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Michel Boudart, Principal Investigator

Department of Chemical Engineering

Stanford University

Stanford, California 94305

DISCLAIMER

O_2 Chemisorption, ESR Spectroscopy, and Hydrodesulfurization Activity on Sulfided $CoMo/\gamma\text{-}Al_2O_3$

Michel Boudart, Xiao Hong Kang, Jorge Sánchez Arrieta, and Daniel G. Löffler

Department of Chemical Engineering

Stanford University

Stanford, CA 94305

ABSTRACT

Oxygen chemisorption and electron spin resonance spectroscopy (ESR) have been used to characterize sulfided $CoMo/\gamma\text{-}Al_2O_3$ catalysts with different atomic Co/(Co+Mo) ratios (α). Chemisorption of O_2 on sulfided $Mo/\gamma\text{-}Al_2O_3$ and $CoMo/\gamma\text{-}Al_2O_3$ samples was proportional to the Mo content, but was only slightly affected by addition of Co. Neither chemisorption of O_2 nor oxo-Mo^{+5} ESR signal intensity correlated with thiophene or benzothiophene hydrodesulfurization (HDS) activity of sulfided $CoMo/\gamma\text{-}Al_2O_3$.

INTRODUCTION

Oxygen chemisorption and ESR spectroscopy have been widely used to characterize both reduced and sulfided Mo/Al_2O_3 and $CoMo/Al_2O_3$ samples. Correlations have been found between O_2 chemisorption and propylene hydrogenation activity on reduced $Mo/\gamma\text{-}Al_2O_3$ [1], O_2 chemisorption and thiophene HDS activity on unsupported MoS_2 [2], or bulk Mo sulfides [3], and O_2 chemisorption and thiophene HDS on sulfided $Mo/\gamma\text{-}Al_2O_3$ [4] and reduced $CoMo/Al_2O_3$ samples [5].

The relationship between O_2 chemisorption and HDS activity of sulfided $CoMo/\gamma\text{-}Al_2O_3$ catalysts is not clear. Tauster and Riley [6] found that the catalytic activity for the HDS of a gas oil feed correlated with the chemisorption of O_2 on sulfided $CoMo/\gamma\text{-}Al_2O_3$, but other authors [7,8] failed to find a correlation between O_2 chemisorption and thiophene HDS activity. The rapid oxygen adsorption on sulfided $CoMo/\gamma\text{-}Al_2O_3$ has been found to be proportional to the Mo content, but it increases only slightly with Co present [9]. Recently, Bodrero and Bartholomew [10] suggested that O_2 chemisorption may not be specific to sulfur removal sites.

Several different signals have been found in the ESR spectra of unsupported and supported sulfided Co(Ni)Mo(W) samples [3,11-16]. Some of these signals have correlated with the activity. Voorhoeve [17] reported a linear relationship between benzene hydrogenation activity and the intensity of an ESR signal in sulfided nickel-tungsten samples. Hagenbach et al. [13] found a parallel between the curves of thiophene hydrogenolysis, cyclohexene hydrogenolysis and cyclohexene isomerization, and the intensity of a low-temperature ESR signal versus the atomic ratio (α), in unsupported cobalt sulfide-molybdenum sulfide mixtures. Recently, Silbernagel et al. [3] found a linear correlation between sulfur coordinated Mo^{+5} defects and dibenzothiophene HDS activity for both unsupported and supported sulfided Mo samples.

In the present contribution we present results of O_2 chemisorption and ESR spectroscopy studies on Mo/Al_2O_3 and $CoMo/\gamma\text{-}Al_2O_3$ samples with different values of the atomic ratio α. These results are compared with previously reported data for thiophene [18] and benzothiophene [19] HDS activity.

EXPERIMENTAL

All samples were prepared by impregnation (incipient wetness method). The $\gamma\text{-}Al_2O_3$ powder used as support (from Chevron Research Company, BET surface area = 200 m^2g^{-1}) was heated in air at 773 K for 2 h.

