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AN IN-SITU INFRARED CELL AND ITS APPLICATION IN STUDY OF SULFIDATION OF A MODEL Co/Mo CATALYST

T. SZILÁGYI, T.I. KORÁNYI, Z. PAÁL

Institute of Isotopes of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B. 77, Hungary

J. TILGNER

Zentrum für wissenschaftlichen Gerätebau der Akademie der Wissenschaften der DDR, 1199 Berlin, Rudower Chaussee 6, GDR

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A flow cell was constructed to measure infrared spectra of catalyst samples with controlled heating at 673 K. We monitored sulfidation of an unsupported Co-Mo catalyst by thiophene. Correlation was found between the intensity changes and frequency shifts of the metal-oxygen IR bands and the appearance of oxythiomolybdate bands and the simultaneous increase of thiophene conversion. These results point to short-living cobalt-oxythiomolybdates which may have highest HDS activity.

1. Introduction

Relatively few attempts [1–4] have been made for the complex characterization of the hydrodesulfurization (HDS) catalytic system; i.e. the simultaneous investigation of the surface and structure of the catalyst together with its catalytic properties in HDS. Infrared (IR) spectroscopy is widely applied for the study of catalytic systems but its use in this field was concentrated to the examination of suitable probe molecules (O_2, NO, CO, thiophene, etc.) adsorbed on the catalyst surface [2,3,5,6]. In those studies catalyst samples are generally applied in form of self supporting wafers in static systems. Sample wafers are relatively thick and absorb IR light completely in those spectral regions where the strong bands of catalysts occur. Therefore no direct spectral information indicating catalyst structure or its changes during a reaction can be obtained from such measurements. Because of the static conditions, the comparison with other catalytic data (activity, selectivity, etc.) may be rather difficult.

In our laboratory preliminary measurements were performed to follow the activation of unsupported oxidic cobalt-molybdenum catalysts of different Co/Mo ratio by the conventional nujol-mull IR technique [7]. Bands of MoO_3, a-$CoMoO_4$ and Co_3O_4 were found in the spectra of calcined catalysts but no reasonable spectra could be recorded even after the very beginning of sulfidation. Therefore we decided to construct an experimental system suitable for observing spectral changes of the solid catalyst during reduction and/or sulfidation under flow conditions parallel to the measurement of HDS activity and butene hydrogenation (HYD) selectivity over these samples. We report here the performance of this system during sulfidation of a selected model Co/Mo catalyst.

2. Experimental

2.1. INFRARED CELL AND APPARATUS

The device we developed combines an IR flow cell with a catalytic microreactor which allows to monitor the IR spectrum of the catalyst sample "in situ" during reaction (fig. 1a). The front surface of a stainless steel base plate is covered by gold and carefully polished. A thin layer (ca 0.1 mm) of catalyst powder is placed on that surface within a circular shaped spacer and covered with a caesium iodide infrared window (KBr or NaCl windows being much more sensitive to thermal treatment). With the relatively soft CsI window and well-polished contacting surfaces satisfactory sealing was achieved without any gasket. Uniform heating of the catalyst layer is effected from behind, the temperature could be, in principle controlled up to ca 800 K. However, the vapor pressure of CsI being 5 * 10 exp 3 at 800 K, work at this temperature is not recommended.

Gas transfer lines are also attached to the base plate permitting a continuous gas flow during pretreatment and reaction. The gas chromatographic analysis of the reaction products could be performed by intermittent sampling.

IR spectra were measured by a DIGILAB FTS-20C Fourier-transform infrared spectrophotometer. The flow cell is situated in the sample chamber (fig. 1b) but the original light path is changed so that the focus is imaged on the catalyst layer. Thus the incident beam transmitted through the window passes twice the sample since it is reflected back by the polished gold surface acting, in fact, as a mirror.

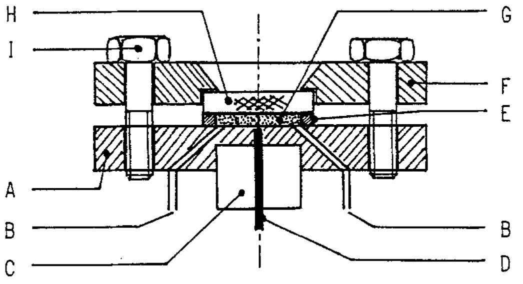

Fig. 1a. Scheme of the IR cell. A-base plate, B-gas inlet and outlet, C-heater element, D-thermocouple, E-spacer, F-flange, G-catalyst sample, H-window, I-fixing screws.

