Catalysis Letters 37 (1996) 167–172

The dissociation kinetics of H_2S over an alumina supported Co–Mo sulphide catalyst

S.C. Moffat and A.A. Adesina [1]

School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Received 16 August 1995; accepted 20 November 1995

In this study, a high surface area 4Co : 6Mo : 100γ-Al_2O_3 sulphide prepared using precipitation from homogeneous solution (PFHS) has been used for the catalytic splitting of hydrogen sulphide into H_2 and elemental sulphur. The activity of this new formulation was significantly better than previously reported recipes. Kinetic data collected over a wide range of H_2S partial pressures between 883 and 983 K revealed that, although the decomposition followed a first-order law, a mechanism involving H_2S adsorption on co-ordinative unsaturation sites of the Co–Mo sulphide catalyst gave a Langmuir–Hinshelwood rate expression that yielded satisfactory model parameters. In particular, the scission of the surface H–S bond appeared to be the rate determining step.

Keywords: dissociation; kinetics; Co–Mo sulphide; H_2S

1. Introduction

The hydroprocessing of petroleum, coal and minerals yields large quantities of toxic H_2S which must be removed or reduced to environmentally-acceptable levels before disposal. Annual H_2S production from these sources is about 2.7 billion tonnes [1] and thus, in addition to H_2S present in natural gas, the utilisation of H_2S is a major objective of gas processing technology. Presently, H_2S finds limited low level use in the manufacture of sulphides, various organosulphur compounds and heavy water. However, Raymont [2] has pointed out the beneficial economics of H_2 recovery from H_2S. Extant technology for removing H_2S from industrial gaseous effluents depends primarily on either the Claus process in which H_2S is burnt releasing water and saleable sulphur, or the absorption of H_2S into caustic or amine solutions such as the Selexol Process, Hot Carbonate Process or the Alkazid Process [3]. In the minerals processing industries, H_2S may also be removed via a number of thermochemical cycles involving metal oxide sulphidation followed by revivification as in the Dry-Box Process. While the net energy released from these routes may be used for low grade process heat requirements, it is evident that hydrogen utilised originally in the desulphurisation process (either for crude petroleum, coal or mineral ores) is ultimately discarded as water. Consequently, the splitting of H_2S into valuable H_2 which can be recycled and sulphur has attracted investigation within the last two decades following Raymont's economic analysis. At least five possible routes have been proffered for the decomposition of H_2S. These include

- direct thermolysis of H_2S [4,5],
- photo-assisted decomposition [6],
- thermochemical open and closed loop processes [7],
- electrolytic splitting [8],
- catalytic decomposition [9–11].

Of these, the most promising appears to be the catalytic dissociation over transition metal sulphides. Zazhigalov et al. [12] reported that activity decreases in the order

$$CoS_2 = NiS > WS_2 > MoS_2 > FeS_2 > AgS_2 > CuS > CdS > MnS > ZnS\,.$$

However, the stability and regenerability of these catalysts have been debated. Fukuda et al. [8] found that, while disulphides of Mo and W were efficient over long periods of use, monosulphides of Fe, Co and Ni experienced only short-lived activity (up to about 8 h) because they were converted to catalytically inactive higher sulphides. The series Cr_2S_3, MoS_2, WS_2, VS and V_2S_3 has also been investigated by Chivers et al. [10,13]. They observed that MoS_2 was the most effective above 873 K and XRD analysis of spent catalysts did not show any change in bulk composition. There is, however, a paucity of information on the catalytic kinetics of H_2S decomposition. Kaloidas and Papayannakos [14] reported a reversible Langmuir–Hinshelwood rate equation for the decomposition over an unsupported commercial MoS_2. They concluded that the cleavage of the H–S bond appeared to be the rate controlling step.

