Based on the oxygenates distribution for the sample in the heated receiv between 625 and 700 hours on stream, and assuming similar oxygenates distribution for products collected in the heated receiver during the rest of the run, the weight percents of paraffins, olefins, alcohols and aldehydes in the carbon number range of C_2 -C_{19} during the first 825 hours in Run 47 were made, as shown in Figure 5-301b.

The oxygenates that were detected in the Fischer-Tropsch product are not expected to pose a problem in downstream processing for fuels applications. On the other hand, these oxygenates are very high-valued chemicals and potentially are recoverable from Fischer-Tropsch products.

5.3.5 Elucidation of the Relation Between Properties and Function of the New Modified Ruthenium Catalyst

In order to elucidate the relation between properties and function of the new modified ruthenium catalyst, both the fresh catalyst and the catalyst used in Run 46 were characterized by various techniques and compared to the unmodified ruthenium catalyst with the same ruthenium level tested in Run 47. These catalytic properties were then correlated with the observed catalytic performances.

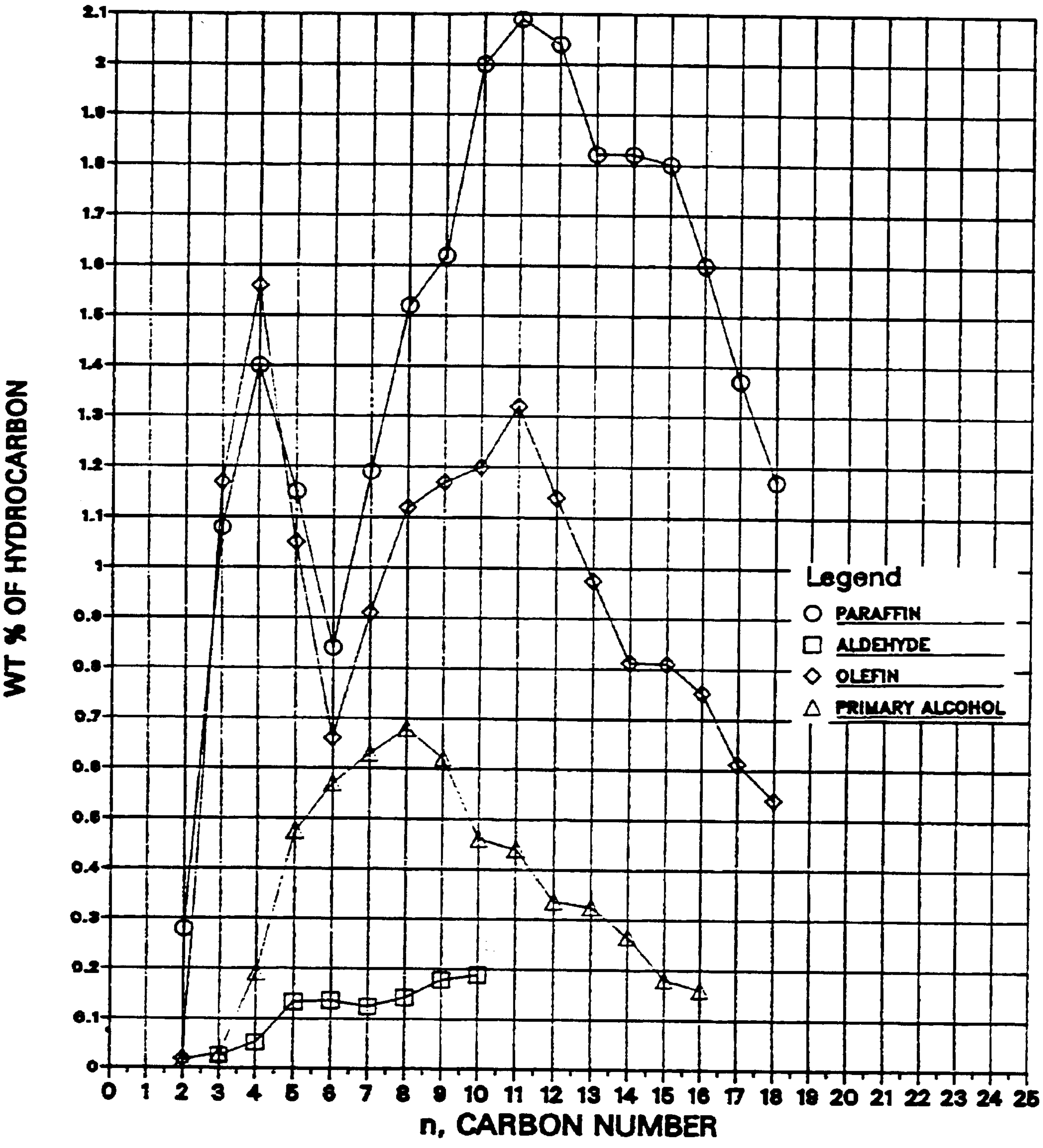
5.3.5.1 Characterization of Fresh Catalysts