One series of $CoMo/\gamma\text{-}Al_2O_3$ samples was prepared in the following way. A batch of $Mo/\gamma\text{-}Al_2O_3$ was prepared by impregnating the calcined $\gamma\text{-}Al_2O_3$ at room temperature with ammonium molybdate (81.9% MoO_3, J.T. Baker Chemical Co.) in ammonium hydroxide solution. The sample was then dried and heated in air at 773 K for 2 h. Then samples with different values of α were obtained by impregnation of $Mo/\gamma\text{-}Al_2O_3$ with appropriate amounts of $Co(NO_3)_2.6H_2O$ (Min 99%, Allied Chemical Co.) in aqueous solution. The samples were dried at room temperature in air and heated in air at 773 K for 2 h, resulting in a series with approximately constant Mo content. In addition, one sample containing only Co (6.5% wt) was prepared by two successive impregnations with an aqueous solution of the Co nitrate following the same procedure as above. The sample was heated in air between the two impregnations.

Another series of $Co(2\%)Mo/\gamma\text{-}Al_2O_3$ was prepared separately by impregnating Mo and Co successively in such a way that the Co loading was held constant at 2%, but the Mo content was varied. Conditions of preparation were the same for both series of Co-Mo samples.

The composition of the $CoMo/\gamma\text{-}Al_2O_3$ was determined by atomic absorption spectroscopy and is listed in Table 1. The surface area of these samples was

determined using the BET method and N_2 physical adsorption and is shown in Figure 5.

CoMo/γ-Al_2O_3 samples were also examined by X-ray diffraction (XRD). No pattern of bulk molybdena was found for these samples. Above α = 0.44, Co_3O_4 lines were observed in the XRD pattern. High purity O_2 and H_2 (99.95%, Liquid Carbonic Co.) and N_2 (99.98%, Liquid Carbonic Co.) were used as received for the sample treatment.

The samples were sulfided with a premixed UHP Matheson H_2S/H_2 mixture (2% vol. H_2S) according to fixed program. Each sample was heated from room temperature to 503 K in H_2 (3 ℓ/h) and held at 503 K for 0.5 h. Then the samples were sulfided with the H_2S/H_2 mixture (6 ℓ/h) for 0.5 h at 503 K, 0.5 h at 553 K, and 1.5 h at 613 K. After the sulfidation, N_2 was flowed through the sample bed (3.3 ℓ/h) for 1 h and then the sample was cooled to room temperature. The sample was then transferred to a high vacuum system without air contact. There the sample was evacuated at 613 K for 2 h (residual pressure is less than $5x10^{-3}$ Pa) before O_2 uptake and ESR measurement.

O_2 chemisorption measurements were carried out volumetrically in a glass high vacuum system. After the sulfided sample was cooled <u>in vacuo</u> in a Dry-Ice acetone bath (195 K) for 2/3 h, the first O_2 isotherm was determined. Then the sample was evacuated for 1 h at 195 K and the second O_2 adsorption isotherm was measured at 195 K.

Electron spin resonance spectra of the CoMo/γ-Al_2O_3 samples were obtained at room temperature with a Varian E-3 Spectrometer. The working frequency was 9.5 GHz with modulation frequency of 100 kHz. The magnetic field was calibrated by means of a Varian Strong Pitch sample. The relative intensity of the Mo signal was calculated with the formula [19]:

$$I = \frac{W^2 R}{G} \qquad (1)$$

where W is the peak-to-peak separation, R is the peak-to-peak height of the recorded first derivative curve, and G is the amplification factor (gain). A series of $MgSO_4$ and $MnSO_4$ references were used to obtain the Mo^{+5} spin density of $CoMo/\gamma\text{-}Al_2O_3$ samples.

RESULTS

O_2 Chemisorption

Typical adsorption isotherms are shown in Figure 1. Curve A corresponds to reversible plus irreversible adsorption, and Curve B to the reversible adsorption. The amount of O_2 chemisorption is taken as the difference between the two isotherms.

