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PREPARATION AND ACTIVITY OF A SULFIDED Co-Mo/Al_2O_3 CATALYST PREPARED BY THERMODECOMPOSITION OF $Co(CO)_3NO$

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IR characterization and activity measurements of a sulfided Co-Mo/Al_2O_3 catalyst (3.6% CoO; 14% MoO_3) prepared by thermodecomposition of $Co(CO)_3NO$ on a sulfided Mo/Al_2O_3 sample are compared to those of the conventional Co-Mo/Al_2O_3 industrial catalyst. The ex-carbonyl preparation leads to a higher degree of promotion for the Co-Mo couple, as evidenced by a two-fold increase in HDS activity and by a more intense signal of adsorbed CO on the promoted sites. On the other hand, the hydrogenation activity is not sensitive to the method of preparation.

1. Introduction

The most common catalysts used in industrial hydrotreating processes are the well known Co-Mo and Ni-Mo/Al_2O_3 sulfided catalysts. They are prepared by impregnation of alumina with metal salts, followed by calcination and sulfidation. The active phase is described as a MoS_2-like structure which is able to accommodate individual Co or Ni promoter ions at the edges of the MoS_2 slabs [1]. According to this "decoration" model, it seems possible to introduce the promoter directly on the sulfided form of a Mo/Al_2O_3 catalyst. Attempts reported with different metal salts or complexes lead to Ni-Mo/Al_2O_3 catalysts matching up to the conventional preparations with respect to hydrogenation activities [2]. Another approach has been performed using the carbonyl $Ni(CO)_4$ as the promoter precursor [3]. IR spectra of adsorbed CO indicated indeed a very high degree of promotion of the mixed sulfided phase. Unfortunately, the catalyst sensitivity to air prevented any activity test in a classical reactor. We report here the first results obtained from $Co(CO)_3NO$. This compound has a high vapor pressure at r.t. which makes its deposition an easy operation as already reported by Roustan [4].

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2. Results

The preparation of the Co-Mo/Al_2O_3 catalysts has been studied by FTIR with a Nicolet MX-1 spectrometer. $Co(CO)_3NO$ [Ventron] is first contacted at r.t. ($P_{eq} = 400$ Pa) with a disc of 10 mg of conventional Mo/Al_2O_3 (14% MoO_3) already sulfided at 673 K by H_2-H_2S 10% in the IR cell. Adsorption and thermal decomposition of the carbonyl have been followed in situ up to 673 K. Then a CO pressure (1330 Pa) has been introduced at r.t. to probe the active sites in the promoted catalyst as previously described [5]. Results have been compared to those obtained on the industrial Co-Mo/Al_2O_3 catalyst HR 306 (Procatalyse; 3% CoO, 14% MoO_3) sulfided in the same conditions.

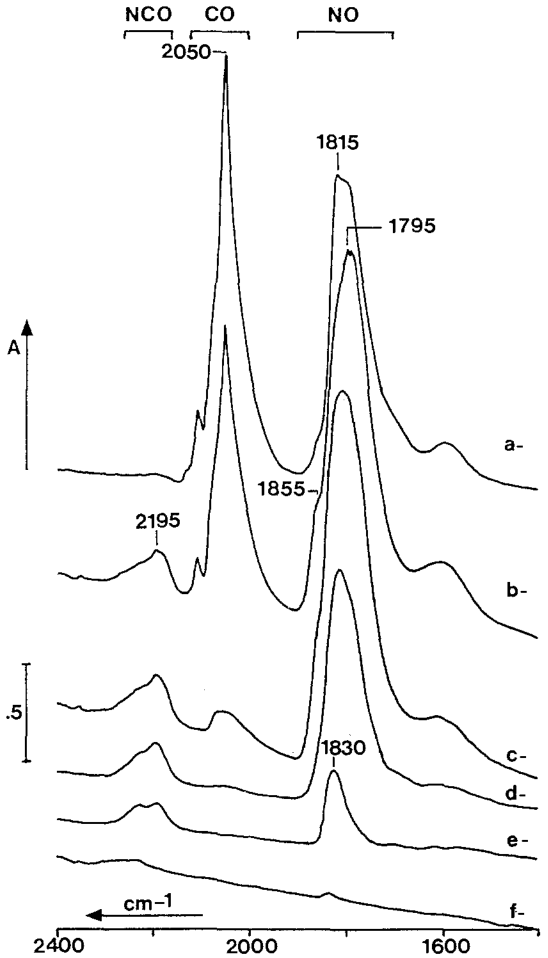

Fig. 1. IR spectra observed: a) After deposition of 400 Pa $Co(CO)_3NO$; b) After one hour of contact; c–f) After evacuation respectively at r.t., 373 K, 473 K and 573 K.

