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PREPARATION AND CHARACTERIZATION OF HIGHLY ACTIVE RUTHENIUM SULPHIDE SUPPORTED CATALYSTS

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Ruthenium sulphide catalysts supported on alumina were prepared using different precursor salts [ruthenium (III) chloride trihydrate, ruthenium (III) acetylacetonate and triruthenium dodecacarbonyl] and sulphided under various atmospheres. The properties of the catalysts in thiophene hydrodesulphurization are interpreted in relation to the XPS characterizations. These results show the importance of the sulphidation step in the absence of hydrogen in order to obtain a well sulphided, well dispersed and highly active catalyst.

1. Introduction

The catalysts usually employed to remove sulphur and nitrogen in petroleum feedstocks are Co- and Ni-promoted Mo or W sulphides supported on alumina or silica-alumina. Over the last few years extensive research on other transition metal sulphides (TMS) in hydrotreating reactions have been carried out [1–7]. Ruthenium sulphide was found to exhibit prominent catalytic activities. According to Pecoraro and Chianelli [1], bulk RuS_2 appeared to be 13 times more active than MoS_2 for dibenzothiophene hydrodesulphurization (HDS). Lacroix et al. [2] reported a hydrogenation (HYD) activity 6 times higher than that of MoS_2. In both studies unsupported RuS_2 displayed one of the highest activities in comparison with other TMS. Several interesting properties could be expected if RuS_2 catalysts were to be deposited on a high surface area support.

However, there is a large discrepancy within the literature concerning the performance of supported ruthenium. On one hand, zeolite- or carbon-supported RuS_2 showed outstanding hydrodenitrogenation (HDN) properties [3–5]; on the other hand, it has been observed that alumina-supported ruthenium samples

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exhibited lower activity as HDS or as HDN catalysts than a molybdenum-based sample [3,6,7]. Nevertheless, Kuo et al. [7] reported interesting observations on the sulphidation process of alumina-supported metallic ruthenium but reactivity comparisons were difficult to interprete owing to the rate calculation basis. In this later work, a 3.7% Ru/Al_2O_3 possessed ca. seven fold higher thiophene conversion rates than CoMo/Al_2O_3 when compared per estimated square meter of active area, while thiophene HDS rates were ca. 7-fold lower over Ru/Al_2O_3 catalyst than over CoMo/Al_2O_3 when compared per gram of catalyst.

In view of the above studies it was of interest to investigate the steps involved in the activation of supported Ru catalysts. Therefore, we examined first the impregnation using several precursors and then we investigated the crucial sulphidation step.

2. Experimental

The alumina supported ruthenium catalyst was prepared by incipient wetness impregnation of the "$RuCl_3 \cdot H_2O$" precursor salt. Ruthenium (III) acetylacetonate- and $Ru_3(CO)_{12}$-based catalysts were prepared by impregnating the support with a solution of the complex in benzene-cyclohexane, then by stirring overnight under an inert atmosphere. The solvent was evaporated in a stream of nitrogen. The impregnated samples were then oven-dried at 383 K for 16 hours.

Prior to the catalytic tests, the materials used were sulphided in a flow reactor for 4 hours at 673 K under an atmosphere containing H_2S [N_2/H_2S(15%), H_2/H_2S(15%)] or pure H_2S. The identification of the catalysts in relation to the precursor salt and to the activation mixture is given in table 1.

The XPS experiments were carried out with a Hewlett Packard 5950A spectrometer using monochromatic Al Kα radiation. To minimize the exposure to air, the sulphided samples kept in a sealed bottle under argon were transferred rapidly to the spectrometer. The binding energies were referenced to Al 2p at 74.3 eV.

