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NOTES

Effect of γ-Irradiation on the Sulphur Poisoning of Ru/Alumina Methanation Catalyst

Catalyst deactivation due to the presence of sulphur compounds in reactant gases is a well known phenomenon (*1*). We recently reported (*2*) on the various products formed in the interaction of CS_2 with Ru/alumina.

It has also been found (*3, 4*) that though γ-irradiation may not significantly alter the activity of metal catalysts, large enhancements in their activities could be achieved under irradiation, if metal supported on wide-band materials was used. It was, therefore, of interest to know how γ-irradiation would alter the sulphur poisoning of supported catalysts. We report here the effect of γ-irradiation on the yields of species formed in the CS_2–H_2 reaction over Ru/alumina at 400–650 K and on the poisoning of this catalyst for CO methanation.

The catalyst and the experimental methods have been described elsewhere (*2–4*). One gram of Ru (1.6 wt%)/alumina catalyst (60–80 mesh, BET area 177 ± 5 m^2 g^{-1} and metal surface area 8 ± 1 m^2 g^{-1}) was used in each experiment. CS_2 vapor–H_2 gas mixture, obtained by passing H_2 (32 ml min^{-1}) through a bubbler containing liquid CS_2 and maintained at 275 K was passed over the catalyst and the product gases were estimated at regular intervals using a gas chromatograph. The reacting gas mixture contained ~1 μmol CS_2/ml of gas and was regularly analyzed before admitting to the catalyst reactor to ensure the constant proportion of H_2/CS_2 throughout the experiment.

To examine the influence of γ-radiation on the sulphur poisoning of catalyst activity for CO methanation reaction, pulses of CO (1.6 μmol) and CS_2 vapor (2.0 ± 0.1 μmol) were alternately injected into H_2 carrier gas (34 ml min^{-1}) flowing over the catalyst and the CH_4 formed from both CO and CS_2 were estimated. The radiation experiments were performed under similar conditions after maintaining the catalyst in the γ-source for 2 hr.

(*a*) *Radiation Effect on Yields from CS_2–H_2 Reaction*

When CS_2 vapor–H_2 gas mixture (1 μmol CS_2 ml^{-1}) was passed over the catalyt, the effluent was found to contain CH_4, H_2S, and a small amount of CO (cf. Ref. (*2*)). The catalyst temperature remaining constant, the yields of CH_4, and H_2S increased with time and within 15 min reached a constant value. Also, the yields of CH_4 and H_2S increased with increasing temperature. It was of interest to note that each catalyst sample continued to produce CH_4 and H_2S from CS_2–H_2 reaction for at least 4 consecutive days (corresponding catalyst exposure ~77 mmol of CS_2) without requiring any regeneration.

When the catalyst assembly was kept in a γ-radiation chamber (γ-dose ~ 0.6 *M* rad h^{-1}), the yields of CH_4 and H_2S were found to be enhanced while that of CO reduced. The yields of all the product gases reached a saturation value after about 1 hr of irradiation. On discontinuing the γ irradiation, the catalyst activity was gradually restored to nearly the preirradiation level. The saturation yields of CH_4 and H_2S at different catalyst temperatures without and under γ irradiation are given in Fig. 1.

The γ-dose-dependent growth behavior of CH_4 and H_2S yields and subsequent post-irradiation decay were similar to those found in the case of CO and CO_2 methanation reactions (*3, 4*). Figure 2 shows the

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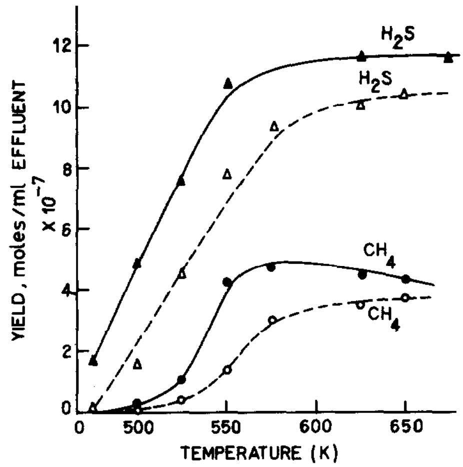

