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Methanation over Transition-Metal Catalysts

V. Ru/Al_2O_3—Kinetic Behavior and Poisoning by H_2S

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Hydrogenation of CO over Ru films supported on Al_2O_3 was investigated in a gradientless, all-quartz, internal-recycle reactor at temperatures between 523 and 673°K, at CO concentrations from 0.1 to 4%, and at H_2S concentrations between 0 and 100 ppb in H_2 at atmospheric pressure. Methane is the major reaction product. The measured activation energy of 27 ± 1 kcal/mole is in good agreement with the values reported for highly dispersed Ru catalysts. Methanation is strongly inhibited by CO in the gas phase at temperatures between 523 and 673°K. AES studies of aged catalysts show that there is no carbon present either on the surface or in the subsurface regions. In the presence of 13 ppb H_2S in the gas phase the methanation activity is reduced by more than 10^3-fold at 663°K. The activation energy remains 27 kcal/mole indicating that poisoning of Ru by H_2S is primarily a geometric effect. AES studies show the formation of a saturated two-dimensional surface sulfide, corresponding to each sulfur atom blocking two surface Ru atoms. There is no subsurface sulfur. This poisoning by sulfur is in marked contrast with the tolerance of Ru to poisoning by SO_2 during NO reduction by NH_3, and suggests that the nature of the reaction environment (strongly reducing vs mildly reducing) may have a significant effect on the tolerance of a catalyst to poisoning by sulfur.

INTRODUCTION

There has been much recent emphasis on developing a sulfur-tolerant catalyst for the catalytic hydrogenation of CO to CH_4 and higher hydrocarbons. Other publications from our laboratory (*1*, *2*) describe the poisoning by H_2S of Al_2O_3-supported Ni and Co, CO hydrogenation catalysts. Ru, also active for CO hydrogenation (*3*, *4*), has been reported to be more sulfur tolerant than other Group VIII transition metals (*5*–*8*). Another recent study (*9*) indicates that Ru is more sensitive to poisoning by sulfur than Ni catalysts. The results obtained in these previous studies are either based on the rate of deactivation or on the basis of a different reaction environment; quantitative data to establish the true sensitivity of Ru to poisoning by sulfur are lacking. The objective of this study was to determine the sulfur tolerance of Ru in CO hydrogenation under transport-free conditions.

EXPERIMENTAL

The quartz recycle reactor for testing catalysts, the gas chromatographic analysis system, and the Auger electron spectrometer used in the surface studies of aged catalysts have been described earlier (*1*, *2*, *10*). All gases used in catalyst testing were of ultrahigh purity and were passed over appropriate beds to remove traces of any impurities in the feed stream (*2*, *10*).

The catalyst was prepared by impregnating fused α-Al_2O_3 plates with ruthenium salt solution. To prepare the salt solution, 2 vol of 10 wt% ruthenium nitrate solution in water (Englehard Chemical Division) was added to 1 vol of 10 wt% ammonium bicarbonate solution. The addition of ammonium

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bicarbonate solution to the ruthenium nitrate solution was to keep the pH of the impregnating medium as close to 7 as possible to prevent dissolution of aluminum ions into the solution. The Al_2O_3 plate was soaked in the solution for 30 sec, and then heated in flowing He (~100 cm^3/min) at 313°K for 3 hr, before being loaded into the reactor.

The methanation activity, the activation energy, and the CO concentration dependence of the rate of methanation over Ru/Al_2O_3 were investigated between 523 and 673°K, at atmospheric pressure, and with CO concentrations from 0.05 to 10% in H_2.

An important part of this investigation was the examination of the surface of used catalysts by Auger electron spectroscopy. The reactor shutdown procedure for the runs was to shut off the CO in the feed and purge the reactor at reaction temperature with H_2 for 2 hr, then cool it to room temperature in flowing H_2. Studies showed that Ru/Al_2O_3 catalysts could be transferred to the Auger electron spectrometer without subsequent contamination.

Two types of sulfur poisoning studies were carried out. In prepoisoning studies the catalyst was equilibrated at reaction temperature (663°K) in a H_2 stream containing 13–95 ppb H_2S, and then the CO was added to the feed. In the *in situ* poisoning runs, the prepoisoning step was eliminated.

RESULTS AND DISCUSSION

Sulfur-Free Reaction Studies

Figure 1 shows transient methanation activity of Ru/Al_2O_3 at 573°K with 4% CO in H_2 as the feed gas. Since the reactor used in the present study is well mixed, the CO concentration in the effluent stream always represents the reactor gas-phase composition. There is an initial ~60-min period during which the CO concentration in the reactor increased from 0% to very close to the feed value of 4%. This is the reactor transient response to a step change in CO input concentration, which, as we show later, has a strong inhibiting effect on the rate of methanation. As shown in Fig. 1, the methanation activity dropped by more than an order of magnitude during this initial period. There follows a slow continued deactivation which is approximated by an exponential decay with a time constant of 0.11 hr^{-1} over the first few hours and a time constant of 0.0132 hr^{-1} over the 20- to 45-hr period, corresponding to a pseudo-steady state. Measurements of activation energy and CO partial pressure dependence were made in the pseudo-steady-state regions. To ensure that the catalytic activity had not changed during these kinetic measurements, periodic activity checks were made under the original operating conditions.

