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AN AUGER ELECTRON SPECTROSCOPY STUDY OF THE ACTIVATION OF IRON FISCHER-TROPSCH CATALYSTS[1]

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I. Introduction

Promoted iron catalysts are commonly used for Fischer-Tropsch (F-T) synthesis. Copper, potassium and silica are frequently employed as promoter species, either singly or in combination. The number of different iron catalyst formulations which have been investigated for F-T synthesis is enormous and there does not yet appear to be a general consensus as to the optimum catalyst composition. In addition, questions regarding the effects of variations in catalyst activation and reaction conditions are still open. Because of the large number of parameters involved in the development of F-T catalysts, a great deal of work remains to be done before the factors affecting catalyst performance are fully understood.

In this paper one of these factors, namely the effects of variations in activation procedure on the surface composition of iron based F-T catalysts, will be investigated. Two different catalysts were studied. The first catalyst, with a composition of 100 Fe/5 Cu/4.2 K/25 SiO_2 (parts by weight) shows little variation in activity with activation procedure [1]. Activation in 1 atm. hydrogen at 220°C or 280°C for one hour, or in 1 atm. CO at 280°C for 12 hours, all give initial CO conversions of 65-75% when tested in a slurry phase reactor at 250°C and 1.48 MPa total pressure, with a H_2 to CO ratio of 0.67 and a space velocity of 2 nL/g-catalyst-hr. The second catalyst (100 Fe/3 Cu/0.2 K) displays wide variations in activity with activation procedure [2]. Initial CO conversion, measured in a fixed bed reactor at 250°C and 1.48 MPa total pressure, with a H_2 to CO ratio of 1.0 and a SV of 2 nL/g-catalyst-hr., increases from 30% to 80% in the order H_2, 280°C, 24 hrs. < H_2, 280°C, 8 hrs. < H_2, 250°C, 24 hrs. < H_2, 250°C, 8 hrs. < CO, 280°C, 24 hrs. Surface compositions of these two catalysts were measured, after the activation treatments described above, using Auger electron spectroscopy (AES). It will be shown that the variations in catalyst activity observed by Bukur, *et al.* [1,2], correlate well with variations in surface composition, offering insights into the optimum conditions for catalyst activation.

II. Experimental

The experimental apparatus used in this study is shown schematically in figure 1. The system consists of an ultra high vacuum (UHV) chamber (base pressure = 3×10^{-10} Torr) equipped with a single pass cylindrical mirror analyzer with an integral electron gun (Perkin-Elmer, Model C15-155) for AES, and a quadrupole mass spectrometer (Hiden Analytical, Model PC301) for residual gas analysis. Coupled to the UHV chamber is an atmospheric pressure gas phase reactor. Samples can be transferred from the reactor into the UHV analysis chamber without exposure to air. This capability is crucial to the success of these experiments since activated iron catalysts can be extremely reactive toward oxygen.

The catalyst samples were mounted on the end of a long transfer rod coupled to a welded bellows assembly, which allows movement between the reactor and the UHV analysis chamber. Each sample consisted of ~30 mg of catalyst pressed onto a tungsten mesh at 2000 psi. The tungsten mesh was suspended between two electrical feedthroughs by means of copper clamps and heated by passing current through the mesh. Temperature was measured with a chromel-alumel thermocouple spot welded to the mesh.

Prior to all pretreatments, the samples were calcined in 130 Torr O_2 for 3 hours to remove adventitious carbon, ensure complete conversion of surface iron to Fe_2O_3, and maintain consistency with the procedures followed by Bukur, *et al.* [2] during the activity measurements. Pretreatments were performed by heating the sample to the desired temperature and isolating it in

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the reactor by closing the gate valve. Either hydrogen or CO was then introduced into the reactor at atmospheric pressure (630 Torr in Albuquerque). After the pretreatment was complete, the reactor was evacuated while holding the sample at the pretreatment temperature. In this manner, readsorption of pretreatment product gases (CO_2 and H_2O) during evacuation was avoided. The gate valve was opened after the reactor pressure fell to less than 5×10^{-8} Torr, and the sample was lowered into the UHV chamber and cooled prior to analysis.

Pretreatments for times longer than four hours were done in several stages. This procedure allowed changes in surface composition to be monitored as a function of pretreatment time, and also ensured that buildup of product gases (CO_2 and H_2O) did not affecting the results. The first stage of pretreatment typically lasted four hours with subsequent pretreatment stages lasting six hours.

Hydrogen (Alphagaz, research grade) and oxygen (Alphagaz, research grade) were used as received. Carbon monoxide (Alphagaz, research purity) was passed through a glass wool filled U-tube immersed in liquid nitrogen to remove carbonyls.

III. Results and Discussion

A. 100 Fe/5 Cu/4.2 K/25 SiO_2

AES spectra of the 100 Fe/5 Cu/4.2 K/25 SiO_2 catalyst following the various pretreatments are shown in figure 2. The spectra for the three different activations are essentially indistiguishable. This observation is consistent with activity measurements, which show little variation in CO conversion between the different activation procedures [1].

