Ru/Alumina and Ru–Mo/Alumina Catalysts: An XPS Study

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Ru/Al$_2$O$_3$ and Ru–Mo/Al$_2$O$_3$ catalysts have been prepared by impregnating respectively γ-Al$_2$O$_3$ and calcined Mo/Al$_2$O$_3$ with aqueous solutions of ruthenium (III) acetate. XPS spectra of catalysts dried at 393 K, calcined in air at 873 K, and sulfided in H$_2$/H$_2$S are reported. Ru and Mo species in the catalysts, according to the respective binding energies, were ruthenium dioxide and oxo-molybdenum (VI) in catalysts calcined at 873 K and a ruthenium sulfide and MoS$_2$ in the sulfided catalysts. Unusually low Ru binding energies were found for some catalysts. The properties of the catalysts in thiophene HDS are interpreted with the aid of the XPS results. © 1987 Academic Press, Inc.

INTRODUCTION

The ability of cobalt to modify the activities and selectivities of molybdenum disulfide hydrodesulfurization (HDS) catalysts is well known. In sulfided Co–Mo/Al$_2$O$_3$ catalysts cobalt is located at the edges of patches of MoS$_2$ dispersed over the alumina support (1, 2). Cobalt is usually described as the promoter, although the active species is a new cobalt–molybdenum sulfide phase (1, 2). We were interested in extending the range of catalysts beyond the familiar cobalt or nickel and molybdenum or tungsten pairs in order to see if we could further modify the properties of the catalyst, for example, the hydrogenation function. We were particularly interested in ruthenium since RuS$_2$ is an excellent catalyst in its own right, for example, for the HDS of dibenzothiophene (3).

A preliminary report of our catalytic work on Ru–Mo catalysts has been published (4). The catalytic properties of the catalysts described in the present paper are summarized in Table 1. The Ru–Mo/Al$_2$O$_3$

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catalysts were active for the HDS of thiophene but were no better than Co–Mo or Ni–Mo catalysts. The promoter effect of ruthenium depended on the pretreatment. Synergy between ruthenium and molybdenum was observed for those catalysts which had not been calcined after the addition of ruthenium. However, promotion by ruthenium was not observed for catalysts

TABLE 1

Thiophene Conversion at 673 K[a]

Catalyst[b]	Thiophene conversion[c]	
	nc	c
Mo(6.94)/Al$_2$O$_3$	—	56.7
Mo(3.47)/Al$_2$O$_3$	—	28.4
Ru(8.74)/Al$_2$O$_3$	20.5	29.1
Ru(4.37)/Al$_2$O$_3$	10.2	14.6
Ru(4.37)–Mo(3.47)/Al$_2$O$_3$	53.5	37.8
Ru(4.37)/Al$_2$O$_3$ + Mo(3.47)Al$_2$O$_3$[d]	38.6	43.0 (38.4)[e]

[a] From Ref. (4).
[b] Figures in parentheses are weight percent.
[c] Percentage; nc, not calcined; c, calcined in air at 873 K.
[d] From linear interpolation (Ref. (4)).
[e] The value 38.4 takes into account the poorer ruthenium sulfide dispersion (Table 2) in the sulfided Ru–Mo catalyst: (new conversion) = [conversion over Mo(3.47)/Al$_2$O$_3$] + [conversion over calcined Ru(4.37)/Al$_2$O$_3$] × [dispersion of Ru in calcined Ru(4.37)–Mo(3.47)/Al$_2$O$_3$]/[Ru dispersion in calcined Ru(4.37)/Al$_2$O$_3$] = 28.4 + 14.6 × 0.15/0.22.

which had been calcined (i.e., heated in air at 873 K) after the addition of ruthenium.

A feature of thiophene HDS over both uncalcined and calcined Ru–Mo/Al₂O₃ catalysts was a much higher proportion of butane in the products than that over Co- or Ni-promoted catalysts. Evidently, the hydrogenation function of the HDS catalysts was greater over the Ru-promoted catalysts.

