JOURNAL OF CATALYSIS 76, 164–168 (1982)

Hydrogenation of Propene Catalyzed by Cobalt and Nickel Dispersed in Zinc Sulfide

M. BHADURI,[1] R. BURCH, AND P. C. H. MITCHELL

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England

Received May 22, 1981; revised February 4, 1982

The mixed sulfides $M_xZn_{(1-x)}S$ (M = Co, Ni; $0 \leq x \leq 0.1$) were prepared and their X-ray diffractograms and uv-visible diffuse reflectance spectra were recorded. Hydrogenation of propene over the mixed sulfides was carried out in a static reactor at 480°C and 345 Torr initial pressure (hydrogen : propene = 1 : 1). CoS was more active than NiS. Increasing amounts of Co^{2+} ions in the Co–Zn–S system did not show any significant increase of activity but for the Ni–Zn–S system the activity increased with the Ni^{2+} ion content from $x = 0.0$ to 0.1 making the activity of $Ni_{0.1}Zn_{0.9}S$ greater than that of NiS. Cobalt or nickel ions in octahedral coordination by S^{2-} ions are thought to be the active species in the catalytic hydrogenation of propene.

INTRODUCTION

The object of the work described in this paper was to compare the activities in the hydrogenation of propene of cobalt and nickel sulfide catalysts. Co^{2+} and Ni^{2+} ions were dispersed in a zinc sulfide lattice in the hope of producing ions with well-defined chemical (i.e., sulfide) and structural environments (tetrahedral and octahedral coordination). In this way we hoped to compare well-dispersed Co and Ni sulfides of different structures. The solid solutions $M_x Zn_{(1-x)}S$ with x varying from 0 to 10 mole% are likely to provide a series of catalysts in which the active species Co^{2+} or Ni^{2+} are highly dispersed and their number varies systematically while the other parameters affecting the catalyst remain unaltered. Hydrogenation of propene was used as a test reaction which was followed by monitoring pressure drop with time in a static reactor. Studies on the catalytic activities of this type of sulfide solid solution have not been reported, although a good deal of research has been carried out on the preparation, characterization, and activity of solid solutions of metal oxides (*1*).

EXPERIMENTAL

Zinc sulfide (99.9%, Alpha), nickel sulfide (99.9%, Alpha), and cobalt sulfide (precipitated by passing hydrogen sulfide into a warm alkaline solution of cobalt nitrate under nitrogen (*2*)) were used as the starting materials for preparing catalysts. Mixtures of zinc sulfide and cobalt or nickel sulfide were heated in evacuated (10^{-5} Torr) sealed silica tubes (Co, 950°C, 50 h; Ni 700°C, 100 h) which were quenched in water at room temperature to give a series of catalysts containing up to 10 mole% cobalt or nickel in zinc sulfide. The heating temperatures were close to but below the melting points of the dopant CoS or NiS. Samples of ZnS were also treated in the same way as the mixed sulfides in each system.

Samples with more than 10 mole% Co or Ni were not studied since our objective was to have a solid solution with good dispersion of the dopant and avoid interaction between dopant ions. At high concentrations of dopant there is also the possibility of segregation of a new phase.

X-Ray diffractograms were recorded by using a Philips X-ray generator (PW 1130)

---

[1] Present address: School of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, England.

0021-9517/82/070164-05$02.00/0

equipped with a Ni filtered CuK_α radiation source and a horizontal goniometer (PW 1380). A Beckman spectrophotometer (ACTA MIV) was used to obtain uv-visible diffuse reflectance spectra with barium sulfate as reference.

The static reactor, a Pyrex tubular vessel of about 100 ml in volume, containing the catalyst (0.25 g) spread uniformly along its length (10 cm), was placed horizontally in a furnace, and was evacuated down to $\sim 3 \times 10^{-5}$ Torr. The temperature was raised to 480°C and after about 2 h a gas mixture containing 50 vol% propene in hydrogen was introduced to the reactor until the pressure attained 345 Torr and the reactor was then isolated from the rest of the apparatus by a greaseless tap. The pressure drop with time in the static reactor due to hydrogenation of propene was monitored continuously by a previously calibrated pressure transducer and a chart recorder. All the experiments were carried out for ~24 h and some of them were repeated for ~8 h. At the end of each experiment, the reaction products were analyzed by GLC. A blank experiment without catalyst demonstrated that the walls of the reactor did not catalyze propene hydrogenation.

