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Sulfur Poisoning of Nickel Methanation Catalysts

I. *In Situ* Deactivation by H_2S of Nickel and Nickel Bimetallics[1]

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The effects of exposure to dilute H_2S during reaction on the methanation activity of alumina-supported nickel, cobalt, and nickel bimetallic catalysts in powder, pellet, and monolith form were investigated. Results of activity tests at 525°K, 1 atm, and a space velocity of 30,000 hr^{-1} with 10 ppm H_2S in the reactant stream show that cobalt and most nickel bimetallic catalysts are not significantly more or less sulfur tolerant than nickel; Ni–MoO_3, however, is more active before, during, and after exposure to H_2S. The data also indicate that monolithic catalysts are significantly more sulfur resistant than either powder or pellet catalysts. All of these catalysts, however, are completely deactivated within a period of 2–3 days under the conditions investigated. During reaction in the presence of H_2S, there is an exponential decrease in activity accompanied by a gradual breakthrough of the poison. Less sulfur is adsorbed on the catalyst during reaction than would be if equilibrium adsorption occurred. Data showing the roles of temperature, gas composition, and catalyst geometry in the poisoning process and the results of regeneration experiments are presented and discussed.

INTRODUCTION

Poisoning of nickel catalysts by sulfur compounds is a serious problem in a number of important catalytic processes, including methanation of coal synthesis gas. Yet the adsorption of sulfur compounds such as H_2S has seen relatively little study (*1*, *2*) and the basic mechanisms of poisoning are poorly understood. Effects of H_2S on the specific methanation activity of nickel were only recently studied by Dalla Betta *et al.* (*3*, *4*) and Bartholomew *et al.* (*5–7*). These studies show that H_2S causes significant loss of activity upon several hours exposure to a reaction mixture containing 1 to 10 ppm H_2S.

The present study of alumina-supported Ni, Co, and bimetallics of Ni with Co, Pt, Rh, Ru, and MoO_3, in powder, pellet and monolithic form, was undertaken to determine effects of catalyst composition, metal loading, and support geometry on the poisoning by H_2S during reaction of methanation catalysts. Effects of temperature and reactant gas composition as well as several regeneration treatments were also investigated.

EXPERIMENTAL

Analytically pure metal salts and Kaiser SAS 0.32-cm alumina spheres (301 m^2/g) were used in preparation of the supported catalyst beads and powders. Cordierite monolith supports (Corning Glass Works) with 31 square channels/cm^2 of cross section were washcoated with Al_2O_3 powder

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(Kaiser SA Medium) and used in preparation of monolithic catalysts. Samples were prepared by simple impregnation or coimpregnation to incipient wetness of the support with aqueous metal salt solutions followed by oven drying at 355 to 375°K for 5 hr. The impregnated, dried samples were reduced in flowing hydrogen at a space velocity of 1000 to 2000 hr^{-1} while heating at less than 5°K/min to 725 to 775°K with a 2-hr temperature hold at 500°K and 10 to 16 hr at 725 to 775°K. Samples of 50 to 100 g of catalyst reduced in a separate reduction system were carefully passivated with 1% air in nitrogen. Additional details regarding the preparation and characterization of these catalysts have been reported elsewhere (*5–9*).

Metal surface areas were determined by means of hydrogen chemisorption at 298°K (*9–11*) [375°K for ruthenium-containing catalysts (*12*)] using a conventional volumetric apparatus capable of 1.3×10^{-7} kPa. Hydrogen adsorption uptake was determined as a function of pressure and the isotherm was extrapolated to zero pressure to obtain the amount chemisorbed. Catalyst compositions (in weight percent by metallic constituent) and hydrogen adsorption uptake data are shown in Tables 1 and 2. For the purpose of simplicity, catalysts are hereafter designated by total metal loading, e.g., 20% Ni–Co rather than 10% Ni/10% Co/Al_2O_3.

The state of metal reduction in the Ni/Al_2O_3 catalysts was determined by O_2 oxidation (*9*). The results indicate these catalysts have 70–90% of the nickel re-

TABLE 1

Effects of H_2S Poisoning on Methanation Activity of Nickel and Nickel Bimetallic Catalysts (525°K, 110 kPa, GHSV = 30,000 hr^{-1}, in 95% N_2, 4% H_2, 1% CO, 10 ppm H_2S)

Catalyst[a]	H_2 adsorption[b] (μmoles/g cat)	Percentage CO conversion (fresh catalyst)	Turnover number[c] × 10^3 (fresh catalyst)	Percentage activity after 24 hr	Percentage activity at time/H_2 uptake[d] of 0.5 hr/μmole H_2
3% Ni/P	35	7.5	5.1	<1	31
14% Ni/P	179	41	6.7	45	37
10% Ni/10% Co/P	107	29	6.5	40	40
2.5% Ni/3% MoO_3/P	19	4.8	10.8	13	54
2.5% Ni/0.5% Ru/P	52	7.8	5.3	<1	9
2.5% Ni/0.5% Rh/P	30	6.6	6.2	<1	34
15% Ni/0.5% Pt/P	130	24	6.2	38	35
12% Ni/M	75	93	23.4	50	50
5.5% Ni/5.5% Co/M	54	88	25.5	35	41
6% Ni/6% MoO_3/M	25	85	41.5	40	62
11% Ni/0.6% Pt/M	73	75	17.7	49	45
6% Ni/1.2% Ru/M	31	37	18.8	—[e]	59

[a] P denotes powdered alumina supported catalyst; M denotes Al_2O_3-coated monolithic support.