FIG. 1. Saturation CH_4 and H_2S yields from CS_2–H_2 gas mixture (1.01 μmol CS_2 ml^{-1}) reacting over Ru/alumina catalyst at different temperatures. – – –, No irradiation. —, Under γ-irradiation.

data for a typical catalyst temperature of 550 K. The yields of CH_4 and H_2S during the "growth period" have been plotted as

$$-\ln\left(1 - \frac{y_t - y_0}{y_{\max} - y_0}\right)$$

versus irradiation time, where $y_{\max}$ refers to the limiting yields under irradiation and y_0 to the saturation thermal yields before irradiation. The data for postirradiation decay period are plotted in this figure as

$$-\ln\left(\frac{y_t' - y_0'}{y_{\max} - y_0'}\right)$$

versus time, y_0' being the saturation yields of H_2S or CH_4 subsequent to removal of the catalyst chamber from the γ-source. The near straight line plots in Fig. 2 clearly suggest that radiation induced enhancement is a result of simultaneous growth and decay of certain "centers" having a short "life time." Similarly, the yields in postirradiation period may be attributed to exponential decay of these centers.

(*b*) *Radiation Effect on Catalyst Poisoning*

In the experiments when pulses of CO (1.6 μmol) and CS_2 (~2.0 μmol) were alternately injected over the catalyst in the presence of H_2, CH_4 yields were higher with the catalyst under irradiation, the extent of enhancement being substantial in the temper-

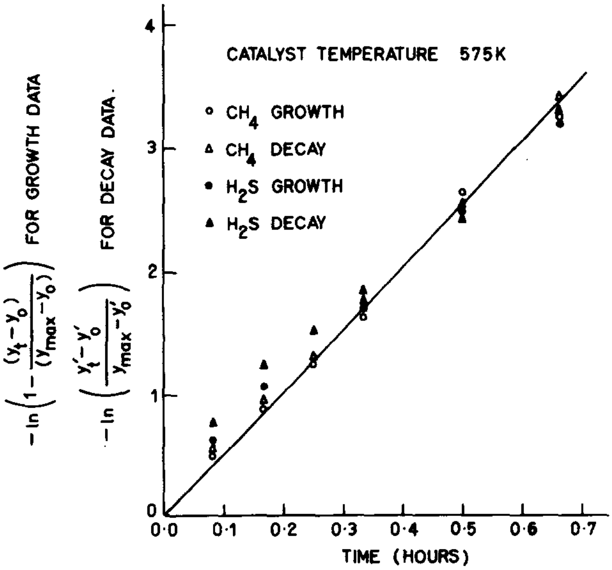

FIG. 2. Yields of CH_4 and H_2S from CS_2–H_2 reaction under γ-irradiation [plotted as $-\ln(1 - (y_t - y_0/y_{\max} - y_0))$ vs irradiation time] and during postirradiation decay (plotted as $-\ln(y_t' - y_0'/y_{\max} - y_0')$ vs time).

ature range 500–600 K. The typical yields of CH_4 from successive injections of CO and CS_2 at 575 K are given in Fig. 3. While the CH_4 from CO ceased to form after the eighth CS_2 pulse injection with unirradiated catalyst, it required 10 CS_2 pulse injections with the catalyst under irradiation. Also, the CS_2 continued to react with H_2 to form CH_4 even after CO ceased to be methanated; however, the yield of CH_4 was drastically reduced at about the same point when the catalyst was deactivated for CO methanation. Similar data were obtained with other concentrations of CS_2 and CO pulses and at other catalyst temperatures. For example, when pulses containing 0.8 μmol CS_2 were used, the catalyst deactivation for CO methanation at 475 K was observed after injection of 19 CS_2 pulses with no irradiation while the number of CS_2 pulses required in the presence of γ-radiation was 24.

