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CATALYTIC PROPERTIES IN HYDROGENATION AND HYDRODESULPHURIZATION REACTIONS OF RUTHENIUM SULPHIDE SOLID SOLUTIONS CONTAINING IRON, COBALT OR NICKEL

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Solid solutions $M_xRu_{1-x}S_2$ (M = Ni, Co, Fe) were prepared by sulphidation of mixtures of hydroxides at 673 K; their crystallographic properties were studied by X-ray diffraction. These new materials present interesting properties in biphenyl hydrogenation and in thiophene hydrodesulphurization. The catalytic properties are strongly dependent on the nature of the metal associated to ruthenium. Cobalt-ruthenium catalysts present a good activity for hydrodesulphurization but very low activity for hydrogenation, iron catalysts exhibit low activity for both reactions, and nickel catalysts possess remarkable properties in hydrogenation and hydrodesulphurization (twice the activity of pure ruthenium sulphide). A comparison has been established with the properties of molybdenum sulphide catalysts promoted by the same elements.

Ruthenium sulfide for hydrogenation and hydrodesulphurization

1. Introduction

Ruthenium sulphide catalysts, either unsupported or supported by various carriers such as carbon, zeolite or alumina, are very active for performing hydrodesulphurization, hydrodenitrogenation and hydrogenation reactions [1–6]. In addition to these promising uses of RuS_2 in catalysis, it has been shown that this chalcogenide may form ternary compounds with other pyrite type sulphides like CoS_2 or RhS_2 [7], CoS_2, NiS_2 or FeS_2 [8]. For the nickel-ruthenium system, solid solutions were synthesized at 1073 K in the whole range of composition [9]. These new materials are very active in biphenyl hydrogenation even for high Ni content ($x < 0.83$). Such results led to the assumption that other $M_xRu_{1-x}S_2$ compounds may also present interesting catalytic properties.

The aim of this study was to extend the previous work on the nickel-ruthenium sulphide catalysts to the iron- and cobalt-ruthenium sulphides. Members of the system $Co_xRu_{1-x}S_2$ and $Fe_xRu_{1-x}S_2$ were prepared, the homogeneity range of the pyrite structure was examined and the catalytic properties were determined for model reactions characteristic of hydrotreatment i.e. the hydrogenation of biphenyl and the hydrodesulphurization of thiophene. Moreover, the properties of these ruthenium based catalysts were compared with the properties of the more conventional molybdenum sulphide based catalysts containing the same elements, i.e. iron, cobalt or nickel.

2. Experimental

CATALYSTS PREPARATION AND CHARACTERIZATION

The synthesis of the members of the $M_xRu_{1-x}S_2$ system was performed by sulphidation of the coprecipitated hydroxides. The latter were prepared by adding dropwise and simultaneously aqueous solutions of Ni (Co, Fe) chloride, Ru chloride and ammonium triethylamine to a large volume of water maintained at room temperature and vigorously stirred. In these conditions, the precipitations were complete and the resulting slurries were filtrated, washed with water and dried at room temperature. The oxidic precursors were then sulphided by a $2 l.h^{-1}$ H_2S flow in a reactor maintained at 673 K during 2 hours (heating rate 100 $K.h^{-1}$) and cooled to room temperature under the same atmosphere. A pure RuS_2 was prepared according to the same procedure.

The molybdenum based catalysts were prepared by the homogeneous sulphide precipitation method developed by Candia et al. [10]. A dilute solution of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$, $4H_2O$ and nickel nitrate $Ni(NO_3)_2$, $6H_2O$ (or cobalt or iron nitrate) with a predetermined concentration $r = M'/(M' + Mo) = 0.3$ was heated at 343 K and vigorously stirred. A dilute solution of $(NH_4)_2S$ was added slowly. The slurry was stirred at the same temperature under reduced pressure until complete evaporation of the liquid phase. The resulting precursor was heated in a flow of H_2-H_2S 15% up to 673 K, kept at this temperature for 4 hours and cooled to room temperature under the same atmosphere. A sample of pure molybdenum sulphide was obtained by decomposition of ammonium thiomolybdate.

