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Catalytic Properties of a $CoMo/Al_2O_3$ Catalyst Presulfided with Alkyl Polysulfides: Comparison with Conventional Sulfiding

J. van Gestel, J. Leglise, and J.-C. Duchet

Laboratoire de Catalyse et Spectrochimie, URA CNRS 0414, ISMRA, Université de Caen, 6 Bd. Maréchal Juin, 14050 Caen Cedex, France

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A $CoMo/Al_2O_3$ hydrotreating catalyst has been sulfided in different ways: (i) by conventional *in situ* sulfiding in a high-pressure reactor with a H_2S/H_2 or dimethyldisulfide (DMDS)/H_2 mixture at 350°C and 4 MPa; or (ii) by a preliminary presulfidation with di-*tert*-nonyl or di-*tert*-dodecyl pentasulfides followed by one of the above conventional *in situ* sulfidations. The presulfidation was performed in two steps: impregnation of the oxidic catalyst with the polysulfide and then thermal treatment under flowing nitrogen at 130°C. The catalysts were evaluated for their catalytic properties at 280–350°C and 4 MPa for the simultaneous hydrodesulfurization of thiophene and hydrogenation of cyclohexene. Compared to H_2S/H_2, *in situ* DMDS/H_2 sulfiding of the $CoMo/Al_2O_3$ catalyst enhanced the C–S hydrogenolysis at 280°C but not the hydrogenation; however, the apparent activation energy for hydrogenation was markedly increased. The presulfidation with the polysulfides followed by H_2S/H_2 sulfidation yielded improved activities at 280°C for both hydrogenation and C–S bond breakage and did not influence the apparent activation energies. The highest activities were obtained by combining presulfiding and DMDS/H_2 sulfidation. These results are discussed in terms of the genesis of the supported sulfide phase with various sulfur species.

INTRODUCTION

Hydrotreating catalysts containing cobalt (nickel) and molybdenum supported on alumina are generally available in the oxidic form. They are transformed to sulfides after treatment with a mixture of sulfur-containing feed and hydrogen.

This treatment is typically carried out in the reactor itself since the metal sulfides are unstable under oxygen. The initial and the final states of the supported phases have been the subject of detailed characterizations by means of numerous physicochemical techniques. The essential features are gathered in several reviews (1–5). The dominant Mo species identified on the oxidic precursor are polymolybdate (Mo^{6+}) entities spread as a monolayer on the carrier and bonded to alumina through Mo–O–Al linkages. Cobalt is recognized in various environments, mainly Co_3O_4 and surface spinel species. Activation with H_2S/H_2 results in sulfidation and reduction to Mo^{4+}; under mild conditions (ca. 200°C) it yields primarily patches of MoS_2-like structure in highly dispersed form, still interacting with the support. In the sulfided catalyst, cobalt species of interest are reported as cobalt ions adsorbed on the edges of the MoS_2 slabs and as Co_9S_8 individual sulfide. Structural rearrangement occurs upon prolonged treatment at higher temperature, resulting in MoS_2 crystallites of greater size and stacking, which are detached from the carrier. Increased amounts of Co_9S_8 are also observed under such conditions.

It is now well established that only the edge and corner sites of the MoS_2 slabs are active for the catalytic reactions involved in hydrotreatment (6, 7). Moreover, the intrinsic activity is strongly dependent on the interaction of the Mo sulfides with the alumina surface (8). Hence, the genesis of the supported sulfide is of critical importance for catalyst performance. However, less is known about the processes occurring during the buildup of the active phase from the oxidic precursor. From temperature-programmed sulfiding (9, 10) and Raman spectroscopy (11, 12) studies, it is concluded that sulfiding a Mo/Al_2O_3 catalyst with H_2S/H_2 starts at room temperature with an O–S exchange reaction up to 130°C. Reduction to Mo^{4+} follows by rupture of Mo–S bonds, producing elemental sulfur which is evolved as H_2S. The results point to an easy sulfidation to MoS_2, which is almost complete at 200–300°C. The same steps were identified on mixed cobalt–molybdenum catalysts; the presence of cobalt seems to increase the dispersion of the molybdenum sulfide.

The sulfidation process is likely to be influenced by the nature of the sulfiding agent and the conditions of its implementation. Indeed, the activity and the selectivity of a $CoMo/Al_2O_3$ catalyst for hydrodesulfurization (13, 14), for hydrogenation (13), and for hydrodenitrogenation (14) have been found to be very sensitive to the mode of sulfiding.