It is interesting to note that for all activation procedures studied, the iron surface remains in a partially oxidized state; substantial amounts of oxygen are still present and the Fe(MVV) Auger transition displays two peaks at 43 and 52 eV, characteristic of oxidized iron [3,4]. Metallic iron, in contrast, displays a single peak in the MVV region at 47 eV. By comparing O(511 eV)/Fe(703 eV) peak ratios of the activated catalysts with that of the calcined catalyst (not shown) it is found that partial reduction of iron does occur during activation. The O/Fe Auger ratio drops from ~5.0 for the freshly calcined catalyst to ~3.5 for the activated catalysts. Also, prior to activation, the sample is electrically insulating, making acquisition of Auger spectra difficult. Following hydrogen treatment, the sample displays good electrical conductivity, supporting the conclusion that partial reduction occurs during hydrogen activation. Based on these observations it is concluded that reduction of Fe_2O_3 to Fe_3O_4 or FeO occurs during activation of this catalyst under the conditions investigated here. The complete absence of a peak at 47 eV in the Fe(MVV) region indicates that little if any metallic iron is present. No buildup of either graphitic or carbidic carbon is observed during activation in CO.

During the course of this investigation it was found that prolonged exposure to the electron beam resulted in changes in the surface composition of the sample. In particular, electron stimulated desorption of potassium and silicon was observed. This effect was used to investigate the effects of decreasing potassium and silica concentrations on catalyst activation. Accordingly, three different regions of the 100 Fe/5 Cu/4.2 K/25 SiO_2 catalyst were exposed to the electron beam (3 kV, 0.04 A/cm^2) for 0, 2 and 4 hours. The sample was then calcined at 300°C for 2 hours and activated in 1 atm. H_2 for 4 hours. Results are shown in figure 3. As the potassium and silica concentrations decrease, the extent of reduction of surface iron clearly increases, as evidenced by decreases in the O(511 eV)/Fe(703 eV) ratio as well as changes in the Fe(MVV) peak shape. Similar results are observed for CO activation. The (MVV) peak shape in the bottom curve of figure 3 indicates essentially complete reduction of surface iron to the metallic state [3-5], even though substantial amounts of oxygen can still be observed. This residual oxygen is associated with silica, as well as potassium, which is believed to be present as an oxide, hydroxide, or peroxide species in iron F-T catalysts. Some sulfur buildup can be seen in the reduced regions of the catalyst in figure 3. The presence of this sulfur will be discussed below (Section III B.).

These results clearly show that either potassium or silica is inhibiting reduction of this iron F-T catalyst. Based on the work presented here, it is not possible to seperate the effects of these two components. Earlier work using Mossbauer spectroscopy has shown, however, that potassium alone can inhibit the *bulk* reduction of iron catalysts [6].

B. 100 Fe/3 Cu/0.2K

i. Activation in Hydrogen

Figures 4 and 5 show the effects of hydrogen activation at 250°C and 280°C, respectively, on the surface composition of the 100 Fe/3 Cu/0.2 K catalyst. In contrast to the results for the 100 Fe/5 Cu/4.2 K/25 SiO_2 catalyst (Section III A.), nearly complete reduction of surface iron to the metallic state is observed for all activation times and temperatures investigated. At 250°C, minor changes in the Fe(MVV) lineshape, and decreases in the O/Fe ratio for activation times greater than 4 hours, indicate that a small portion of the surface iron is not reduced until the activation time exceeds 10 hours. Other than this slight variation in the extent of iron reduction, the only significant difference among the spectra in figures 4 and 5 is the sulfur concentration. Sulfur concentration is seen to increase with both activation temperature and time. The source of the sulfur is most likely a bulk impurity in the catalyst, which segregates to the surface upon reduction of the iron. The metal nitrates used to prepare the precipitated iron catalysts [2] generally contain small amounts of sulfate as an impurity.

Comparison of the sulfur levels in figures 4 and 5 with the CO conversions measured for the various activation procedures [2] shows that CO conversion is inversely related to sulfur concentration, consistent with the well known poisoning effect of sulfur on the F-T reaction. This correlation between sulfur concentration and activity provides valuable insight into the optimum conditions for activation of iron F-T catalysts in hydrogen. Clearly, efforts should directed toward inducing as little sulfur segregation as possible, while at the same time ensuring reduction of most of the iron. Based on the results presented here and in reference [2], this goal can most readily be achieved by employing the mildest reduction conditions possible. Of course, rigorous exclusion of sulfur containing impurities during catalyst synthesis would also avoid the sulfur poisoning observed here. It may be, however, that the procedures necessary to further purify starting materials would be prohibitively expensive for commercial application.

ii. Activation in Carbon Monoxide

Figure 6 shows the effects of CO activation at 280°C on the surface composition of the 100 Fe/3 Cu/0.2 K catalyst. As is the case for hydrogen activation, complete or nearly complete reduction of iron to the metallic state occurs after 4 hours of activation. Reduction is evident from the low O(511 eV)/Fe(703 eV) ratios seen in the spectra. Unfortunately, the Fe(MVV) region, which would provide corroborating evidence for iron reduction, is obscured by the carbon peak at 28 eV. The concentration of carbon on the surface can be seen to grow with activation time in CO. The featureless shape of the carbon peak at 272 eV indicates that the carbon is in a graphitic form. None of the fine structure characterisitic of carbidic carbon [5] is visible in figure 6.