The powder diffraction patterns were obtained with a SIEMENS D 500 diffractometer (Cu-Kα radiation: 1.5418 Å) equipped with an automatic identification of phases according to JCPDS index. For all samples, a scan speed of 1° min^{-1} was used and the 2θ range between 26 and 70 degrees was investigated. The lattice parameter of the cubic pyrite structure was calculated according to the least squares analysis method.

CATALYTIC ACTIVITIES

The hydrogenation of biphenyl was carried out in a continuous flow microreactor (SOTELEM RDP 830) under medium high pressure conditions. The experimental conditions were the following:

$P_{H2} = 23 \times 10^5$ Pa, $P_{H2S} = 17 \times 10^2$ Pa, $P_{BP} = 8 \times 10^2$ Pa,

temperature range: 510–560 K.

The hydrogen sulphide partial pressure utilized in the present study was higher than that utilized previously in order to avoid the deactivation observed at reaction temperature higher than 550 K using low hydrogen sulphide partial pressure. It was checked that no important deactivation occurred for all the catalysts up to 573 K.

In these conditions, biphenyl is mainly converted into cyclohexylbenzene and dicyclohexyl.

The hydrodesulphurization of thiophene was performed in a continuous flow microreactor at atmospheric pressure. The test conditions were:

$P_{H2} = 1 \times 10^5$ Pa, $P_{Th} = 17 \times 10^2$ Pa,

temperature range: 550–650 K.

In these experimental conditions, a small deactivation was observed for all catalysts during the first hours on-stream. Nevertheless, the pseudo-stationary state was reached quickly in all cases. The activities reported here were determined after at least 16 hours on-stream.

For both reactions, the total conversion was kept lower than 15% by adjusting the catalyst weight. The intrinsic rates were calculated using the following equation:

$$r_i = \frac{Q}{m \cdot S_f} \tau$$

with

Q = hydrocarbon flow rate,
m = catalyst weight,
τ = conversion,
S_f = surface area of the catalyst after test.

Intrinsic rates can be used for the comparison of the different samples since it has been demonstrated that in cubic systems like RuS_2 catalytic activities are proportional to surface areas [2]. For molybdenum based catalysts such a relationship has also been observed for samples prepared at similar sulphiding temperatures [11].

3. Results and discussion

CHARACTERIZATION OF $M_xRu_{1-x}S_2$ SOLID SOLUTIONS

The XRD patterns of the $Ni_xRu_{1-x}S_2$ compounds obtained by the sulphidation of hydroxides at 673 K can be interpreted on the basis of a cubic pyrite

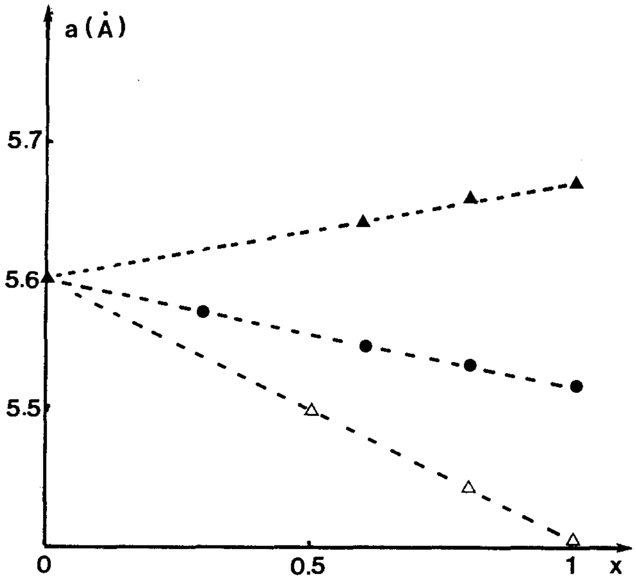

Fig. 1. Variation in lattice parameter *a* (A) for $Ni_xRu_{1-x}S_2$ (▲), $Co_xRu_{1-x}S_2$ (●), and $Fe_xRu_{1-x}S_2$ (△) catalysts obtained at 673 K from hydroxides.

structure. As reported in fig. 1, the lattice parameters were found to verify the Vegard's law. The linear change of the cell parameter with the composition is proof of solid solution formation. These results are similar to those obtained previously using a higher sulphidation temperature (873 K). The lowering of the sulphidation temperature allows the preparation of samples presenting higher surface areas.