In situ H_2S/H_2 gas sulfiding is a common practice in laboratory experiments, but is not recommended in refineries, mainly because of "hot-spotting" (15). In fact,

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commercial sulfidation is conducted by wetting the catalyst with a sulfiding feed under pressure; this leads to higher activity (16–18). It can be applied successfully with the sulfur from the feedstock itself or preferably with a light gas-oil spiked with a sulfur compound which releases H_2S at low temperature; this seems to be a key factor in reaching a high level of sulfiding and activity. CS_2 and mercaptans should be avoided because of environmental problems; organic sulfides are now popular, typically dimethyldisulfide (DMDS), which decomposes more easily than dimethylsulfide.

In a recently marketed novel commercial technology (19–21), the oxidic catalyst is presulfided *ex situ* with organic polysulfides brought to the catalyst by impregnation, followed by a heat treatment which partially converts the metal oxides to sulfides. The activation is achieved in the reactor only with hydrogen or with the feedstock diluted in hydrogen. This procedure avoids the use of a spiking agent. The patents claim that the startup of the unit is shorter and safer (22). The increased industrial interest and the lack of published fundamental study prompt research on this subject.

EXPERIMENTAL

1. Catalysts

a. Base catalyst. The oxidic catalyst was a $CoMo/Al_2O_3$ (KF 742-1.3Q) from Akzo which had been used in a hydrotreating plant and had been regenerated. It is designated hereafter as KR. Elemental analysis (CNRS, Vernaison) gave the following: Co, 2.8 wt%; Mo, 9.3%; C, 0.5%; and S, 0.6% as sulfate species. It is free from nickel and vanadium. BET surface area was 210 $m^2\,g^{-1}$ and pore volume 0.63 $cm^3\,g^{-1}$. Metal composition and texture were similar to those of a fresh KF 742 catalyst. Moreover, in our study we checked that regeneration did not affect the activity.

b. Presulfided catalyst. Two organic polysulfides $R\text{-}S_n\text{-}R$ (ELF Atochem), with ligands R either *t*-nonyl or *t*-dodecyl and with an average sulfur chain length $n = 4.8$ or 4.4, respectively, were used as presulfiding agents. In fact, the polysulfides were composed of several linear polysulfides with sulfur chain lengths ranging from 2 to 8. The oxidic base catalyst (10 g) was contacted for 1 week at room temperature with 25 ml of a solution of the polysulfide in isooctane. The concentration of the impregnating solution was chosen to incorporate an amount of sulfur exceeding that required by the stoichiometry Co_9S_8 and MoS_2 in the final catalyst, i.e., 7.6 wt%. After equilibrium, the solid was filtered and dried at room temperature. The impregnated catalyst was then treated at 130°C under flowing nitrogen for 2 h. The evolved products were collected and analyzed by chromatography. During this presulfiding step the catalyst color turned black. The presulfided catalysts were then stored under air before the catalytic tests. They are designated KRN or KRD according to the use of *t*-nonyl or *t*-dodecyl polysulfide, respectively.

c. Sulfur and carbon content. The solids were analyzed for their sulfur and carbon content by microcombustion performed by CNRS (Vernaison) at different stages of their preparation: (i) after impregnation of the base catalyst with the polysulfide solution and drying at room temperature until constant weight; (ii) after the subsequent presulfidation at 130°C; (iii) after *in situ* sulfidation at 0.1 MPa; and (iv) after catalytic test at 4 MPa. The sulfidation at atmospheric pressure (2.5 h at 400°C with H_2S (15 vol%)/H_2 and a temperature rise of 3°C min^{-1}) was followed by flushing with Ar at 400°C for 0.5 h, whereas after the catalytic test the solid was cooled under H_2S/H_2 and then flushed with H_2 at 80°C. The absolute deviation on the S and C contents amounted to 0.2% for the catalysts sulfided at 0.1 MPa, but to 0.5% for the catalysts tested at 4 MPa.

2. Catalytic Test

The catalytic properties were studied in a flow microreactor operating at 4 MPa total pressure. The reactor was loaded with 30 mg of presulfided or oxidic base catalyst (sieved 0.6–1.0 mm) and diluted with 7 g of SiC (1–2 mm).

a. Activation of the catalyst. The samples were sulfided *in situ* at 4 MPa in the gas phase, with a mixture of either H_2S/H_2 (10 vol% H_2S, produced by decomposition of dimethyldisulfide, DMDS, in a prereactor) or DMDS/H_2 (5 vol% DMDS) at a total flow rate of 2.4 liters h^{-1}. The procedure was as follows: After pressurization of the system, the temperature of the reactor was raised at 3°C min^{-1} to 350°C under the sulfiding mixture and then maintained for 12 h. In the case of DMDS/H_2, the activation was started with 1 vol% DMDS up to 130°C to prevent condensation; the concentration was then adjusted to 5 vol% and the temperature increased as above.