In the present paper we report an XPS study of a Ru/Al₂O₃ catalyst and a 1:1 Ru–Mo/Al₂O₃ catalyst in the synergic region. Our object was to discover the nature of the species in the calcined and sulfided catalysts, to ascertain whether there was any interaction between ruthenium and molybdenum or alumina, and to determine the dispersion of ruthenium and molybdenum on the alumina support.

EXPERIMENTAL

Preparation of Materials

We prepared two types of Ru and Ru–Mo catalyst supported on alumina, namely those calcined after the addition of ruthenium, designated Ru (c), and those not calcined, Ru (nc).

Catalysts consisting of ruthenium or ruthenium and molybdenum supported on γ-Al₂O₃ were prepared by the pore-filling method. In a typical preparation γ-Al₂O₃ (1.0 g) or a calcined Mo/Al₂O₃ catalyst was impregnated with an aqueous solution of ruthenium (III) acetate (1.7 cm³) (5). The material was dried at room temperature and overnight at 393 K. Part of each sample was calcined in dry air at 873 K for ca. 2 h.

The uncalcined and calcined samples were sulfided with a mixture of H₂(90)–H₂S(10) at 673 K for 4 h. Samples, after cooling, were transferred to the spectrometer without contact with air.

X-Ray Photoelectron Spectroscopy (XPS)

An A.E.I. ES200B spectrometer was used to record XPS spectra. The samples were pressed on indium foil attached to the sample probe.

We report core-electron binding energies relative to C 1s at 285.0 eV, or, for alumina-supported samples, Al 2s at 119.6 eV and Al 2p at 74.8 eV, full peak widths at half-maximum intensity (FWHM), and intensities as relative peak areas determined by planimetry.

Catalytic Activities

Thiophene conversions were determined in a flow reactor at 1 atm and 523–673 K. Details are in Ref. (4).

RESULTS AND DISCUSSION

Typical XPS spectra are shown in Figs. 1 and 2. Binding energies, peak widths, peak intensities relative to alumina, and assignments (6–14) are given in Table 2.

Binding Energies and Assignments

Ru/Al₂O₃ catalysts. The most intense ruthenium peak is the Ru $3d_{3/2-5/2}$ doublet. The $3d_{3/2}$ component is hidden by a C 1s peak from hydrocarbon contaminant in the
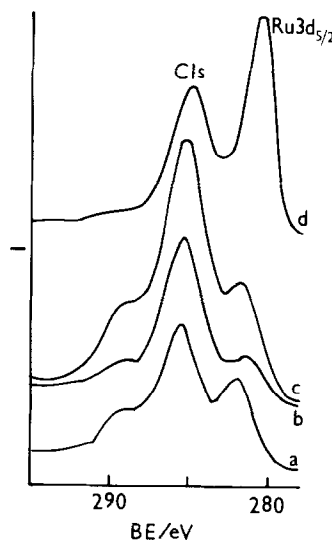

FIG. 1. XPS spectra of catalysts in the oxide form showing Ru binding energies (BE) vs intensities (*I*) of uncalcined (nc) and calcined (c) Ru/Al₂O₃ and RuMo/Al₂O₃ catalysts: (a) Ru(nc)/Al₂O₃, (b) Ru(c)/Al₂O₃, (c) RuMo(nc)/Al₂O₃, (d) RuMo(c)/Al₂O₃.
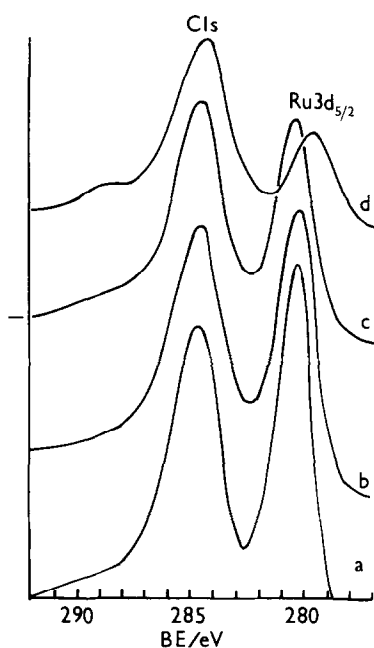
FIG. 2. XPS spectra of sulfided catalysts showing Ru binding energies (BE) vs intensities (I) of catalysts prepared by sulfiding uncalcined (nc) and calcined (c) oxide forms of the catalysts: (a) Ru(nc)/Al$_2$O$_3$, (b) Ru(c)/Al$_2$O$_3$, (c) RuMo(nc)/Al$_2$O$_3$, (d) RuMo(c)/Al$_2$O$_3$.