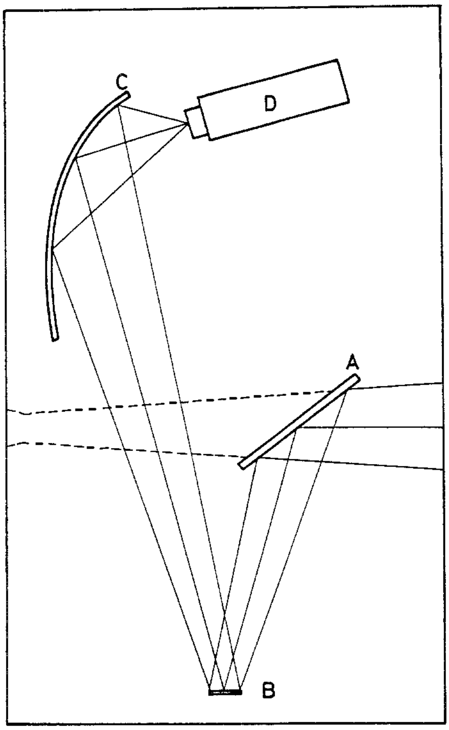

Fig. 1b. Optical layout. A-plane mirror, B-sample position, C-elliptic mirror, D-detector. Dotted lines show the original IR beam.

The transmitted IR light is then collected by an elliptical mirror on a DGTS detector.

2.2. CATALYST AND PROCEDURE

Aqueous solutions of $(NH_4)_6Mo_7O_{24} \times 4H_2O$ and $Co(NO_3)_2 \times 6H_2O$ (Reanal puriss grade each) were mixed in a mole fraction of $r = Co/(Co + Mo) = 0.68$. The solution was dried at 390 K overnight and calcined in air at 723 K for 4 h. The calcined catalyst was placed at the IR cell. The cell was heated in 40 ml/min hydrogen flow ramping by 10 K/min which was followed by 2 hours isothermal reduction at 673 K. After prereduction, a 35 : 1 mixture of hydrogen and thiophene (H_2/T) was introduced at 673 K with the same flow rate ($p = 1$ bar). Thiophene decomposed at the catalyst surface: one of its product, viz. S sulfided the catalyst [8]. The main change monitored was this solid-state transformation of the Co-Mo oxide catalyst precursor. This leads to the formation of 3–8 overlayers of MoS_2 containing also Co-sulfides [4b].

The vapor pressure of CsI is 5 · 10 exp − 5 at 673 K. Considering the evaporation rate of a solid at 760 Torr surrounding pressure, about 9 · 10 exp 17 molecules leave the surface during 3 h [10]. If all of it had been taken up by Co-Mo oxide (about 5 · 10 exp 18 surface atoms), about 18% of the surface would have been covered by CsI. We have no reason to assume, however, that essentially inert CsI could effectively compete with highly reactive H_2 and thiophene for surface sites. The likely residence time of CsI on the surface is small; further, as we shall see from our results, reduction and sulfidation of the catalyst may take place even in its presence.

3. Results

Thiophene conversions (X) and hydrogenation selectivities (HYD) increase with increasing reaction times (fig. 2). This indicates that the catalyst reaches its most active state gradually during its contact with thiophene. This is in agreement with data obtained in a conventional flow [4a] and circulation [9] reactor. 70% thiophene conversion with 30% HYD selectivity was found at the highest activity state of $r = 0.68$ catalyst in a flow reactor on a sample pressed in a holder appropriate for subsequent XPS measurements [4]. In the present study, the conversions were lower (3%, see fig. 2); the high level of HYD selectivity (60%) indicates the lack of poisoning effect of the adsorption of thiophene and/or hydrogen sulfide on the catalytically active sites [11]. The two curves run almost parallel. This does not mean the identity of HDS and HYD active sites, but indicates rather that the hydrogenation reaction of butenes is really a subsequent reaction to HDS. Whereas solid-state transformations and catalytical processes manifesting themselves as HDS are hardly separable (in fact, during the run shown the former should prevail), HYD is a purely catalytic reaction.