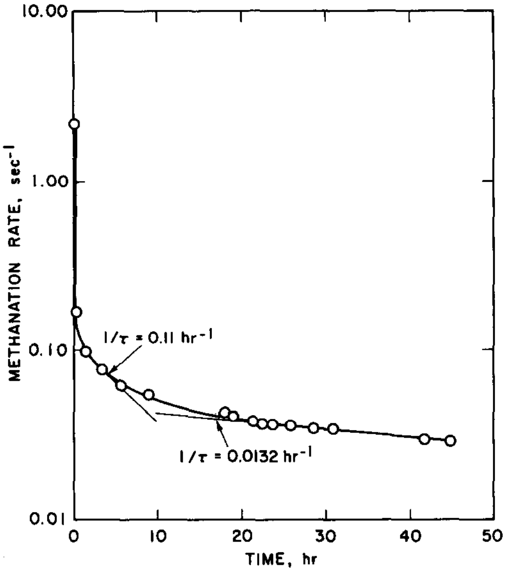

FIG. 1. Transient methanation activity of Ru/Al_2O_3 under sulfur-free conditions. Reaction conditions: 573°K, 4% CO in H_2. τ = exponential decay time constant.

When the CO concentrations in the reactor were reduced to 0.1%, a slow but continued regeneration of the deactivated catalyst occurred. Complete regeneration to the initial activity was achieved upon removing CO from the feed and treating the deactivated catalyst with H_2 at 673°K for 16 hr. Transient activity behavior of Ru/Al_2O_3

was identical in other runs carried out at temperatures between 523 and 673°K. In each case the above-mentioned regeneration procedure resulted in complete recovery of the lost activity. Elliott and Lunsford (*11*) have reported a similar regeneration procedure for Ru/Al_2O_3. These observations are also in agreement with those of Rabo *et al.* (*12*), who reported that Ru–C species formed via CO dissociation at 673°K were hydrogenated to methane and ethane at 296°K. The ease with which a deactivated Ru catalyst can be regenerated is in sharp contrast with the regeneration behavior of Ni and Co, CO hydrogenation catalysts (*1*, *2*).

Under our reaction conditions employed, CH_4 was the major reaction product with a trace of higher hydrocarbons; CO_2 was not detected (detection limit ~100 ppm). Sachtler *et al.* (*13*) have reported that disproportionation of CO is slower on Ru than on Ni and Co; hence the absence of CO_2, as observed in our study, is consistent with their results. Among higher hydrocarbons, only C_2H_4 and C_2H_6 were observed at 573°K, whereas only C_2H_4 was formed at 525°K. The molar ratio of C_2H_4 to CH_4 was 0.05 at 525°K with 4% CO in H_2, and this molar ratio did not change with the deactivation of Ru catalyst. At 573°K, both C_2H_4 and C_2H_6 were detected in equimolar amounts; $\Sigma C_2/C_1$ ratio increased as the CO concentration in feed was increased from 1.75 to 4%. No hydrocarbons other than CH_4 were detected at 673°K up to CO concentrations of 4.0%.

The effect of CO concentration on the rate of methanation over Ru/Al_2O_3 was examined at three temperatures: 525, 573, and 673°K. The concentration of CO was varied between 0 and 4%; variation in the H_2 concentration which constituted balance of the feed gas, was negligible during these measurements. Figure 2 shows that the rate of methanation over Ru/Al_2O_3 at 573°K is strongly inhibited by CO. Replotting the data (Fig. 2) as the methanation rate vs $1/X_{co}$ shows that the rate is inversely proportional to CO mole fractions (X_{co}) between 0.005 and 0.04. Similar results were obtained at 525 and at 673°K. Our results are in agreement with similar observations made with different reactor and catalyst configurations by Vannice *et al.* (*14*) and by Ekerdt and Bell (*15*).

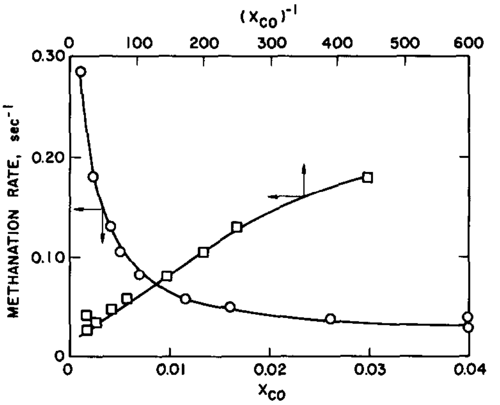

FIG. 2. CO partial pressure dependence of the rate of methanation over Ru/Al_2O_3 under sulfur-free conditions. Reaction conditions: 573°K, CO in balance H_2. The measurements were made with both increasing and decreasing CO concentration.