Practically all H_2S decomposition catalysts investigated in the literature are low surface area mono-metallic unsupported specimens. The role of γ-Al_2O_3 supported Co–Mo sulphide catalysts for hydrodesul-

---

[1] To whom correspondence should be addressed.

phurisation is well established [15]. Topsøe et al. [16] extensively investigated the importance of cobalt in enhancing the ability of the CoS–MoS_2/γ-Al_2O_3 during desulphurisation. They suggested that the addition of cobalt to MoS_2 led to the formation of a new Co–Mo–S type species which possess better catalytic ability than that of the pure sulphide. These catalysts are, however, often prepared via high temperature sulphidation of the metal or metal oxide [17,18]. Since H_2S decomposition is essentially a desulphurisation reaction, the catalysts for this decomposition are often prepared by the same technique. In general, reported activities appeared stymied by low surface areas [9–12], hence the development of a high surface area active Co–Mo/γ-Al_2O_3 would be desirable for future process design. In a recent paper, Rao et al. [19] reported the preparation of a new class of hydrotreating catalysts which has superior activity over those obtained from sulphidation of the metal oxide. The technique, termed precipitation from homogeneous solution (PFHS) ensured excellent dispersion over the high surface area support and is particularly well suited for the preparation of bimetal sulphides. Consequently, kinetics of the H_2S decomposition reaction over a supported Co–Mo catalyst obtained from the PFHS warrant inquiry.

2. Experimental

Fig. 1 is a diagrammatic illustration of the experimental rig. The gas manifold system consisted of three cylinders containing high purity argon, H_2S and argon/H_2S gases. Gas flow rates were regulated and metered by independent rotameters before mixing in a stainless steel chamber to the desired composition. The mixed gases were then sent to the reactor made from a quartz tube (i.d. = 5 mm) containing typically 0.2 g of 200–250 μm particles of the Co–Mo catalyst. It was placed axially in a pre-calibrated PID temperature-controlled furnace such that the position of the catalyst bed was always in the gradientless temperature zone. The reactor effluent was passed through an acetone/ice mixture condenser to remove the sulphur product as solid. Continuous on-line sulphur composition measurement is difficult with a TCD-gas chromatograph since the sulphur vapours will condense at temperatures below 717 K and block either the injector port (maintained at 403 K) or the column (kept at 360 K). Hence, it was necessary to remove the sulphur in an acetone/ice trap before the GC. The remaining gases were filtered before entering a Shimadzu 8A gas chromatograph in which a Haysep-Q column separated the H_2 and H_2S prior to identification on a TCD and peak area determination on an electronic integrator. The waste gases were then bubbled through caustic solution before atmospheric venting. A total feed volumetric flow rate of 2.5 ml s^{-1} (measured at STP) combined with the relatively small catalyst particle size employed ensured that the kinetic data collected were free from heat and mass transport intrusions.

Catalyst preparation

Hydrodesulphurisation (HDS) catalysts are usually prepared from Co–Mo sulphide mixtures containing up to about 4 wt% Co [15]. In a recent investigation [20], we observed that for supported MoS_2 catalysts, optimum H_2S decomposition activity was obtained at 6–10% Mo loading. As a result, a 4Co : 6Mo : 100γ-Al_2O_3 composition is a logical choice for the present study. Two monometal sulphide catalysts, namely 4% CoS/γ-Al_2O_3 and 6% MoS_2/γ-Al_2O_3, were also prepared for comparative purposes and to determine, if any, the extent of synergy in the Co–Mo system.

All three catalysts were prepared using the PFHS procedure. The 6% MoS_2 catalyst was prepared from an aqueous solution (A) made from 10 ml of 0.1 M MoO_3 solution, 1 g urea, 1 ml 0.75 M HNO_3 and 30 ml of thioacetamide solution. 1.5 g of the γ-Al_2O_3 support (Nor-