According to STEM examination both the new modified ruthenium Catalyst 4966-180 and the unmodified Catalyst 4966-198 had about 85% of the ruthenium particles in the 4-6 nm size range, while the rest of the articles were 3-4 nm and 6-20 nm. EXAFS was used to determine whether the modifier was in ruthenium's local coordination environment. CO FTIR was used to determine whether the modifier has changed the CO adsorption strength on ruthenium. XPS was used to determine whether the modifier altered ruthenium's chemical state.

Figure 5-301b

FISCHER-TROPSCH SYNTHESIS WITH Ru CATALYST

PLANT 700A - FIXED BED REACTOR, RUN 46, HOURS: 0-825
209 C, 900 PSIG, 2.0 H2/CO FEED



5.3.5.1.1 EXAFS Measurements

Figure 5-302 shows the normalized EXAFS Chi function obtained for the new modified Catalyst 4966-180, the unmodified ruthenium Catalyst 4966-198 and the ruthenium metal standard. It is apparent that good correspondence of essentially every feature in the metal standard spectrum can be found in both catalyst samples. This was made even more apparent when all three data sets are overlayed, as has been done in Figure 5-303. This result indicates that ruthenium in the catalyst samples is essentially ruthenium metal-like. No differences can be observed between the modified and unmodified ruthenium catalysts. It is particularly important to note that even the high frequency features in all three spectra agree very well. The higher frequency features are produced through backscattering from ruthenium neighbors more distant than nearest neighbors. This indicates also very good "long range" correspondence between the ruthenium structures in the catalysts with those in the ruthenium metal.

The data were Fourier transformed and back-transform filtered to isolate only the contributions from shells less than about 3.2Å distant. These results are overlayed in Figure 5-304. Again, the two catalysts cannot be distinguished from each other and from the metal standard.

It is important to note that EXAFS is a bulk technique and is not sensitive to surface features for 4-6 nm ruthenium particles. The results summarized here indicate that the modifier probably was not in the local coordination environment of ruthenium in any significant amount inside the particles, while such a conclusion cannot be made for the surface of ruthenium particles.

5.3.5.1.2 CO FTIR Measurements

The CO adsorption spectra for the modified ruthenium Catalyst 4966-180 and unmodified ruthenium Catalyst 4966-198 are overlayed in Figure 5-305. The

Figure 5-302. Comparison of EXAFS at the Ru K Absorption Edge for Ruthenium Metal, Unmodified Ruthenium Catalyst 4966-198 and Modified Ruthenium Catalyst 4966-180