The XRD patterns of the $Co_xRu_{1-x}S_2$ samples also evidenced homogeneous solutions and the lattice parameters were found to change linearly with the composition in the range $0 < x < 1$. Values of the cell parameter (fig. 1) agree well with the ones reported by Foise et al. [12] for solid solutions prepared by heating stoichiometric quantities of pentaamine cobalt (III) chloride and ammonium hexachlororuthenate (IV) at 1073 K in hydrogen sulphide.

Concerning the members of the $Fe_xRu_{1-x}S_2$ system, it has been previously reported that preparation using $FeCl_3$, $2H_2O$ did not lead to solid solutions in the whole range of composition [8]. New attempts were made with the iron (II) chloride dihydrate. Under these conditions, a monophasic system appears to be obtained for $0 < x < 1$, the lattice parameters are given on fig. 1.

CATALYTIC ACTIVITIES OF RUTHENIUM BASED CATALYSTS

Hydrogenation of biphenyl

In a previous paper [9], it was reported for the $Ni_xRu_{1-x}S_2$ catalysts sulphided at 1073 K, that the addition of 20% of nickel atoms into the RuS_2 structure leads

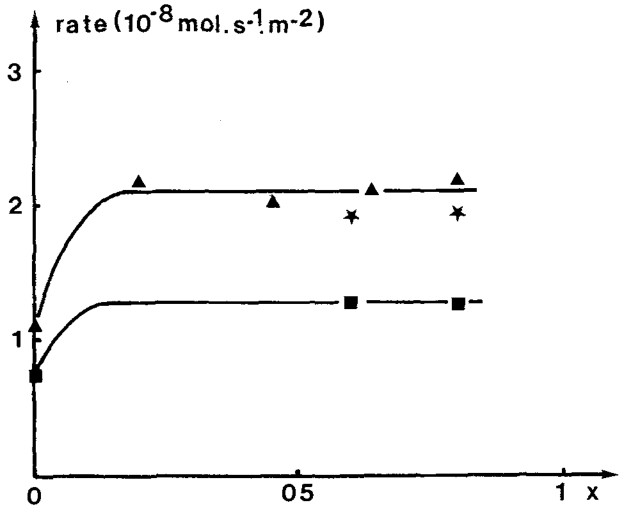

Fig. 2. Catalytic activities versus composition in biphenyl hydrogenation. ▲ catalysts prepared at 1073 K and tested under $P_{H2S} = 4.5 \times 10^2$ Pa. (from ref. [9]). ★ catalysts prepared at 673 K and tested under $P_{H2S} = 4.5 \times 10^2$ Pa. ■ catalysts prepared at 673 K and tested under $P_{H2S} = 17 \times 10^2$ Pa.

to a twofold increase of the activity of pure RuS_2. A further increase of the Ni content does not affect the hydrogenation properties (fig. 2) which remain constant up to $x = 0.83$.

Table 1
Catalytic activities for catalysts prepared at 673 K.

Catalysts	Biphenyl hydrogenation			Thiophene hydrodesulphurization	
	P_{H2S} ($10^2 \cdot$Pa)	S_f $m^2 \cdot g^{-1}$	r_i (530 K) $mol \cdot s^{-1} \cdot m^{-2}$	S_f $m^2 \cdot g^{-1}$	r_i (573 K) $mol \cdot s^{-1} \cdot m^{-2}$
$Ni_{0.8}Ru_{0.2}S_2$	4.5	20	1.90	22	7
$Ni_{0.8}Ru_{0.2}S_2$	17	20	1.25	–	–
$Ni_{0.6}Ru_{0.4}S_2$	4.5	37	1.90	39	7.4
$Ni_{0.6}Ru_{0.4}S_2$	17	37	1.30	–	–
$Co_{0.8}Ru_{0.2}S_2$	17	32	0.16	39	4.4
$Co_{0.6}Ru_{0.4}S_2$	17	44	0.20	–	–
$Co_{0.3}Ru_{0.7}S_2$	–	–	–	35	4.1
$Fe_{0.8}Ru_{0.2}S_2$	17	15	0.03	15	0.5
$Fe_{0.5}Ru_{0.5}S_2$	17	21	0.03	20	0.4
RuS_2	17	43	0.73	38	4
MoS_2	17	15	0.10	18	0.31
NiMoS	17	12	0.95	23	3.2
CoMoS	17	11	0.11	15	2.3
FeMoS	17	6	0.05	6	0.2

Using the same H_2S partial pressure as previously, the intrinsic activities obtained for $Ni_{0.6}Ru_{0.4}S_2$ and $Ni_{0.8}Ru_{0.2}S_2$ prepared at 673 K are similar to those obtained for catalysts prepared at a higher temperature. For $P_{H2S} = 17 \times 10^2$ Pa, the intrinsic activities vary similarly with Ni addition but are slightly smaller than in the first case which is due to the inhibiting effect of H_2S generally observed in hydrogenation reactions.