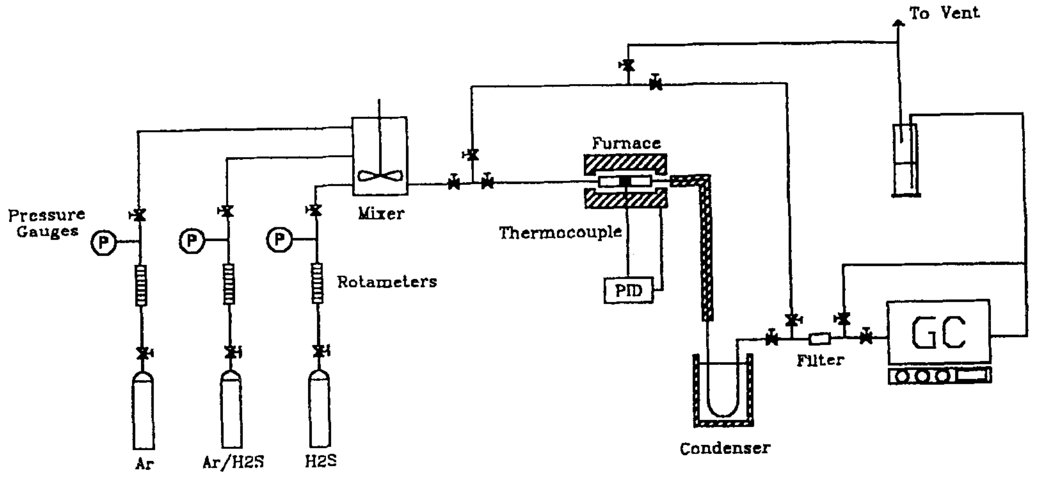

Fig. 1. Experimental apparatus.

ton, USA) was suspended in 100 ml of solution A in a 250 ml conical flask and diluted with distilled water to the mark. The conical flask was then placed in continuous shaker water bath set at 110 rpm and 365 K for about 3 h. At the end of this period, the solution was filtered and the resultant solids washed and dried at 383 K for 14–16 h. The dried solid was further calcined at 1023 K in argon environment for 3 h. The 4% CoS specimen was produced in the same manner except that in the make-up of solution A, the 0.1 M MoO_3 solution was substituted with calculated amount of $Co(NO_3)_2$ solution. However, the bimetal Co–Mo sulphide was prepared from a further suspension of 1.41 g of 6% MoS_2 in 100 ml of the aqueous solution containing 10 ml 0.1 M $Co(NO_3)_2$ with subsequent steps as previously described.

3. Results and discussion

3.1. Catalyst characterisation

All catalysts were characterised using BET method, XRD analysis and ICP emission spectroscopy. The BET surface areas for the three catalysts were measured at liquid N_2 temperature on an ASAP 2000 Micromeritics unit and found to be 187, 235 and 204 $m^2 g^{-1}$ for the Co, Mo and Co–Mo samples respectively. The surface area of the pure γ-Al_2O_3 support was similarly determined as 221 $m^2 g^{-1}$. The comparable surface areas between the pure support and the sulphide catalysts are consistent with the claims of Rao et al. [19]. Although chemisorption studies were not conducted, it would seem that at the metal loading used, the relatively little change in surface area is indicative of small crystallites and hence, efficient dispersion of the metal sulphide. Ordinarily, as metal loading on the support increased, one would expect a corresponding decrease in total surface area due to pore blockage by the crystallites. However, the Co–Mo catalyst has an intermediate surface area between the two monometal sulphides in spite of its higher metal loading (10%). Under the catalyst preparation conditions, intimate interaction between the Co and Mo species is expected. Thus, the BET data suggest the possible formation of a new surface phase containing a Co–Mo–S complex. ICPES analysis confirmed the expected catalyst composition. The X-ray diffractogram for the MoS_2 gave the characteristic signal for MoS_2 species at a double angle of about 14.7°. As may be seen in fig. 2, this peak disappeared in the Co–Mo sample suggesting that this phase probably no longer existed and hence the possibility of a new unidentified Co–Mo phase. However, the Co catalyst was essentially XRD amorphous either due to the low metal loading (ca. 4%) used or the formation of very fine crystallites. In an earlier Mössbauer spectroscopy study, Topsøe et al. [16] reported a Co–Mo–S phase in their catalyst.