As the catalyst samples retain their activity for the CS_2–H_2 reaction even when they are completely poisoned for CO methanation (Fig. 3, also see Section (a)), it may be concluded that CS_2 decomposition and hydrogenation require Ru sites of "lesser" activity as compared to that for CO decomposition. Also, the fact that at the stage at which the catalyst is poisoned for CO methanation the CH_4 yields from CS_2–H_2 reaction are also drastically reduced suggests that the Ru sites compete for decomposition of both CO and CS_2, thus explaining the poisoning behavior of CS_2 for CO methanation.

The radiation-induced enhancement in activity for the CS_2–H_2 reaction (Fig. 1) agrees with our previous work (*3, 4*) on methanation of CO and CO_2. With the help of thermoluminescence studies, it has been shown earlier (*3, 4*) that the radiation-induced enhancement in activity of supported

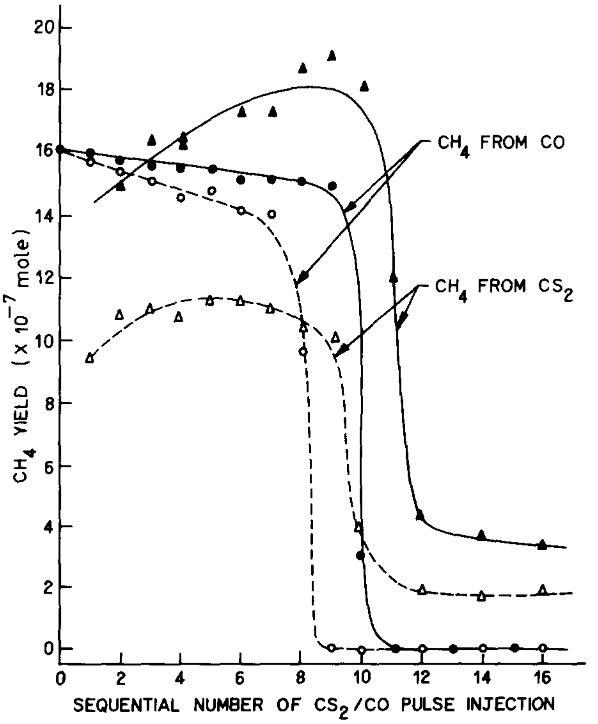

FIG. 3. Effect of γ-irradiation on CH_4 yields from successive pulses of CO (1.6 μmol) and CS_2 (2.0 ± 0.1 μmol) injected alternatively over Ru/alumina catalyst in the presence of H_2 carrier gas. – – –, No irradiation. —, Under γ-irradiation.

metal catalysts may be attributed to the generation of charge-trapped centers in the support matrix and their thermal detrapping. The energy released during recombination of charge centers would be equally available to the different species present at the catalyst surface, thus altering their chemical reactivity to the same extent. This is in agreement with the almost identical growth and decay yields of CH_4 and H_2S as shown in Fig. 2. The slope of the curve in Fig. 2 is thus an indication of the effectiveness of the support material for radiation-induced enhancement of catalytic activity and a better support will give a more positive slope depending on the band gap and related properties of the material.

As complete decomposition of CS_2 takes place over catalyst surfaces even in the absence of radiation to give rise to elemental carbon and sulphur (*2*), it may be surmised that the pumping of thermally released stored energy from the support to Ru sites alter the Ru–C or Ru–S bond vibrations thus affecting the subsequent hydrogenation of C and S.

If the amount of sulphur left on the catalyst surface in the experiments of Section (a) above is calculated on the basis of eluted H_2S (Fig. 1), presuming all exposed CS_2 undergoes decomposition, it is found that γ-irradiation reduces sulphur coverage by about 35%. A catalyst used under γ-irradiation is therefore likely to require less rigorous regeneration treatment.

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