Based on the spectra in figure 6 it is difficult to explain why the CO activated catalyst displays higher activity than the hydrogen activated catalysts. Since graphitic carbon is known to be a poison for F-T reactions [7,8], the initial activity of the CO activated catalyst might be expected to be less than that of the hydrogen activated catalysts. There are several possible explanations for this apparent discrepancy. First, the CO activated catalysts do not appear to have the high levels of sulfur seen on hydrogen activated surfaces. Assuming that sulfur is a more severe poison than graphitic carbon, it would then be possible for the CO activated catalyst to display higher activity than the hydrogen activated catalysts. Note, however, that since the mean free path (MFP) of sulfur Auger electrons is much shorter than the MFP of the iron Auger electrons [9], the S(150 eV)/Fe(703 eV) ratio on the CO activated catalyst may be severely attenuated by the presence of the carbon overlayer, such that actual sulfur levels on the CO activated catalyst surface may be similar to those on the hydrogen activated catalysts. A second explanation involves the morphology of the carbon overlayer. If the graphitic carbon forms in an island structure, then the reaction could occur on essentially carbon free regions of the surface between the graphitic carbon islands. A high specific activity on the carbon free regions could more than compensate for the decrease in clean metal surface area caused by the formation of graphitic carbon islands. Alternatively, the carbon could be growing in a filamentous form, leaving large areas of the surface carbon free. Clearly, more research is needed to understand the effects of CO activation on the F-T activity of this catalyst. TEM experiments are currently underway to investigate the morphology of the carbon overlayers.

IV. Conclusions

The effects of activation procedures on the surface composition of two different iron F-T catalysts have been studied. For both catalysts, the surface composition correlates well with activity measurements performed on the same catalysts. For a 100 Fe/5 Cu/4.2 K/25 SiO2 catalyst, no significant variation in surface composition was seen as a function of activation procedure, in agreement with the fact that measured initial CO conversion over this catalyst is also independent of activation procedure. For all activation procedures attempted with this catalyst, only partial reduction of the surface iron was observed and no evidence for metallic iron was seen. Lowering silica and potassium levels by electron stimulated desorption demonstrates that one or both of these components is responsible for inhibiting iron reduction.

A 100 Fe/3 Cu/0.2 K catalyst displays significant variations in activity with pretreatment procedures, and these differences are reflected in surface composition. For hydrogen activation, essentially complete reduction to the metallic state is observed for all activation treatments. In addition, segregation of sulfur to the surface occurs during activation. The surface sulfur concentrations are correlate inversely with catalyst activity, consistent with the known poisoning effect of sulfur on F-T activity. Based on these results, it is clear that optimum hydrogen activation conditions for this catalyst involve the lowest temperature and shortest time necessary to ensure complete reduction of iron. Under these conditions, segregation of sulfur to the catalyst surface is minimized.

CO activation of the 100 Fe/3 Cu/0.2 K catalyst also results in reduction of iron to the metallic state, accompanied by formation of graphitic carbon. Several possible explanations of the high activity of the CO activated catalyst are proposed, but a definitive explanation awaits the results of further experiments.

Acknowledgement

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Figure Captions

Figure 1: Schematic diagram of the experimental apparatus.