RESULTS AND DISCUSSION

X-Ray Diffraction

X-Ray diffractograms of $Co_xZn_{1-x}S$ catalysts did not show any lines additional to those of ZnS. Therefore, no second phase was present and the Co^{2+} ions had become incorporated in the ZnS lattice. For the $Ni_xZn_{1-x}S$ catalysts samples with $x \leq 0.05$ similarly formed a single phase solid solution incorporating all the Ni^{2+} ions in the ZnS lattice. However, for samples with $x = 0.07$ and 0.1 there was evidence of a second phase, probably some Ni^{2+} ions present as NiS. Diffraction angles (2θ) and relative intensities of lines in the diffractograms are listed in Table 1. Lattice parameters a were calculated from the 2θ values assuming a cubic structure and are plotted against composition x in Fig. 1. In the $Ni_xZn_{1-x}S$ system, the value of a hardly changed with composition. This is consistent with the lower extent of incorporation of Ni^{2+} into the ZnS lattice. However, the a value for $Co_xZn_{1-x}S$ decreased as the composition changed from $x = 0$ to 0.05, beyond which it remained unchanged. The discontinuity at $x = 0.05$ could indicate a structural change for the Co^{2+} ion.

TABLE 1

X-Ray Diffraction of $Ni_xZn_{1-x}S$ Samples

Composition x	Diffraction angle, 2θ, and relative intensity[a]
0.0[b] and 0.01-0.05	27(4), 28.6(100), 33.1(10), 47.5(4), 47.75(32), 56.5(25), 56.6(14)
0.07[c]	34.6(4), 45.75(4)
0.10[c]	30.1(8), 30.6(8), 34.6(2), 45.75(4)

[a] Intensities (in parentheses) relative to the strongest line in each diffractogram taken as 100.

[b] ZnS heated at 750°C for 100 h in vacuum.

[c] For these samples, only diffraction angles additional to those observed for samples with $x = 0$ and $x = 0.01-0.05$ are shown.

We conclude from the diffraction studies that the ability to form a solid solution in ZnS (i.e., to substitute for Zn^{2+} ions) is greater with Co^{2+} than Ni^{2+}. This is in accordance with the greater tetrahedral site preference of Co^{2+} compared with Ni^{2+}.

Reflectance Spectra

The spectra of ZnS and the mixed sul-

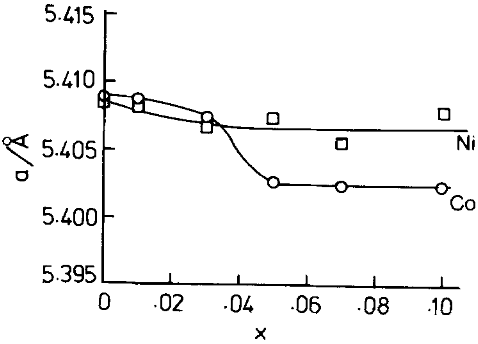

FIG. 1. Plots of lattice parameter, a, vs composition, x, for samples of the $Co_xZn_{1-x}S$ and $Ni_xZn_{1-x}S$ systems.

