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NOTES

About the Nature of Hydrogen Activation on Unsupported Ruthenium Sulphide

Transition metal sulphides have been widely studied, due to their important industrial applications as catalysts for hydrodesulphurization (HDS), hydrodenitrogenation (HDN), and aromatics hydrogenation (HN). The screening of the HDS and HN properties of various transition metal sulphides has evidenced the prominent catalytic activity of ruthenium sulphide. This catalyst appeared to be 13 times more active than molybdenum sulphide in HDS and 6 times more active in HN (*1–4*).

In order to explain these large differences in catalytic activities, several interpretations were proposed. In all the models developed until now, it has been assumed that the hydrocarbon adsorption takes place on coordinatively unsaturated cations. These vacancies would be formed in the conditions used for hydrotreatment reactions by removal of superficial sulphur atoms. The S_2^{2-} pairs present in RuS_2 could be more reactive toward hydrogen than the S^{2-} anion of MoS_2, which would lead to numerous or (and) more active sites and therefore to highest catalytic activities.

Another important difference between MoS_2 and RuS_2 might arise from the hydrogen activation process namely heterolytic or homolytic dissociation. Recent studies performed on lamellar sulphides support the hypothesis of the formation of heterolytic hydrogen adsorption on coordinatively unsaturated Mo or W edge sites (*5–8*). However, another possible mechanism for hydrogen adsorption could be the homolytic dissociation on $(S\text{–}S)^{2-}$ groups. Such a possibility of hydrogen activation was demonstrated in molecular coordination chemistry by Rakowski-DuBois and co-workers (*9*). Recently, Polz *et al.* (*10*) suggested that disulphide species located at edge planes of MoS_2 might be also considered as potential sites for homolytic dihydrogen dissociation. If this hypothesis is correct, this type of hydrogen activation would be more important on RuS_2 where all the anions are S_2^{2-} pairs. In fact, recent studies of Tatarchuk and co-workers on a series of ruthenium catalysts either reduced, mildly sulphided, or fully sulphided led to such a conclusion; i.e., the active sites for hydrogen dissociation and retention could be coordinatively unsaturated S–S anion pairs which provide the dual-site requirement for hydrogen adsorption (*11, 12*). Moreover, the same authors showed that bulk sulphidation of metallic ruthenium was difficult and therefore the intermediate states might be only metallic ruthenium catalysts modified by sulphur adsorption (mild sulphidation) or a "skin" of crystalline RuS_2 on top of metallic ruthenium.

To address this important question of hydrogen activation on ruthenium sulphide, we have chosen to take the fully sulphided state as the starting point and to evaluate the influence of progressive desulphurization on hydrogen activation. The H_2–D_2 exchange reaction was utilized because this reaction may proceed at low temperature without changing the stoichiometry of the catalyst.

Ruthenium sulphide was prepared by precipitation at room temperature from an aqueous solution of $RuCl_3$ by pure H_2S and by further sulphidation in an H_2S flow at 400°C for 2 h. The catalyst was cooled down to room temperature under the same atmo-

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sphere and flushed with an inert gas. X-Ray diffraction was similar to that of RuS_2 reported in the JCPDS index, and elemental analysis indicated a stoichiometry S/Ru = 2.15.

The surface area of such a sample determined by N_2 physisorption was 70 m^2 g^{-1}, and no porosity was detected from the calculation of the pore size distribution. Therefore, the crystallite mean diameter calculated from the surface area gives an idea about the average particule size. In the present case, the solid may be considered as formed by a collection of cubes having an average length of about 140 Å. Taking into account the crystallographic data of RuS_2, a geometrical model similar to the one developed for MoS_2 by Kasztelan *et al.* (*13*) has been built up (*14*). This model allows the calculation of the stoichiometry of the catalyst with the assumption that each superficial ruthenium atom is still in a 6 fold coordination state. This excess of sulphur can be either S–S pairs (2 sulphur atoms per superficial ruthenium atom), bridged S–S pairs, or SH groups (one sulphur atom per superficial ruthenium atom). With both assumptions, the calculated stoichiometries lie between 2.24 and 2.12, which is close to the S/Ru ratio found by chemical analysis.

The desulphurization of the catalyst was carried out in a dynamic microreactor which allowed us to measure the amount of H_2S removed under hydrogen by the use of a specific UV photodetector (HNU Photoionization detector equipped with a 10.21 eV UV light source). The amount of H_2S evolved from the solid is simply quantified after the detector is calibrated with a known concentration of hydrogen sulphide diluted in hydrogen. The sample was first flushed with a nitrogen flow and then contacted with a hydrogen flow of 40 cm^3/min at room temperature. The temperature was then increased stepwise and the sample was left 3 h at each temperature of reduction.

The curve giving the variation of the H_2S evolved during the reduction process presents two different domains (Fig. 1). Below 300°C, mild reduction takes place which leads to the elimination of ca. 4000 μmol g^{-1} of hydrogen sulphide. According to the geometrical model, this partial reduction would correspond to the elimination of the superficial sulphur atoms between 50 and 200°C. Then, a progressive reduction involving more internal anions could proceed. At 300°C the depth of reduction corresponds roughly to the desulphurization of two ruthenium layers. These results are similar to the ones observed by Wambeke *et al.* (*15*) concerning molybdenum sulphide reduction assuming that large variations in the S/Mo ratio can result only in the removal of peripheral sulphur atoms without changing the core of MoS_2.