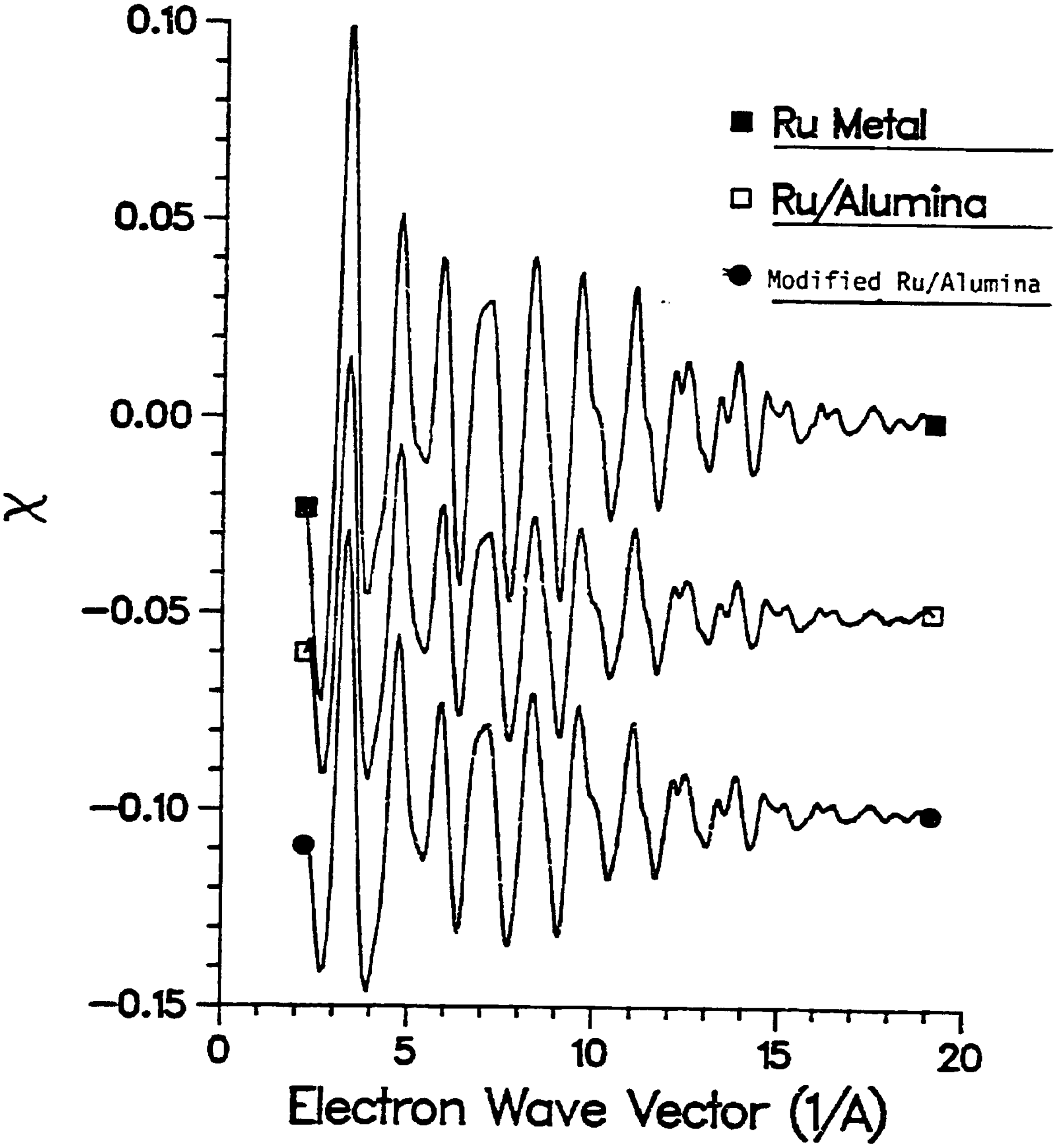


Figure 5-303. EXAFS at the Ru K Absorption Edge: Overlayed Results for Ruthenium Metal, Unmodified Ruthenium Catalyst 4966-198 and Modified Ruthenium Catalyst 4966-180

