Use of CO as probe molecule for characterization of mixed Ru-Ni sulphide phases supported over alumina

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Infrared spectroscopy was used to characterize mixed ruthenium-nickel sulphides prepared by step-wise impregnation over alumina and further sulphidation. The hydrogenation of biphenyl was compared over samples containing different amounts of nickel and ruthenium and a large increase was observed for a catalyst with an atomic Ni/(Ni+Ru) ratio near 0.4. Infrared spectra of adsorbed CO indicate that the increase in catalytic activity is ascribed to the presence of a very large number of Ru-Ni sites.

Keywords: Nickel; ruthenium; sulphide; CO adsorption; hydrogenation

1. Introduction

Conventional hydrotreating catalysts [Co(Ni)-Mo(W)/Al_2O_3] have been widely characterized by the adsorption of probe molecules [1,6]. Particularly, CO adsorption on alumina-supported Ni-Mo and Ni-W has provided new valuable information about active sites involved in hydrodesulfurization (HDS). Promoted sites in sulphided Ni-W/Al_2O_3 have been associated with an intense band at 2085 cm^{-1} which partially resists to evacuation at room temperature [6].

More recently, ruthenium sulphide (either supported or unsupported) has received considerable attention since this chalcogenide displayed prominent hydrodesulfurization, hydrogenation (HYD) and hydrodenitrogenation (HDN) activities [7]. Furthermore, some of us have reported the synthesis of ruthenium sulphur ternary compounds with Ni, Fe or Co and the outstanding HDS and HYD properties of the $ni_xRu_{1-x}S_2$ systems [8]. These $Ni_xRu_{1-x}S_2$ systems have been prepared supported on alumina [9] and the aim of this work was to characterize the Ru-Ni catalysts by infrared spectroscopy using CO as probe molecule.

2. Experimental

2.1. CATALYSTS PREPARATION

The Ni, Ru and Ru-Ni/Al_2O_3 catalysts, containing 7 total wt.-% of metal, were prepared by pore filling impregnation. The outgassed carrier was first contacted with an appropriate precursor salt solution, then oven dried at 383 K for 16 h. The Ru-Ni/Al_2O_3 samples were prepared by sequentially adding Ru and Ni, as described elsewhere [9]. Calcination was avoided for the Ru-based samples while the Ni/Al_2O_3 catalyst was calcined at 623 K. "$RuCl_3.3H_2O$" (Aldrich Chemie) and $NiCl_2$ (Merck) were used as precursor salts and a fraction (0.08–0.12 mm) of γ-alumina (BET surface area 236 $m^2.g^{-1}$) from Rhône-Poulenc was employed as a support.

The Ru-Ni/Al_2O_3 catalysts will be denoted by the atomic ratio "r", defined as the number of Ni atoms charged in the catalyst divided by the total number of Ni and Ru atoms in the sample, $r = \mathrm{Ni}/(\mathrm{Ni} + \mathrm{Ru})$.

2.2. ADSORPTION MEASUREMENTS

The dried impregnated catalyst (0.01 g) was pressed into a self-supporting wafer, trimmed to fit the catalyst holder and then activated. Sulphidation was carried out under $2 \cdot 10^4$ Pa of H_2S at 873 K, followed by an evacuation at the same temperature. Later, CO ($P = 1.3 \cdot 10^3$ Pa) was introduced into the IR cell at room temperature (rt). Then, spectra of the adsorbed species were recorded using a Nicolet 605X FTIR spectrometer. The spectra reported in the figures were subtracted from the reference one and from that of gaseous CO. Bands associated with the species retained after evacuation at rt characterize the irreversible adsorption state.

2.3. REACTION TESTS

Prior to catalytic tests, the catalysts were sulphided in a flow reactor for 4 h under a N_2/H_2S (15%) mixture at 873 K (heating rate 0.16 $K \cdot s^{-1}$). After cooling to rt, the samples were flushed with a nitrogen flow and stored in sealed bottles under argon in order to preserve the catalysts from oxidation.