Table 1
Composition, denomination and specific rates in thiophene HDS at 623 K of the catalysts

Sample identication	Catalyst precursor	Sulphidation mixture	Ru (wt.%)	r_s (10^{-8} mol·s^{-1}·g^{-1})
RuCl(H_2/H_2S)	"$RuCl_3 \cdot 3H_2O$"	H_2–H_2S(15%)	7.0	64
RuCl(N_2/H_2S)		N_2–H_2S(15%)	7.0	560
RuCl(N_2/H_2S) [a]		N_2–H_2S(15%)	7.0	355
RuCl(H_2S)		H_2S(100%)	7.0	495
RuCO(N_2/H_2S)	$Ru_3(CO)_{12}$	N_2–H_2S(15%)	6.5	290
RuACAC(N_2/H_2S)	Ru(ACAC)$_3$	N_2–H_2S(15%)	7.2	275
HR346	–	H_2–H_2S(15%)	–	700

[a] Sample calcined at 673 K.

The thiophene conversions were determined in a dynamic differential reactor operated at 573–623 K. ($P_{H_2} = 101$ kPa, $P_{\text{thiophene}} = 2.4$ kPa).

3. Results and discussion

3.1. INFUENCE OF THE PRECURSOR

In order to select the ruthenium salt leading to the best catalyst, experiments on the influence of the precursor in thiophene hydrogenolysis (table 1) were carried out. The HDS activity of the ruthenium chloride-based catalyst is 1.5 times higher than those of carbonyl-based or acetylacetonate-based solids. These results can be explained by differences in the dispersion of Ru on Al_2O_3 and are in good agreement with previous observations in the literature [3]. Further characterizations will contribute to the understanding of the influence of the precursor on the HDS activity. Henceforth all our studies will be based on a ruthenium chloride-prepared catalyst.

3.2. INFLUENCE OF THE SULPHIDING MIXTURE

The results in table 1 indicate that large differences for thiophene HDS were observed in relation to the sulphiding mixture. Thus the $RuCl(H_2/H_2S)$ was almost ten times less active than both $RuCl(H_2S)$ and $RuCl(N_2/H_2S)$ samples were. The $RuCl(N_2/H_2S)$ sample displayed the highest specific rate, that was only marginally lower than that of the industrial $NiMo/Al_2O_3$ (HR346 from PROCATALYSE).

XPS spectra of supported Ru catalysts were recorded on samples taken at different steps of the preparation. The spectra for Ru binding energies shown in fig. 1 correspond to the impregnated dried sample (1a), the calcined solid (1b), and the uncalcined catalysts sulphided under three atmospheres (1c, 1d, 1e). Concerning the uncalcined and unsulphided sample, it is difficult to determine the Ru oxidation state since the linersharps are complicated. For these findings two reasons can be stated: (i) the precursor salt (commercial ruthenium chloride) is a heterogeneous mixture of variable oxidation-state, oxochloro and hydrochloro complexes [8], (ii) surface carbon at the surface (B.E. 284.5 eV). Regarding the calcined solid, Ru binding energies were ca. 2 eV less than those in the impregnated catalyst and were similar to the Ru binding energies present in ruthenium oxides [10]. Finally, the Ru binding energies for the sulphided solids agree with the previous results on unsupported RuS_2 [6,9]. Those values do not differ significantly for the samples sulphided under the three mixtures although an additional band is observed for $RuCl(H_2/H_2S)$. This photopic at 282.6 eV suggests the presence of other entities such as an oxychloride and cannot be considered as reoxidized ruthenium (B.E. 280.7 eV) [10].