spectrometer or, for some samples, unde-composed acetate. The position of the Ru $3d_{3/2}$ peak can be determined with a precision of ±0.2 eV.

Oxide catalysts. The Ru XPS of the Ru/Al$_2$O$_3$ sample which had not been calcined is assigned to ruthenium (III) acetate (Table 2). The binding energies are close to those observed for the well-defined molecular compound Ru(acac)$_3$ (where acac is the anion of acetylacetone).

The Ru binding energies of calcined Ru/Al$_2$O$_3$ were 0.3–0.4 eV less than those for the uncalcined material. The binding energy decrease is due to decomposition of the impregnating salt. The values correspond to RuO$_2$ or RuO$_2 \cdot$ xH$_2$O (Table 2).

Sulfided catalysts. Binding energies of ruthenium in the sulfided catalysts were ca. 1–2 eV less than those in the oxide catalysts (Table 2) and were similar to the Ru binding energies in ruthenium sulfides

formed by sulfiding a Ru(0)/Al$_2$O$_3$ sample made by reducing Ru/Al$_2$O$_3$ in hydrogen or precipitated from a solution of RuCl$_3$ in glacial acetic acid with H$_2$S. The sulfided catalysts therefore contain Ru–S species.

Ru–Mo/Al$_2$O$_3$ catalysts, oxide catalysts. According to the Ru binding energies (Table 2) the Ru species in the uncalcined Ru–Mo/Al$_2$O$_3$ catalyst is ruthenium (III) acetate as in the Ru-only catalyst. The Ru binding energies of calcined Ru–Mo/Al$_2$O$_3$ are, however, appreciably less than those of calcined Ru/Al$_2$O$_3$. The significant decrease in the Ru binding energies in the presence of molybdenum could be due either to a chemical interaction between ruthenium and molybdenum or an increased particle size of the RuO$_2$ formed (see below).

Sulfided catalysts. The Ru binding energies of sulfided uncalcined Ru–Mo/Al$_2$O$_3$ are close to those of sulfided Ru/Al$_2$O$_3$ and are assigned to ruthenium sulfide. The Mo binding energy corresponds to MoS$_2$. The presence of molybdenum does not affect the Ru binding energies in the uncalcined catalysts.

The Ru spectra of the sulfided calcined Ru–Mo/Al$_2$O$_3$ are strikingly different from those of the other catalysts (Fig. 2). The binding energies (279.6 and 461.5 eV) are close to, or slightly less than, those of ruthenium metal (279.9 and 461.2–462.2 eV) (6, 12–14). The low values are not an artifact since all other levels, including the support, were as expected. The reproducibility, checked in two separate experiments, was ±0.2 eV. The Mo binding energies again corresponded to MoS$_2$. Exceptionally low Ru binding energies have been reported (15) for reduced ruthenium catalysts supported on calcium oxide. Possible interpretations are discussed later.