Zdrazil [17] has pointed out that synergy is a common feature of many bimetallic desulphurisation catalysts. Synergetic effects may be due to an increase in the total number of active sites from the two original distinct sites (in this case CoS and MoS_2 species) which retain their separate properties. This is termed textural synergy. However, in chemical synergy, intricate interaction between the two metal centres can lead either to the formation of completely new active sites or a co-operative action between the two metal centres. From the catalyst characterisation data, it would seem that chemical synergy is evident in the present Co–Mo sulphide system. Incidentally, both Co–Mo and Ni–Mo sulphide catalysts are known to exhibit chemical synergy for the HDS reaction [21].

3.2. Activity and kinetic studies

Homogeneous thermolysis of H_2S commenced at

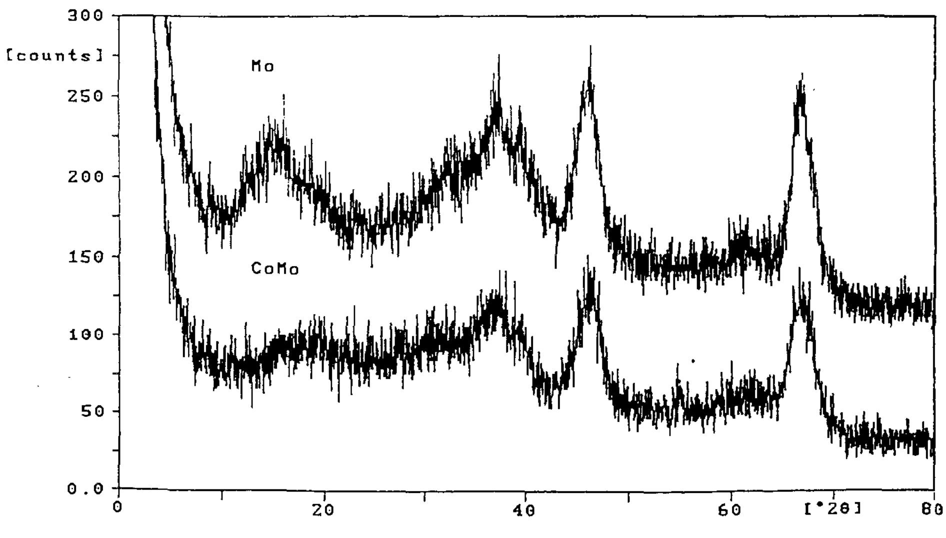

Fig. 2. X-ray diffractograms for Mo and Co–Mo sulphide catalysts.

about 1013 K [5], thus the standard catalyst activity test was carried out at 101 kPa total pressure in the quartz reactor over a temperature band of 883–983 K using a 48% H_2S/Ar mixture. Prior to activity measurements, the fresh catalyst was always pretreated in the H_2S/Ar stream at 923 K until such a time when the reactor exit H_2S composition remained constant. Although an initial overshoot in H_2S consumption rate was always observed, the relaxation to steady-state rate was often achieved within 15–20 min. Furthermore, activity was routinely monitored after every six runs using the 48% H_2S/Ar mixture to confirm stable catalyst performance over the experimental period. The catalyst was also left under an argon blanket when not in use.

Using 48% H_2S/Ar feed, the rates of H_2S decomposition as a function of temperature over the three catalysts are shown in fig. 3. As a comparison, the data for the unsupported MoS_2 [14] and CoS [22] under the same experimental conditions are re-presented. As may be seen, the new Co–Mo catalyst exhibited the most superior activity at all temperatures investigated. Activation energy values for the supported catalysts were generally smaller (60, 64 and 95 kJ mol^{-1} for Co–Mo, Mo and Co sulphide respectively) than the unsupported samples (120 and 106 kJ mol^{-1} for MoS_2 and CoS respectively). Incidentally, the previous work on MoS_2 was done with a commercial catalyst which has a surface area of 4–5 m^2 g^{-1} [14]. Also, CoS employed in our earlier work [22] had a BET surface area of about 2.5 m^2 g^{-1}. There appears to be a positive correlation between surface area and activity for these sulphide catalysts. It is apparent that the superior activity of the PFHS catalysts is indication that efficient dispersion (and hence small metal sulphide particle size) ensured greater accessibility of H_2S reacting molecules to more metal sulphide atoms (sites for the adsorption) than the unsupported samples. In fact Okamoto et al. [23] have found that the desulphurisation activity of transition metal sulphides increased with BET surface area. Thus, the higher H_2S decomposition activity of the PFHS catalysts may be attributed to its high surface area.