[b] Total adsorption measured at 298°K.

[c] Turnover numbers have units of molecules CH_4 per site per second. Conversions were very high for the monolithic catalysts (80 to 90%); however, effectiveness factors were nearly unity and mass transfer film resistance was negligible under these conditions. Turnover numbers for the fresh catalysts were determined before H_2S was added.

[d] H_2 uptake based on 1 cm^3 of sample and corrected for the appropriate density of each sample. Powder densities ranged from 0.36 to 0.56 g/cm^3; monolithic catalyst densities ranged from 0.6 to 0.8 g/cm^3.

[e] Data were taken over a period of 12 hr at which time 60% of the activity remained.

TABLE 2

Effects of H_2S Poisoning on Methanation Activity of Nickel and Nickel Bimetallic Catalysts (525°K, 110 kPa, GHSV = 30,000 hr^{-1}, in 99% H_2, 1% CO, 10 ppm H_2S)

Catalyst[a]	H_2 adsorption[b] (μmoles/g cat)	Percentage CO conversion (fresh catalyst)	Turnover number[c] $\times 10^3$ (fresh catalyst)	Percentage activity after 24 hr	Percentage activity at time/H_2 uptake[d] of 0.5 hr/μmole H_2
3% Ni/P	35	27	31	0	2.5
20% Ni/P	213	90	13	35	4
20% Co/P	76	90	35	12	4
10% Ni/10% Co/P	107	85	26	23	7
10% Ni/10% MoO_3/P	92	60	20	25	16
3% Ni/S	35	22	25	0	4.5

[a] P denotes powdered alumina-supported catalyst; S denotes 0.32-cm Al_2O_3 spheres.

[b] Total adsorption measured at 298°K.

[c] Turnover numbers have units of molecules CH_4 per site per second. Conversions were very high (20 to 90%); however, effectiveness factors were nearly unity and mass transfer film resistance was negligible under these conditions.

[d] H_2 uptake based on 1 cm^3 of sample and corrected for the appropriate density of each sample. Powder densities ranged from 0.36 to 0.56 g/cm^3.

duced to the metallic state. The phase compositions of alumina-supported nickel and nickel bimetallics were previously investigated by X-ray diffraction (*5, 11*). The results reveal the presence in these catalysts of well-dispersed clusters ranging from 3 to 7 nm in diameter and provide positive evidence for formation of alloy clusters in Ni–Co, Ni–Ru, and Ni–Rh. The X-ray data for the nickel molybdenum oxide catalyst, however, do not provide evidence for alloy formation or enable the determination of the oxidation state of molybdenum. Hence, the composition of this catalyst will be arbitrarily designated as Ni–MoO_x where $x = 3$, although x could vary from 0 to 3 throughout the sample. The possibility of metallic molybdenum cannot be ruled out since MoO_3 can be reduced to the metal in hydrogen at about 770°K (*13*) which is near reduction temperatures used in this work.

Sulfur poisoning tests were conducted at 1 atm, 525°K, and a space velocity of 30,000 hr^{-1} using 1 cm^3 of catalyst sample in an isothermal glass reactor equipped with O-ring stopcocks and preheater. In the case of monolithic catalysts, 1.3-cm-long by 2.5-cm-diameter samples were used, some of the channels of which had been plugged with cement to obtain 1 cm^3 of volume. The reactant mixture contained 95% N_2, 4% H_2, 1% CO, and 10 ppm H_2S or alternatively 99% H_2, 1% CO, and 10 ppm H_2S (gas compositions expressed in molar percent and ppm by volume). Chromatographic samples were taken every 0.5 hr over a period of 12–24 hr. Gas phase H_2S concentrations and catalyst sulfur contents were determined analytically using techniques described previously (*2*).

RESULTS

Deactivation Measurements during Reaction

Normalized activity versus time data are plotted in Fig. 1 for 3 and 14% Ni/Al_2O_3 powders and a 12% Ni/Al_2O_3-coated monolith tested in a reaction mixture containing 95% N_2, 4% H_2, 1% CO, and 10 ppm H_2S. Normalized activity (hereafter

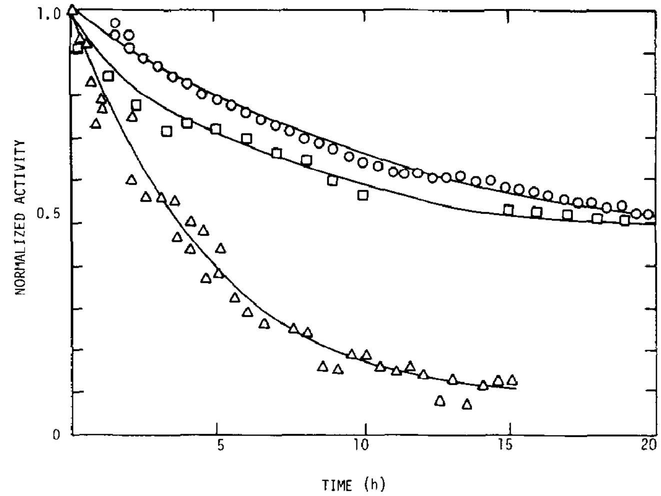

FIG. 1. Normalized activity vs time curves for H_2S poisoning of nickel catalysts during reaction at 525°K, 110 kPa, and 30,000 hr^{-1}. Reaction mixture: 95% N_2, 4% H_2, 1% CO, 10 ppm H_2S. ○, 12% Ni monolith; □, 14% Ni/Al_2O_3 powder; △, 3% Ni/Al_2O_3 powder.