Figure 2 shows the chemisorption of O_2 on sulfided $Mo/\gamma\text{-}Al_2O_3$ and $Co(2\%)Mo/\gamma\text{-}Al_2O_3$ samples. The chemisorption of O_2 on sulfided $Mo/\gamma\text{-}Al_2O_3$ obtained by Chung and Massoth [8] and Silbernagel *et al.* [3] are also plotted in Figure 2. The O_2 chemisorption data on our sulfided $Mo/\gamma\text{-}Al_2O_3$ samples is in very good agreement with the data of these investigators.

The chemisorption of O_2 increases less than 30 percent with the incorporation of 2% of Co in the $Mo/\gamma\text{-}Al_2O_3$ samples. This increment mainly takes into account the chemisorption of O_2 on the Co phase, since the O_2 chemisorption is not zero at 0% Mo content. In the sulfided $CoMo/\gamma\text{-}Al_2O_3$ samples, with approximately constant Mo content, the chemisorption of O_2 increases slightly as Co content varies from 0 to 10% wt (Figure 3).

ESR Measurements

A typical series of ESR spectra of a sulfided sample containing 7.2% Mo and 3.5% Co is shown in Figure 4. Curves A, B, and C correspond to the ESR spectrum of this sample after sulfidation, after O_2 chemisorption at 195 K, and after reaction with O_2 at 473 K, respectively.

Two signals can be observed in all the CoMo/γ-Al_2O_3 samples after sulfidation. Signal I has an asymmetric curve with g = 1.93 and ΔH = 80 G, and signal II is centered around g = 2.01. Signal I has been observed by other authors [3,10,11,13-15] in sulfided Mo/γ-Al_2O_3 and CoMo/γ-Al_2O_3. This signal has been assigned to oxo-Mo^{+5} defects.

Konings et al. [14] identified signal II as originating from the MoS_2 phase in sulfided CoMo/γ-Al_2O_3 samples. (Silbernagel et al. [3] assigned this signal on Mo/γ-Al_2O_3 to a similar thio Mo^{+5} defect on MoS_2.)

The ESR spectrum of the sulfided samples after O_2 chemisorption at 195 K showed Signal I and a doublet peak signal. Then, after the sulfided sample reacted with O_2 at 473 K, a well-defined triplet signal (g1 = 2.039, g2 = 2.013, g3 = 1.988) and Signal I were observed. This triplet signal has been assigned by Lojacono et al. [21] to a paramagnetic type of sulfur.

The oxo-Mo^{+5} signal was used to estimate the ESR spin density in all sulfided CoMo/γ-Al_2O_3 before and after O_2 chemisorption. The ratio of oxo-Mo^{+5} defects/Mo atom decreases as the Co concentration increases, and decreases slightly after O_2 chemisorption. These samples have from 27×10^{-3} to 8×10^{-3} oxo-Mo^{+5} defects/Mo atom, for α varying from 0 to 0.72.

DISCUSSION

Figures 2 and 3 show how the chemisorption of O_2 depends on the Co and Mo content in sulfided Co-Mo/γ-Al_2O_3 samples. It is clear in these figures that chemisorption of O_2 increases linearly with the Mo content, and increases only slightly with the Co content. The chemisorption of O_2 on Co(2%)Mo/γ-Al_2O_3 increases 120% when the Mo content varies from 4 to 10% wt. On the other hand, the chemisorption of O_2 increases only 16% when the Co content varies from 2.3 to 6.2% wt.

The activity of the sulfided CoMo/γ-Al_2O_3 samples for thiophene and benzothiophene HDS has been measured in different experimental systems, and the results have been reported elsewhere [18,19]. The nominal turnover rates (based on total Mo atoms) for thiophene consumption and for benzothiophene conversion to ethylbenzene are shown in Figure 5 along with our data for O_2 chemisorption, oxo-Mo^{+5} ESR signal intensity and BET area. It is observed that while chemisorption of O_2 increases slightly with addition of Co, the HDS activity increases substantially. As an example, chemisorption of O_2 on the sample with $\alpha = 0.33$ is only 5% greater than chemisorption of O_2 on the sample with $\alpha = 0$, while HDS activity is more than seven times greater. As we mentioned in the introduction, similar results were obtained by several authors [7-9], but not by Tauster *et al.* [6]. We think that the disagreement is related to the structural changes in the Co-Mo phases occurring when the Co/Mo ratio is changed [19]. These structural changes did not affect Tauster *et al.* results because they compared chemisorption of O_2 and HDS activity on a sample with constant Co/Mo ratio before and after coke deposition.