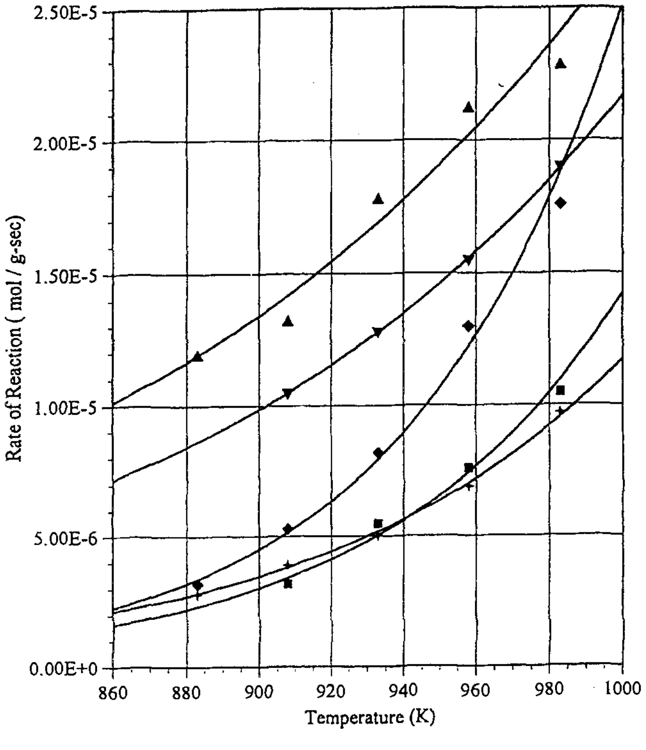

Fig. 3. Performance of various catalysts using 48% H_2S feed. (◆) MoS_2 (ref. [14]), (■) CoS (ref. [22]), (+) 4% Co (this work), (▲) 4% CoS + 6% MoS_2 (this work), (▼) 6% Mo (this work).

Kinetic data were collected at five temperature levels using seven different feed compositions over the Co–Mo–S catalyst. Fig. 4 shows that the reaction rate increases almost linearly with H_2S partial pressure up to about 40% H_2S/Ar feed. In fact a fit of all rate data to a power law expression yielded

$$-r_{H_2S} = 2.415 \times 10^{-3} e^{-61336/RT} P_{H_2S}^{0.763} . \tag{1}$$

The mechanism for the decomposition of H_2S has always been assumed to proceed via the thermochemical regenerative cycle involving the sulphidation of the catalyst followed by the reversible decomposition of the higher sulphide to release the lower sulphide [9–11] in accordance with

$$M_pS_q + xH_2S \rightarrow M_pS_{q+x} + xH_2 \tag{2}$$

$$M_pS_{q+x} \rightarrow M_pS_y + (q + x - y)S \tag{3}$$

Evidently if $y = q$ the original sulphide catalyst has been regenerated. However, non-stoichiometric sulphides may be formed in which $q \not\simeq y$. In particular, if the higher sulphide M_pS_{q+x} is not easily decomposed, catalyst activity would be lost over a relatively short period. In the present study, catalyst activity was constant over a three-week period of continuous use and was periodically checked in between kinetic runs with the standard

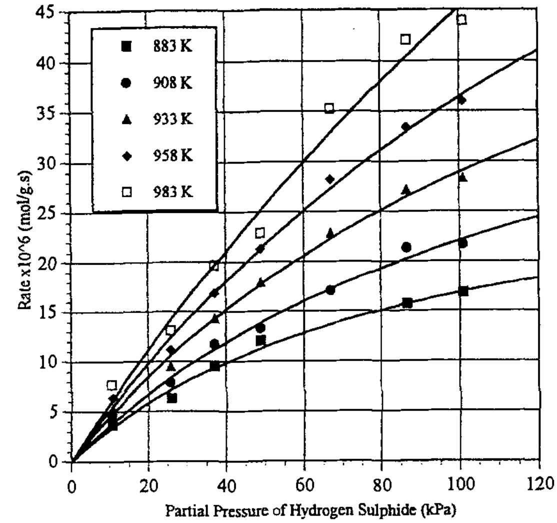

Fig. 4. Rate–composition–temperature behaviour of the Co–Mo sulphide catalyst.