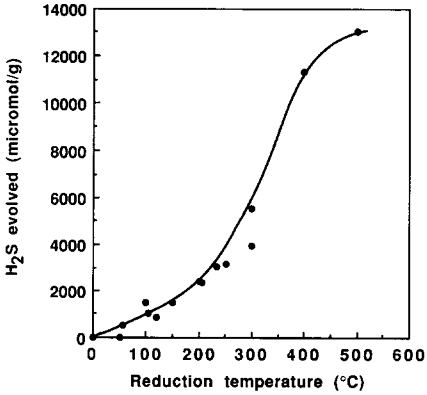

FIG. 1. Amount of H_2S evolved as a function of the reduction temperature.

Above 300°C, the drastic change in slope may be ascribed to a severe bulk reduction which provokes surface collapsing (Fig. 1) and phase segregation leading to the presence of an important concentration of bulk metallic ruthenium. As a matter of fact, the XRD patterns of a solid reduced at 400°C contained the diffraction lines ascribed to both metallic ruthenium and ruthenium sulphide (*14*). This phase segregation is in good agreement with previous studies which demonstrated that apart from pyrite RuS_2 no other Ru–S phase can be obtained (*16*).

At 500°C, the reduction of the solid is almost complete and the total amount of

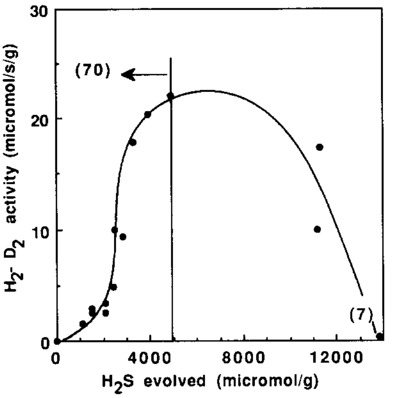

FIG. 2. H_2–D_2 exchange activity in micromol of HD per s and per g of catalyst versus the amount of H_2S eliminated by reductive treatment. Typical surface areas (in m^2/g) of the sample after these treatments are given in brackets. The vertical line shares the amount of H_2S evolved into two domains corresponding to distinct textural properties (on the left surface areas are constant, on the right surface areas are decreasing from 70 to 7 m^2/g).

removed sulphur is close to the initial stoichiometry observed by chemical analysis.

After each reduction at a given temperature and measurement of the amount of H_2S evolved from the solid, the plug flow microreactor was isolated from the open air and transferred to the catalytic unit designed for the H_2–D_2 exchange experiments. The latter were performed at 0°C by using an equimolecular H_2–D_2 mixture ($P_{H_2} = P_{D_2} = 50$ torrs) diluted in argon. The analysis of the effluent gases was performed by mass spectrometry. As the exchange reaction was always carried out at temperatures much lower than the reduction temperature, no H_2S, HDS, or D_2S was detected in the effluent gases which indicated that no further reduction of the sample occurred during the exchange reaction course.

As shown in Fig. 2, an increase in the degree of desulphurization of the solid brings about a large increase of the catalytic activity as long as the specific area of the catalyst remains constant. For highest reduction of the solid (above 300°C or ca. 5000 μ mol g^{-1} of H_2S removed), the activity decreases down to an almost inactive state. At this stage of reduction, the solid contains a noticeable amount of bulk metallic ruthenium as evidenced by XRD. As the catalytic properties drastically fall down, the resulting metal phase is obviously poisoned by residual sulphur atoms, since sulphur poisoned metallic ruthenium has been recognized to be inactive for hydrogen activation (*11, 12, 16, 17*). Thus, the decrease in the H_2–D_2 exchange activity may be ascribed to the replacement of the active sulphide phase by an inactive poisoned metallic phase.

The major increase of the catalytic properties with desulphurization, in the temperature range of surface area stability, clearly rules out that hydrogen dissociation occurs mostly on S_2^{2-} pairs. Accordingly, the catalytic sites able to activate H_2 have to be assigned either to small metallic patches resistant to sulphur poisoning or to surface sulphur defects. The presence of small metallic particules is unlikely, since it has been checked that H_2S adsorption carried out on a reduced sample inhibited any further hydrogen adsorption. On the other hand, this inhibiting effect is consistent with the presence of surface sulphur vacancies which adsorb H_2S. These vacancies appear therefore to be essential for dihydrogen activation. However, a too high desulphurization induces a decrease of activity and a structural rearrangement of the catalyst. By pointing out the major role of surface vacancies for hydrogen activation, it may be tentatively suggested that a heterolytic splitting of dihydrogen is most likely, as already proposed for molybdenum sulphide (*5–7*). Nevertheless, the homolytic dissociation of hydrogen on two vacancies cannot be excluded. Further studies concerning the adsorption of probe molecules and especially hydrogen in relation with the amount of H_2S eliminated are in progress.

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