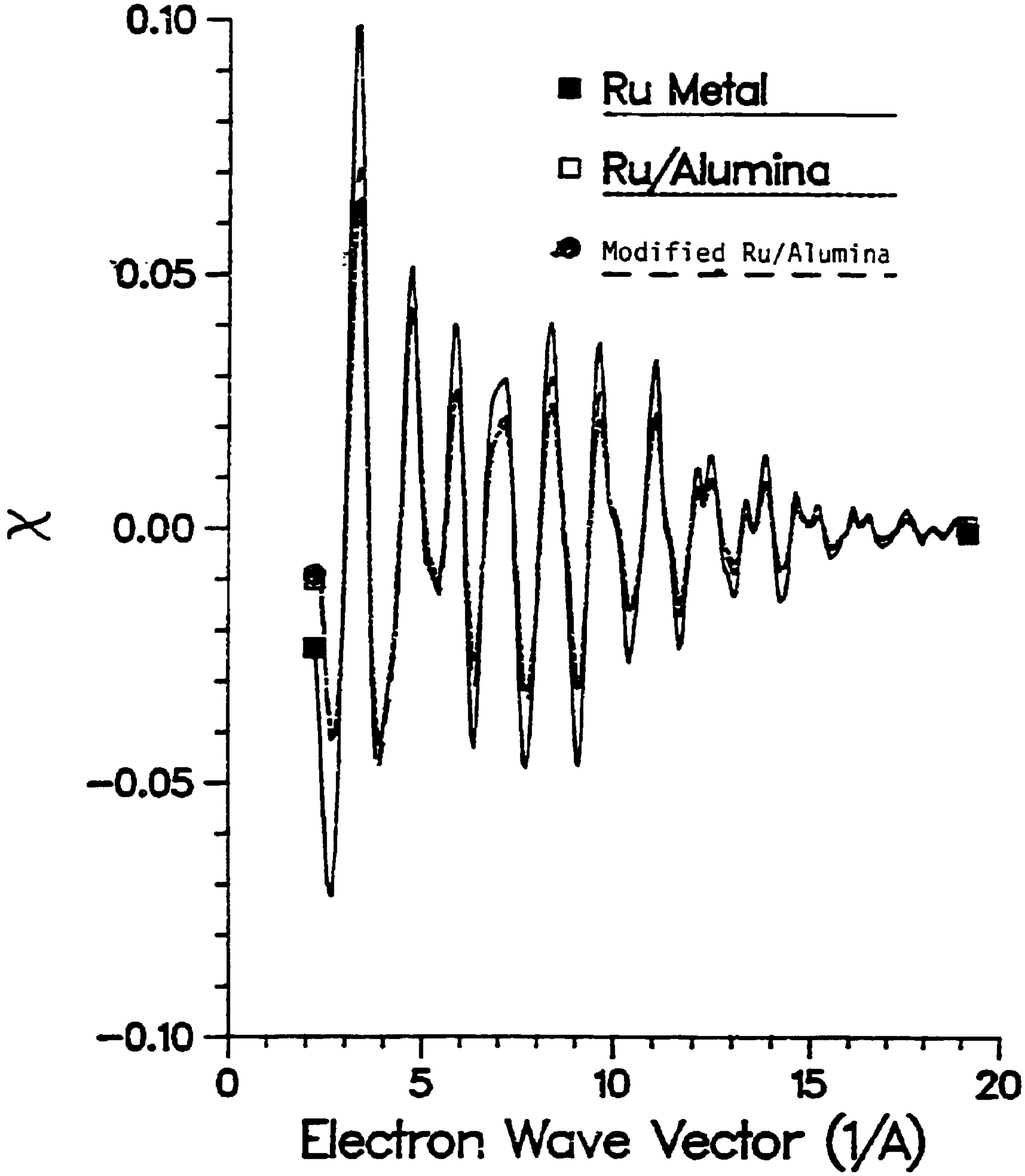


Figure 5-304. EXAFS at Ru K Absorption Edge: Overlayed Results of the Isolated Nearest Neighbor Signal for Ruthenium Metal, Unmodified Ruthenium Catalyst 4966-198 and Modified Ruthenium Catalyst 4966-180