H_2S/Ar mixture to ensure reproducible activity. Thus, the formation of higher catalytically inactive sulphides was unlikely. Although sulphur was collected as solid product over the three-week run, the spent catalyst did not show any visible yellow coloration due to sulphur deposition in the catalyst pores or on the surface. This suggests that the catalyst did not act as a "sponge" for sulphur species during reaction. Sulphur balance could not be carried out since only steady-state H_2 and H_2S compositions were known. However, on a H_2 basis, most runs gave a 96–99% closure. This calculation assumes that sulphane (H_2S_X, $X = 2, 3, \ldots, 8$) species are negligible – a valid thermodynamic assertion at the operating temperature of 883–983 K [4].

Sugioka and Aomura [24] have also provided an alternative explanation for the mechanism of H_2S decomposition. They proposed that the co-ordinative unsaturation sites of the sulphide catalyst is responsible for the adsorption of the H_2S and upon H–S bond cleavage, this site can anchor the sulphur species which may then be released during the desorption step. According to Tanaka and Okuhara [25] transition metal sulphides may possess up to three different types of co-ordinative unsaturation sites (depending on the axis selected for the cleavage of the crystal structure) on which various types of ligands may be bonded and hence their effectiveness. Under reaction conditions (> 673 K), Chianelli and Pecorado [26] observed that transition metal, for example, ruthenium, exists as the sulphur-deficient Ru_{2-x} rather than RuS_2. With the PFHS technique interaction between CoS and MoS_2 species can lead to sulphur-bridging between the Co and Mo atom centres to form a new sulphur-deficient Co–Mo–S surface species active for H_2S decomposition. Hydrogen sulphide molecule adsorbs on this site via the sulphur atom [27]. The splitting of the hydrogen–sulphur bond releases hydrogen and a labile sulphur atom which may then desorb to regenerate the vacant co-ordinative unsaturation site. As noted before, XRD data did not implicate the existence of individual CoS and MoS_2 in the Co–Mo catalyst. Again, the lower activation energy of the Co–Mo catalyst than either of the monometal sulphides indicates the possibility for chemical synergy between Co and Mo metal centres by way of co-operative action in a new surface entity such as the sulphur-bridged Co–Mo site proposed here. The extent of synergy, α, has been defined by Zdrazil [17] as

$$\alpha = \frac{a_{\text{Co–Mo}}}{a_{\text{Co}} + a_{\text{Mo}}}, \tag{4}$$

where a_i is the specific activity of the particular catalyst. For chemical synergy, $\alpha \geqslant 1$. For the supported catalyst, the specific activity was defined as the global H_2S decomposition rate per unit surface area. Specific activity on an areal basis was employed because all three catalysts were supported on the same material and with the high dispersion (also confirmed by the XRD data), the metal sulphide surface area would be proportional to the BET total surface area. Fig. 5 is a plot of the specific activity vs. temperature for the three catalysts. It is evident that α is at least unity at the temperatures investigated and a mechanism involving H_2S adsorption on a Co–Mo–S co-ordinative unsaturation site such as that in fig. 6 may be proffered.