The determination of the catalytic activities was performed in the vapour phase into a dynamic flow-microreactor working at medium pressure (Total pressure $23 \cdot 10^5$ Pa, biphenyl pressure $8 \cdot 10^2$ Pa and added H_2S pressure $435 \cdot 10^2$ Pa) at 530 K. Specific rates were determined after 16 h on stream in the pseudo-stationary state.

3. Results

3.1. ADSORPTION MEASUREMENTS

The spectrum of CO adsorbed species on the Ru/Al_2O_3 catalyst sulphided at 873 K is shown in fig. 1. The total spectrum in this figure consisted of one broad band at 2052 cm^{-1} (low frequency, LF) and of another second weaker band at 2112 cm^{-1} (high frequency, HF_2). Moreover, a shoulder was observed at ca. 2072 cm^{-1} (high frequency, HF_1). After evacuation, only partial removal of the bands occurred and the HF_1 band was more definite.

CO adsorption on a catalyst sulphided at 873 K and treated under H_2 in the same conditions, gave spectrum B in fig. 2. The LF band and the HF_1 shoulder shifted to lower wave numbers which was also more precisely evidenced on the irreversible spectrum (not reported here for reason of clarity). Resulphiding the catalyst allowed us to obtain a spectrum (fig. 2C) analogous to that obtained for the prior sulphide sample (fig. 2a).

An additional experiment performed for CO adsorption on a Ru/Al_2O_3 sample reduced directly under H_2, showed a major band centered at 2026 cm^{-1} (see fig. 2D). The intensity of the band was several times more important when comparing with the sulphided samples.

The sulphided Ni/Al_2O_3 sample was contacted with CO in a similar way. As already reported in the literature [5,6], the IR spectrum showed one weak band

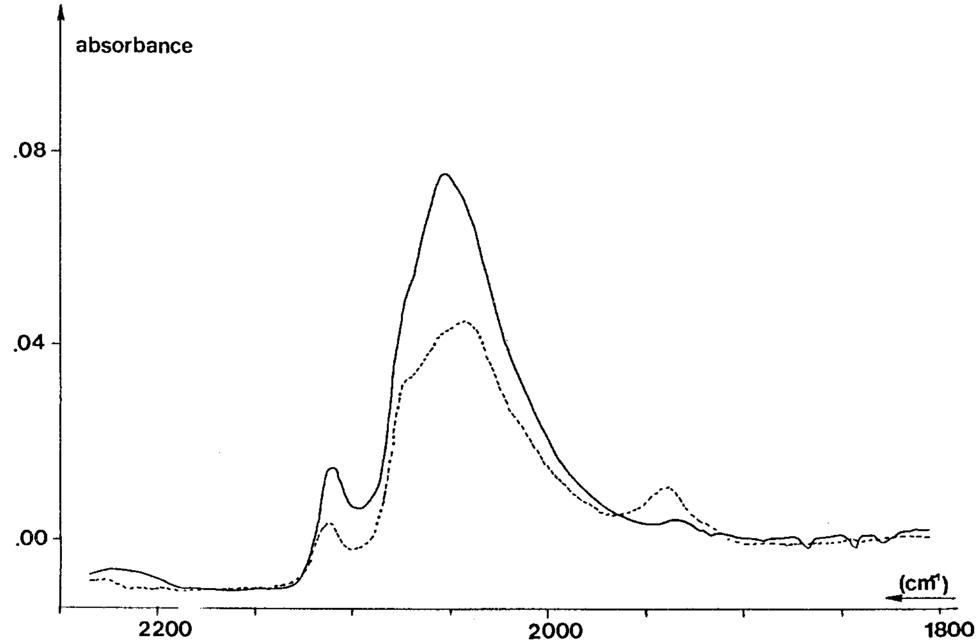

Fig. 1. Infrared spectra of CO adsorbed on the Ru/al_2O_3 sample sulphided at 873 K: ——: total adsorption; - - - - - -: irreversible species.