Sulfur binding energies. The S 2p binding energies in the sulfided catalysts (Table 2) are assigned to the sulfide (S^{2-}) ion. The S binding energies in the catalysts are ca. 1 eV less than those in bulk ruthenium sulfide prepared by sulfiding the supported metal

TABLE 2

XPS Data[a] for Ru/Al$_2$O$_3$ and Ru–Mo/Al$_2$O$_3$ Catalysts[b]

Catalyst	Binding energy (BE) and intensity (I)					Species
	Ru 3$d_{5/2}$			Ru 3$p_{3/2}$		
	BE (eV)	FWHM (eV)	I	BE (eV)	FWHM (eV)	
Ru/Al$_2$O$_3$[c]						
Oxide						
nc	281.9	2.0	0.66	463.6	4.8	Ru(III) acetate[d]
c	281.5	2.2	0.39	463.3	5.4	RuO$_2$[e]
sulfide						
nc	280.2	2.0	0.59	461.1	4.2	RuS$_2$[f]
c	280.4	2.0	0.43	461.2	4.6	RuS$_2$[f]
Ru–Mo/Al$_2$O$_3$[g]						
oxide						
nc	281.8	3.0	0.27	462.8	5.3	Ru(III) acetate[d]
c	280.8	2.0	0.38	462.5	5.3	Ru–O[e]
sulfide						
nc	280.5	1.8	0.33	461.7	4.2	RuS$_2$[f]
c	279.6	2.3	0.15	461.3	5.0	Ru–S[f]

	Mo 3$d_{5/2}$					
	BE (eV)	FWHM (eV)	I			
Ru–Mo/Al$_2$O$_3$[g]						
oxide						
nc	233.0	2.6	0.25			Mo(VI)–O[h]
c	233.1	2.8	0.25			Mo(VI)–O[h]
sulfide						
nc	228.6	2.0	0.21			MoS$_2$[i]
c	228.7	2.1	0.22			MoS$_2$[i]

	S 2p					
	BE (eV)	FWHM (eV)	I			
Ru/Al$_2$O$_3$[c]						
sulfide						
nc	162.2	2.6	0.20			S^{2-}[j]
c	162.6	4.0	0.28			S^{2-}[j]
Ru–Mo/Al$_2$O$_3$[g]						
sulfide						
nc	162.0	2.6	0.19			S^{2-}[j]
c	162.6	2.5	0.16			S^{2-}[j]

[a] Binding energy (BE in eV) relative to Al 2s, 119.6 eV; full width at half-maximum peak height (FWHM in eV); integrated intensity (I) relative to Al 2s.

[b] Catalysts in the oxide and sulfide forms; nc, not calcined after adding Ru(III) acetate; c, oxide form calcined at 873 K in air.

[c] Ru, 8.74 wt%.

[d] Cf. Ru(acetylacetonate)$_3$: 282.2, 463.7 (this work).

[e] Cf. RuO$_2$: 282.1, 463.2 (Ref. (6)); 280.7 (Ref. (7)); 281.0, 281.9 (Ref. (8)); hydrated RuO$_2$: 281.4 (Ref. (7)).

[f] Not pyrites-type RuS$_2$ (see text). Cf. RuS$_2$ precipitated by H$_2$S from RuCl$_3$ in ethyl acetate: 280.1, 460.8 (this work); RuS$_{0.6}$ from reduced RuCl$_3$ reacted with H$_2$/H$_2$S (10%) at 643 K, 4 h: 280.6, 461.6 (this work).

[g] Ru, 4.37; Mo, 3.47 wt%.

[h] Cf. MoO$_3$/Al$_2$O$_3$: 232.7 (Ref. (9)).

[i] Cf. MoS$_2$/Al$_2$O$_3$: 229.0–229.4 (Ref. (10)).

[j] Cf. S^{2-} in MoS$_2$: 162.5 (Ref. (10)); S$_2^{2-}$ in RuS$_2$: 163.1, 163.4 (this work).

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or ruthenium trichloride (see Table 2). The higher binding energy corresponds to the disulfide ion (11) as we would expect for RuS_2 which has a pyrites structure. Thus the sulfur species in the catalysts is sulfide and so different from the species, disulfide, in bulk RuS_2.