A third activation procedure using pure H_2 up to 350°C was also carried out.

b. Reaction conditions. At the end of the activation period, the catalyst was cooled to 280°C; the liquid feed was then introduced by a metering pump at a dosing rate of 1.2 ml h^{-1}, and the H_2S/H_2 (2.8 vol% H_2S) flow was increased to 12 liters h^{-1}. The liquid charge containing thiophene (13 vol%), cyclohexene (7%), *m*-xylene (19%), *n*-heptane (51%), and 2-propanol (10%) was totally vaporized in the system. The resulting partial pressures were 14.6, 6.3, 13.2, 30.3, and 12.0 kPa, respectively. The presence of 2-propanol prevented gumming of the pump head.

On-line analysis of the reaction products was carried out every 2 h with a gas chromatograph equipped with a CPSIL-5B capillary column and a FID detector. The analysis did not resolve the butenes and butane arising from the thiophene reaction. Steady-state conversions were measured after 12 h on stream, whereafter the reaction temperature and liquid hourly space velocity were varied in the range 280–350°C and 12–50 h^{-1}, respectively, with the partial pressures kept constant. The activity of the catalysts was stable over a period of 2 weeks.

c. Kinetic analysis. Pseudo-first-order rate equations were integrated and kinetic parameters (rate constants and activation energies) were computed by means of a nonlinear Marquardt method. Langmuir–Hinshelwood rate expressions could be reduced to pseudo-first-order equations because of the large excess of H_2S (110 kPa) compared to the organic reactants.

RESULTS

1. Carbon and Sulfur Analysis

Table 1 lists the sulfur and carbon contents of the catalysts after each stage of their activation.

The S/(S+C) weight ratios of the impregnated catalysts, dried at room temperature, were close to those of the organic polysulfides, i.e., 0.42 or 0.33 for the *t*-nonyl or *t*-dodecyl polysulfide, respectively. No isooctane solvent remained after drying.

The subsequent step at 130°C under flowing nitrogen occasioned a substantial decrease in the carbon content, indicating a decomposition of the polysulfides. Indeed, hydrocarbons were detected in the collected products: mainly nonenes for the KRN and dodecenes for the KRD catalyst. The patents also mentioned reaction of the alkylpolysulfides in the same temperature range (19, 20). The sulfur loss during the presulfidation step (Table 1) was due to distillation of the lighter fraction of the starting polysulfides.

After the final *in situ* sulfidation at atmospheric pressure with H_2S/H_2 at 400°C, all the carbon from the polysulfide was removed. The degree of sulfidation (D.S.) of the final catalyst was calculated as the ratio of the measured sulfur content (S wt% in Table 1), subtracting the sulfate species contribution (0.6%) to the stoichiometric sulfur as Co_9S_8 and MoS_2 (7.6%). The correction of 0.6% was justified by the stability of sulfate species on alumina (23). Moreover, sulfiding a fresh catalyst (KF 742) at 400°C yielded the same D.S. as that obtained on the regenerated KR used in this study (0.88, Table 1), indicating that sulfidation was almost complete. The D.S. values determined for the presulfided catalysts lay in the same range. The sulfur content of the catalysts sulfided and tested under high pressure was somewhat lower (D.S. about 0.70). Similar low D.S. values under hydrogen pressure have been reported (13, 24). Therefore, a possible influence of water on the sulfur uptake produced from 2-propanol can be reasonably discarded.

2. Model Reactions: Product Distribution and Reaction Scheme

n-Heptane and *m*-xylene did not react under the experimental conditions. 2-Propanol was converted 90–100% into C_3 hydrocarbons and H_2O. Therefore, the catalysts were tested only for the meaningful thiophene and cyclohexene model reactions.

The presence of water during the catalytic test may affect the activity results. However, Satterfield and Smith found only a moderate effect of water on the HDN of quinoline run with H_2S (25). In our case, the effect of water was minimized by the large excess of hydrogen sulfide. Furthermore, the partial pressures were kept constant, allowing a comparative study of the catalysts.

TABLE 1

Sulfur and Carbon Content (wt%)[a] at Different Stages of the Catalyst Activation

	Impregnated with polysulfides		Presulfided *ex situ*		Sulfided *in situ*[b]			Sulfided *in situ*[c] and tested		
Catalyst	C	S	C	S	C	S	D.S.[d]	C	S	D.S.[d]
KF 742	—	—	—	—	<0.2	6.7	0.88	—	—	—
KR	—	—	—	—	0.5	7.3	0.88	1.3	6.3	0.75
KRN	18.7	12.6	5.2	11.2	0.4	6.7	0.80	1.0	5.7	0.68
KRD	20.2	10.6	6.3	6.6	0.4	7.0	0.84	1.0	6.3	0.75

[a] Percentage weight of the catalyst sulfided at 0.1 MPa, 400°C.