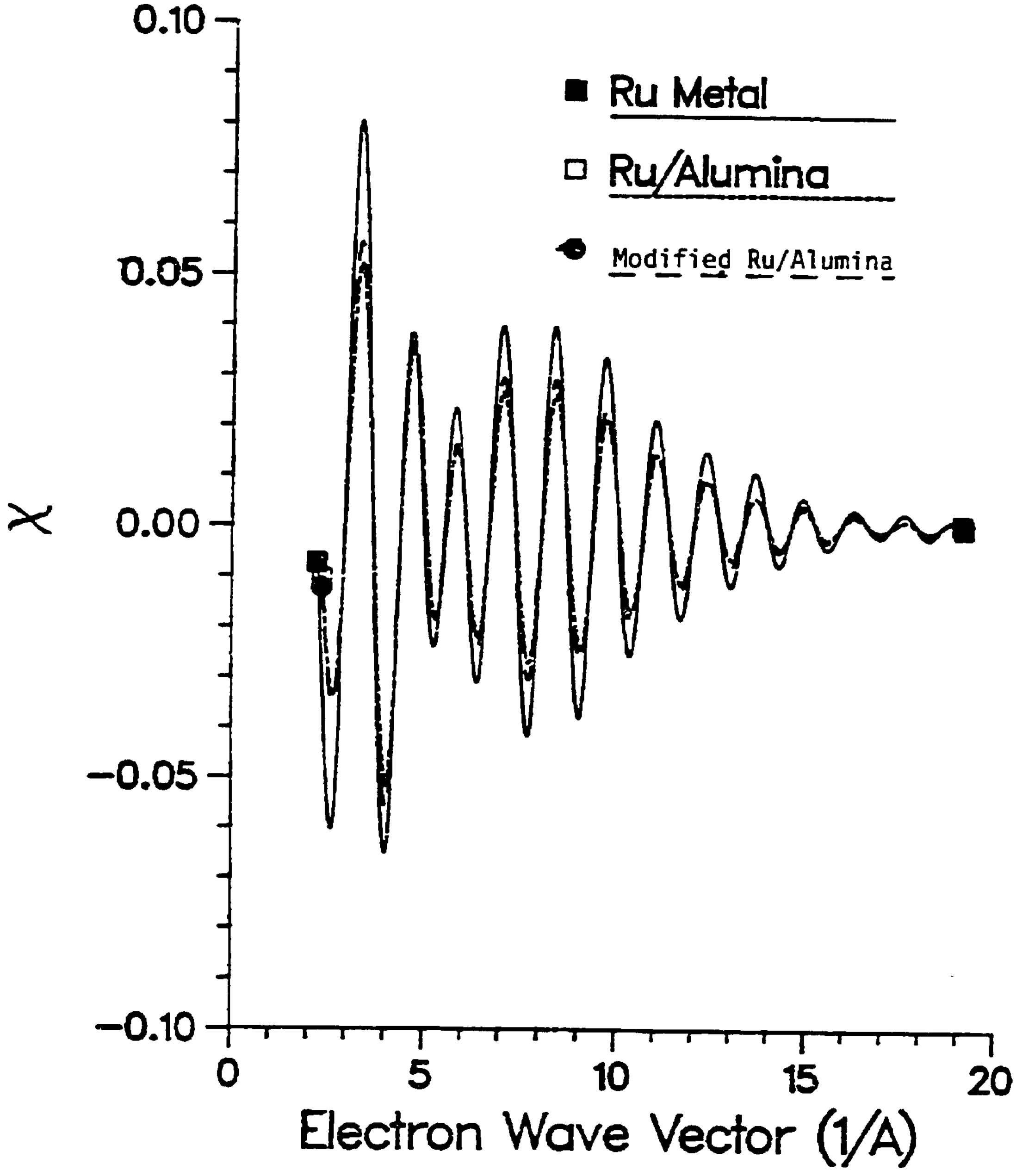
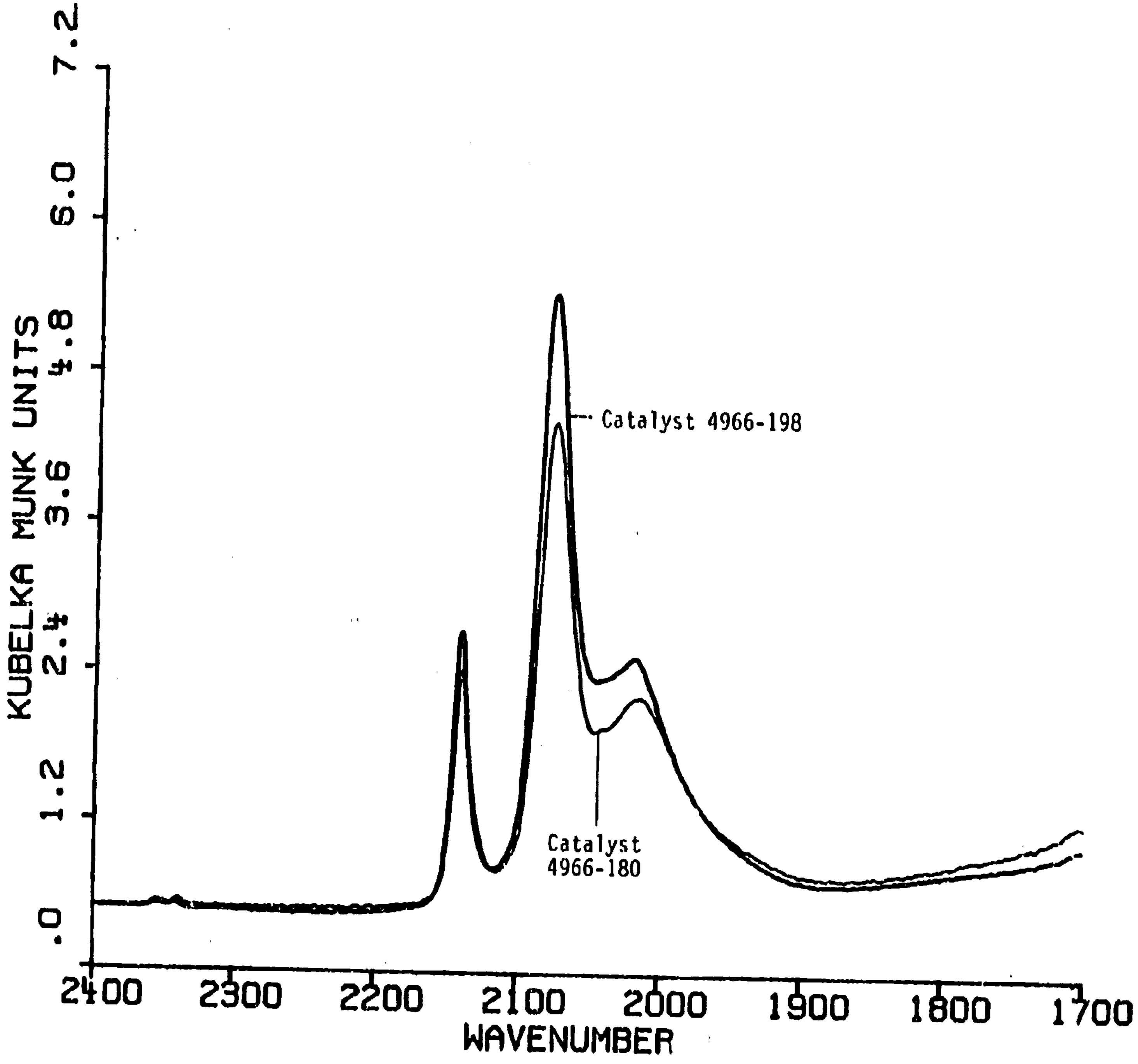