The activation energy for catalytic methanation over Ru/Al_2O_3 was 27 ± 1 kcal/mole. The very reproducible measurements are summarized in Fig. 3, where each symbol denotes a different run at a constant CO concentration. The methanation activation energy is independent of the CO concentration in the gas phase; identical values for the activation energy were obtained with 0.87% CO and with 4% CO in H_2. The methanation activity with 4% CO in H_2 shown in Fig. 3 is in agreement with the kinetic effect of CO concentration, shown in Fig. 2. The same is not true, however, for the runs with 0.87% and 1.0% CO in H_2 (Fig. 3). This is believed to result from the fact that Ru surface areas may not have been reproduced exactly in different batches of catalyst preparation; each run was made with a freshly prepared batch of Ru/Al_2O_3. Our activation energy measurements are in excellent agreement with the value of 27 kcal/mole (*14*), and the value of

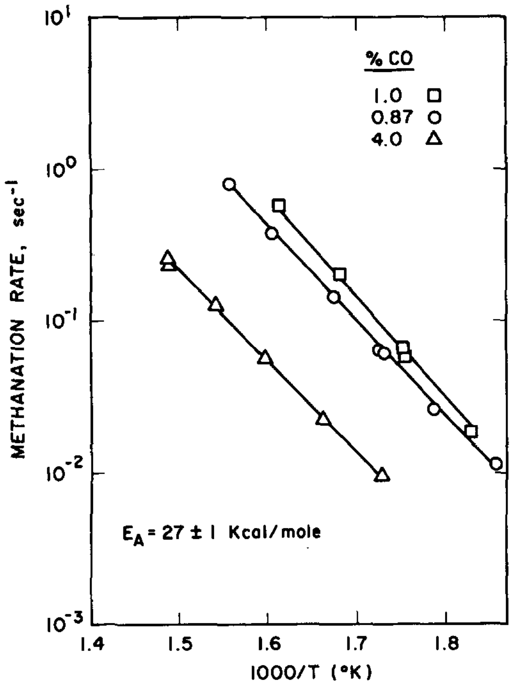

FIG. 3. Temperature dependence of the rate of methanation over Ru/Al_2O_3 under sulfur-free conditions. Each symbol denotes a new run with a freshly prepared batch of Ru catalyst. The concentration of CO was maintained at a constant value, as indicated, during each individual run.

26.8 ± 0.8 kcal/mole (*11*) obtained for highly dispersed Ru catalysts.

AES Analysis of Sulfur-Free Aged Ru/Al_2O_3

Figure 4 shows the AES spectra of a Ru/Al_2O_3 catalyst which had been used in the reactor at 673°K with 1% CO in H_2 for 150 hr. The run had been terminated with the catalyst operating in the pseudo-steady-state region with methanation activity more than an order of magnitude lower than that of a fresh Ru catalyst. Figure 4A shows that the AES spectrum of the aged catalyst before any treatment in the vacuum chamber is the same as that for clean Ru/Al_2O_3. There is no carbon present on the Ru surface; a small nitrogen peak may be the result of contamination during sample transfer. The oxygen peak is from the alumina, and is indicative of a discontinuous Ru surface. The low-energy Al peak is masked by a Ru peak, but the presence of Al_2O_3 was established by the presence of a high-energy (~1400 eV) Al peak. The catalyst surface shown in Fig. 4A was heated in the AES chamber at 673°K and at 10^{-8} Torr for 1 hr, with no change in the AES spectrum. The surface was then sputtered with an Ar^+ beam for 2 min. The resulting AES spectrum (Fig. 4B) remains basically unchanged except that (i) the nitrogen peak intensity increased, presumably the result of contamination of the sputtering gas with N_2, a fact that was confirmed by residual gas analysis, and (ii) the low-energy Al peak was no longer resolved from the wide low-energy Ru peak although the high-energy (~1400 eV) Al peak was still present. There was no carbon present in the subsurface regions either. AES analysis of other catalysts aged under sulfur-free conditions gave similar results—carbon was not present either on the surface or in the subsurface regions.

The absence of subsurface carbon indicates that rate inhibition on Ru is a surface process, presumably an accumulation of carbonaceous species, which reduced the number of active sites during methanation but were readily hydrogenated during the reactor shutdown. It has been reported that carbon can be hydrogenated off a Ru surface at room temperature (*12*). Similar results have been reported in another study (*13*), where surface carbon on Ru may not be as dominant a route to CH_4 formation, as it has been reported for Ni and Co. The absence of carbon on deactivated Ru/Al_2O_3 is in sharp contrast to the surface and bulk carburization observed with Co/Al_2O_3 (*10*) and Ni/Al_2O_3 (*1*); the reaction conditions used and the procedure used for run termination were the same in all three cases. This is in agreement with the literature reports (*16*) that whereas Fe, Co, and Ni form bulk carbides, Ru does not.