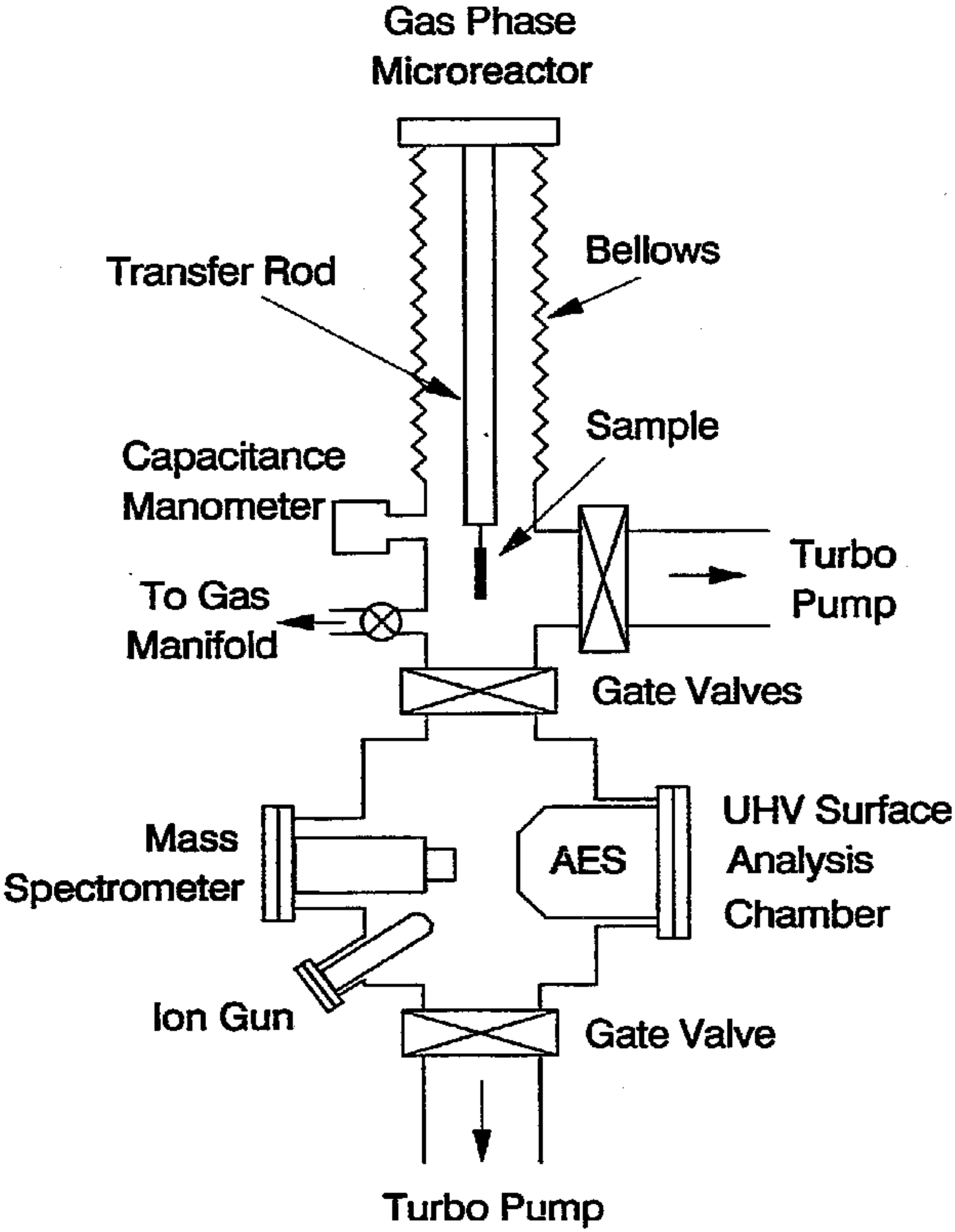
Figure 2: Effect of various activation procedures on the surface composition of the 100 Fe/5 Cu/4.2 K/25 SiO_2 catalyst.

Figure 3: Effect of lowering silica and potassium levels on the surface composition of the 100 Fe/5 Cu/4.2 K/25 SiO_2 catalyst following activation in hydrogen. Similar results are observed for activation in CO.

Figure 4: Variation of surface composition of 100 Fe/3 Cu/0.2 K catalyst with activation time in one atmosphere of hydrogen at 250°C.

Figure 5: Variation of surface composition of 100 Fe/3 Cu/0.2 K catalyst with activation time in one atmosphere of hydrogen at 280°C.

Figure 6: Variation of surface composition of 100 Fe/3 Cu/0.2 K catalyst with activation time in one atmosphere of carbon monoxide at 280°C.