referred to as activity) is defined here as the rate of methanation of CO at any given time divided by the initial rate of reaction. The decrease in activity with time appears to be exponential in nature. The 3% Ni powder, however, loses activity at a substantially greater rate than either the 14% Ni powder or 12% monolith. The higher rate of deactivation for the 3% Ni is likely a consequence of its lower metal surface area or sulfur adsorption capacity relative to the other two samples, as indicated by the hydrogen adsorption uptake data in Table 1. The rates of deactivation for the 14% Ni powder and 12% Ni monolith are approximately the same, although the hydrogen uptake for the monolithic catalyst is substantially smaller.

Figure 2 shows activity and outlet H_2S concentration as a function of time for a 3% Ni–Rh powder tested in the same nitrogen-diluted, H_2S-containing mixture. The data reveal that under reaction con-

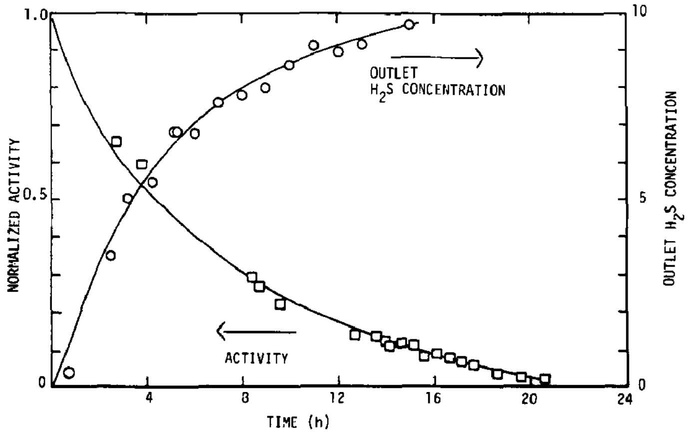

FIG. 2. Normalized activity and outlet H_2S concentration (ppm vol) vs time curves for H_2S poisoning of 3% $Ni\text{-}Rh/Al_2O_3$ powder at 525°K, 110 kPa, and 30,000 hr^{-1}. Reaction mixture: 95% N_2, 4% H_2, 1% CO, 10 ppm H_2S. □, Activity; ○, outlet H_2S concentration.

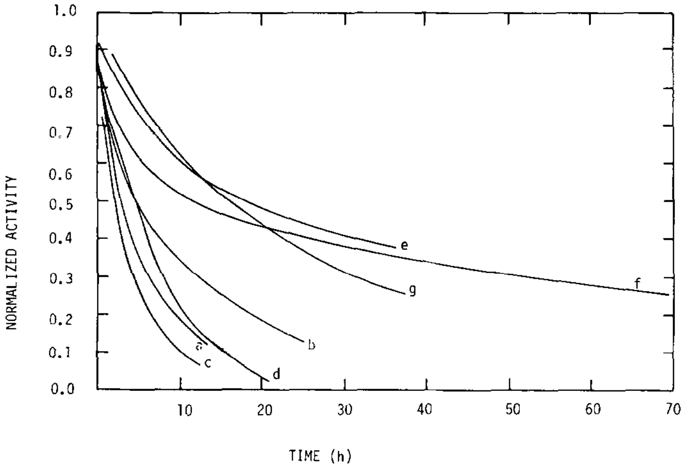

FIG. 3. Smoothed activity vs time curves for H_2S poisoning during reaction at 525°K, 110 kPa, and 30,000 hr^{-1}. Reaction mixture: 95% N_2, 4% H_2, 1% CO, 10 ppm H_2S. (a) 3% Ni/P; (b) 3% Ni-MoO_3/P; (c) 3% Ni-Ru/P; (d) 3% Ni-Rh/P; (e) 14% Ni/P; (f) 20% Ni-Co/P; (g) 15.5% Ni-Pt/P. (/P denotes powdered alumina-supported catalyst.)

ditions at high space velocity, H_2S breakthrough occurs before the sample is completely deactivated. For example, after 8 hr approximately 30% of the original activity remains, while the outlet H_2S concentration is about 8 ppm. In higher metal loading (10 to 20%) catalysts the breakthrough of H_2S was much more gradual; for instance, the 12% Ni/M catalyst displayed 50% activity with only 20% H_2S