IR spectra measured during sulfidation are shown in fig. 3. Those are difference spectra, i.e. a single beam spectrum taken in a certain state was ratioed

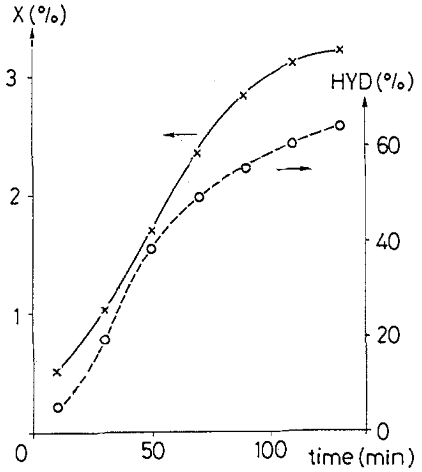

Fig. 2. Thiophene conversions (X(%)) and hydrogenation selectivities (HYD(%) = (isobutane + n-butane)/(C_4 hydrocarbons) × 100) measured over catalyst $r = 0.68$ at various reaction times.

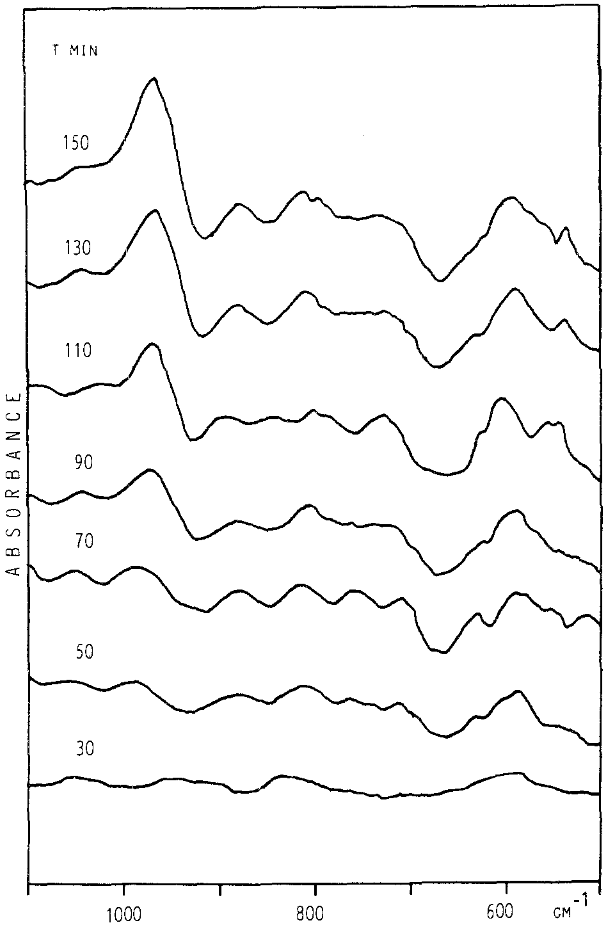

Fig. 3. Difference IR spectra of the catalyst as a function of sulfidation time.

against that of the prereduced but unsulfided catalyst. The spectra show progressive solid-state transformations which can be compared with the activity measurements as a function of reaction time. Though more experiments are necessary for a detailed analysis of all the spectral features, some of them can be tentatively interpreted at this point. It was already shown [7] that our calcined catalyst contains – besides of $CoMoO_4$ – excess cobalt in the form of Co_3O_4. In fig. 4 spectra of these substances are shown for comparison with the difference spectrum corresponding to the longest sulfidation period. The negative feature at 660 cm^{-1} can be interpreted as a decrease of the corresponding band of Co_3O_4 indicating that the Co-oxide is sulfided. However, it might be also resulted by diminished intensity of the broad tail observed in the spectrum of a-$CoMoO_4$. Above 900 cm^{-1} a prominent derivative-shaped feature is seen on the difference spectra. It is characteristic of a band that is shifted to higher frequencies (i.e. the 930 cm^{-1} band of Co-molybdate). Hence it is explained that the corresponding