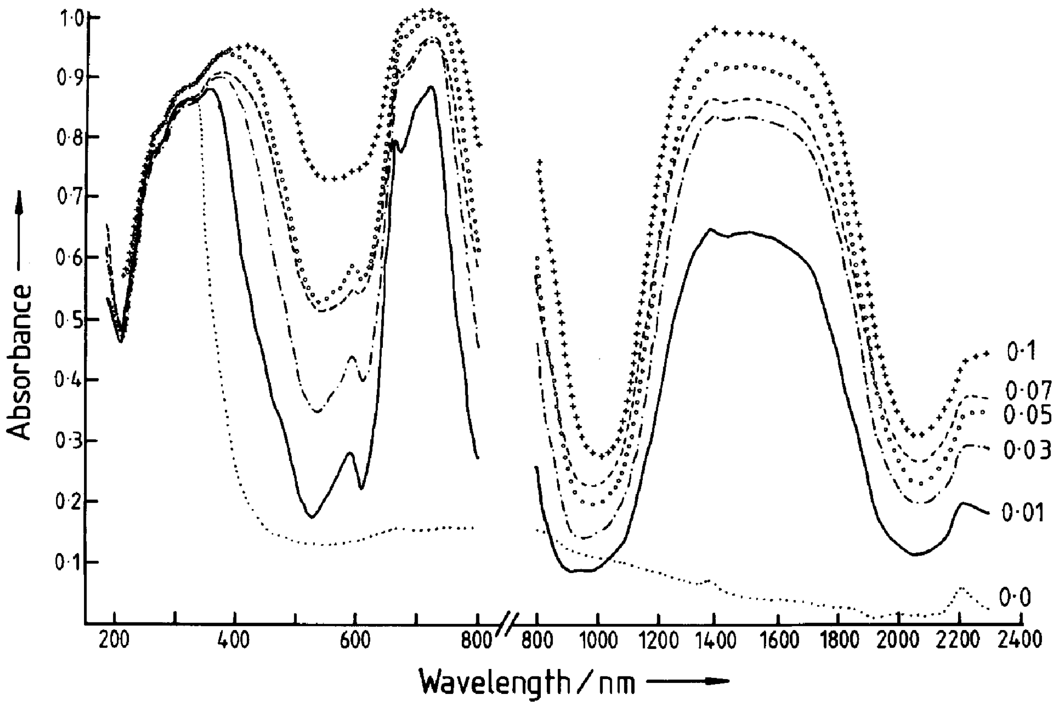

FIG. 2. Ultraviolet-visible near ir diffuse reflectance spectra of samples of the $Co_xZn_{1-x}S$ ($0 \le x \le 0.1$) system. Numbers on the curves are the values of x.

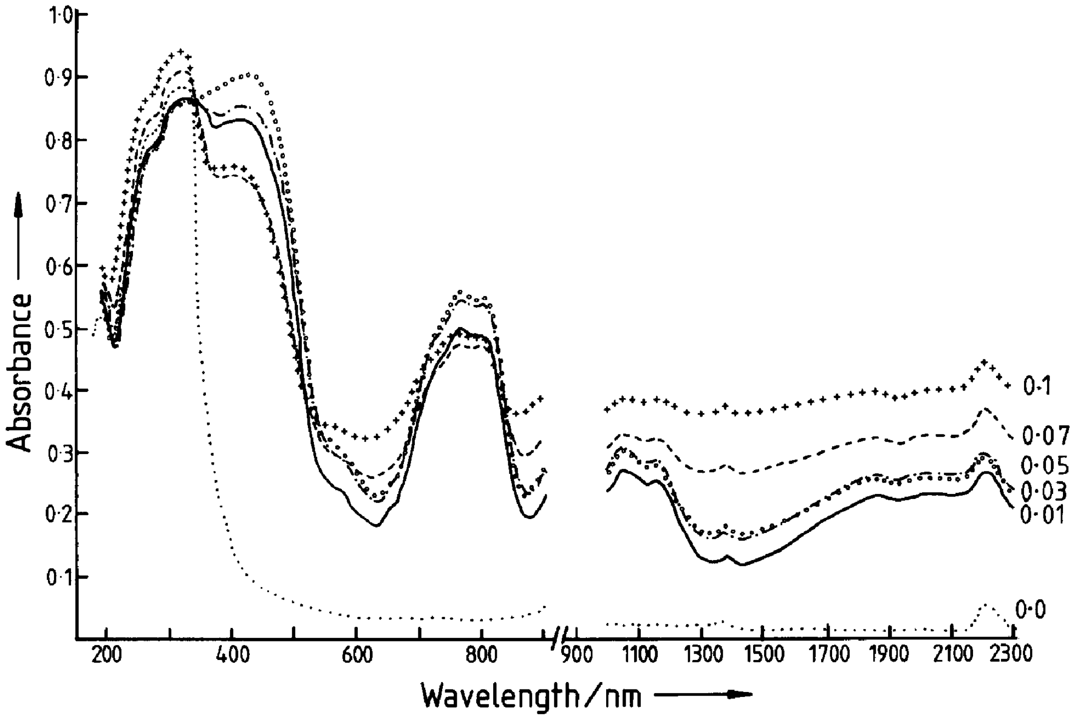

FIG. 3. Ultraviolet-visible near ir diffuse reflectance spectra of samples of the $Ni_xZn_{1-x}S$ ($0 \le x \le 0.1$) system. Numbers on the curves are the values of x.