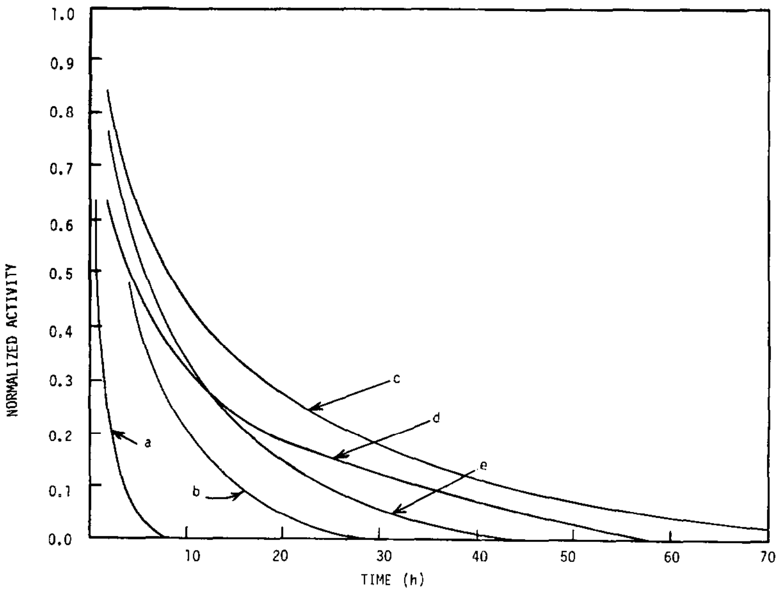

FIG. 4. Smoothed activity vs time curves for H_2S poisoning during reaction at 525°K, 110 kPa, and 30,000 hr^{-1}. Reaction mixture: 99% H_2, 1% CO, 10 ppm H_2S. (a) 3% Ni/P; (b) 20% Co/P; (c) 20% Ni/P; (d) 20% Ni-MoO_3/P; (e) 20% Ni-Co/P.

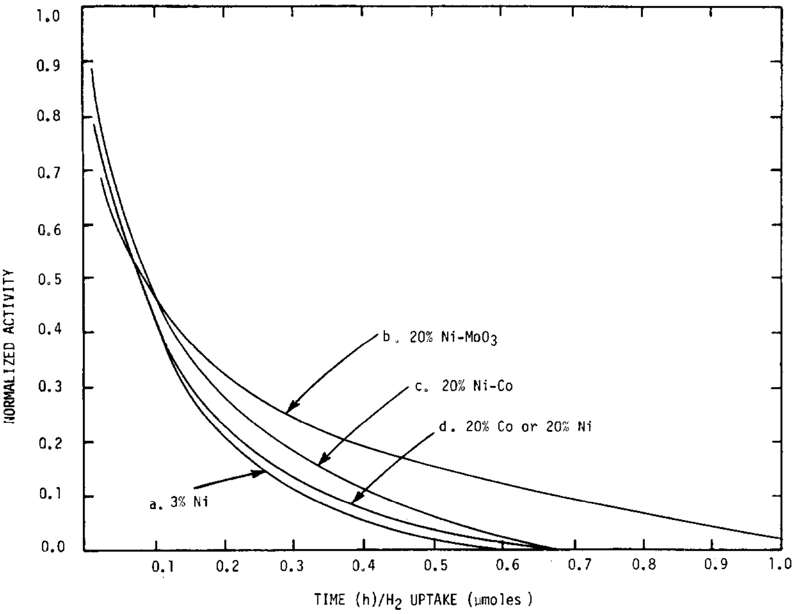

FIG. 5. Smoothed activity vs surface area normalized time during reaction at 525°K, 110 kPa and 30,000 hr^{-1}. Reaction mixture: 99% H_2, 1% CO, 10 ppm H_2S. (a) 3% Ni; (b) 20% Ni-MoO_3; (c) 20% Ni–Co; (d) 20% Ni or 20% CO. (All powders supported on alumina.)

breakthrough after 17 hr. Complete breakthrough was not observed for the 10–20% catalysts even after 2 to 3 days.

Smoothed activity-versus-time curves are shown in Figs. 3 and 4 for Ni, Ni–Co, Ni–MoO_3, Ni–Pt, Ni–Rh, and Ni–Ru catalyst powders tested in the nitrogen-diluted reaction mixture containing 10 ppm H_2S and for Ni, Co, Ni–Co, and Ni–MoO_3 powders tested in a hydrogen-rich mixture (99% H_2, 1% CO, 10 ppm H_2S). From the data in both figures, it is apparent that the 3 to 6 wt% catalysts lose activity at a substantially greater rate in the first 10 to 20 hr than do the 14 to 20 wt% catalysts, again most probably because of the larger adsorption capacity for the latter group. It would be tempting to attempt to compare the relative sulfur resistances of the different catalysts from the curves in Figs. 3 or 4. However, because of the significant differences in surface areas for these catalysts (see Tables 1 and 2) such a comparison is not meaningful, unless these differences are taken into account.

Figure 5 shows activity plotted versus time divided by hydrogen uptake (surface area normalized time) for 1-cm^3 powdered samples of 3% Ni, 20% Ni, 20% Co, 20% Ni–Co, and 20% Ni–MoO_3 tested in 99% H_2, 1% CO, and 10 ppm H_2S. The results of normalizing the effects of surface area are very interesting. The deactivation curves for 3 and 20% nickel are very nearly coincidental. The curves for 20% Ni and 20% Co are essentially the same and are represented by a single curve. The curve for Ni–Co shows slightly higher activity compared to Ni for values of the abscissa from 0.1 to 0.5. The activity of 20% Ni–MoO_3/Al_2O_3, however, is significantly higher for values of the abscissa above 0.2.