We also observed that the oxo-Mo^{+5} defects/Mo atom ratio decreased with the incorporation of Co, and slightly decreased after O_2 chemisorption at 195 K . A comparison of oxo-Mo^{+5} defects/Mo atom ratio and chemisorption of

O_2 shows that the O/Mo ratio is 10-30 times greater than oxo-Mo^{+5} defects/Mo atom ratio. Also, we found that whereas oxo-Mo^{+5} ESR intensity decreases, the thiophene HDS activity increases when α is less than 0.33. Therefore, these oxo-Mo^{+5} defects are not the sites where HDS and O_2 chemisorption take place.

Chemisorption of O_2 measures all anion vacancies present in the Co and Mo phases on CoMo/γ-Al_2O_3 samples, only a fraction of which are active sites for HDS. Silbernagel et al. [3] found that thio-Mo^{+5} ESR intensity and chemisorption of O_2 correlate with dibenzothiophene HDS activity, but the ratio of O_2 chemisorption thio-Mo^{+5} intensity was 10-20. Then, we cannot expect to correlate chemisorption of O_2 with the HDS activity on a series of CoMo/γ-Al_2O_3 samples.

CONCLUSION

Based on our results, we conclude that the chemisorption of O_2 increases linearly with the Mo content in Mo/γ-Al_2O_3 and Co(2%)Mo/γ-Al_2O_3, and the incorporation of Co on Mo/γ-Al_2O_3 only slightly increases the chemisorption of O_2. Chemisorption of O_2 and the oxo-Mo^{+5} defects/Mo^{+5} atom ratio do not correlate with thiophene and benzothiophene HDS activity of CoMo/γ-Al_2O_3 samples.

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Table 1

Composition of $CoMo/\gamma\text{-}Al_2O_3$ samples in the oxide form

wt %		
Mo	Co	α
7.66	0.0	0.00
7.40	0.67	0.13
7.55	2.3	0.33
7.20	3.5	0.44
6.70	6.2	0.60
6.00	9.5	0.72
0.00	6.5	1.00

FIGURE CAPTIONS

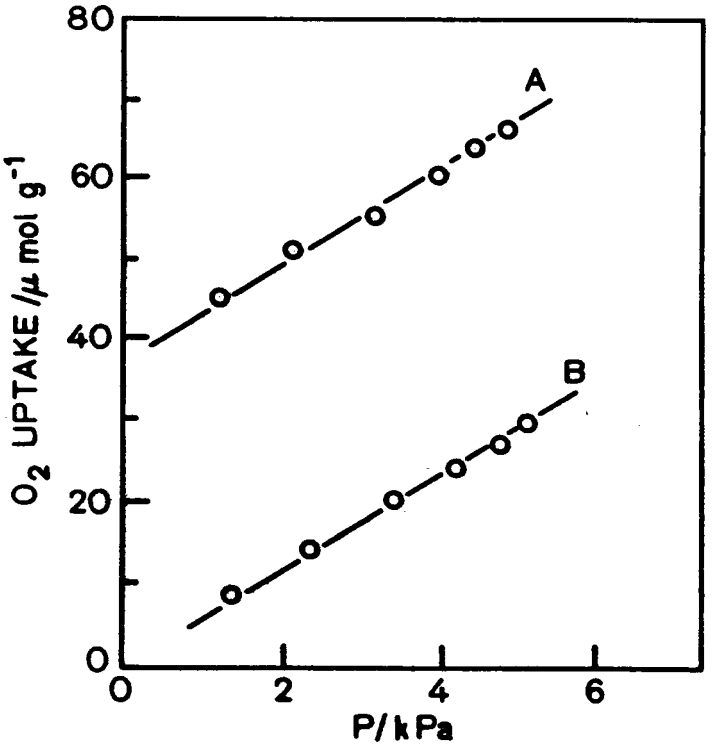
Figure 1 Oxygen uptake at 195 K on sulfided CoMo/γ-Al_2O_3 with α = 0.33. A) Reversible plus irreversible O_2 uptake; B) reversible O_2 uptake.

