Promotion and Inhibition by Hydrogen Sulfide of Thiophene Hydrodesulfurisation over a Sulfide Catalyst

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The reaction of thiophene has been studied between 300 and 400 °C and 0.1 MPa over a sulfided CoMo–Al_2O_3 catalyst with various amounts of H_2S; besides the usual inhibiting effect, it has been found that low levels of H_2S promoted the reaction above 380 °C.

Molybdenum-based sulfide catalysts are widely used in the hydroprocessing of petroleum fractions where sulfur compounds are converted into hydrocarbons and H_2S. Therefore, the various reactions involved in hydro-treatment, mainly hydro-desulfurisation, hydro-denitrogenation and hydrogenation, are affected by the level of H_2S production.

The influence of H_2S has been extensively studied on model compounds for the three main types of reaction involved in hydro-treatment. Although the results appear contradictory, it is mostly found that H_2S inhibits S removal,[1] enhances C–N bond breakage,[2] and has almost no effect on hydrogenation.[3,4]

Recently, we reported that H_2S inhibits the conversion of thiophene to C_4 at 4 MPa and 280 °C.[5] Under these conditions, the reaction of thiophene (T) was found to proceed mainly through the thiolane (THT) intermediate (Scheme 1). The hydrogenation step to THT is in fact favoured by H_2S, whereas the C–S bond breakages are depressed.

Here we report evidence for the promoting effect of H_2S on the global conversion of thiophene performed at atmospheric pressure.

Fig. 1 shows reaction rate as a function of the actual level of H_2S measured† at four temperatures. Below 380 °C, the usual inhibiting effect of H_2S is observed, but at 400 °C, the curve shows a slight maximum around 1% H_2S. This result shows that H_2S promotes thiophene conversion, and should be considered in the mechanism. The continuous decrease of the rate of thiophene disappearance at high H_2S levels indicates that inhibition and promotion occur simultaneously. Their relative influence depends upon the reaction conditions: inhibition predominates at high H_2S level and low temperature while promotion prevails at low H_2S level and high temperature.

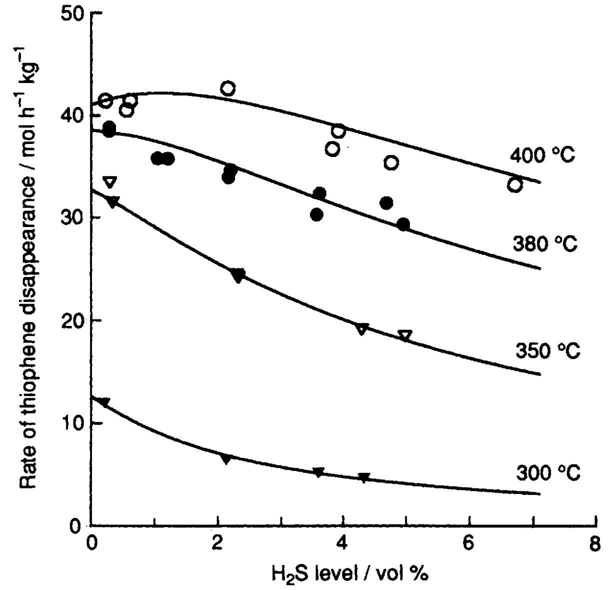
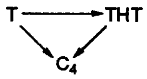


Fig. 1 Rate of thiophene disappearance (mol h^{-1} kg^{-1}) as a function of the actual H_2S level (vol%) at various temperatures



Scheme 1

This behaviour at atmospheric pressure is consistent with other results obtained under different pressures.[5] Therefore the triangular reaction scheme demonstrated under pressure (Scheme 1) is also likely to hold at atmospheric pressure. Indeed we detected, as others,[6,7] the hydrogenated intermediate THT at atmospheric pressure. Based on this, the kinetics of thiophene disappearance may well account for the observed curves. Measuring rates at low conversion simplifies Scheme 1 to two parallel routes, hydrogenation to THT and C–S bond breakage of thiophene.

The competition between promotion and inhibition can be interpreted by heterolytic dissociation of both H_2 and H_2S on the surface.[8,9] Hydrogenation would involve electrophilic H^+ species arising from H_2 or H_2S.[5] Then, H_2S influences hydrogenation in two ways: (*i*), it provides protonic species required for hydrogenation; (*ii*), it inhibits reaction rate by competitive adsorption with thiophene. Since H_2S is more strongly adsorbed than hydrogen, this should yield a higher concentration in active protonic species. At low H_2S levels, the promoting action of H_2S may predominate. The C–S bond breakage route is assumed to involve nucleophilic species, similarly to C–N bond breakage.[5] Among them, SH^- is known to be less active than the hydridic H^-. In that case, H_2S is inefficient for breaking a C–S bond, and acts simply as an inhibitor by adsorbing on the hydrogenolysis sites. Progress in modelling the rate equations supports the above interpretation.

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† The reaction of thiophene was studied in a flow reactor operating between 300 and 400 °C at atmospheric pressure. The reactor was loaded with 30 to 100 mg of sieved (0.2–0.5 mm) CoMo–Al_2O_3 catalyst from AKZO (KF 742). The oxidic catalyst was sulfided at 400 °C for 2.5 h under a H_2S–H_2 (15–85 vol%) flow. Then the reactor was fed with thiophene (8 vol%) and H_2S (0 to 6 vol%), balanced by H_2. The total flow rate ranged from 50 to 150 ml min^{-1}. Under these conditions, the conversion was below 7%. The major compounds were H_2S, butenes and butane, but traces of THT were evidenced after trapping the effluent of an experiment performed at 400 °C. The actual H_2S level is the average of the vol% H_2S at inlet and outlet of the reactor. The rate of thiophene disappearance, $r = x\ F^o/W$, was measured after 3 h on-stream, where x is the conversion, F^o the molar flow of thiophene at inlet and W the catalyst weight. Under our conditions, the reaction rates were free from diffusion limitations.

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