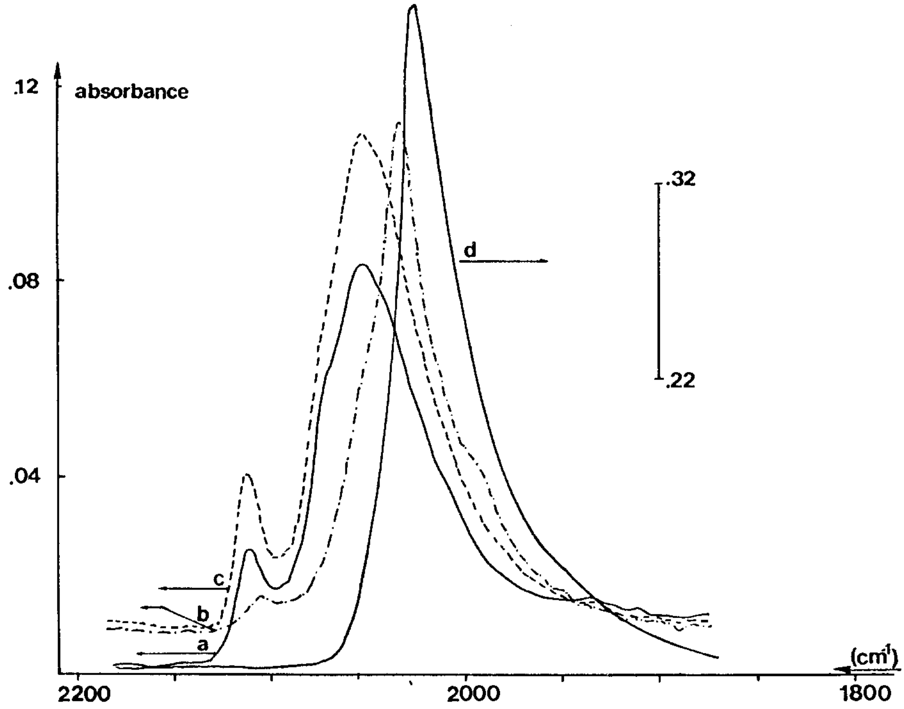

Fig. 2. Infrared spectra of adsorbed species resulting from CO adsorption on Ru/Al_2O_3 samples: a) sulphided H_2S at 873 K, B) reduced H_2 at 873 K, C) re-sulphided H_2S at 873 K and D) directly reduced H_2 at 873 K.

at 2080 cm^{-1} which was completely removed after evacuation. Its weak intensity is probably due to Ni migration into the alumina lattice when sulphiding at 873 K.

Adsorption of CO was performed on a series of Ru-Ni catalysts activated under H_2S at 873 K. CO adsorbed species on Ru Ni(0.14) exhibited several maxima at 2055, 2077, 2094 and 2113 cm^{-1} (fig. 3A). After evacuation, the bands situated at 2055, 2077 and 2113 cm^{-1} remained almost unchanged, indicating adsorbed species resembling to those observed for the supported ruthenium sulphide. The band centered at 2094 cm^{-1} completely disappeared and therefore, it can be attribuable to sulphided Ni. Fig. 3B gives the CO spectrum for the Ru Ni(0.35) catalyst. Three maxima are observable at 2055, 2090 and 2112 cm^{-1}. However, the spectrum was apparently different from that shown in fig. 3A. On evacuating, the spectrum of the irreversibly adsorbed entities exhibited a three bands spectrum, as for the supported ruthenium sulphide. This feature suggests that the asymmetric band at 2090 cm^{-1} may correspond to Ni and may overlap the HF_1 band (associated with CO adsorbed on Ru). Adsorption on the Ru Ni(0.77) sample gave rise to one major asymmetric band at 2091 cm^{-1} (see fig. 3C) along with shoulders at 2050, 2078 and 2115