[b] H_2S/H_2, 0.1 MPa, 400°C.

[c] H_2S/H_2, 4 MPa, 350°C.

[d] Degree of sulfidation defined in the text.

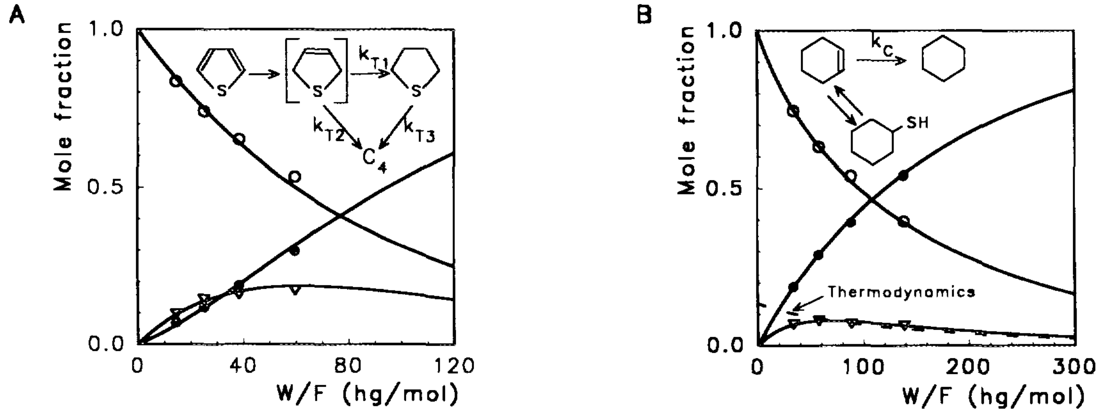


FIG. 1. Product distribution and reaction scheme for thiophene (A) and cyclohexene (B) at 280°C and 4 MPa on the KR catalyst, sulfided *in situ* with H_2S/H_2: ○, thiophene or cyclohexene; ●, C_4 hydrocarbons or cyclohexane, ▽, thiolane or cyclohexanethiol. Dashed line in (B): thermodynamic mole fraction of cyclohexanethiol.

Figure 1 shows typical product distributions versus space–time for the two reactions at 280°C for the KR catalyst sulfided with H_2S/H_2. Clearly, the hydrodesulfurization of thiophene (Fig. 1A) into C_4 hydrocarbons proceeds through the intermediate thiolane. Computed kinetics allow one to derive a proper reaction scheme. A poor fit was obtained with the simple consecutive scheme thiophene → thiolane → C_4. The triangular kinetic scheme

$$\begin{tikzcd}
\text{Thiophene} \arrow[rr, "1"] \arrow[dr, "2"'] & & \text{Thiolane} \arrow[dl, "3"] \\
& C_4 &
\end{tikzcd}$$

proved more satisfactory. However, C–S bond rupture from the aromatic thiophene ring is not expected to occur directly. It should involve several semihydrogenated intermediates, such as dihydrothiophenes. Although not evidenced, dihydrothiophenes have been suggested as the first products of the thiophene reaction (26, 27) with subsequent parallel hydrogenation to thiolane and C–S bound rupture yielding C_4 hydrocarbons and H_2S. The simplified reaction scheme is depicted in Fig. 1A. The high reactivity of the semihydrogenated intermediates prevents direct access to the rate constant of the limiting dearomatization step. Therefore, the rate constants k_{T_1} and k_{T_2} are calculated directly from the conversion of thiophene to thiolane and to C_4 hydrocarbons. The rate constant values listed in Table 2 indicate that the main route to C_4 hydrocarbons proceeds via thiolane, as expected under high hydrogen pressure.

The product distribution for the cyclohexene reaction is plotted in Fig. 1B. Cyclohexane was the main product, but a significant amount of cyclohexanethiol was observed. Isomerization into methylcyclopentene was negligible at 280°C. The thiol formation results from a reversible addition of H_2S to the olefin. The fraction of the thiol at thermodynamic equilibrium in the mixture decreased with cyclohexene conversion, as drawn in Fig. 1B. It fits the experimental fractions at sufficiently high space–time, which means that the establishment of the equilibrium is fairly slow. It is, however, catalyzed by the sulfide phase since in a separate experiment much slower rates were observed on the alumina support itself. Other sulfur compounds such as dicyclohexylsulfide were not found. Therefore, the simple scheme depicted in Fig. 1B describes the reaction of cyclohexene; the computed curves agree well with the experimental data.