Turnover numbers (molecules of methane produced per site per second) at 525°K for fresh samples and activities at 24 hr and at a surface area normalized time of 0.5 hr/µmole H_2 are listed in Tables 1 and 2 for powdered and monolithic catalysts tested in the nitrogen-diluted and

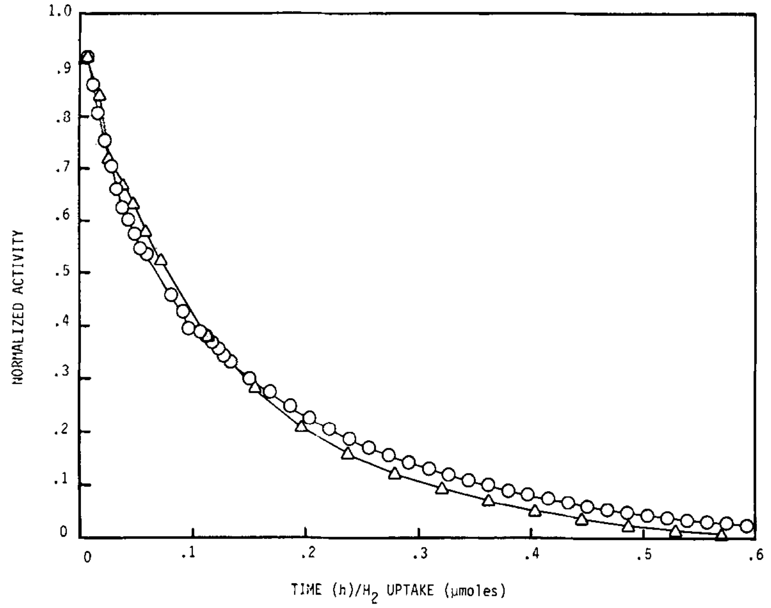

FIG. 6. Normalized activity vs surface area normalized time for 3% Ni in powder and pellet form during reaction at 525°K, 110 kPa, and 30,000 hr^{-1} in 99% H_2, 1% CO, 10 ppm H_2S. ○, 0.32 cm pellets; △, powder.

hydrogen-rich reactant gas mixtures, respectively. For a given catalyst geometry and reactant gas mixture, the activities of the fresh catalysts are not significantly different than observed for Ni, with the exception of Co and Ni–MoO_3 which are

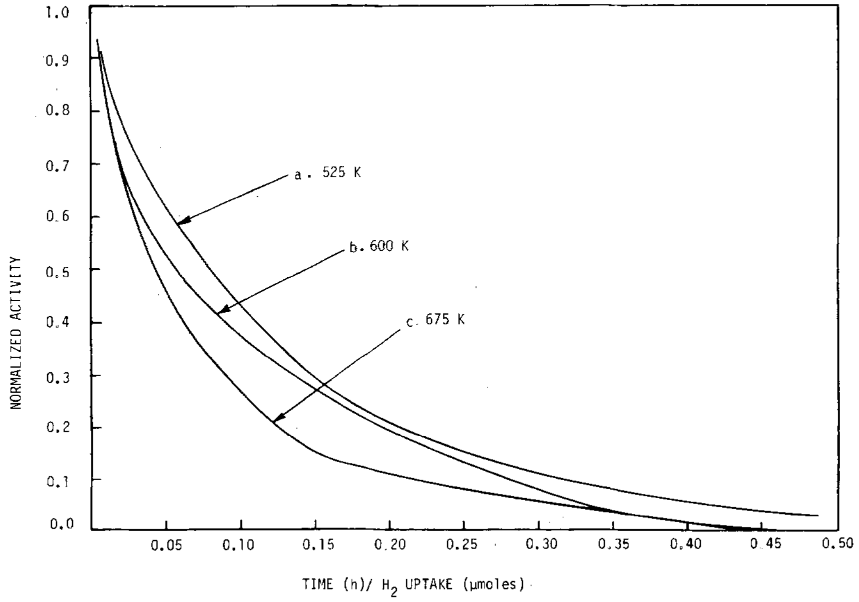

FIG. 7. Normalized activity vs surface area normalized time for 3% Ni/P during reaction at 525, 600, and 675°K, 110 kPa, and 30,000 hr^{-1} in 99% H_2, 1% CO, and 10 ppm H_2S. (a) 525°K; (b) 600°K; (c) 675°K.

about a factor of 2 more active. Catalyst geometry apparently influences the specific rate to the same or even greater extent than catalyst composition, as the data in Table 1 reveal that the turnover numbers for the fresh monolithic catalysts are 2 to 4 times larger than those for the fresh powders. That initial activity is also influenced by reactant gas composition is evidenced by a comparison of the data in Tables 1 and 2 for the powders; that is, the turnover numbers determined for fresh catalysts in the hydrogen-rich reactant mixture ($H_2/CO = 99$) are 2 to 3 times higher than those determined in the nitrogen-diluted mixture ($H_2/CO = 4$).

According to the data in Table 1, after 24 hr of exposure to the nitrogen-diluted, H_2S-containing mixture the monolithic samples with metal loadings of 8 to 12 wt% range in activity from 35 to 50% while the 14 to 20 wt% powders retain 38 to 45% of the original activity. The 3 wt% catalyst powders, however, retain less than 1% of their original activity after 24 hr.

Based on their higher activities for the same surface area normalized time in Table 1, the monolithic catalysts appear to be significantly (10 to 20%) more sulfur resistant than the catalyst powders. On the other hand, activity data in Table 2 and Fig. 6 for 3% Ni/Al_2O_3 in powder and spherical pellet form show very little difference, i.e., the activity of the pellets is not more than 2 to 3% higher than that of the powder at any given time. Thus, the monolithic catalysts are probably somewhat more sulfur resistant than catalysts in pellet form.