Intensities and Stoichiometries

Relative intensities are presented as the ratio of peak areas of a component of the catalyst and the aluminium of the support. Intensity ratios are given in Table 2. The Ru $3d_{5/2}$ peak area is easy to measure but the overlapping carbon peak causes problems with Ru $3d_{3/2}$. We may assume a symmetrical signal and a peak area ratio of 1.5 between the split peaks separated by 4.2 eV. We can then calculate the Ru $3d_{3/2}$ peak area.

From the ratio of areas of characteristic peaks of two elements in one sample we can determine the stoichiometry by using the relationship

$$I_A/I_B = (n_A/n_B)[(K.E.(A))/$$
$$(K.E.(B))]^{(1+n)} \times (\sigma_A/\sigma_B).$$

Here I_A and I_B are the areas of two peaks of the sample, for example, O $1s$ and Ru $3d$; n_A and n_B are the stoichiometries in the sample depth analyzed; K.E.(A) and K.E.(B) are the kinetic energy (K.E.) for peaks A and B; σ_A and σ_B are the photoelectron cross sections (16). For a homogeneous sample n_A and n_B will be the bulk stoichiometry.

The term $[(K.E.(A))/(K.E.(B))]^{(1+n)}$ takes into account that (a) the transmission factor of the spectrometer is proportional to K.E. and (b) the mean free path of the photoelectrons is proportional to $(K.E.)^n$, where n is between 0.5 and 0.8 (we used 0.8). For the high surface area supported catalysts we expect from the Kerkhof–Moulijn model (17) that the intensity ratio, for example, I_{Ru}/I_{Al} or I_{Mo}/I_{Al}, is proportional to the bulk composition if the supported species (Ru, Mo) are well dispersed in a monolayer. Then, considering the Ru $3d$, Al $2s$, and Mo

$3d$ levels and for $n = 0.8$ we have

$$(I_{Ru}/I_{Al})_{theoretical} = 13.0(nRu/nAl)$$

and

$$(I_{Mo}/I_{Al})_{theoretical} = 10.85(nMo/nAl).$$

We can now predict the following theoretical monolayer values for our samples

$(I_{Ru3d}/I_{Al2s})_{theoretical}$	(I_{Mo3d}/I_{Al2s})
Ru(8.75)/Al$_2$O$_3$	
0.63	
Ru(4.37)–Mo(3.47)/Al$_2$O$_3$	
0.31	0.22

Ru/Al$_2$O$_3$ catalysts. The I_{Ru}/I_{Al} ratio (0.66) for uncalcined Ru/Al$_2$O$_3$ was close to the theoretical monolayer value (0.63, above) which means that the Ru species was well dispersed. After calcination the ratio was less (0.39), presumably because of sintering which gave poorly dispersed RuO$_2$.

After sulfiding, the I_{Ru}/I_{Al} ratio of calcined Ru/Al$_2$O$_3$ remained almost the same (0.39 to 0.43) and so sulfiding hardly changed the dispersion of ruthenium. For both uncalcined and calcined sulfided Ru/Al$_2$O$_3$ the S/Ru stoichiometry was close to 2.

Ru–Mo/Al$_2$O$_3$ catalysts. The I_{Ru}/I_{Al} ratio of the Ru–Mo/Al$_2$O$_3$ catalysts increased slightly after calcination (0.27 to 0.38). These values are near the theoretical monolayer value (0.31) showing that ruthenium is well dispersed in the calcined catalyst as well as in the uncalcined catalyst. Evidently molybdenum prevented sintering of RuO$_2$.

The I_{Mo}/I_{Al} ratio did not change after calcination. The value (0.25) was close to the theoretical one (0.22) deduced from the Kerkhof–Moulijn model. Therefore molybdenum is well dispersed in both the uncalcined and calcined Ru–Mo/Al$_2$O$_3$ catalysts.