Figure 2 Oxygen chemisorption vs. Mo content on sulfided Co(2%)Mo/γ-Al_2O_3 (triangles) and Mo/γ-Al_2O_3 (squares). Full and open circles denote data for O_2 chemisorption on sulfided Mo/γ-Al_2O_3 reported in references [3] and [9], respectively.

Figure 3 Oxygen chemisorption vs. Co content on sulfided CoMo/γ-Al_2O_3 samples with Mo content as shown in Table 1.

Figure 4 ESR signal from a sulfided sample with α = 0.44. A) After sulfidation; B) after O_2 chemisorption at 193 K; C) after reaction with O_2 at 473 K. Signals I and II have been attributed to oxo-Mo^{+5} and thio-Mo^{+5} defects, respectively [3].

Figure 5 Plot of BET area, O/Mo and oxo-Mo^{+5} defects atom ratios on sulfided $CoMo/\gamma\text{-}Al_2O_3$ samples vs. α. Also shown are the nominal turnover rates for thiophene (NTR_T) and benzothiophene (NTR_{BT}) HDS from references [18] and [19].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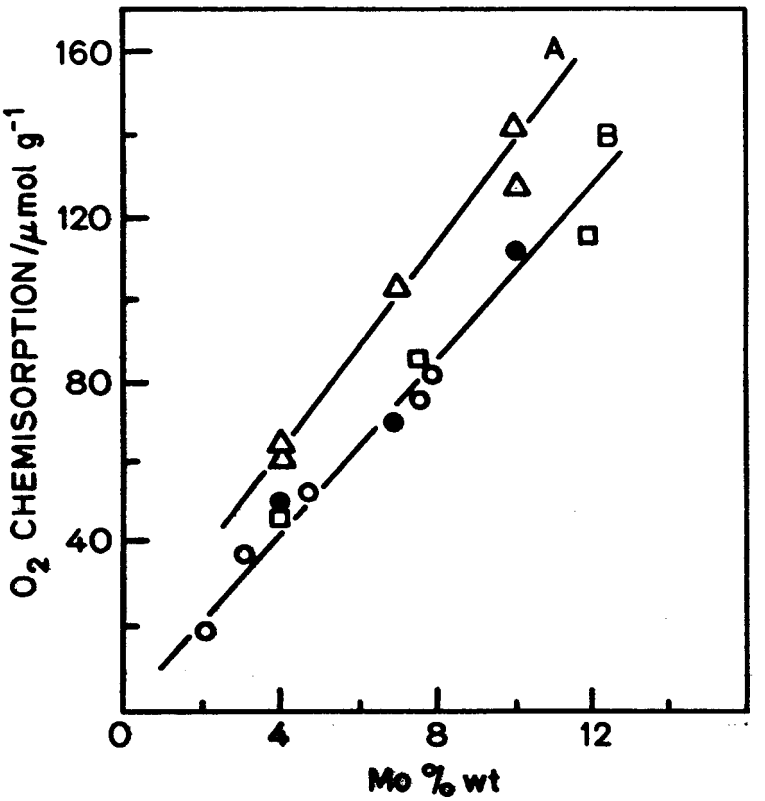
60
40
20
0
0
2
4
6
A
B
O_2 UPTAKE /μ mol g^{-1}
P/kPa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80
40
0
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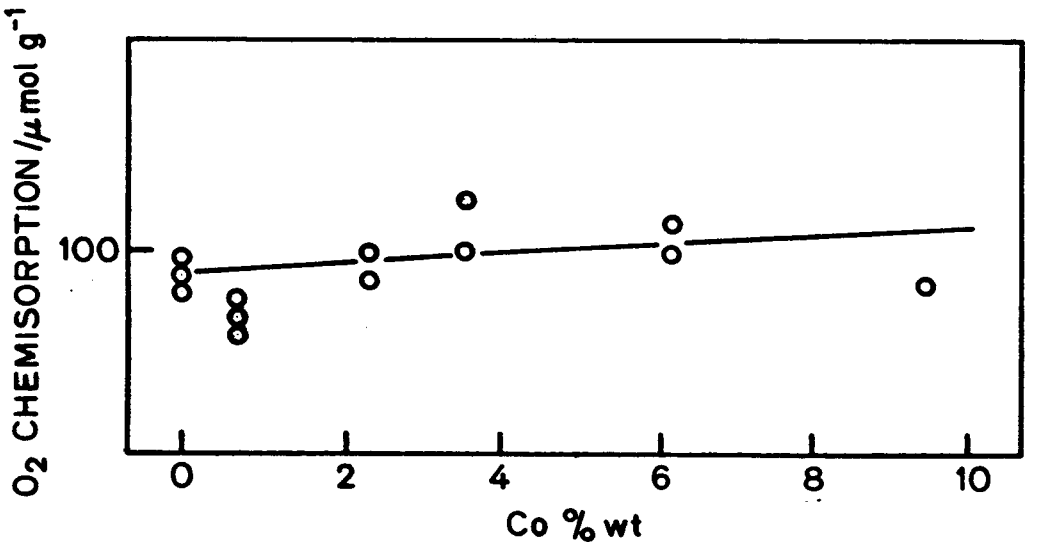
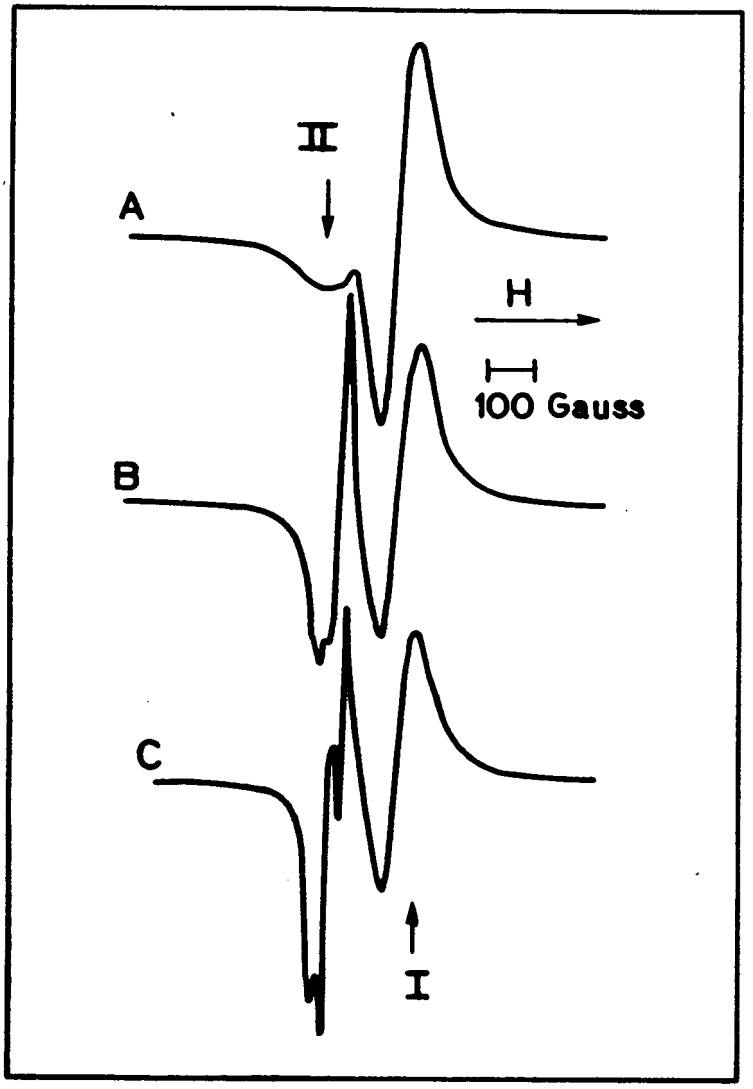
8
12
A
B
O_2 CHEMISORPTION/μmol g^{-1}
Mo % wt