Qualitatively similar trends were observed for the regenerability of deactivated

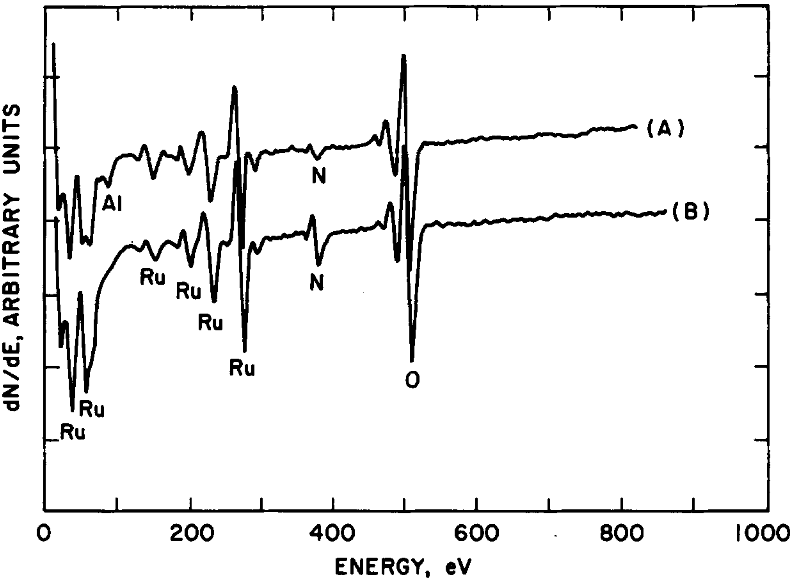

FIG. 4. AES spectra of aged Ru/Al_2O_3. Reaction conditions: 673°K, 1% CO in H_2 for 150 hr. (A) Before any treatment in the vacuum chamber; (B) after sputtering with Ar^+ beam (~10 $\mu A/cm^2$) for 2 min.

catalysts. Deactivated Ru catalysts could be easily regenerated by H_2 treatment; Ni (*1*) and Co (*10*) could not be so easily regenerated by the identical H_2 treatment. This difference between the Ru and the Ni and Co during methanation appears to be well correlated with their ability to form carbides.

Sulfur-Poisoning Reactor Studies

Figure 5 shows the transient CO concentration and methanation activity of Ru/Al_2O_3 at 663°K during *in situ* poisoning. Here, the reactor was brought to 663°K in H_2, and then the feed composition was switched to 55 ppb H_2S and 1% CO in H_2. The transient concentration of H_2S in the reactor is shown in Fig. 6. The initial activity of the Ru/Al_2O_3 is the value expected in a sulfur-free run. The concentration of CO in the gas phase increased from 0 to 1% over an initial period of 16 hr. As the catalyst activity decreased under the combined effects of poisoning by sulfur and rate inhibition by an increasing concentration of

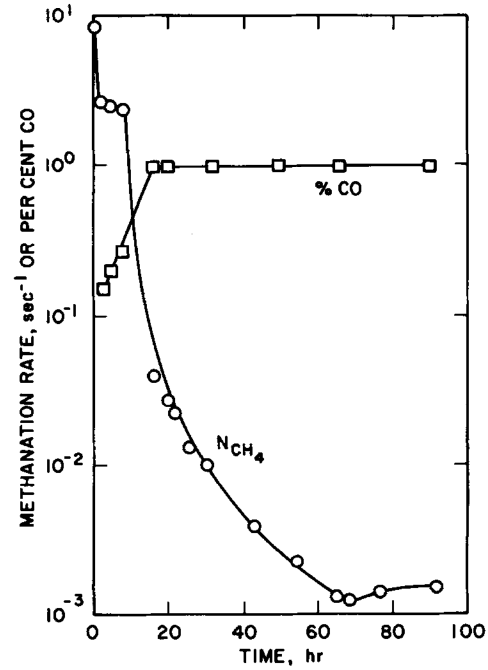

FIG. 5. Transient CO concentration and methanation activity profiles during *in situ* poisoning of Ru/Al_2O_3. Reaction conditions: 663°K, 55 ppb H_2S and 1% CO in H_2; H_2S concentration was reduced from 55 to 13 ppb after 68 hr.

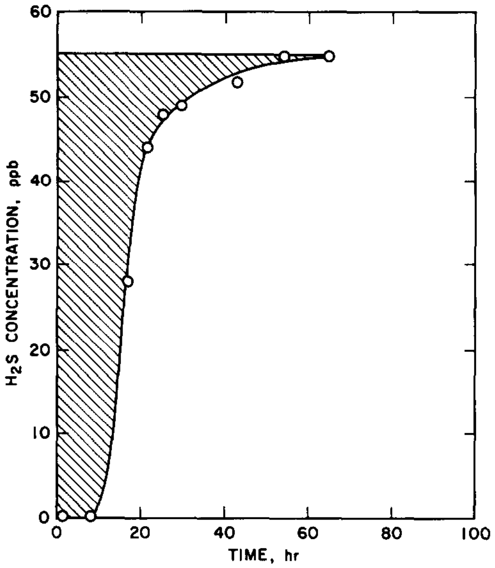

FIG. 6. Transient H_2S concentration profile in the reactor gas phase. Reaction conditions: same as those in Fig. 5. The hatched area represents the total amount of sulfur adsorbed on the catalyst.

CO, the surface was being poisoned by sulfur during this period.