TABLE 2

Pseudo-first-order Rate Constants (liters h^{-1} g^{-1}) at 280°C for Thiophene and Cyclohexene Reaction Steps[a]

Catalyst	*In situ* treatment at 350°C	Thiophene k_{T_1}	Thiophene k_{T_2}	Thiophene k_{T_3}	Cyclohexene k_c
KR	H_2S/H_2	57±3	16±2	90±18	85±3
KRN		65±4	25±2	95±11	104±2
KRD		60±4	31±2	86±9	114±2
		(67±7)[b]	(105±10)	(147±7)	(67±3)
KR	$DMDS/H_2$	53±2	22±2	119±9	80±1
KRN		59±3	23±2	142±11	94±1
KRD		57±2	25±2	145±9	99±1
		(101±7)	(109±14)	(168±7)	(84±3)
KR	H_2	28±2	10±2	22±20	58±2
KRN		51±2	17±2	103±13	72±1
KRD		56±5	16±5	61±30	69±2

[a] According to the schemes depicted in Figs. 1A and B.

[b] Numbers in parentheses are the apparent activation energy (kJ mol^{-1}).

The two model reactions allow evaluation of hydrogenation activity by the rate constants k_{T_1} for thiophene and k_C for cyclohexene; measurements for an extended series of catalysts activated in different ways showed that these two rate constants appeared fairly well correlated. However, k_C is more accurate, due to the simpler reaction scheme, and better quantifies the hydrogenation function. On the other hand, the correlation for the extended series failed with k_{T_2} and k_{T_3}, both of which reflect C–S bond rupture. This points to different mechanisms for sulfur removal from dihydrothiophene and from thiolane.

3. *Effect of Presulfiding on the Activity*

Activity results for thiophene and cyclohexene conversions at 280°C on the three catalysts KR, KRN, and KRD are expressed in terms of rate constants with their 95% confidence intervals in Table 2.

a. In situ sulfidation with H_2S/H_2. Preliminary presulfiding with polysulfides markedly improved the activity of the reference KR catalyst sulfided with H_2S/H_2 (Table 2). The presulfidation using *t*-dodecyl polysulfide was the most efficient (catalyst KRD). The rate constant k_C for cyclohexene hydrogenation was enhanced by a factor of 1.4, and the constant k_{T_2} for direct C–S bond rupture of thiophene by a factor of 2. The hydrogenation of thiophene to thiolane (k_{T_1}) and the C–S bond rupture of thiolane (k_{T_3}) were not significantly affected.

Apparent activation energies determined in the range 280–350°C are also quoted in Table 2. Both hydrogenation rate constants, k_C and k_{T_1}, were activated to the same level (67 kJ mol^{-1}). For the sulfur removal from thiophene, k_{T_3} was much more activated (147 kJ mol^{-1}) than k_{T_2} (105 kJ mol^{-1}), which again suggests different mechanisms for the two C–S bond breakages. Presulfiding with