Results obtained for both sets of composition for cobalt and iron-ruthenium systems show the same variations of the activities with the concentration (table 1). Nevertheless, values of the intrinsic rates are much lower and follow the order: $FeRu \ll CoRu \ll RuS_2 < NiRu$. Therefore, the addition of nickel promotes the catalytic activities of ruthenium sulphide whereas cobalt and iron function as poisons.

Hydrodesulphurization of thiophene

The catalytic activities of nickel, cobalt or iron ruthenium sulphide phases are given in table 1. For nickel catalysts a twofold increase of the activity is observed for $x = 0.5$ and $x = 0.8$ by comparison to the activity of RuS_2. An activity higher than that of RuS_2 was also observed for cobalt catalysts for $x = 0.3$ and 0.8. The iron catalysts are very poor for both compositions. The hydrodesulphurization intrinsic rates follow the order: $FeRu \ll RuS_2 < CoRu < NiRu$.

For the reactions considered, the catalytic properties are strongly dependent on the nature of the metal associated to ruthenium. Moreover, the classification of the activities is different in hydrogenation and hydrodesulphurization. These results are consistent with the existence of mixed solid solutions whose electronic and therefore catalytic properties are dependent on the nature of all the components. It should also be noticed that the variation of the catalytic properties are observed for quite low amount of promoter. Then, the activity is almost constant for all concentrations of the second metal compatible with the existence of a pyrite phase.

COMPARISON WITH CONVENTIONAL MOLYBDENUM BASED CATALYSTS

The promoting effect of group VIII metals on the catalytic activities of molybdenum sulphides is generally maximal for a concentration of promoter corresponding to a value of $r = M'/(M' + Mo)$ close to 0.3. Therefore such a concentration has been chosen for the comparison with ruthenium based catalysts.

Results given in table 1 indicate that hydrogenation activities vary in a large range according to the sequence: $FeMoS \ll MoS_2 < CoMoS \ll NiMoS$, while the hydrodesulphurization intrinsic activities follow the order: $FeMoS \ll MoS_2 \ll CoMoS < NiMoS$.

In both cases the catalytic activities of molybdenum based catalysts are smaller than the activities of ruthenium based catalysts.

For Mo (or W) based catalysts, the promoter atoms are located at the edges of the lamellar disulphide, which means at the surface of the dichalchogenide, whereas in pyrite solid solution X-ray diffraction evidence homogeneous materials. Nevertheless, the comparison of the two series of samples indicate some similarities: very small activity of iron catalysts, high activity for nickel catalysts, good activity of cobalt catalysts in hydrodesulphurization. Therefore, it can be assumed that in both systems (ruthenium and molybdenum) the components behave as "synergetic pairs", the members of these pairs work together or cooperate.

This idea of "mixed sites" is in agreement with the concepts of electronic promotion [13–15]. It could also explain why cobalt has a different promoting effect in hydrogenation reaction for the ruthenium and the molybdenum based catalysts and the observation that ruthenium catalysts are more active than molybdenum catalysts in all reactions.

4. Conclusion

The sulphidation at 673 K of a mixture of hydroxides allow to prepare the polycrystalline members of the $M_xRu_{1-x}S_2$ systems in the whole range of composition.

Some of these new materials are highly active in biphenyl hydrogenation or in thiophene hydrodesulphurization even for high Ni or Co content ($x = 0.8$). Compared to NiMoS, CoMoS and FeMoS catalysts, the ruthenium solid solutions present higher activities.

Some parallelism may be drawn between the two series of samples. This similarity suggests that in both cases the promoting effect (or poisoning effect) is due to the existence of mixed sites whose electronic and catalytic properties are related to the nature of the components.

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