Although the concentration of CO in the gas phase reached a steady value of 1% after 16 hr of reactor operation, it took about 68 hr for the H_2S concentration in the reactor to reach steady state, as shown by the equality of the reactor inlet and outlet H_2S concentrations at this time (Fig. 6). During this same period, methanation activity decreased by more than 10^3-fold, with a close approach to steady-state activity (Fig. 5). However, such a large activity reduction meant that the CH_4 concentration in the exit stream was reduced to less than 1 ppm, a level where accurate analysis was difficult. To circumvent the difficulty in measuring CH_4 concentrations below 1 ppm, the concentration of H_2S in the gas phase was reduced from 55 to 13 ppb. The methanation activity increased slightly from 1.20×10^{-3} to 1.6×10^{-3} sec^{-1}. This is about 2000-fold lower than the steady-state methanation activity of Ru/Al_2O_3 at 663°K with 1% CO in H_2 (3.5 sec^{-1}), showing that Ru/Al_2O_3 is almost as sensitive to poisoning by H_2S as Ni (*1*) and Co (*2*).

The total amount of sulfur adsorbed on the Ru surface can be estimated by integrating the hatched area shown in Fig. 6. Piecewise integration of this area gives the fraction of sulfur adsorbed as a function of on-stream poisoning time. AES studies showed that the poisoning was due to the formation of a two-dimensional surface sulfide, corresponding to a sulfur-saturated Ru surface. The fraction of sulfur adsorbed expressed as the fraction Θ_s of a saturated sulfur layer is shown in Fig. 7. The rate of sulfur adsorption ($\alpha d\Theta_s/dt$) is constant to $\Theta_s = 0.65$, and then it decreases as the surface becomes saturated with sulfur. Identical sulfur adsorption behavior has been observed for Ni (*1*) and Co (*2*). A direct correlation between the methanation activity of Ru and the fraction Θ_s of surface covered with sulfur can thus be obtained, but it is not simple; linear relationships between the methanation activity and $(1 - \Theta_s)^2$, that were observed for the sulfur poisoning of Ni (*1*) and Co (*2*), could not be established for Ru. This results from the strong coupling of sulfur poisoning and CO inhibition effects with Ru/Al_2O_3. Similar

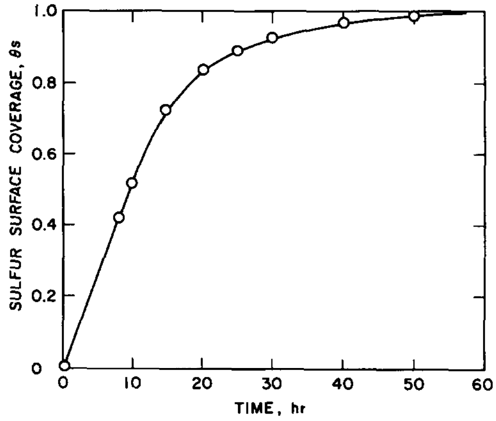

FIG. 7. Fraction of surface coverage by sulfur, Θ_s, as a function of time during *in situ* poisoning of Ru/Al_2O_3. Reaction conditions: same as those in Fig. 5.

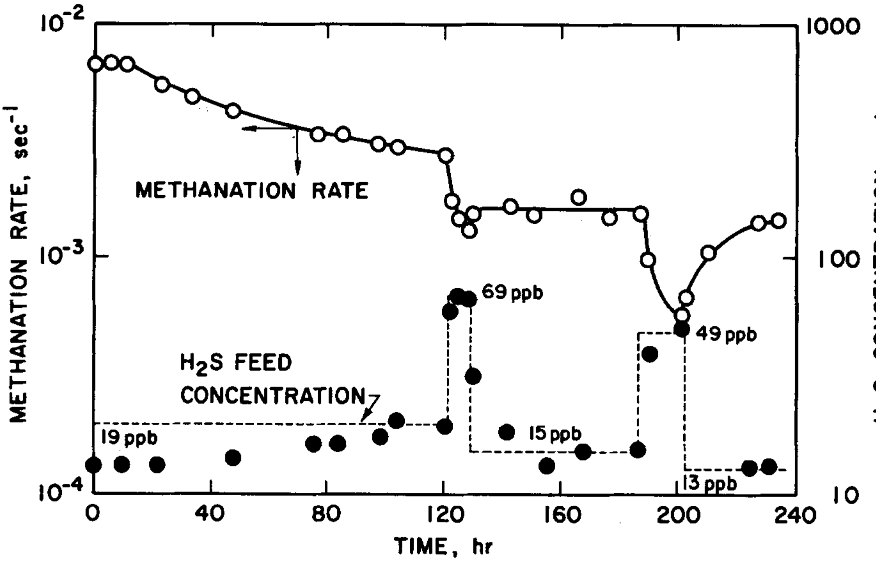

FIG. 8. Transient H_2S concentration and methanation activity profiles for prepoisoned Ru/Al_2O_3. Prepoisoning conditions: 663°K, 19 ppb H_2S in H_2 for 161 hr. Reaction conditions: 663°K, 13 to 69 ppb H_2S and 1% CO in H_2. The broken line indicates H_2S concentration in the feed gas; the solid circles represent the H_2S concentration in the reactor gas phase.

coupling effects were observed in other *in situ* poisoning runs with Ru/Al_2O_3.