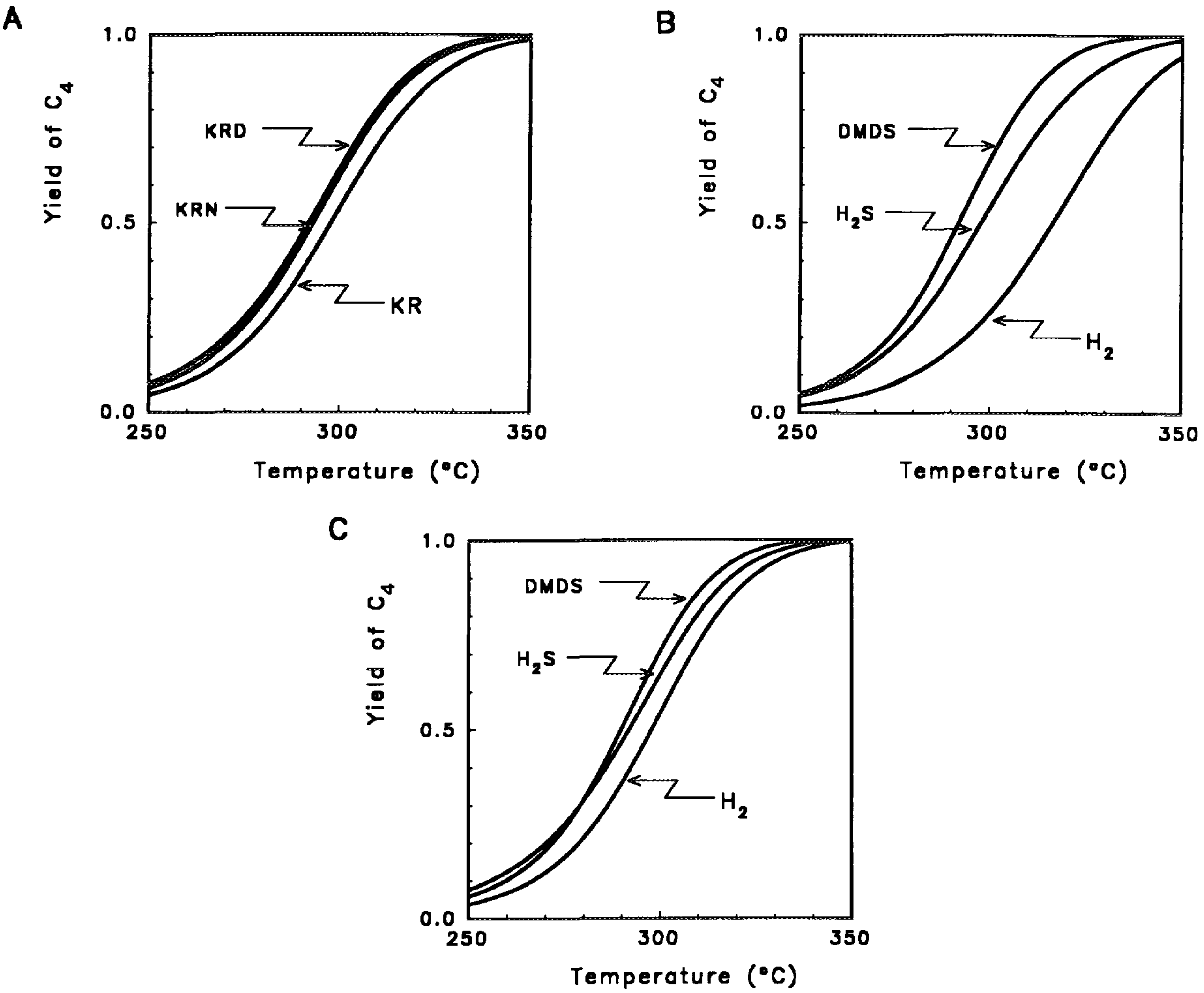


FIG. 2. Simulated production of C_4 hydrocarbons at W/F_T = 60 h g mol^{-1} as a function of temperature. (A) KR, KRN, and KRD catalysts sulfided with H_2S/H_2; (B) KR catalyst sulfided with H_2S/H_2 or DMDS/H_2, or prereduced with H_2; (C) KRD catalyst sulfided with H_2S/H_2 or DMDS/H_2, or prereduced with H_2.

polysulfides did not modify the values found for the KR catalyst sulfided with H_2S/H_2.

The advantage of presulfiding is evident from Fig. 2A, which shows the results of a simulation of C_4 hydrocarbon production from thiophene at fixed space-time versus temperature from the rate constants and activation energies listed in Table 2. As a consequence of the presulfidation, half conversion of thiophene into C_4 hydrocarbons is obtained about 6°C lower than after a classical sulfiding alone.

b. In situ sulfidation with DMDS/H₂. Sulfiding the oxidic KR catalyst with DMDS/H_2 instead of H_2S/H_2 significantly increased the activity for C–S bond rupture (k_{T_2} and k_{T_3} in Table 2). However, the main effect of DMDS/H_2 compared to H_2S/H_2 sulfidation was to increase the apparent activation energy for hydrogenation of both thiophene (k_{T_1}) and cyclohexene (k_C). Thus, the advantage of DMDS/H_2 over H_2S/H_2 sulfiding with respect to activity should be more pronounced when the catalyst is tested at higher temperature; this is simulated for the hydrodesulfurization of thiophene in Fig. 2B.