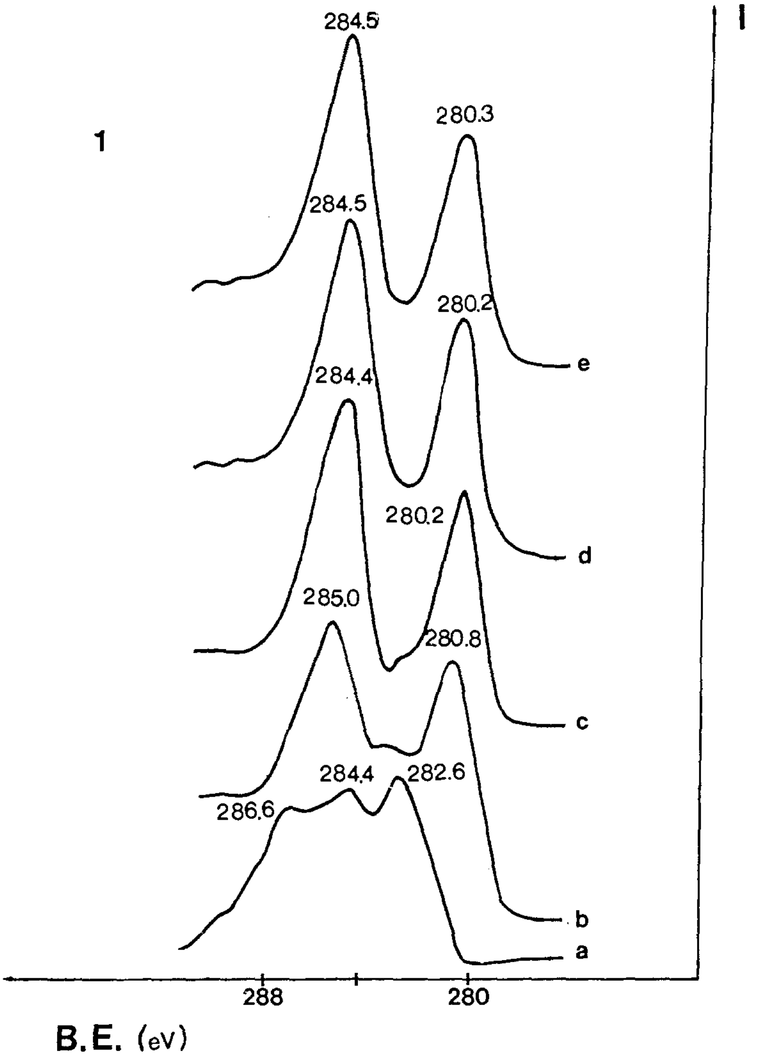

Fig. 1. Ru $3d_{3/2}$ and Ru $3d_{5/2}$ XPS spectra of RuCl catalysts: a) not calcined, not sulphided; b) calcined at 673 K, not sulphided; c) sulphided under H_2/H_2S^{nc}; d) sulphided under N_2/H_2S^{nc}; e) sulphided under H_2S^{nc}. (^{nc}: not calcined.)

The S2p binding energies for the samples sulphided in the absence of hydrogen (figs. 2a, 2b) are assigned to the $(S-S)^{2-}$ ion. Those values are close to the characteristic band of the bulk RuS_2 [6,9] which has a pyrite structure (B.E. 162.5 eV). As can be seen from the figure mentioned above, the S 2p peaks are not very symmetric indicating the presence of a small amount of elemental sulphur at the surface. The S 2p binding energy for $RuCl(H_2/H_2S)$ (fig. 2c) decreases slightly implying the presence of S^{2-} species as suggested by Mitchell et al. [6]. More detailed examination of fig. 2c reveals that the peak near 168.5 eV (sulphate) has