The I_{Ru}/I_{Al} ratio for the uncalcined Ru–Mo catalyst increased slightly after the catalyst had been sulfided (0.27 to 0.33) but decreased for the calcined catalyst (0.38 to

0.15). If we assume S/Mo = 2 then S/Ru is also 2.

The I_{Mo}/I_{Al} ratios for sulfided Ru–Mo/Al$_2$O$_3$ were 0.19 and 0.22 for the uncalcined and calcined catalysts, respectively. This means no change of dispersion.

Species in the Catalysts and the Interaction between Ruthenium and Molybdenum

The species in the oxide catalysts (Table 2) are oxomolybdenum (VI) and either ruthenium (III) acetate or RuO$_2$, before or after calcining, respectively. In the sulfided catalysts both ruthenium and molybdenum are completely sulfided since the stoichiometries deduced from the XPS intensities were 2S : 1Mo or 1Ru. Molybdenum is present as MoS$_2$ but the ruthenium sulfide is apparently not pyrites-type RuS$_2$ since the S binding energies correspond to sulfide, not disulfide.

It is apparent also that calcination of the Ru–Mo oxide catalysts induces an interaction between ruthenium and molybdenum since the Ru binding energies are 1 eV less in the calcined than in the uncalcined catalysts.

The Ru $3d_{5/2}$ binding energy in the catalyst prepared by sulfiding calcined Ru–Mo/Al$_2$O$_3$ (279.6 eV) is slightly lower than that for Ru metal (279.9 eV) (6, 12–14) and Ru/Al$_2$O$_3$ reduced in hydrogen (ca. 280 eV) (8, 14). Also the ratio I_{Ru}/I_{Al} in the sulfided calcined catalyst is about half the ratio in the uncalcined catalyst (Table 2). Thus sulfiding by our procedure (H$_2$–H$_2$S) of the Ru–O–Mo species in the calcined catalyst is accompanied by sintering and formation of a new Ru sulfide species.

The unusually low binding energy of ruthenium in the sulfided calcined Ru–Mo catalyst could be due to charge transfer from molybdenum to ruthenium making the ruthenium more negative and similar to electron transfer to reduced ruthenium catalysts supported on calcium oxide (15). However, compensating changes of the Mo

binding energies are not apparent: Mo binding energies are the same in the calcined oxide form of the Ru–Mo catalyst (233.1 eV) as in the uncalcined form (233.0 eV) and the corresponding sulfided catalysts (228.7 and 228.6 eV). The bandwidth was greater in the calcined catalyst; possibly any charge transfer is restricted to peripheral Mo atoms of the single slabs.

An alternative possibility is that the changes in the Ru binding energies are due to changes in particle size of the Ru (or possibly Ru–Mo) oxide and sulfide species. As a matter of fact, observed binding energy differences can be attributed to physical effects other than the real chemical shift which implies a change in the valence electron charge density. In particular, extraatomic relaxation energy for small particles may be different from that for larger ones or bulk compounds. This effect has been reported for Ru binding energies in both Ru metal and RuO$_2$ which are sensitive to particle size variations (8). Larger particles (>ca. 15 Å diameter) can have binding energies ca. 1 eV less than smaller particles. In our Ru–S system, it is expected that the smallest particles should have Ru binding energies higher than those of bulk RuS$_2$ (280.1–280.6 and 460.8–461.6 eV for the $3d_{5/2}$ and $3p_{3/2}$ levels, respectively; see Table 2, footnote f). This is not found experimentally so that a particle size explanation is not correct to account for the low observed binding energy.

According to our XPS intensities (Table 2), the Ru dispersion is poorer in the sulfided calcined Ru–Mo/Al$_2$O$_3$ catalyst than in the corresponding sulfided uncalcined catalyst. In the oxide forms of the catalysts the Ru XPS intensity is greater in the Ru–Mo catalyst than in the Ru-only catalyst; this could be due to an interaction between ruthenium and molybdenum which prevents ruthenium from being lost from the surface by entering the alumina lattice. The higher Ru surface concentration in the Ru–Mo catalyst could then give rise to a bigger RuO$_2$ particle size.