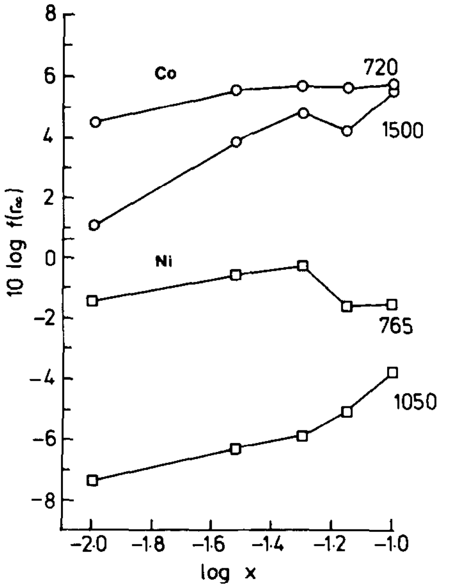

FIG. 4. Log-log plots of the Kubelka-Munk function, $f(r_\infty)$, against composition, x, for samples of the $Co_xZn_{1-x}S$ and $Ni_xZn_{1-x}S$ systems. Numbers on the curves are wavelengths (λ in nm).

fides recorded relative to $BaSO_4$ are shown in Figs. 2 and 3. We assign the absorption peaks in the visible and near ir regions to ligand field transitions of Co^{2+} and Ni^{2+}. For the low Co and Ni catalysts ($x \leq 0.05$) the number and positions of the peaks correspond to tetrahedral Co^{2+} (720 and 1500 nm) and Ni^{2+} (765 and 1050 nm) (*3*, *4*). We express the intensities of absorption as the Kubelka-Munk function, $f(r_\infty)$, calculated (*5*) at various wavelengths. The relation between $f(r_\infty)$ and the concentration, x, of an absorbing species is given by

$$\log f(r_\infty) = \log x + \log \epsilon/s$$

where ϵ is the extinction coefficient and s the scattering coefficient. For a homogeneous dispersion of the absorbing species in the ZnS lattice we expect a linear relation between $\log f(r_\infty)$ and $\log x$. Values of $\log f(r_\infty)$ at selected wavelengths are plotted against $\log x$ in Fig. 4. We see a negative deviation from linearity and a discontinuity at $x = 0.05$. Our interpretation is that with increasing x, the fraction of octahedral Co^{2+} and Ni^{2+} increases. This would cause a decrease in absorbance since the extinction coefficients for the octahedral species are less than those of the tetrahedral species. The deviation is most pronounced for the Ni catalysts showing a greater proportion of octahedral structure with Ni^{2+} than with Co^{2+} in agreement with the X-ray diffraction data and the greater octahedral site preference of Ni^{2+}. For the Ni^{2+} catalysts there is a significant decrease in absorbance at $x \geq 0.07$ for the absorption band at 765 nm. This corresponds to the presence of a separate phase according to the X-ray diffraction patterns. Thus this phase consists predominantly of Ni^{2+} in octahedral coordination by S^{2-} ions. However, segregation of a new phase probably causes background variation in the infrared region of the spectrum and thus the absorbance at 1050 nm seems to increase more strongly for $x \geq 0.07$.

Catalytic Measurements

The reaction studied is the hydrogenation of propene to propane

$$CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$$

which is accompanied by a pressure drop at constant volume. The composition of the gas mixture was determined by analysis of gas samples withdrawn after 8 and 24 h (a separate run). The 8-h samples contained

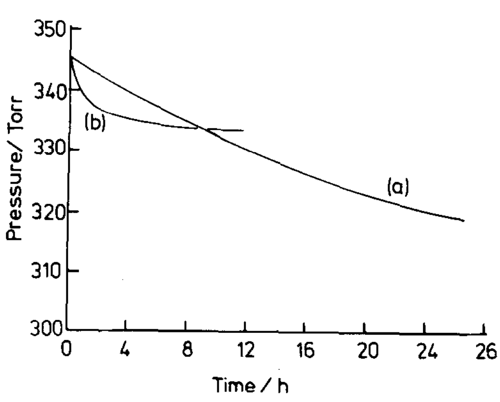

FIG. 5. Change of pressure with time in the static reactor during the hydrogenation of propene at 480°C on (a) $Co_{0.05}Zn_{0.95}S$ and (b) CoS.