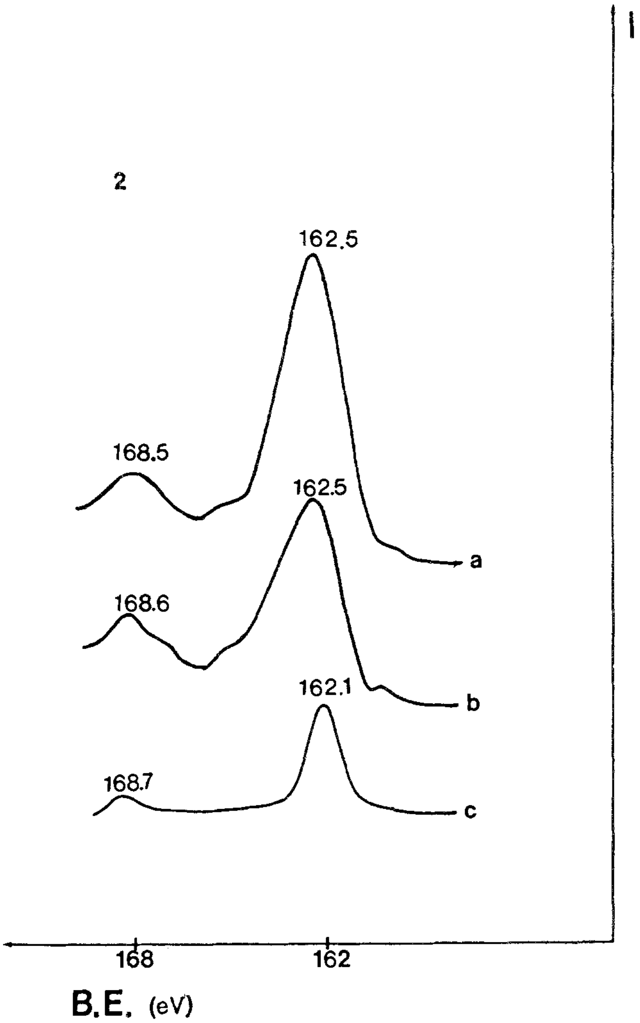

Fig. 2. S $2p_{1/2}$ and S $2p_{3/2}$ XPS spectra of RuCl catalysts: a) sulphided under H_2S^{nc}; b) sulphided under N_2/H_2S^{nc}; c) sulphided under H_2/H_2S^{nc}. (^{nc}: not calcined.)

a weak intensity. This fact confirms that little or no reoxidation occurs during air exposure prior to surface analysis.

The atomic ratios calculated from the peak intensities of the elements presented in the catalysts are given in table 2. Ru $3d_{5/2}$ was employed only to avoid the Ru $3d_{3/2}$ peak which is overlapped by the C 1s band. For an uncalcined and unsulphided sample, the Ru/Al intensity ratio is close to the value obtained from bulk chemical analysis (Ru/Al = 0.038) and suggests an excellent dispersion of Ru on the support. Generally speaking this ratio decreases after sulphidation. The highest Ru/Al value, observed for the RuCl(N_2/H_2S) sample, and the slightly lower value, obtained for RuCl(H_2S), correlate with the differences in the hydrogenolysis activities.

Table 2
XPS data for Ru/Al_2O_3 catalysts

Sample	Binding energy (eV)		XPS ratios	
	Ru $3d_{5/2}$	S_{2p}	$\frac{Ru}{Al}$	$\frac{R}{Ru}$
$RuCl(H_2/H_2S)$ – sulphided[nc]	280.2	162.1	0.019	1.8
$RuCl(H_2S)$ – sulphided[nc]	280.3	162.5	0.022	3.6
$RuCl(N_2/H_2S)$ – sulphided[nc]	280.2	162.5	0.025	4.2
RuCl				
– not sulphided[nc]	282.6	–	0.038	–
– not sulphided[c]	280.8	–	0.028	–

nc: not calcined before sulphidation.
c: calcined at 673 K before sulphidation.

The S/Ru stoichiometric value for ruthenium disulphide is 2, whereas the S to Ru XPS intensity ratios range from 1.8 to 4.2 (table 2), depending on the sulphiding mixture. Thus, the $RuCl(H_2S)$ and the $RuCl(N_2/H_2S)$ catalysts must be completely sulphided while the $RuCl(H_2/H_2S)$ is incompletely sulphided. Doubtless, excess sulphur incorporation cannot be ruled out since bulk compositions determined by atomic absorption agree with those values. A high S/Ru ratio has already been considered in the literature [11] for MoS_2 on alumina. Analogous behaviour could be expected for small crystallites of RuS_2. The presence of elemental sulphur at the surface also contributes to such an excess.