Catalytic Properties

In the uncalcined Ru–Mo/Al$_2$O$_3$ catalyst ruthenium promotes thiophene hydrodesulfurization (HDS), the activity of the catalyst being greater than the sum of the activities of the individual ruthenium and molybdenum catalysts (Table 1). However, the activity of the calcined Ru–Mo/Al$_2$O$_3$ catalyst is less than the sum of the separate ruthenium and molybdenum activities; ruthenium deactivates, rather than promotes, the calcined catalyst. This is so even if we take into account the poorer dispersion of ruthenium in the calcined catalyst (see Table 1). The general effect of ruthenium, even at low concentrations, in a series of Ru–Mo catalysts is deactivating toward thiophene conversion (4).

We now consider whether our XPS measurements help us to understand how ruthenium deactivates the calcined Ru–Mo catalyst. The significant observation is the low binding energy of ruthenium in the calcined catalyst. Let us assume that the low Ru binding energy is due to charge transfer from molybdenum to ruthenium; then the positive charge on those molybdenum atoms associated with ruthenium has increased. We know that promoters like cobalt act by transferring charge to molybdenum, so enhancing the ability of molybdenum to donate to, and thereby activate, molecules of, for example, thiophene (18). On the contrary, a metal which withdraws charge from molybdenum will have an effect opposite to promotion, i.e., deactivation. Copper is such a metal. We suggest that ruthenium in the calcined Ru–Mo catalyst behaves in the same way as copper, withdrawing charge from, and deactivating, molybdenum atoms of the catalyst. The molybdenum atoms affected need not be all the molybdenum atoms of the catalyst, but only those, the peripheral atoms, which participate in the catalysis.

The hydrogenation function of the catalysts, as deduced from the proportion of butane in the products of thiophene HDS, is the same for the calcined and uncalcined Ru–Mo/Al$_2$O$_3$ catalysts and shows a pronounced synergy (4). For example, the amount of product butane at 40% thiophene conversion over a Ru–Mo catalyst is nearly three times the amount over a molybdenum-only catalyst. The hydrogenation is clearly associated with the presence of ruthenium since the hydrogenation is greater for the Ru-promoted catalysts than for Co- or Ni-promoted catalysts (4). Note, however, that very little butane is produced over Ru-only catalysts. It appears, then, that hydrogenations do not take place on ruthenium sulfide but rather on MoS$_2$ (at sites different from the desulfurization sites). The way in which ruthenium acts as a promoter of hydrogenation is not apparent from our work. One possibility would be hydrogen spillover from ruthenium sulfide to MoS$_2$ as has been suggested for Co$_9$S$_8$ (19).

CONCLUSIONS

Our main conclusion is that, when a Ru–Mo/Al$_2$O$_3$ catalyst in the oxide form is calcined, interaction between ruthenium and molybdenum leads to a new Ru–O–Mo species. When this species is sulfided in a H$_2$/H$_2$S mixture a ruthenium–molybdenum sulfide species is formed which is less active in desulfurization of thiophene than the individual ruthenium and molybdenum sulfides. In effect the ruthenium poisons the MoS$_2$. The reason for this is probably a charge transfer interaction between Ru and Mo which leads to withdrawal of charge from the molybdenum. The effect of ruthenium is then similar to that of copper in deactivating a MoS$_2$ catalyst. If the Ru–Mo/Al$_2$O$_3$ oxide catalyst is sulfided before being calcined, then ruthenium promotes the desulfurization activity. In both types of catalyst ruthenium promotes the hydrogenation function. The calcination step is clearly crucial in determining whether ruthenium promotes or deactivates a MoS$_2$ catalyst. We plan further work with unsupported Ru–Mo catalysts to obtain more

information on the Ru–Mo species involved.

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