Comparison of the activity data at a surface area normalized time of 0.5 hr/μmole H_2 for catalysts of different metal composition (any given geometry and reactant gas composition) in Tables 1 and 2 reveals that Ni–MoO_3 catalysts (Ni–Co catalysts to a lesser extent) retain a higher percentage of their initial activity, i.e., exhibit greater resistance to H_2S than Ni or other Ni bimetallics.

TABLE 3

Effects of Poisoning and Regeneration Treatments on Normalized Activity

Catalyst[a]	Treatment	Percentage activity[b] after treatment
14% Ni/P	35 hr in reaction mixture[c] containing 10 ppm H_2S at 525°K	39
	2 hr in pure H_2 at 725°K	0
20% Ni–Co/P	88 hr in reaction mixture[c] containing 10 ppm H_2S at 525°K	20
	3 hr in CO; then 30 min in air and 11 hr in H_2 all at 525°K	37
	1 hr in H_2 at 725°K	0
	0.5 hr in O_2 and 1 hr in H_2 at 525°K	12
	0.5 hr in H_2 at 725°K	0
12% Ni/M	27 hr in reaction mixture[c] containing 10 ppm H_2S at 525°K	33
	3.5 hr temperature ramp from 525 to 675°K and 2.5 hr at 675°K in reactant mixture[c]	30
	30 hr in H_2 at 675°K	22

[a] P denotes powdered alumina-supported catalysts; M denotes Al_2O_3-coated monolithic support.

[b] Percentage of initial activity, i.e., normalized activity.

[c] Reactant mixture contained 1% CO, 4% H_2, 95% N_2.

A comparison of the activities of 3% Ni/P and 20% Ni–Co/P after 24 hr or at 0.5 hr/μmole between Tables 1 and 2 shows, as does comparison of Figs. 3 and 4, that the rates of deactivation are significantly greater for catalysts tested in the hydrogen-rich mixture.

Figure 7 shows the activity versus surface area normalized time curves for the 3% Ni powder in the hydrogen-rich reaction mixture at 525, 600, and 675°K,

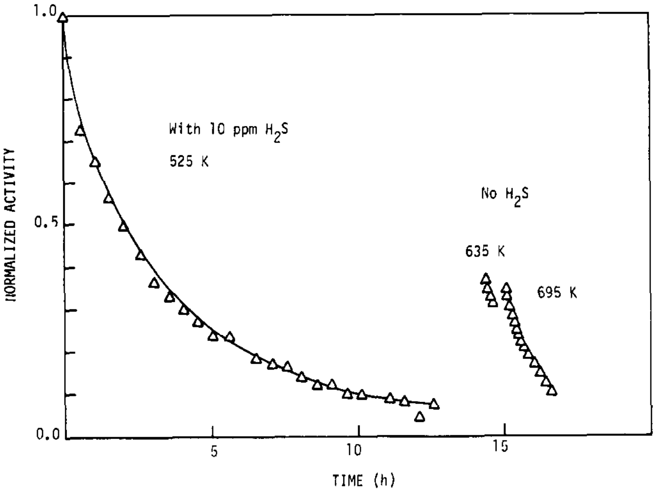

Fig. 8. Normalized activity vs time for H_2S poisoning of 3% Ni-Ru/Al_2O_3 during reaction at 525°K followed by attempted regeneration in H_2S-free reaction mixture at 635 and 695°K (110 kPa and 30,000 hr^{-1}). Reaction mixture: 95% N_2, 4% H_2, 1% CO, 10 ppm H_2S.

respectively. The data show that the rate of deactivation increases slightly with increasing temperature.

Regeneration Experiments

Attempts were made to regenerate selected poisoned catalysts with flowing hydrogen, carbon monoxide, oxygen, or a H_2/CO reaction mixture. Representative results are shown in Table 3. Several poisoned catalyst powders (such as the 14% Ni in Table 3) treated in flowing hydrogen at 725°K for 0.5 to 2 hr lost all remaining measurable activity and surface area. Although 5% of the surface area (measured by H_2 chemisorption at 298°K) could be recovered by a 24-hr treatment in H_2 at 725°K, no measurable activity was recovered. However, a Ni–Co powder treated in CO for 3 hr, then in air for 30 min followed by an 11-hr reduction in H_2 at 525°K showed an increase in activity (measured at 525°K) from 20 to 37%. Upon treatment at 725°K in H_2 all remaining activity was lost; nevertheless, a treatment in O_2 followed by H_2 reduction at 525°K restored 12% of its activity.

Figure 8 shows the effect of attempted regeneration of 3% Ni–Ru/P in the nitrogen-diluted reaction mixture. After the H_2S component was removed from the reaction mixture and the temperature increased to 635°K, the rate of deactivation increased rapidly; an increase in temperature to 695°K caused even more rapid and essentially complete loss of activity within a few minutes.

Monolithic catalysts showed similar further loss of activity when treated in pure H_2 or an H_2S-free reactant mixture, although the rate and extent of deactivation were not as great as for the powdered samples. For example, a decrease in activity from 30 to 22% was observed for poisoned 12 wt% Ni/M upon exposure to hydrogen for 30 hr at 675°K.