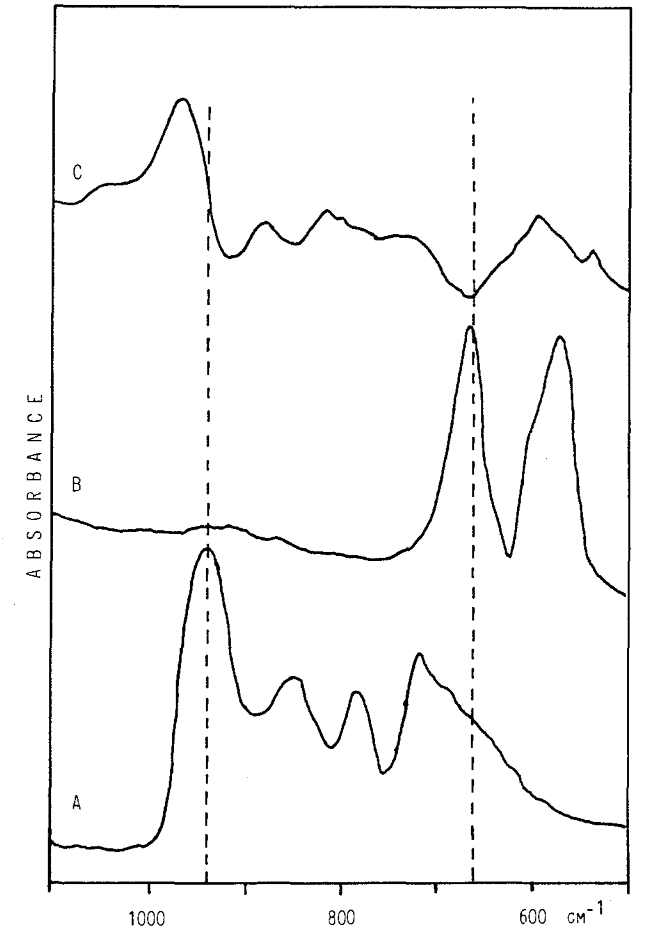

Fig. 4. Comparison of IR spectra. A-spectrum of a-$CoMoO_4$, B-spectrum of Co_3O_4, C-difference spectrum of catalyst after 150 min sulfidation. (A and B measured in nujol mull.)

Mo-O bond (sometimes referred to as Mo-O bond with terminal oxygens [12,13]) is strengthened due to partial sulfidation of the molybdate structure. It is in agreement with the fact that the Mo-O bond order, force constant and consequently the IR absorption frequency is increasing in MoO_4^{2-} compounds as oxygen ligands are gradually substituted by sulfur atoms [14]. Hence cobalt-molybdate is partially sulfided and the small intensity bands between 800–900 cm^{-1} and below 600 cm^{-1} are also assigned to different oxythiomolybdate (like $MoO_2S_2^{2-}$, MoO_3S^{2-}, etc.) species. These preliminary results corroborate our previous findings [4] where we have shown the presence of cobalt-oxythiomolybdates ($CoMoS_xO_y$, $x+y=3.8\ldots4$) by X-ray diffraction at the first moments of sulfidation of unsupported calcined Co/Mo catalysts of varying Co content. At the same time, a very high but temporary HDS activity and HYD selectivity were found at these states of the same catalysts. Therefore, we attributed the highest

HDS activity to these short-living cobalt-oxythiomolybdates [4]. The detection of partially sulfided molybdate species by IR spectroscopy at the initial part of sulfidation supports our hypothesis.

Note added in proof

Chi-Lin O'Young, [J. Phys. Chem. 93 (1989) 2016] added alkali metals (Alk = K or Cs) to a Mo/alumina catalyst up to a ratio Mo/Alk > 1. It was found that "at low atomic ratios, Alk/Mo < 1, the Alk–Mo interaction is not strong enough to suppress the reducibility of molybdenum." The IR absorption bands of adsorbed NO probe molecules became, however, weaker. Obviously, subsurface reduction could proceed without any difficulty even in the presence of surface Cs ions.

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