O_2 CHEMISORPTION /μmol g^{-1}
100
0
2
4
6
8
10
Co % wt


II
A
H
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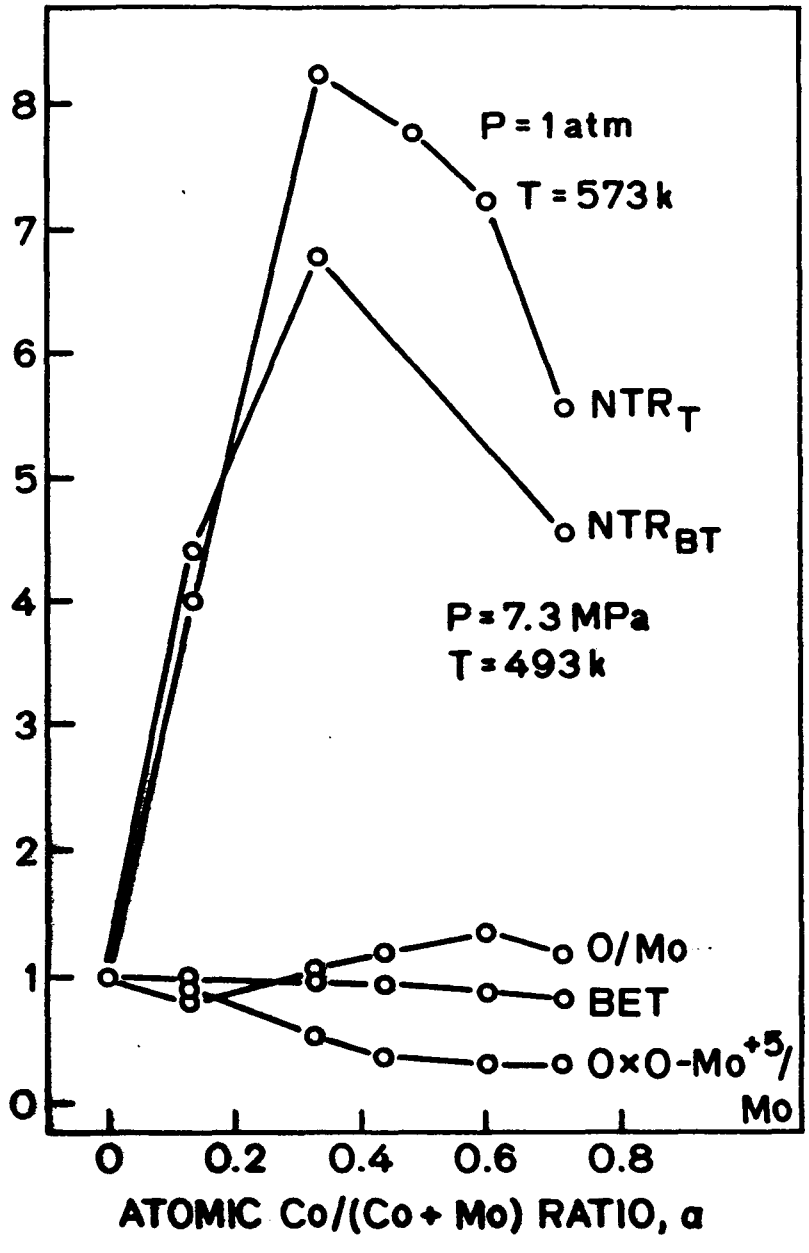
I


P = 1 atm
T = 573 k
NTR$_T$
NTR$_{BT}$
P = 7.3 MPa
T = 493 k
O/Mo
BET
O×O-Mo^{+5}/Mo
0
1
2
3
4
5
6
7
8
0
0.2
0.4
0.6
0.8
ATOMIC Co/(Co + Mo) RATIO, α