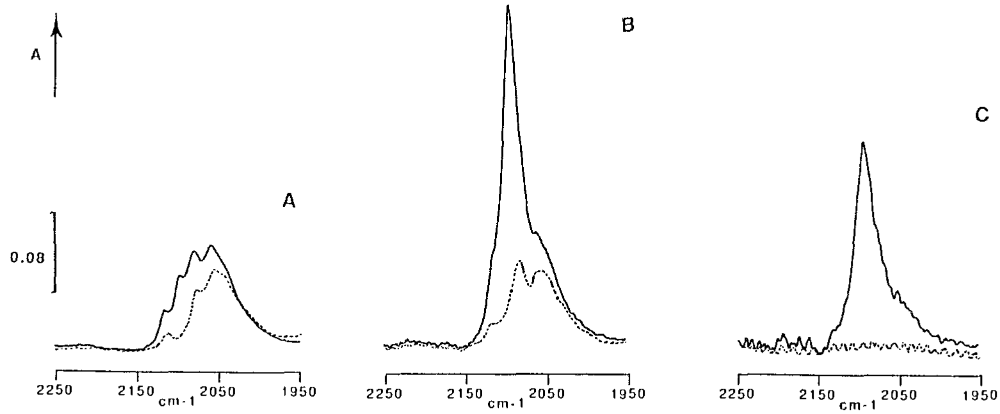

Fig. 3. Infrared spectra of CO adsorbed on the Ru-Ni catalysts: A) $r = 0.14$, B) $r = 0.35$ and C) $r = 0.77$. ———: total adsorption; - - - - - -: irreversible species.

cm^{-1}. The main band may be assigned to CO entities adsorbed on sulphided Ni while the shoulders may be associated to adsorbed entities on Ru. After evacuation, the bands have almost disappeared, owing to the very low Ru content.

3.2. REACTION TESTS

The results of biphenyl hydrogenation on Ru-Ni catalysts are given in fig. 4. As can be seen, a maximum of hydrogenation activity was found for samples with $r \approx 0.35$. The rate corresponding to the maximum was several times higher than the arithmetical sum of the separately measured activities of pure supported sulphided Ru and Ni, pointing out a synergetic effect of both sulphides.

4. Discussion

The band at 2026 cm^{-1} obtained for a H_2 reduced Ru/Al_2O_3 sample is unambiguously assigned to linear CO adsorbed on metallic Ru, as reported in the literature [10,11]. For the sulphided Ru/Al_2O_3 catalyst, the three bands appearing at 2052, 2072 and 2112 cm^{-1} correspond to linear CO and to multicarbonyl CO. The HF bands where identified as tricarbonyl species adsorbed on Ru^{2+} by Yokomizo et al. [11]. The LF band has been observed for linear CO on metallic Ru supported on Al_2O_3 [10] or SiO_2 [12,13], but centred at lower wave numbers. This upward shift observed on sulphided catalysts (compared to metals) has been reported in the literature [12,13] and was related to a decrease in the metal-CO bonding strength, produced when decreasing back donation from the metal to the CO. Therefore, the shift observed for the LF band confirms that CO adsorbs on electron-deficient Ru, induced by the

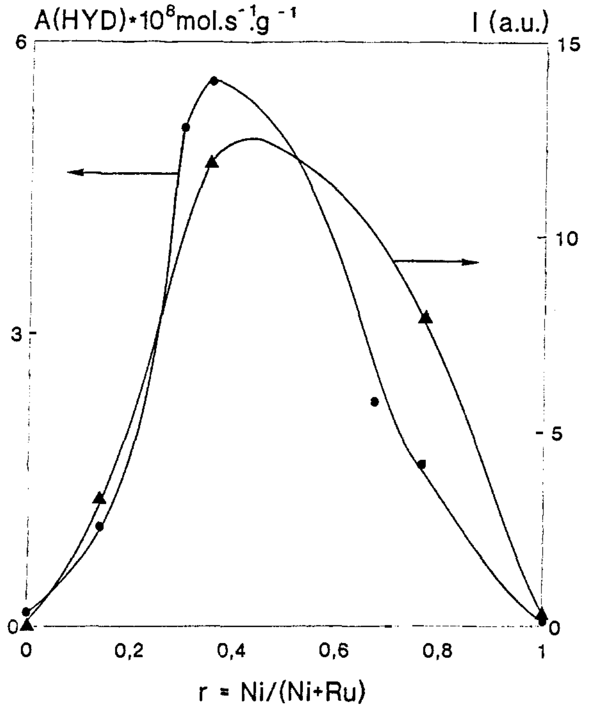

Fig. 4. Effect of the ratio "*r*" on biphenyl hydrogenation and on the 2090 cm^{-1} band intensity. The intensity was calculated by using the integrated area under the 2090 cm^{-1} band.

sulphur-rich environment. From the differences in band intensities between spectra presented figs. 2A and 2C, it appears that sulphur coverage deeply affects the amount of adsorbed CO.