In another set of experiments, a catalyst was prepoisoned with 19 ppb H_2S in H_2 at 663°K for 161 hr. At this time, when the Ru surface appeared to be approaching saturation with sulfur, as indicated by the presence of 14 ppb H_2S in the reactor exit stream, 1% CO was added to the feed gas. Figure 8 shows the resulting transient methanation activity and H_2S concentration profiles; time zero corresponds to the addition of 1% CO to the feed gas. The initial methanation activity was reduced 500-fold by prepoisoning, but this activity continued to decrease during the first 120 hr of reaction as a result of slowly increasing concentration of H_2S in the gas phase. After 120 hr of reactor operation (total 281 hr of sulfur poisoning), the concentration of H_2S in the reactor exit stream equaled that in the feed gas, suggesting that the Ru surface was saturated with sulfur, but the methanation activity continued to decline. We interpret this as indicating that the catalyst was not yet saturated with sulfur, and continued to adsorb sulfur at a rate too small to be detected by H_2S concentration profiles. The 500-fold reduction in initial methanation activity, brought about by prepoisoning with H_2S, indicates that the adsorption of sulfur is the primary cause of reduction in the methanation activity in the presence of CO and H_2S. Carbon may play only a secondary, if any, role in reducing activity. Similar findings have been made over Ni and Co catalysts in our laboratory.

After 120 hr of reactor operation, the concentration of H_2S in the feed was changed in a step-mode as indicated by the broken line in Fig. 8. Solid circles, indicating H_2S concentration in the reactor exit stream, show that any change in the feed conditions is rapidly transformed into the reactor gas-phase composition. Methanation activity also responds quickly to step changes in the feed H_2S concentration. This demonstrates the existence of a dynamic equilibrium between the gas-phase H_2S concentration and the catalyst surface. The steady-state methanation activity of Ru prepoisoned with 13 ppb H_2S is the same (1.6

$\times\ 10^{-3}\ sec^{-1}$) as that obtained from an *in situ* poisoning run (Fig. 5) with the same H_2S concentration, showing steady-state methanation activity of this catalyst is independent of the method of poisoning. Only the initial transient behavior is different in the two cases.

Steady-state methanation activity of Ru/Al_2O_3 at 663°K as a function of H_2S concentration in the gas phase (1% CO in H_2) is shown in Fig. 9. Each symbol represents a different run. Some are with and some are without prepoisoning. Most of the drop in methanation activity results from the first 13 ppb H_2S in the gas phase; higher sulfur concentrations cause much smaller incremental decreases in activity. This extreme sensitivity of Ru/Al_2O_3 to poisoning by H_2S under the strongly reducing conditions of methanation is similar to the behavior observed for Ni/Al_2O_3 (*1*) and Co/Al_2O_3 (*2*) under identical reaction conditions and is in general agreement with the results of Wentrcek *et al.* (*9*), but is in sharp contrast to the resistance of Ru to poisoning by SO_2 under mildly reducing conditions. Tsai *et al.* (*7*) reported that Pt, Pd, and Ni supported on Al_2O_3 lost their catalytic activity in NO reduction by NH_3 by 10^4- to 10^5-fold when 50 ppm SO_2 was introduced into the feed; Ru/Al_2O_3, on the other hand, lost its catalytic activity by only 5-fold under similar reaction conditions. Their results indicated that Ru can be considerably more sulfur resistant than Pt, Pd, or Ni and, by analogy, Co. The present study shows that the reaction surface environment (strongly reducing vs mildly reducing) and the poisoning agent (H_2S vs SO_2) have a marked effect on the catalyst sensitivity to poisoning in the case of Ru and much less so in the case of Ni.

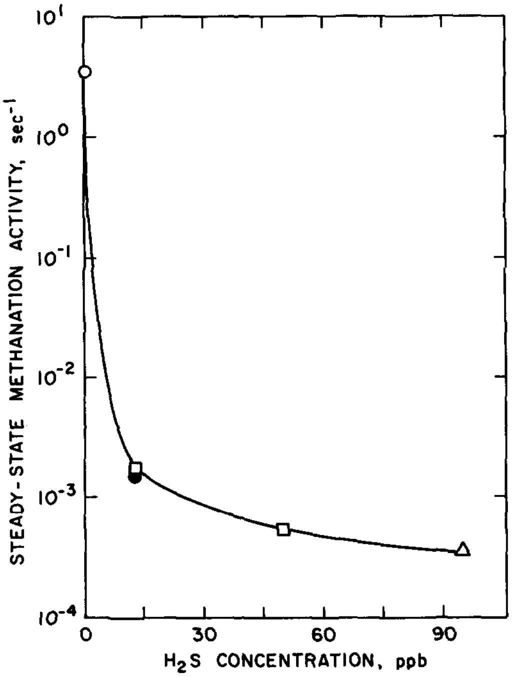

FIG. 9. *Steady-state* methanation activity of Ru/Al_2O_3 as a function of gas-phase H_2S concentration. Reaction conditions: 663°K, 1% CO and H_2S in H_2; each symbol represents a different run.