For this mechanism, the corresponding Langmuir–Hinshelwood steps may be written,

$$H_2S + X \rightleftharpoons H_2S\text{–}X \tag{5}$$

$$H_2S\text{–}X \rightleftharpoons H_2 + S\text{–}X \tag{6}$$

$$S\text{–}X \rightleftharpoons \tfrac{1}{2}S_2 + X \tag{7}$$

where X is the active site. The formation of diatomic sulphur species was proposed since this is the most thermodynamically predominant (about 95% is S_2) allotropic form of sulphur species under reaction conditions [4]. The data described in fig. 4, was most adequately described by the rate model

$$-r_{H_2S} = \frac{kK_{H_2S}P_{H_2S}}{1 + K_{H_2S}P_{H_2S}}, \tag{8}$$

which assumes an irreversible surface reaction involving the liberation of H_2 from adsorbed H_2S as the rate controlling step (rcs), where k is the intrinsic forward rate constant of the surface reaction requiring the cleavage of an H–S bond and K_{H_2S} is the equilibrium adsorption constant for H_2S. Other rate expressions (adsorption and desorption as rcs) were considered with no success either

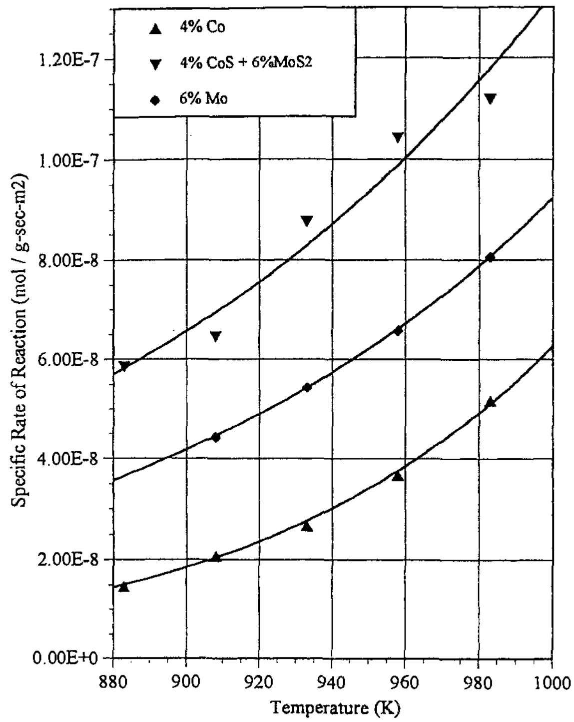

Fig. 5. Specific activity comparison for 4% Co, 6% Mo and 4% Co–6% Mo samples.

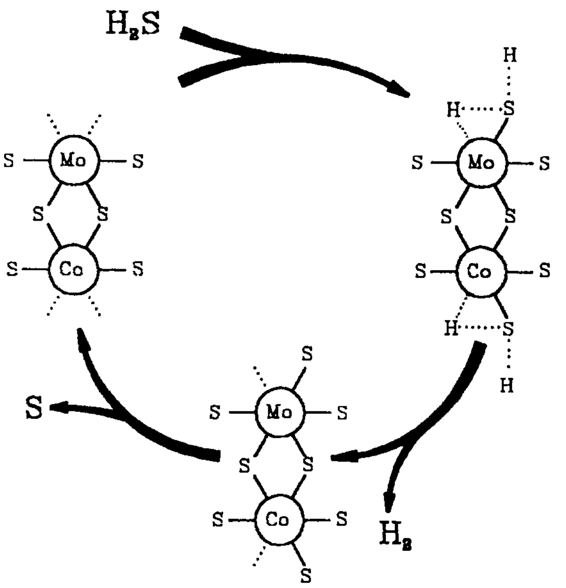

Fig. 6. Proposed H_2S dissociation mechanism.

due to negative parameter estimates or failure to meet statistical criteria (using residual sum of squares) at all five temperatures. The solid curves shown in fig. 4 represent the model prediction and suggest good agreement with the data. Additionally, the parameters, k and K_{H_2S} could be described by

$$k = 1.208\ e^{-78580/RT} \tag{9}$$

and

$$K_{H_2S} = 2.088 \times 10^{-4}\ e^{-30990/RT}\,. \tag{10}$$

As expected, the activation energy of the rate limiting step (eq. (2)) is higher (78.6 kJ mol^{-1}) than the global activation energy (previously evaluated as 61 kJ mol^{-1} from the power law model) since the rate constant in the power law model is a composite of the intrinsic kinetic and equilibrium adsorption/desorption constants.