DISCUSSION

Deactivation during Reaction

The result of exposing nickel-containing catalysts to 10 ppm H_2S for 24 hr during reaction at 525°K (in the nitrogen-diluted reactant mixture) is almost complete deactivation (99%) for 3 wt% samples and 50 to 60% loss of activity for 15 to 20 wt% catalyst powders and 8 to 12 wt%

monolith catalysts. The nearly complete deactivation for the lower metal loading catalysts is in accord with data of Dalla Betta *et al.* (*3*) showing 2 to 3 orders of magnitude loss in activity for 5% Ni/Al_2O_3 during 24-hr *in situ* exposure to 10 ppm H_2S at 525°K. However, when the effects of surface area are normalized (see Fig. 5) high-loading nickel catalysts show time-dependent deactivation behavior almost identical to that of the low-loading nickel.

Nevertheless, the retention of approximately half the initial activity by the powders and monolith catalysts of intermediate to high metal loading after 24 hr exposure to H_2S is quite unexpected, in view of calculations based on previously reported equilibrium adsorption isotherm data for dilute H_2S in H_2 at 725°K (*2*). According to these calculations the catalysts in this study were exposed to 3 to 4 times the amount of H_2S needed to completely saturate the surface if equilibrium adsorption were assumed to occur. The gradual breakthrough curves (see Fig. 2) establish, however, that equilibrium (essentially complete) adsorption does not occur under reaction conditions at high space velocity. In other words, some of the metal sites remain available for reaction. This behavior suggests that the adsorption of H_2S may be affected by the presence of adsorbed reaction intermediates such as carbon, carbon monoxide, and/or COH_2 species as well as other variables such as temperature and residence time.

It should be emphasized that the loss of activity measured for the catalysts in this study was an effect of H_2S poisoning and not an effect of sintering or massive carbon deposition. These catalysts were prereduced in H_2 at high temperatures (725 to 775°K) for 10 to 16 hr resulting in high thermal stability. Therefore, sintering is expected to play a negligible role in the observed deactivation (*14*). Moreover, in long-term steady-state runs using a sulfur-free 95% N_2, 4% H_2, and 1% CO reaction mixture, negligible amounts of deactivation were observed for the 3% Ni/Al_2O_3 at temperatures up to 725°K (*5*, *7*). In fact, significantly higher CO concentrations, higher temperatures (greater than 725°K), and lower H_2/CO ratios (less than 3.0) were found to be necessary before a loss of activity due to carbon deposition could be observed (*5*, *7*).

Effects of Reactant Gas Composition

Although the same catalysts deactivate more rapidly in the hydrogen-rich mixture (99% H_2, 1% CO, 10 ppm H_2S) than in the nitrogen-diluted mixture (95% N_2, 4% H_2, 1% CO, and 10 ppm H_2S), the deactivation rate is still less than would be predicted by equilibrium adsorption. It is interesting that the rate of deactivation for nickel catalysts is greater in the reaction mixture having a lower P_{H_2S}/P_{H_2} and a higher P_{H_2}. This may be further evidence that active carbon deposits (removable by H_2) inhibit the poisoning of the surface by H_2S. This hypothesis finds additional support from the *in situ* poisoning experiments of Dalla Betta *et al.* (*4*) in which nickel catalysts were found to poison more severely if both H_2S and H_2O were added to the reactant mixture rather than only H_2S. These workers reasoned that H_2O inhibits the formation of carbonaceous deposits, thereby rendering the surface more susceptible to attack by H_2S.

Although the value of P_{H_2S}/P_{H_2} for the nitrogen-containing reactant gas mixture of 250×10^{-6} is greater than that predicted from thermodynamics (*15*, *16*) for bulk sulfide formation to occur at 525°K, there was no experimental evidence to indicate that bulk nickel sulfide was formed. On the contrary, the amount of sulfur in Ni/Al_2O_3 samples determined by chemical analysis was just barely sufficient to cover the surface nickel atoms. Nevertheless, there was evidence from chemical analysis of nickel molybdate catalysts (*17*) that additional sulfur was adsorbed and perhaps absorbed by molybdenum oxide to form molybdenum sulfides or oxy-sulfides, which behavior might also account for the greater sulfur tolerance of the molybdenum-containing catalysts.

Effects of Temperature

Since the strength of H_2S adsorption on nickel (at least in pure H_2 mixtures) is observed to decrease with increasing temperature (*1*, *2*) the slightly increasing rate of deactivation with increasing temperature shown in Fig. 7 is the opposite of what might be expected. Nevertheless, the observed behavior in a reacting system may result from a combination of several complex, counteracting effects such as: (i) weaker adsorption of H_2S, (ii) a higher rate of carbon deposition, (iii) an increase in the rate of carbon gasification to methane and (iv) a decrease in surface coverage of competing adsorbed reactant species or intermediates such as carbon, all occurring simultaneously as temperature is increased. The latter two effects may predominate so that the surface coverage of sulfur is increased with increasing temperature.