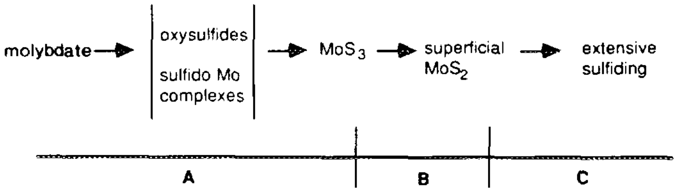
In addition, using DMDS instead of H_2S improves the C–S bond breakage from thiophene (k_{T_3}) on the KRN and KRD presulfided catalysts, while the other steps are slightly decreased (k_{T_2}, k_C) or unaffected (k_{T_1}). DMDS/H_2 sulfiding of the KRN and KRD catalysts increased the apparent activation energies associated with k_{T_1} and k_C, as for the KR catalyst. Then, combining presulfiding with polysulfides and *in situ* sulfidation with DMDS/H_2 yields the highest activity above 280°C (Fig. 2C). Hence sulfur removal is more readily accomplished at temperatures of industrial practice, namely 340–380°C.

c. In situ reduction with H₂. Prereducing the KR catalyst up to 350°C followed by mild sulfidation at 280°C with the feed containing thiophene results in a poorly active catalyst (Table 2 and Fig. 2B) compared to the catalyst sulfided with H_2S/H_2. Remarkably, however, the activity of the catalysts presulfided with polysulfides and then activated with pure hydrogen matches that of the H_2S/H_2 sulfided KR catalyst.

DISCUSSION

1. Genesis of the Active Sulfide Phase

The influence of the activation procedure on the catalytic properties of the $CoMo/Al_2O_3$ catalyst may be interpreted with respect to the genesis of the metal sulfides. The role of cobalt in the final active sulfide phase is still debated in the literature (28–30), but at fixed Co content, the primary factor determining the activity is the dispersion of the molybdenum sulfide. This governs the distribution of exposed metal atoms on edges and corners of the MoS_2 slabs, which are potential active sites (6).



SCHEME 1

The transformation of the supported polymolybdate into dispersed MoS_2 is achieved by sulfidation and reduction steps (16). An intermediate such as MoO_2 (31, 32) is unlikely since reduction of the catalyst before sulfidation yields poor activity (33, 34) (Table 2). The predominant activation mechanism should rather involve the trisulfide MoS_3 indicated by laser Raman spectroscopy (12). The same intermediate was also considered in temperature-programmed sulfiding studies (9). The overall process derived from Payen *et al.* (12) is represented in Scheme 1. Three domains can be arbitrarily distinguished, according to the temperature of treatment. The first region A is pure sulfidation; it starts with successive O–S exchange to oxysulfides, then evolves to sulfidomolybdenum complexes and finally to MoS_3-like species. The reduction into MoS_2 (region B) liberates sulfur desorbed as H_2S. The A and B regions are readily observed under mild conditions, ca. 200°C (12). However, the sulfidation is incomplete at this stage; our $CoMo/Al_2O_3$ catalyst gave a D.S. of 0.60 upon sulfidation by H_2S/H_2 at 200°C. Hence, a more extensive sulfidation requires higher temperatures (region C) at which a fraction of the Mo–O–Al linkages of the partially sulfided Mo species may be broken. This process starts at 300°C (1) and was clearly evident at higher temperatures (8) or after the carrier was changed (35).

From this picture, the dispersion of the catalytic molybdenum disulfide may be determined by the configuration of the MoS_3 intermediate, influenced by kinetic factors in region A. Moreover, region C is determinative with respect to the support interaction and the stacking of the MoS_2 slabs which affect the intrinsic activity of the sites. Indeed, increasing the temperature of sulfidation by H_2S/H_2 from 400 to 600°C modifies the nature of the sites of the supported sulfide (8).

Accordingly, the nature of the sulfiding agent may conceivably influence the different steps of the sulfidation process, and therefore should affect the catalytic properties.

Results obtained by Prada Silvy *et al.* (13) indicate that the effectiveness of the activation can be attributed to balanced reduction and sulfidation reactions. At a treatment temperature below 300°C, sulfidation of the CoMo catalyst is not complete, and the most efficient agent should have the highest ability to sulfide. The sulfur compound should decompose at low temperatures, yielding more active sulfiding than reductive species. At a higher temperature, the sulfidation is complete and the best sulfiding agent yields the lowest carbon deposition (13). Our results are discussed on this basis.

2. *Influence of the Sulfidation Procedure*

a. In situ sulfiding: $DMDS/H_2$ versus H_2S/H_2. Sulfiding the oxidic KR catalyst with $DMDS/H_2$ rather than H_2S/H_2 enhances C–S hydrogenolysis and increases the activation energy for hydrogenation. This is in line with distinct active sites for the two functions of the catalyst (36–39). The sulfur and carbon contents were comparable after these two sulfidations. Thus, the efficiency of $DMDS/H_2$ sulfiding could be due rather to a different buildup of the active phase than to different sulfur stoichiometry.