4. Concluding remarks

The results of this study show that catalysts prepared via precipitation from homogeneous solution exhibited considerably greater activities than those derived from high temperature sulphidation of the metal oxide. In particular, a Co–Mo sulphide catalyst gave the most promising H_2S decomposition rates at all temperatures. Kinetic investigation over this catalyst suggested approximately first-order rate dependency on H_2S at low partial pressure. A mechanism involving the adsorption of H_2S on the coordinative unsaturation site of the Co–Mo–S catalyst has been proposed. The cleavage of the H–S bond to release H_2 appeared to be the rate controlling step.

Acknowledgement

The experimental assistance given by Marx Gwaunza is duly appreciated.

References

[1] E.A. Fletcher, J. Noring and J. Murray, Int. J. Hydr. Energy 9 (1984) 587.
[2] M.E.D. Raymont, Hydrocarbon Process. 54 (1975) 139.
[3] D. Kirk-Othmer, *Encyclopedia Chem. Tech.* Vol. 22 (1984).
[4] V. Kaloidas and N.G. Papayannakos, Chem. Eng. Sci. 44 (1989) 2493.
[5] A.A. Adesina, V. Meeyoo and G. Foulds, Int. J. Hydr. Energy (1995), in press.
[6] O.A. Salman, A. Bishara and A. Marafi, Energy 12 (1987) 1227.
[7] D. Berk, R. Heidemann, W. Svrcek and L. Behie, Can. J. Chem. Eng. 69 (1991) 994.
[8] H. Alqahthany, P.-H. Chiang, D. Eng and M. Stoukides, Catal. Lett. 13 (1992) 289.
[9] K. Fukuda, M. Dokiya, T. Kameyama and Y. Kotera, Ind. Eng. Chem. Fund. 17 (1978) 243.
[10] T. Chivers, J.B. Hyne and C. Lau, Int. J. Hydr. Energy 5 (1980) 499.
[11] L.M. Al-Shamma and S.A. Naman, Int. J. Hydr. Energy 15 (1987) 1.
[12] V.A. Zazhigalov, S.V. Gerei and M. Rubanik, Kinet. Katal. 4 (1975) 967.
[13] T. Chivers, J.B. Hyne and C. Lau, Int. J. Hydr. Energy 12 (1987) 235.
[14] V. Kaloidas and N.G. Papayannakos, Ind. Eng. Chem. Res. 30 (1991) 345.
[15] P.J. Magnus, E.K. Poels and J.A. Moulijn, Ind. Eng. Chem. Res. 32 (1993) 1818.
[16] H. Topsøe, B. Clausen, N. Topsøe and E. Pedersen, Ind. Eng. Chem. Fundam. 25 (1986) 25.
[17] M. Zdrazil, Catal. Today 3 (1988) 269.
[18] B. Delmon, Catal. Lett. 22 (1993) 1.
[19] K.S. Rao, V. Prasad, K. Chary and P.K. Rao, Stud. Surf. Sci. Catal. 44 (1991) 661.
[20] V. Meeyoo, A.A. Adesina and G. Foulds, React. Kinet. Catal. Lett. (1995), in press.
[21] R.R. Chianelli, T.A. Pecorado, T.R. Halbert, W.-H. Pan and E.I. Steifel, J. Catal. 86 (1984) 226.
[22] V. Meeyoo, A.A. Adesina and G. Foulds, *Proc. 44th Can. Chem. Eng. Conf.*, Calgary, 2–6 October 1994, p. 641.
[23] Y. Okamoto, K. Nagata, T. Imanaka and T. Takyu, Bull. Chem. Soc. Jpn. 65 (1992) 1331.
[24] M. Sugioka and K. Aomura, Int. J. Hydr. Energy 9 (1984) 891.
[25] K.I. Tanaka and T. Okuhara, Catal. Rev. Sci. Eng. 15 (1977) 249.
[26] R.R. Chianelli and T.A. Pecorado, J. Catal. 67 (1981) 430.
[27] R.R. Chianelli and S. Harris, J. Catal. 86 (1984) 400.