Effects of Catalyst Composition and Geometry

Of the bimetallic catalysts in this study, only Ni–MoO_3 evidenced substantially greater resistance than nickel to poisoning by H_2S during reaction. This might be explained by (i) the greater sulfur adsorption capacity of molybdenum-containing catalysts (*17*) and (ii) the participation in the reaction of sulfided molybdenum sites which are not taken into account by the H_2 chemisorption measurement at 300°K. A similar phenomenon, namely, the inability of some of the active Ni–MoO_x sites to adsorb H_2 (*5*, *17*, *18*) at lower temperature, may also explain the larger turnover numbers generally observed for fresh Ni–MoO_3 relative to Ni, since these specific rates are based upon H_2 chemisorption at 300°K. It should be noted that Mo/Al_2O_3 and Al_2O_3 have negligible methanation activity under the conditions studied (*17*); hence, the enhanced activity and sulfur tolerance of Ni–MoO_3/Al_2O_3 relative to Ni/Al_2O_3 is evidence of bimetallic synergism.

The somewhat higher sulfur resistance of monolithic catalysts relative to catalysts powders and pellets is interesting but difficult to explain. Since the monolith coating of 0.01 to 0.015 cm thickness has an average pore length 5 times that of the 0.005-cm-diameter particles in the catalyst powder, the effects of eggshell or pore-mouth poisoning might explain the differences in their behavior. However, using the same argument, the 0.32-cm spheres should be more not less sulfur resistant than the monolithic catalysts. It may be possible to explain the geometrical differences in terms of a detailed reactor and selective poisoning model similar to that discussed recently by Lee and Aris (*19*) for nonselective poisoning of monolithic catalysts. The observation of larger intrinsic activities for monolithic catalysts relative to powders and pellets is also interesting and has been discussed in a separate paper (*20*).

Regeneration

The complete loss of measurable activity observed in this study for the poisoned catalyst powders upon exposure to pure H_2 or a sulfur-free reaction mixture at high reaction temperatures (675–725°K) is quite unexpected, in view of the reported partial recovery of activity for poisoned catalysts in the reaction mixture at 675°K reported by Dalla Betta *et al.* (*3*) and the observation in this study that approximately 5% of the adsorbed sulfur could be removed under these conditions.

However, a major difference between this study and Dalla Betta's is that the catalysts tested by Dalla Betta were run for 24 hr at 673°K in a reaction mixture containing up to 20% CO before H_2S was introduced into the reaction mixture. Substantial amounts of carbon would be expected to deposit on the catalyst surface under these conditions. Indeed, Dalla Betta reported significant levels of carbon deposition after 24 hr of reaction at 673°K. This deposited carbon apparently inhibited sulfur poisoning since the nickel catalysts with the lowest steady-state activity (i.e., greatest amounts of carbon deposits) were the most sulfur resistant. Moreover, the deposited carbon layer apparently changed the form of the adsorbed sulfur, allowing some regeneration to occur when the catalysts were treated in the H_2S-free reaction mixture at high temperature.

The complete failure of catalysts in H_2 at high temperatures observed in this study may be explained by thermally induced (i) restructuring of the sulfur species absorbed at 525°K to an inactive metal sulfide, e.g., Ni_3S_2 or NiS or (ii) formation of a sulfospinel such as $NiAl_2S_4$ as suggested by Dalla Betta *et al.* (*3*). Evidence that restructuring of the nickel surface occurs in the presence of adsorbed sulfur was discussed in a previous paper (*2*).

The partial recovery of activity observed for the Ni–Co powder after successive CO and O_2 treatments at 525°K suggests several possibilities, including oxidation of adsorbed sulfur to SO_2 and SO_3, which species are less toxic than H_2S (*21*). Rostrup-Nielsen (*22*) reports that it is possible to regenerate steam-reforming catalysts partially at 800 to 1000°K in H_2O/H_2 atmospheres. Unfortunately, these same conditions would cause substantial sintering of conventional methanation catalysts containing γ-Al_2O_3 as the support (*14*, *23*). In view of the scarcity of data in the literature there is clearly a need to investigate in more depth the regeneration of nickel catalysts in air and other atmospheres.

CONCLUSIONS

(1) Under typical low-pressure reaction conditions for methanation (525°K, 110 kPa, and 30,000 hr^{-1}) in a reaction mixture containing 10 ppm H_2S conventional alumina-supported nickel catalysts lose most of their activity within a period of 2 to 3 days.

However, the rates of deactivation for these catalysts under reaction conditions are lower than would be predicted if equilibrium adsorption occurred. Apparently, the adsorption of H_2S is affected by competitive adsorption of reactants and reactant intermediates as well as residence time and temperature.

(2) The rate of deactivation due to H_2S poisoning increases with increasing H_2/CO ratio, i.e., is greater in a hydrogen-rich reactant mixture, possibly because of a greater rate of carbon gasification.

(3) The effect of increasing reaction temperature from 525 to 675°K is to slightly increase the rate of deactivation due to sulfur poisoning.

(4) Most metal promoters have little effect on the sulfur tolerance of nickel. Ni–MoO_3/Al_2O_3, however, is moderately more and Ni–Co/Al_2O_3 slightly more resistant to sulfur poisoning than Ni/Al_2O_3. The rate of deactivation of Co/Al_2O_3 is essentially the same as Ni/Al_2O_3.

(5) Monolithic catalysts are more sulfur tolerant than catalysts in pellet and powder form.

(6) Sulfur-poisoned catalysts can be partially regenerated with CO/O_2 and O_2 treatments followed by a mild re-reduction. However, treatment in H_2 at 725°K causes complete loss of activity, probably as a result of a surface restructuring phenomenon or phase transition.

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