DMDS decomposes easily with hydrogen under atmospheric pressure on hydrotreating catalysts, producing primarily methanethiol (CH_3SH) at temperatures as low as 170°C (40); the maximum yield reaches 70% at 220°C, while H_2S production starts at about 200°C. Therefore, sulfidation of the catalyst may occur with methanethiol before any action of H_2S. Under pressure, sulfidation may start even at lower temperature, since we observed the decomposition of DMDS into CH_3SH at the beginning of the activation procedure, i.e., 130°C.

As reported by Prada Silvy *et al.* (13), a thiol dissociates either into RS^- and H^+ or into R^+ and HS^- species. Compared to the species issued from H_2S, RS^- would be more effective in sulfidation than HS^-, and R^+ would be less reducing than H^+. Although H_2S is able to initiate sulfidation at room temperature (9), it is likely that the balance between sulfidation and reduction is not optimal. The process would be more favorable with thiol originating from DMDS. Therefore, during the genesis of the active phase (Scheme 1), the two samples should exhibit different MoS_2-like structures at the end of region B.

The marked increase in activation energy for hydrogenation measured on the samples activated with $DMDS/H_2$ suggests that DMDS and H_2S act also differently in region C. In this region, the sulfide adopts its definite structure; the changes in catalytic properties may be related to weakened interactions with the support or to more specific changes in the site environment.

b. Presulfiding with polysulfides. Based on the relative reactivity of organic sulfur compounds, a beneficial action of polysulfides is expected. The decomposition of polysulfides starts at low temperature, i.e., in the range 100–150°C, and is completed around 200°C (19, 20). Compared to DMDS, they may easily release sulfur according to the reaction

$$R\text{–}S_n\text{–}R \rightarrow R\text{–}S_{n-x}\text{–}R + S_x$$

Sulfur is then directly available as a nascent species, acting as such or as a H_2S precursor. Moreover, the polysulfide may undergo S–S or C–S bond splitting, following

$$R\text{–}S_n\text{–}R \rightarrow R\text{–}S_p^- + R\text{–}S_q^+$$

or

$$R\text{–}S_n\text{–}R \rightarrow R\text{–}S_n^- + R^+,$$

with further degradation of the sulfur chain to yield RS^- and elemental sulfur. Moreover, β-elimination, indicated by production of nonenes or dodecenes, yields nascent sulfanes. All these sulfur species are able to start the sulfidation of the metal oxides at the presulfiding stage. This means that the A and B stages of the MoS_2 genesis (Scheme 1) are partially accomplished by the polysulfides, as already evidenced by the color change and confirmed by the activity of these samples even after treatment with pure H_2 (Table 2).

When sulfided with H_2S/H_2, the above sulfiding species from the polysulfides now compete with HS^- from H_2S. The combined presulfiding and *in situ* sulfidation may then influence the MoS_2 buildup and the final activity of the catalyst. The better catalytic results obtained with KRN and KRD indeed suggest an increase in the number of sites. Moreover, since no change in activation energy is observed, the nature of the sites is presumably determined in the last domain (C), where H_2S is the only sulfiding agent. The advantage of using polysulfide may also be related to the presence of hydrocarbons which might hamper the formation of large MoS_2 slabs, without gumming the catalyst (Table 1).

When *in situ* sulfidation of presulfided catalysts is performed with $DMDS/H_2$, the resulting catalysts bear the fingerprint of DMDS, i.e., an increase in the activation energy for hydrogenation. Furthermore, the catalysts presulfided with the polysulfides are more hydrogenating (Table 2). The action of the polysulfide at low temperature should be directed at the dispersion of the MoS_2 particles, whereas high temperature sulfidation by $DMDS/H_2$ seems to govern the nature of the active sites. From a practical point of view, the combination of presulfiding and *in situ* sulfidation with $DMDS/H_2$ allows hydrogenation at temperatures of industrial operation (340–380°C) and meets the first requirement in hydrotreatment.

CONCLUSION

The present study provides evidence for the positive effect of presulfiding with *t*-nonyl or *t*-dodecyl polysulfide followed by *in situ* sulfiding with H_2S/H_2 on the activity of a $CoMo/Al_2O_3$ catalyst. Both hydrogenation and C–S bond rupture are improved by this procedure.

Direct *in situ* sulfidation of the oxidic catalyst with $DMDS/H_2$ instead of H_2S/H_2 also increases the overall activity, mainly at high temperatures of operation, due to a higher activation energy for hydrogenation. Both actions are combined by sulfiding the presulfided catalyst with $DMDS/H_2$.

The polysulfides decomposed easily at low temperature, producing various species able to initiate the sulfidation of the oxidic catalyst and then yielding a better configuration of the final active metal sulfide. DMDS is also an efficient sulfiding molecule. In addition, DMDS changes the nature of the hydrogenation sites compared with H_2S.

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