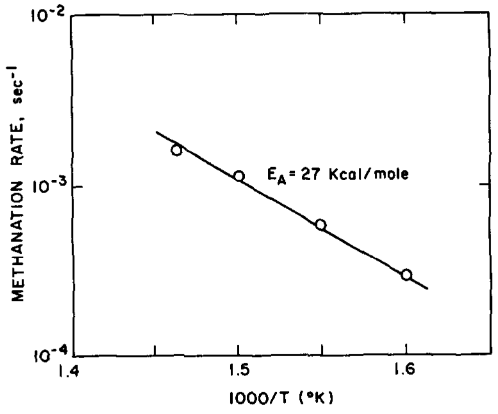

FIG. 10. Temperature dependence of the rate of methanation over sulfur-poisoned Ru/Al_2O_3. Reaction conditions: ~12 ppb H_2S, 1% CO in H_2; steady-state methanation activity had been achieved for Ru/Al_2O_3 surface saturated with sulfur before these kinetic measurements.

The effect of temperature on the rate of methanation over sulfur-poisoned Ru/Al_2O_3 with a feed of 12 ppb H_2S and 1% CO in H_2 is summarized in Fig. 10. The activation energy, 27 kcal/mole, is the same value observed in the sulfur-free kinetic measurements. This is in agreement with Ni/Al_2O_3 data (*1*), but is in striking contrast with Co/Al_2O_3 (*2*) where sulfur poisoning re-

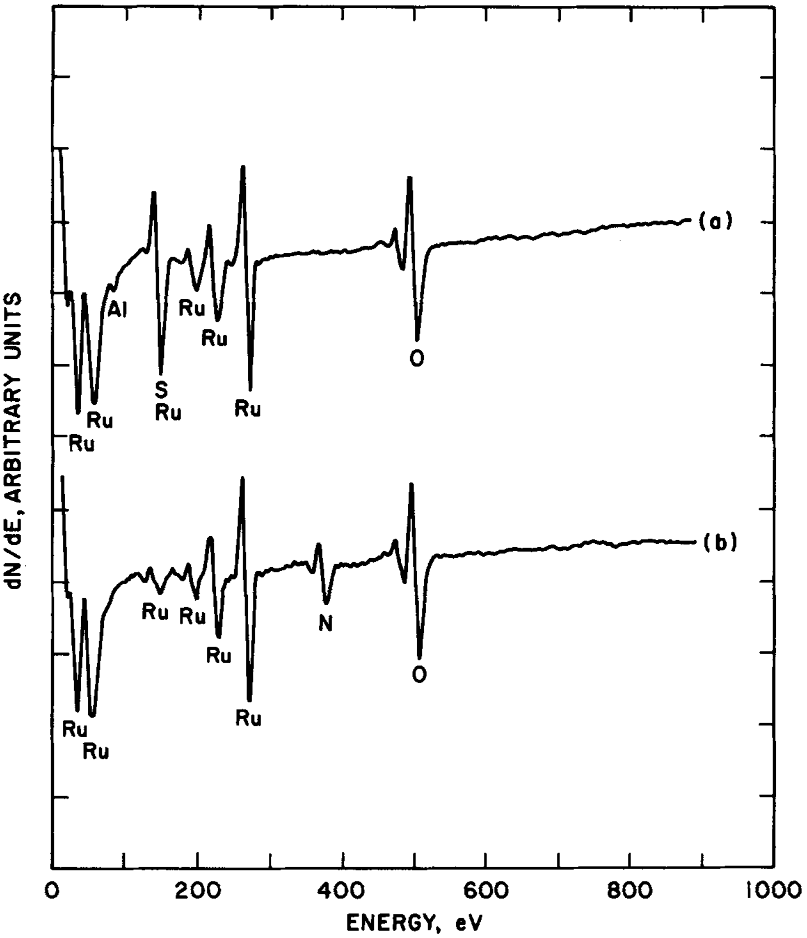

FIG. 11. AES spectra of prepoisoned and aged Ru/Al_2O_3. Poisoning and reaction conditions: same as those described in Fig. 8. (a) Before any treatment in the vacuum chamber; (b) after sputtering with Ar^+ beam (~10 μA/cm²) for 2 min.

duces the activation energy from 28 to 16 kcal/mole. It indicates that the poisoning of Ru by sulfur is primarily a geometric effect where the surface sites active in methanation are blocked by sulfur poisoning.

AES Analysis of Poisoned Ru Catalysts

Figure 11 shows the AES spectra of Ru/Al_2O_3 which had been prepoisoned at 663°K with 13 ppb H_2S in H_2 for 161 hr and then treated with H_2S (13–69 ppb) and 1% CO in H_2 at 663°K for ~235 hr. Figure 11a shows the AES spectrum before any treatment, with no carbon presnt on the surface. The ratio of S (151 eV) to Ru (273 eV) peak is 0.73. The oxygen peak is due to Al_2O_3 which is confirmed by the presence of an Al peak. The surface was sputtered with an Ar^+ beam for total times of 20 sec, 40 sec, 1 min, 2 min, 3 min, and 5 min, and an AES spectrum was taken for each sputtering interval. Carbon was not observed in the surface or in the subsurface layers. The intensity of the sulfur peak was reduced rapidly by sputtering, reaching zero after 2 min, suggesting the presence of sulfur as a surface sulfide. The AES spectrum after 2 min sputtering is shown in Fig. 11b; identical spectra were obtained after 3 and 5 total min of sputtering.