Concerning the sulphided and reduced catalysts, a comparison with the sulphided catalyst and with the H_2 reduced sample indicates that Ru cannot be considered as completely metallic Ru, but as partially reduced Ru.

From the results discussed above, three reference states can be considered as regards ruthenium: (i) Reduced Ru, which can be obtained by treating the precursor under H_2 at convenient temperatures, (ii) Partially reduced ruthenium sulphide, forming when reducing the sulphide, (iii) completely sulphided Ru, which is prepared if the sulphidation is carried out directly on the precursor and in absence of H_2 [7].

A comparison of CO adsorption on Ru-Ni catalysts with that of the unicomponent ones evidences that ν(CO) wavenumbers corresponding to ruthenium sulphide are not modified whereas that attributed to sulphided nickel is shifted to higher wavenumbers (Ni, ν(CO) = 2080 cm^{-1}; Ru-Ni, ν(CO) = 2090 cm^{-1}). It may be envisaged that this shift characterizes Ni sites in an environment modified by Ru. Such sites would involve Ni entities in a more electro-deficient state due to an electronic transfer from Ni to Ru. Such observations of an electronic transfer from Ni toward other metallic atom involved in a sulphide structure has been previously reported in sulphided NiMo and NiW hydrotreating catalysts [14,15] and are consistent with theoretical calculations of Harris et al. [16]. We report in fig. 4 the variation of the intensity of the 2090 cm^{-1} band due to CO adsorption on Ni sites in the Ru-Ni samples versus the Ni/(Ni + Ru) ratio. This intensity curve follows a similar trend to that observed for the HYD activities. Therefore, it is proposed that the large increase of hydrogenation rate for the Ru-Ni catalysts can be ascribed to the presence of a very large number of mixed Ru-Ni sites, both metals would be engaged in a cooperative effect in these types of sites. Complementary physicochemical characterizations are in progress in order to confirm these points.

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References

[1] S.J. Tauster, T.A. Pecoraro and R.R. Chianelli, J. Catal. 63 (1980) 515.
[2] R. Burch and A. Collins, Appl. Catal. 17 (1985) 273.
[3] N.Y. Tøpsoe and H. Tøpsoe, J. Catal. 84 (1983) 386.
[4] D. Ouafi, F. Maugé and J.C. Lavalley, Bull. Soc. Chim. 3 (1989) 363.
[5] M. Angulo, F. Maugé, J.C. Duchet and J.C. Lavalley, Bull. Soc. Chim. Belg. 96 (1987) 925.
[6] J.C. Duchet, JC. Lavalley, S. Housni, D. Ouafi, J. Bachelier, M. Lakhdar, A. Mennour and D. Cornet, Catal. Today 4 (1988) 71.
[7] J.A. De Los Reyes, S. Göbölös, M. Vrinat and M. Breysse, Catal. Lett. 5 (1990) 17, and references cited herein.
[8] M. Vrinat, M. Lacroix, M. Breysse, L. Mosoni and M. Roubin, Catal. Lett. 3 (1989) 405.
[9] J.A. De Los Reyes et al., submitted for publication.
[10] R.A. Dalla Betta, J. Phys. Chem. 79 (1975) 2519.
[11] G.H. Yokomizo, C. Louis and A.T. Bell, J. Catal. 120 (1989) 1.
[12] S.S.C. Chuang, S.I. Pien and C. Sze, J. Catal. 126 (1990) 187.
[13] M.J. Oudar, in: *Deactivation and Poisoning of Catalysts*, eds. M.J. Oudar and H. Wise (Dekker, New York/Basel, 1985) p. 51.
[14] W. Eltzner, M. Breysse, M. Lacroix and M. Vrinat, Polyhedron 5 (1986) 203.
[15] L. Blanchard, J. Grimblot and J.P. Bonnelle, J. Catal. 98 (1986) 229.
[16] S. Harris and R.R. Chiannelli, J. Catal. 98 (1986) 17.