Gas Phase
Microreactor
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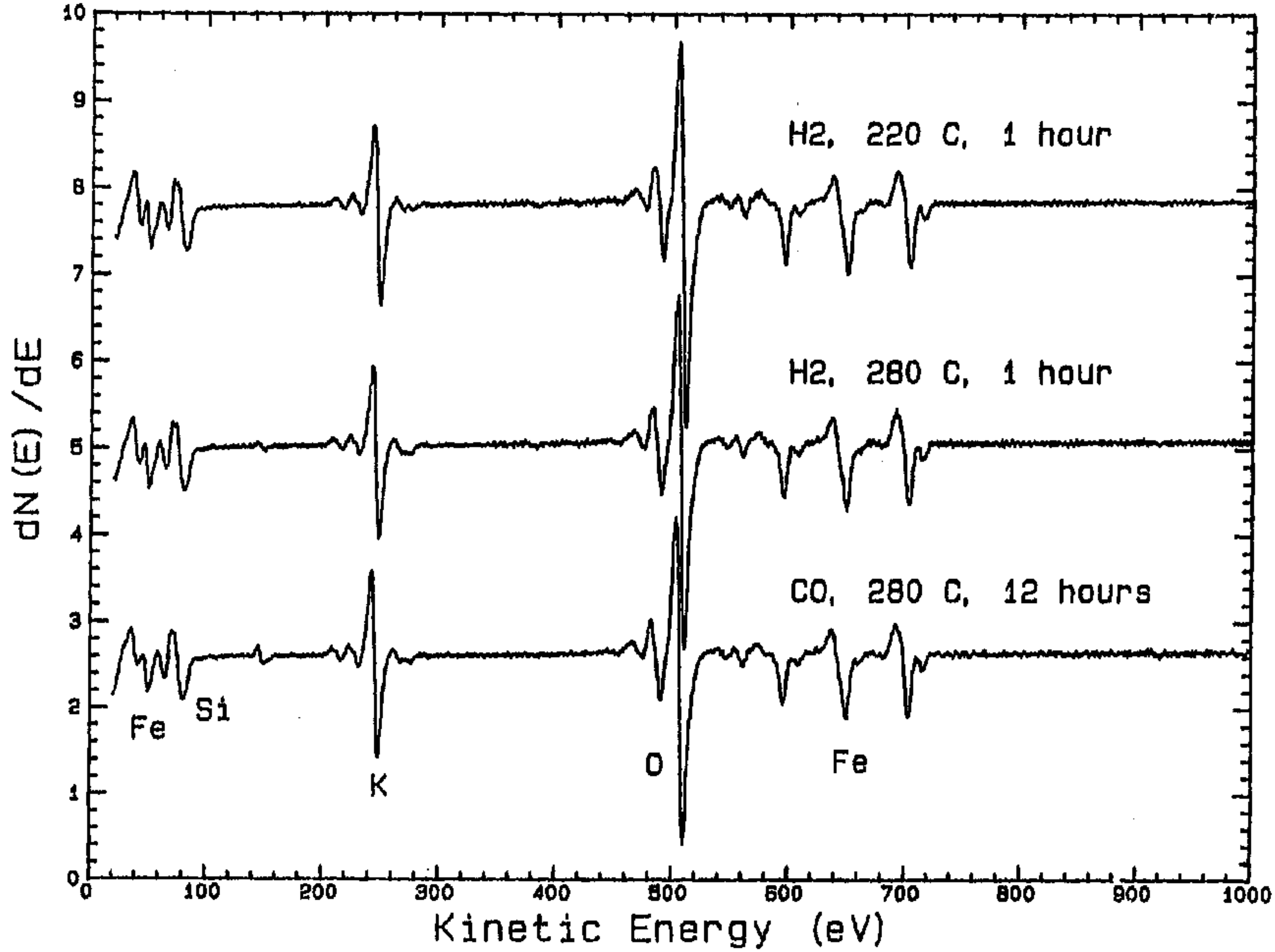
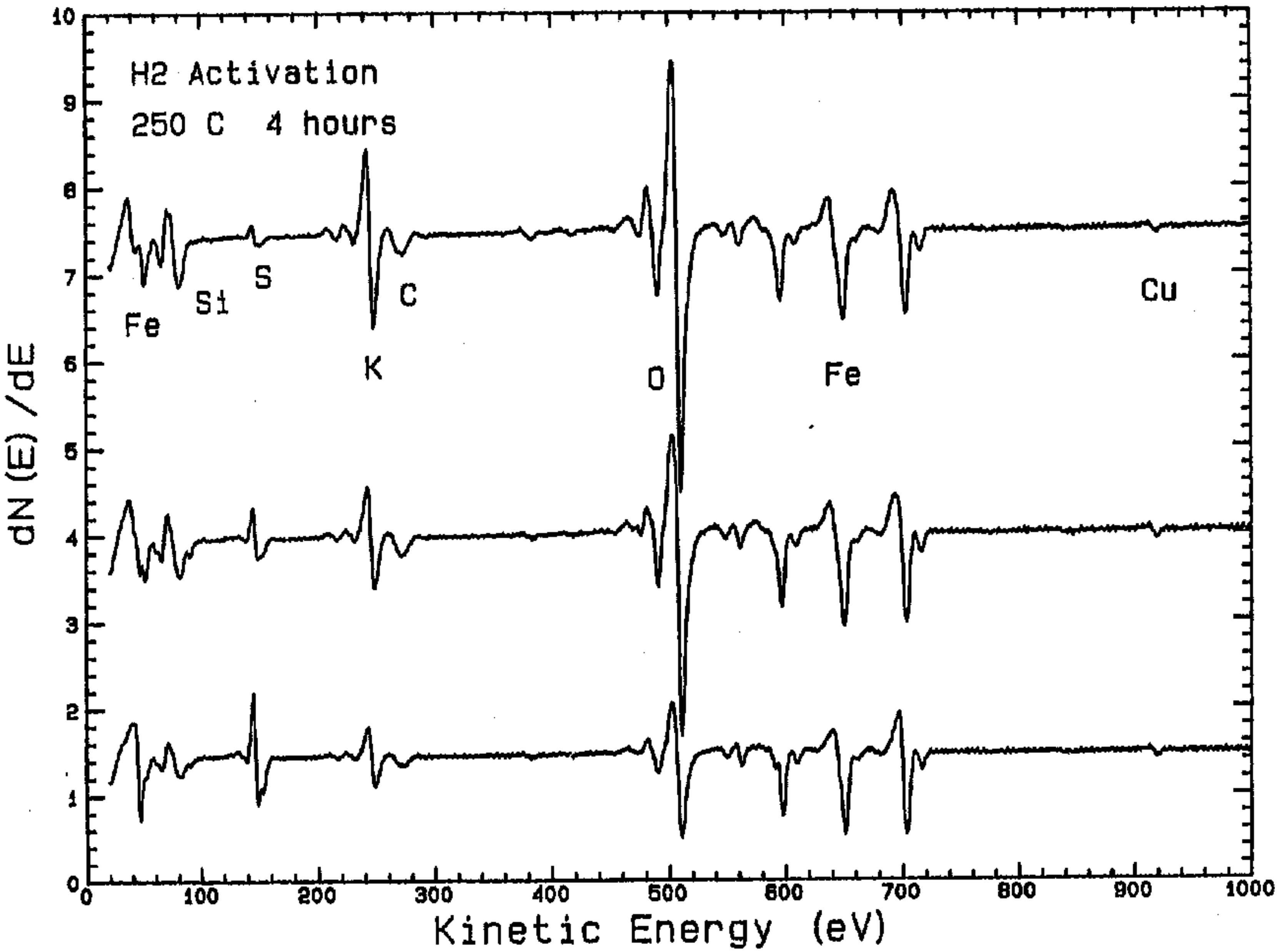
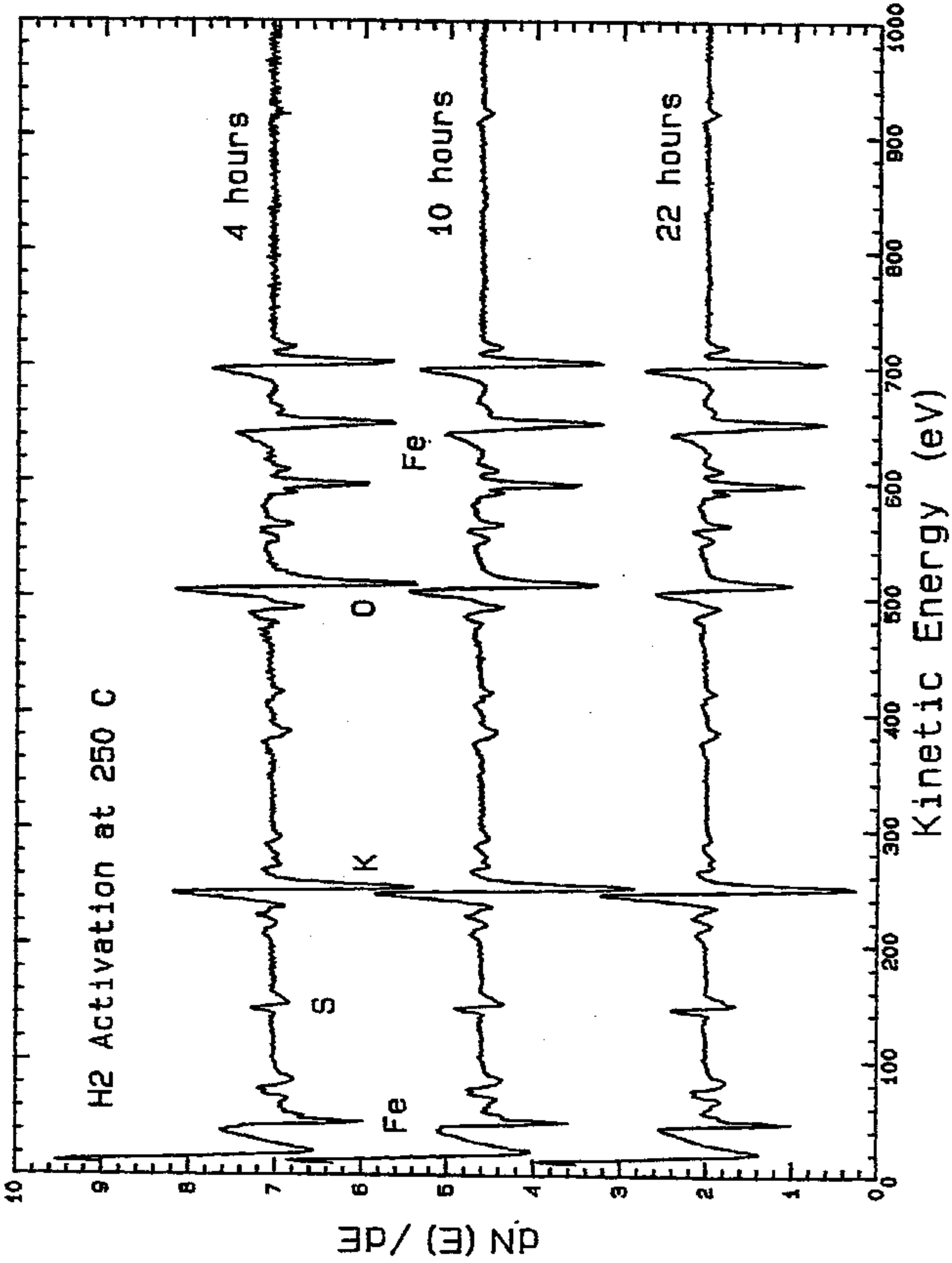
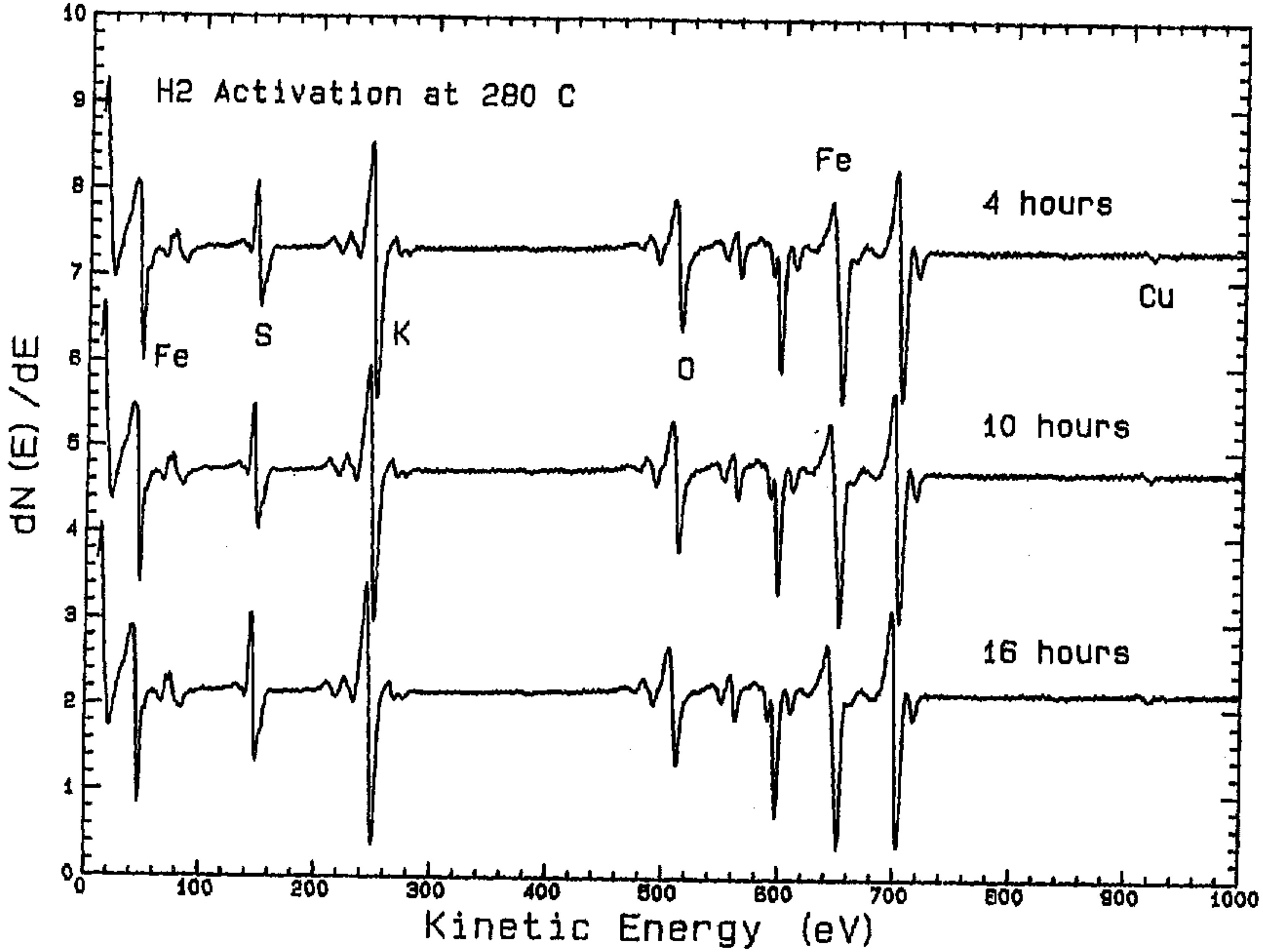
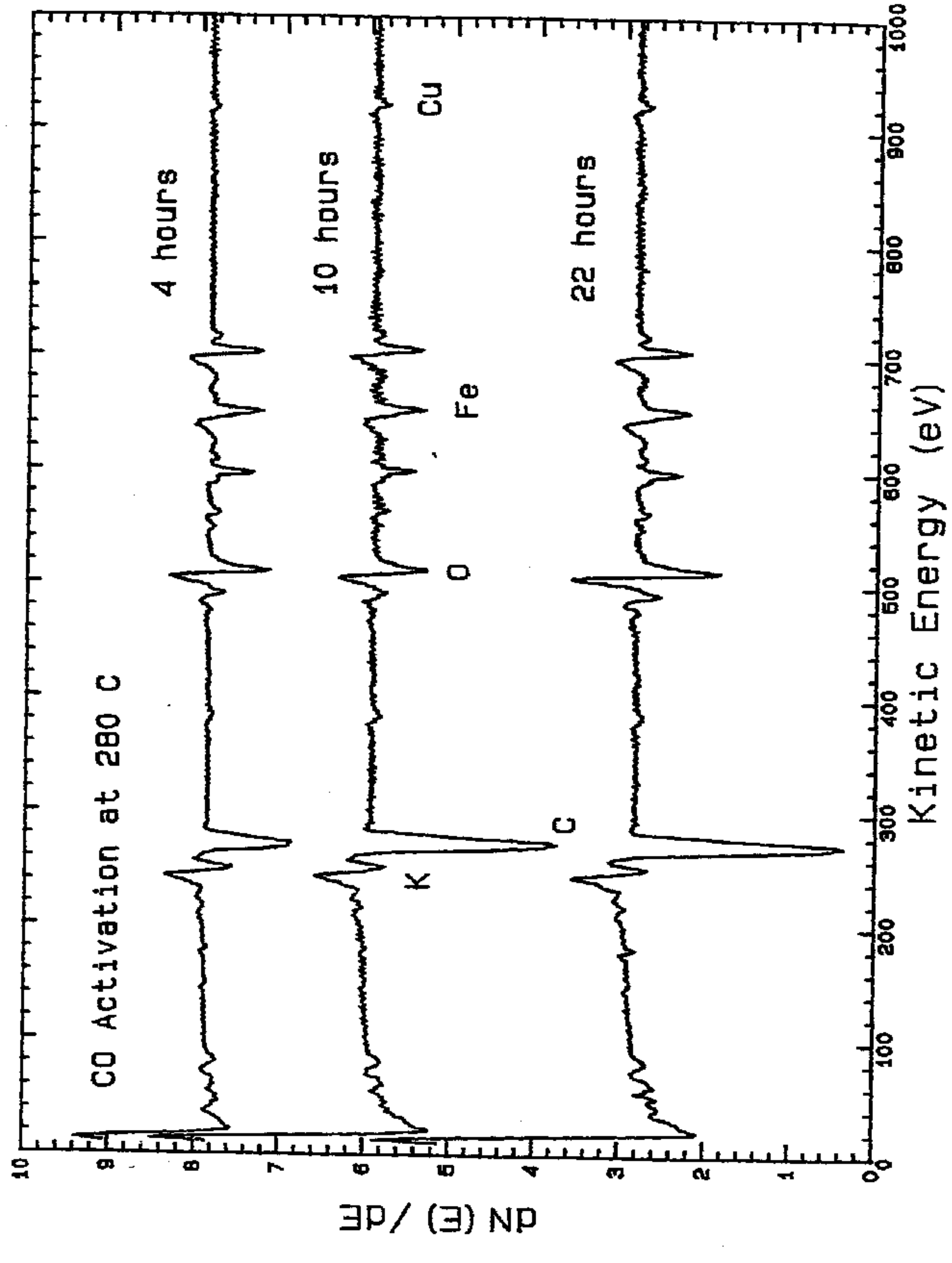


H2, 220 C, 1 hour
H2, 280 C, 1 hour
CO, 280 C, 12 hours
Fe
Si
K
O
Fe
dN (E) /dE
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700
800
900
1000
Kinetic Energy (eV)


H2 Activation
250 C 4 hours
Fe
Si
S
K
C
O
Fe
Cu
dN (E) /dE
Kinetic Energy (eV)
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700
800
900
1000


H2 Activation at 250 C
4 hours
10 hours
22 hours
Fe
S
K
O
Fe
dN (E) /dE
Kinetic Energy (eV)
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700
800
900
1000


H2 Activation at 280 C
Fe
S
K
O
Fe
Cu
4 hours
10 hours
16 hours
dN (E) /dE
Kinetic Energy (eV)
0
1
2
3
4
5
6
7
8
9
10
0
100
200
300
400
500
600
700
800
900
1000


CO Activation at 280 C
4 hours
10 hours
22 hours
Cu
Fe
O
C
K
dN (E) /dE
Kinetic Energy (eV)
0
100
200
300
400
500
600
700
800
900
1000
0
1
2
3
4
5
6
7
8
9
10