With *in situ* poisoned Ru/Al_2O_3 carbon was not present either on the surface or in the subsurface regions. The S (151 eV)/Ru (273 eV) ratio was 0.75, the same as the ratio of 0.73 observed for prepoisoned Ru/Al_2O_3. Again, the intensity of the S peak dropped to zero on sputtering with Ar^+ for 2 min, indicative of the presence of only surface sulfur. These observations lead us to believe that sulfur is present exclusively as a two-dimensional surface sulfide.

Identical S (151 eV)/Ru (273 eV) ratios were obtained in runs with *in situ* poisoning at 663°K with 55 ppb H_2S in H_2, and in a prepoisoning run with 19 ppb H_2S in H_2. The total amount of sulfur absorbed on per unit surface area of Ru was independent of the method of poisoning, and by analogy with Ni and Co, corresponds to one sulfur atom for each two surface Ru atoms. Also, it is supported by the observation that the peak-to-peak height of the S peak in Fig. 11a is approximately the same as that in the AES spectra of two-dimensional saturated surface sulfides of Ni and Co (*1*, *2*).

The fact that increasing the gas-phase H_2S concentration from 14 to 92 ppb reduced the catalytic methanation activity by fourfold, shows that the difference in the residual activity is caused by a difference in the surface sulfur coverage between these two cases. Yet, such a difference is not detectable using Auger electron spectroscopy. The data merely indicate that the kinetic probe is much more sensitive than the surface probe Auger electron spectroscopy.

CONCLUSIONS

The behavior of Ni, Co, and Ru during hydrogenation, particularly in the presence of sulfur, are significantly different. Ruthenium catalysts are strongly poisoned by sulfur and to a lesser extent by carbon. Sulfur geometrically blocks the surface sites active for CO hydrogenation reducing the catalytic methanation activity by several orders of magnitude, but the activation energy for methanation over sulfur-poisoned Ru catalysts is the same as that in sulfur-free studies. This observation is in agreement with that made for Ni (*1*), but is in sharp contrast to that made for Co (*2*).

Carbon is easily hydrogenated off a sulfur-free or sulfur-poisoned Ru surface. Carbon accumulation does not influence the steady-state methanation activity of sulfur-poisoned Ru, although it may affect the transient activity behavior during *in situ* poisoning.

Our data indicate that a saturated two-dimensinal surface sulfide is formed over the Ru surface in the presence of 19 ppb H_2S in H_2 at 663°K, thus making Ru as sensitive to poisoning by sulfur as Ni and Co under strongly reducing conditions of methanation. The markedly different behavior of Ru in its tolerance toward sulfur is observed in the present study and in a previous study (*7*). In previous studies of NO reduction by NH_3 (*7*), the reduction of SO_2 to S^{2-} leading to the formation of metal sulfides resulted in severe activity loss for Pt, Pd, and Ni. Very little sulfur (S (151 eV)/Ru (273 eV) = 0.14) was observed on aged Ru catalysts in the previous studies, and similarly the activity decreased only fivefold. Clearly the tolerance of Ru to SO_2 poisoning was due to lack of sulfide formation, in contrast to Pt, Pd, or Ni. In the present study, the poison was H_2S, already in S^{2-} form, and also more strongly reducing conditions were used which resulted in the formation of a saturated two-dimensional surface sulfide (S (151 eV)/Ru (273 eV) $\cong$ 0.75) and subsequent loss in catalytic methanation activity.

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REFERENCES

1. Fitzharris, W. D., Katzer, J. R., and Manogue, W. H., submitted for publication.
2. Agrawal, P. K., Katzer, J. R., and Manogue, W. H., *J. Catal.* **69**, 327 (1981).

3. Mills, G. A., and Steffgen, F. W., *Catal. Rev.* **8**(2), 159 (1973).
4. Vannice, M. A., *J. Catal.* **37,** 449 (1975).
5. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **40,** 173 (1975).
6. Oliphant, J. L., Fowler, R. W., Pannell, R. B., and Bartholomew, C. H., *J. Catal.* **51,** 229 (1978).
7. Tsai, J., Agrawal, P. K., Foley, J. M., Katzer, J. R., and Manogue, W. H., *J. Catal.* **61,** 192 (1980).
8. Tsai, J., Agrawal, P. K., Foley, J. M., Katzer, J. R., and Manogue, W. H., *J. Catal.* **61,** 204 (1980).
9. Wentrcek, P. W., McCarty, J. G., Ablow, C. M., and Wise, H., *J. Catal.* **61,** 232 (1980).
10. Agrawal, P. K., Katzer, J. R., and Manogue, W. H., *J. Catal.* **69,** 312 (1981).
11. Elliott, D. J., and Lunsford, J. H., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.—Anaheim Meeting,* 462 (March 1978).
12. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
13. Sachtler, J. W. A., Kool, J. M., and Ponec, V., *J. Catal.* **56,** 284 (1979).
14. Vannice, M. A., Lam, Y. L., and Garten, R. L., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.—Anaheim Meeting,* 495 (March 1978).
15. Ekerdt, J. G., and Bell, A. T., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.—Anaheim Meeting,* 475 (March 1978).
16. Toth, L. E., "Transition Metal Carbides and Nitrides," p. 2. Academic Press, New York, 1971.