Upon admission of $Co(CO)_3NO$ on the presulfided Mo/Al_2O_3 sample, IR spectrum presents bands which are close to the gas spectrum (fig. 1). After a contact of one hour at r.t., formation of several types of isocyanate species, with a predominant band at 2195 cm^{-1}, are observed. In the ν(NO) region, a shoulder appears at 1855 cm^{-1}, while the intense band previously at 1815 cm^{-1} shifts to 1795 cm^{-1}. This could account for the formation of dinitrosyl [4]. After evacuation at r.t., the ν(CO) band at 2050 cm^{-1} becomes very weak evidencing a rapid decomposition of tricarbonyl without any formation of bi- and monocarbonyl. Dinitrosyl also disappears since only the intense band at 1810 cm^{-1} characteristic of mononitrosyl, remains after evacuation. By heating under vacuum, intensity of the mononitrosyl band largely decreases while its frequency shifts towards 1830 cm^{-1} at 473 K. The number of isocyanate species stays nearly constant till 473 K. It largely decreases at 573 K, as does the ν(NO) band. No bands persist at 673 K. The same evolution occurs when the $Co(CO)_3NO$ decomposition is performed under H_2-H_2S 10%. The amount of cobalt so deposited is 3.6% CoO. It is noticeable that the adsorption of $Co(CO)_3NO$ on a sulfided Mo/Al_2O_3 sample and its evolution with contact time give rise to spectra which are quite different from those obtained on Al_2O_3 by Morrow's group [4]. Moreover it appears that the amount of cobalt deposited is less important when the Mo/Al_2O_3 is not completely sulfided.

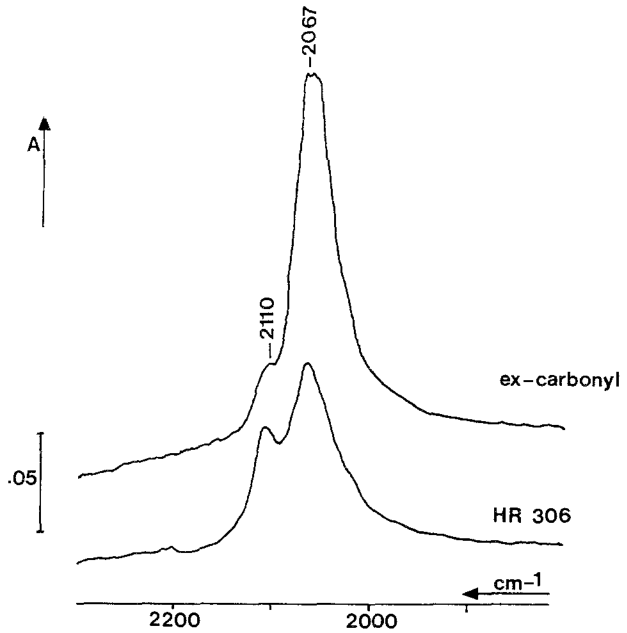

Fig. 2. IR spectra of CO adsorbed on sulfided Co-Mo/Al_2O_3 prepared by thermodecomposition of $Co(CO)_3NO$ or by classical impregnation.

Table 1
Relative activities of Co-Mo/Al_2O_3 catalysts

	HDS thiophene	HN toluene	HN butenes *
Relative reaction rates (ex-carbonyl/conventional catalyst)	1.9	1.0	0.8

* From the consecutive steps in the thiophene reaction scheme:

$\text{thiophene} \xrightarrow{\text{HDS}} \text{butenes} \xrightarrow{\text{HN}} \text{butane}$

CO adsorption on the catalyst after $Co(CO)_3NO$ decomposition under H_2-H_2S at 673 K (ex-carbonyl catalyst) gives rise to IR bands at 2110 cm^{-1} and 2067 cm^{-1} which are close to those observed on on the sulfided industrial HR 306 catalyst (fig. 2). As already reported, these bands characterize respectively unpromoted and promoted Mo sites [5]. However, in the case of the ex-carbonyl catalyst the intensity of the 2067 cm^{-1} band, is fairly high compared to the 2110 cm^{-1} one. Although the composition of both catalysts is nearly similar, it appears that the ratio between the number of promoted and unpromoted sites is much higher than on the conventional HR 306. Therefore the degree of promotion can be increased by the ex-carbonyl preparation.

Both catalysts were tested for their hydrodesulfurization (HDS) and hydrogenation (HN) activities in flow reactors operating at atmospheric pressure (thiophene HDS, $T = 673$ K) or under a H_2 pressure of 4 MPa (toluene HN, $T = 573$ K). Reaction rates at initial conversions are measured in the presence of 2% added H_2S in the H_2 flow. The catalysts precursors were activated at 673 K or 623 K in the atmospheric or pressurized reactors respectively, prior to activity measurements; the carbonyl $Co(CO)_3NO$ previously deposited on a presulfided Mo/Al_2O_3 sample was decomposed under the H_2-H_2S gas mixture used in the test reactions.

Table 1 shows a two-fold increase in thiophene HDS activity for the ex-carbonyl Co-Mo/Al_2O_3 sample compared to the conventional HR 306 catalyst. Therefore, these first results show that the HDS functionality of sulfided Co-Mo/Al_2O_3 catalysts can be largely improved using metal carbonyl as a source of promoter. They confirm that the intensity of the ν(CO) band at 2067 cm^{-1} of adsorbed CO is well related to the HDS active sites.

On the other hand, toluene hydrogenation is not sensitive to the method of preparation of the catalysts. This is confirmed by the relative rates for butenes hydrogenation deduced from the C_4 hydrocarbon fraction of the converted thiophene. The different behaviors with respect to HN and HDS for the two types of catalysts clearly indicate that the selectivity k_{HN}/k_{HDS} strongly depends upon the preparating method. The results confirm that hydrogenation and hydrogenolysis do not occur on the same sites [6].

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