catalyst in sequential gas streams: A) in air, B) in H₂, C) in air.

by FPD(Flame Photometric Detector) installed in the GC.

Since the quartz reactor, quartz wool used to support the catalyst in the reactor, and the gas flow lines are already contaminated with trace amounts of sulfur, the whole reaction unit without catalyst has been baked in flowing air at 550°C before the TPSR experiments until no sulfur is detected in the effluent stream. The reactor is then filled with 0.7g of the sample catalyst, and heated linearly at 10°C/min either in H₂ or in air with the outcoming sulfur detected.

RESULTS AND DISCUSSION

Fig. 1 and 2 show two series of spectra obtained when the TPSR runs are made in two different sequences of reactive gases. The followings are noted in

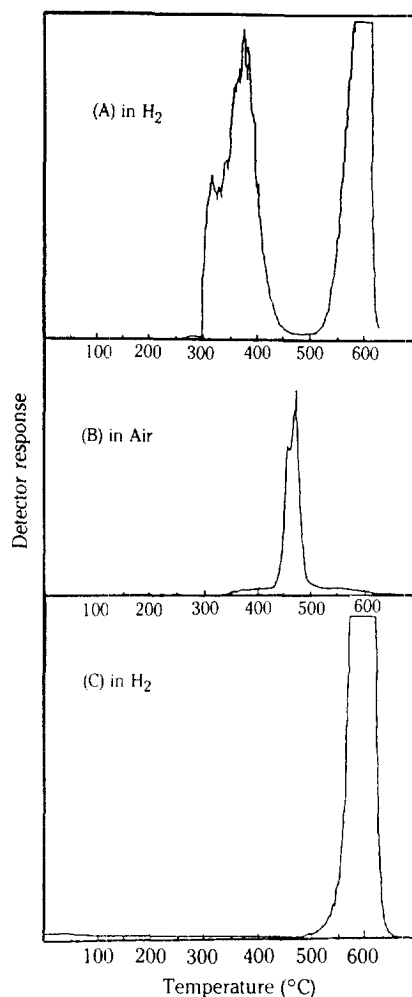


Fig. 2. TPSR spectra obtained by treating sulfur-poisoned Ni/Al₂O₃ catalyst in sequential gas streams: A) in H₂, B) in air, C) in H₂.

the spectra.

1. The spectra show two peaks during the initial TPSR run irrespective of the reactive gases.
2. The low temperature peak appearing below 400°C is not observed from the second run.
3. The peak above 400°C appears at higher temperatures in H₂ than in air.
4. The peaks are smaller in air than in H₂.

The sample catalyst seems to contain two types of sulfur of different reactivity. One is relatively active being removed almost completely at low temperatures, below 400°C, during the initial TPSR run. The other is not so active but reacts slowly so that it remains on the catalyst even after a few TPSR runs. Existence of the two types of sulfur is a characteristic

property of the sample used catalyst.

The sulfur reacts more easily with O_2 than with H_2 in accordance with the previous arguments [1,8]. This is supported by the fact that the peaks above $400^\circ C$ appear at relatively low temperatures when the ambient gas is switched from H_2 to air.

During the oxidation process, however, the sulfur seems to be covered with nickel oxide as proposed by others [8] because the peaks become smaller in air than in H_2 . The smaller peaks in air is not due to the sensitivity change of the detector because the FPD responds almost identically either to SO_2 or H_2S .

Furthermore, the sample treated initially with air consistently shows smaller peaks than one treated initially with hydrogen. This suggests that the sample experiences severer encapsulation of the sulfur by nickel oxide during the initial oxidation process. The encapsulated sulfur is not removed easily even by subsequent treatment in hydrogen. On the other hand, when the sample is initially treated in hydrogen, a large amount of sulfur accumulates on the catalyst surface. The sulfur is then removed considerably by the subsequent gas treatments, showing relatively large TPSR peaks.

Accordingly, our TPSR results seem to support the previous observation that sulfur has lower reactivity with H_2 than with O_2 , and also the notion that the sulfur is buried by nickel oxide during oxidation pro-

cess. We admit that the TPSR provides only an indirect evidence of the above issues. Particularly, the phenomenon of sulfur burial could be proved by a director evidence, e.g., by in-situ XPS analysis of the catalyst surface in different reactive gases. Unfortunately, such an apparatus for in-situ experiments is not available in Korea at the moment.

REFERENCES

1. Windawi, H. and Katzer, J.R.: *J. Vac. Sci. Technol.*, **16**(2), 497 (1979).
2. Bartholomew, C.H. and Pannell, R.B.: *Applied Catalysis*, **2**, 39 (1982).
3. Masagutov, R.M., Kovaleva, L.V., Morozov, B.F. and Spivak, S.I.: *React. Kinet. Catal. Lett.*, **36**(1), 177 (1988).
4. Twigg, M.V.: "Catalyst Handbook", Wolfe Pub. Ltd., London (1989).
5. Bartholomew, C.H., Weatherbee, G.D. and Jarvi, G.A.: *J. Catal.*, **60**, 257 (1979).
6. Holloway, P.H. and Hudson, J.B.: *Surf. Sci.*, **33**, 56 (1972).
7. McCarty, J.G. and Wise, H.: *J. Chem. Phys.*, **72**(12), 6332 (1980).
8. Bartholomew, C.H., Agrawal, P.K. and Katzer, J.R.: *Adv. in Catal.*, **31**, 135 (1982).