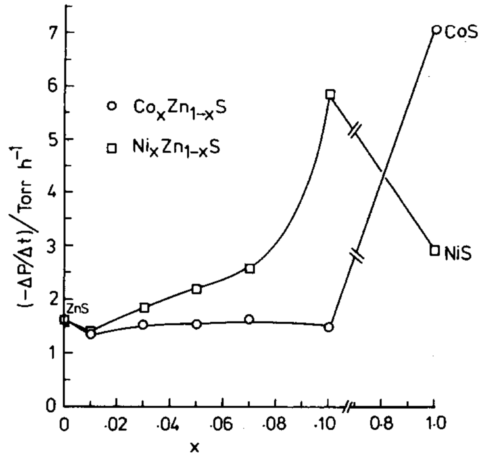

FIG. 6. Variation of the initial rate of hydrogenation ($-\Delta P/\Delta t$) of propene with composition, x, on samples of the $Co_xZn_{1-x}S$ and $Ni_xZn_{1-x}S$ systems at 480°C.

only propane and propene but the 24 h samples contained in addition small quantities of methane and an unidentified compound. Thus over the longer time interval some cracking had occurred but was not significant in the first few hours of the experiment.

The change of pressure at 480°C was used to follow the course of the hydrogenation. In Fig. 5a we show the pressure–time curve for $Co_{0.05}Zn_{0.95}S$ which was typical of the other mixed sulfides and NiS. Pure CoS (Fig. 5b) behaved somewhat differently from the other catalysts showing a high initial activity followed by a leveling off suggestive of poisoning. We express activities as the initial rate of hydrogenation measured by the slope ($-\Delta P/\Delta t$) of the tangent to the pressure–time curve at $t = 0$.

In Fig. 6 we show the initial hydrogenation activity vs composition x of the $M_x Zn_{1-x}S$ (M = Co, Ni) catalysts ($x = 0$–0.10, 1.0). Surface areas were not measured, but in view of the high temperature of preparation there is unlikely to be a great variation between the samples. The slight fall in activity between $x = 0$ and $x = 0.01$, however, is probably not significant in the absence of surface area data.

Further doping with Co hardly affected the activity but with Ni the activity increased considerably. The activity of pure CoS was higher than that of all the doped catalysts. NiS was less active than the doped catalyst with $x = 0.10$ and less active than CoS. Thus the doped Ni catalysts behaved differently from the Co catalysts in that the activity rose with increasing Ni. Presumably over the concentration range studied most Co^{2+} ions enter tetrahedral sites in the ZnS lattice (as suggested by the reflectance spectra and X-ray diffraction patterns) and have no effect on the activity. The higher activity of pure CoS over NiS agrees with our results for the hydrogenation of hex-1-ene over sulfided Al_2O_3-supported catalysts (*6*).

CONCLUSION

We conclude that the nickel–zinc sulfide catalysts are more active than the cobalt–zinc sulfide catalysts over the whole range of composition studied. Co^{2+} or Ni^{2+} ions in octahedral coordination by S^{2-} ions are active in catalyzing propene hydrogenation, but become inactive when in tetrahedral coordination. An active species existing as a separate phase highly dispersed on the matrix (e.g., Ni^{2+} as NiS in $Ni_xZn_{1-x}S$ with $x > 0.05$) is more active than metal ions dispersed in the matrix forming a single phase solid solution.

ACKNOWLEDGMENTS

We would like to thank the Science Research Council for an award of a postdoctoral research fellowship to one of us (M.B.).

REFERENCES

1. Vickerman, J. C., "Catalysis," Vol. 2, p. 107. Chemical Society, London, 1978, and references therein.
2. Glemser, O., *in* "Handbook of Preparative Inorganic Chemistry" (G. Brauer, Ed.), Vol. 2, 2nd ed., p. 1523. Academic Press, New York, 1965.
3. Stephens, D. R., and Drickamer, H. G., *J. Chem. Phys.* **35**, 429 (1961).
4. Weakliem, H. A., *J. Chem. Phys.* **36**, 2117 (1962).
5. Wendlandt, W. W., and Hecht, H. G., "Reflectance Spectroscopy." Interscience, London, 1966.
6. Bhaduri, M., and Mitchell, P. C. H., *J. Catal.*, in press.