It appears from the XPS results that the sulphidation in the absence of hydrogen leads to the formation of bulk RuS_2-like structures, as opposed to a sulphidation carried out under H_2–H_2S [mainly (S^{2-}) ions]. Moreover, some Ru^0 may be present as previously reported for the unsupported RuS_2 tested under high hydrogen pressures [11]. Such metallic ruthenium was recognized to be difficult to sulphide to sulphide by Kuo et al. [7]. It was confirmed in an additional experiment that a Ru/Al_2O_3 sample prereduced under H_2 at 673 K could not be sulphided (even under a N_2/H_2S mixture), displaying a ca. 2 fold lower HDS activity than that of $RuCl(N_2/H_2S)$. It should be noted that XPS is not a suitable technique to identify metallic ruthenium because Ru^0 binding energies (i.e. Ru $3d_{5/2}$ at 280.0 eV) are very close to those of RuS_2 (280.2 eV).

Therefore, these results demonstrate the importance of sulphidation under N_2–H_2S without prereduction in order to obtain a well sulphided and highly active RuS_2 supported catalyst. Similarly, earlier studies in our laboratory [9,13] have shown that the hydrotreating properties of $Ni_xRu_{1-x}S_2$ solid solutions are directly related to the presence of $(S{-}S)^{2-}$ pairs as evidenced by XPS.

3.3. EFFECT OF CALCINATION

From the above XPS characterizations, ruthenium shows a good dispersion on Al_2O_3 after the impregnation step. By contrast, lower values were found after sulphidation. Unfortunately, as shown in table 1, a calcination at 673 K prior to sulphidation appears to reduce the initially high degree of dispersion. As expected, the catalytic performance of a precalcined ruthenium catalyst was lower when compared with the uncalcined sample activity. Not surprisingly, this result might be related to a poorer dispersion on the support as the ratio Ru to Al diminishes (table 2) in agreement with Mitchell's XPS findings [6].

4. Conclusion

The main conclusion which can be drawn from our studies is that sulphidation in the absence of hydrogen permits more complete sulphidation of Ru, induces the formation of the pyrite phase RuS_2, allows a good dispersion on the support and, consequently, a better thiophene HDS activity.

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References

[1] T.A. Pecoraro and R.R. Chianelli, J. Catal. 67 (1981) 430.
[2] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat and M. Breysse, J. Catal. 120 (1989) 473.
[3] T.G. Harvey and T.W. Matheson, J. Catal. 101 (1986) 253.
[4] Eijbouts, V. De Beer and R. Prins, J. Catal. 109 (1988) 217.
[5] S. Göbölös, M. Breysse, M. Cattenot, T. Decamp, M. Lacroix, J.L. Portefaix and M. Vrinat, in: *Advances in Hydrotreating Catalysts*, eds. M.L. Occelli and R. Anthony (Elsevier Science Publishers B.V., 1989).
[6] P.C.H. Mitchell, C.E. Scott, J.P. Bonnelle and J.G. Grimblot, J. Catal. 107 (1987) 482.
[7] Y. Kuo, R.A. Cocco and B.J. Tatarchuk, J. Catal. 112 (1988) 250.
[8] E.A. Seddon and K. Seddon, *The Chemistry of Ruthenium*, 2nd edition (Elsevier, Amsterdam, 1984).
[9] M. Vrinat, M. Lacroix, M. Breysse, A. Bellaloui, L. Mosoni and M. Roubin, in: *Proc. 9th Int. Congr. Catalysis*, Calgary, eds. M.J. Phillips and M. Ternan, 1 (1988) 88.

[10] K.S. Kim and N. Winograd, J. Catal. 35 (1974) 66.
[11] S. Kasztelan, H. Toulhoat, J. Grimblot and J.P. Bonnelle, Appl. Catal. 13 (1984) 127.
[12] A. Bellaloui, L. Mosoni, M. Roubin, M. Vrinat and M. Lacroix, C.R. Acad. Sci. Paris, t. 307 série II (1988) 1171.
[13] M. Vrinat, M. Lacroix, M. Breysse, L. Mosoni and M. Roubin, Cat. Lett. 3 (1989) 405.