Figure 5-305. CO Adsorption Spectra for the Modified Ruthenium Catalyst 4966-180 and the Unmodified Ruthenium Catalyst 4966-198



results indicate that the CO stretching frequencies were identical for the two catalysts. Total amount of adsorption was, however, higher on the unmodified catalyst.

5.3.5.1.3 XPS Measurements

The spectra around the Ru 3p region for the modified ruthenium Catalyst 4966-180, and the unmodified Catalyst 4966-198 are shown in Figures 5-306 and 5-307. Another modified ruthenium Catalyst 4966-196 was prepared by a procedure identical to Catalyst 4966-180 and had a similar ruthenium particle size distribution with this catalyst, according to STEM examination. The spectrum for this catalyst is shown in Figure 5-308. For comparison, the spectrum for the Ir-modified ruthenium Catalyst 4966-174 was also included (Figure 5-309). The binding energies for Ru $3p_{3/2}$ electrons and the percent of the surface occupied by ruthenium for these four catalysts are summarized in Table 5-53.

Table 5-53

Ruthenium Binding Energies in Catalysts
(relative to the Al 2p = 74.40 eV for all samples)

Catalyst	4966-174	4966-196	4966-180	4966-196
Ru $3p_{3/2}$ Binding Energy, eV	461.60	461.47	461.32	461.22
Shift in Binding Energy, eV (relative to unmodified catalyst)	+0.38	+0.25	+0.10	-
% Ru (atomic)	0.29	0.28	0.27	0.35

The modified catalysts all showed slightly higher Ru $3p_{3/2}$ binding energy relative to the unmodified ruthenium catalyst. These results indicate that the modifier may have caused electron deficiency in ruthenium. However, the observed binding energy differences were small, making it difficult to reach definite conclusions.

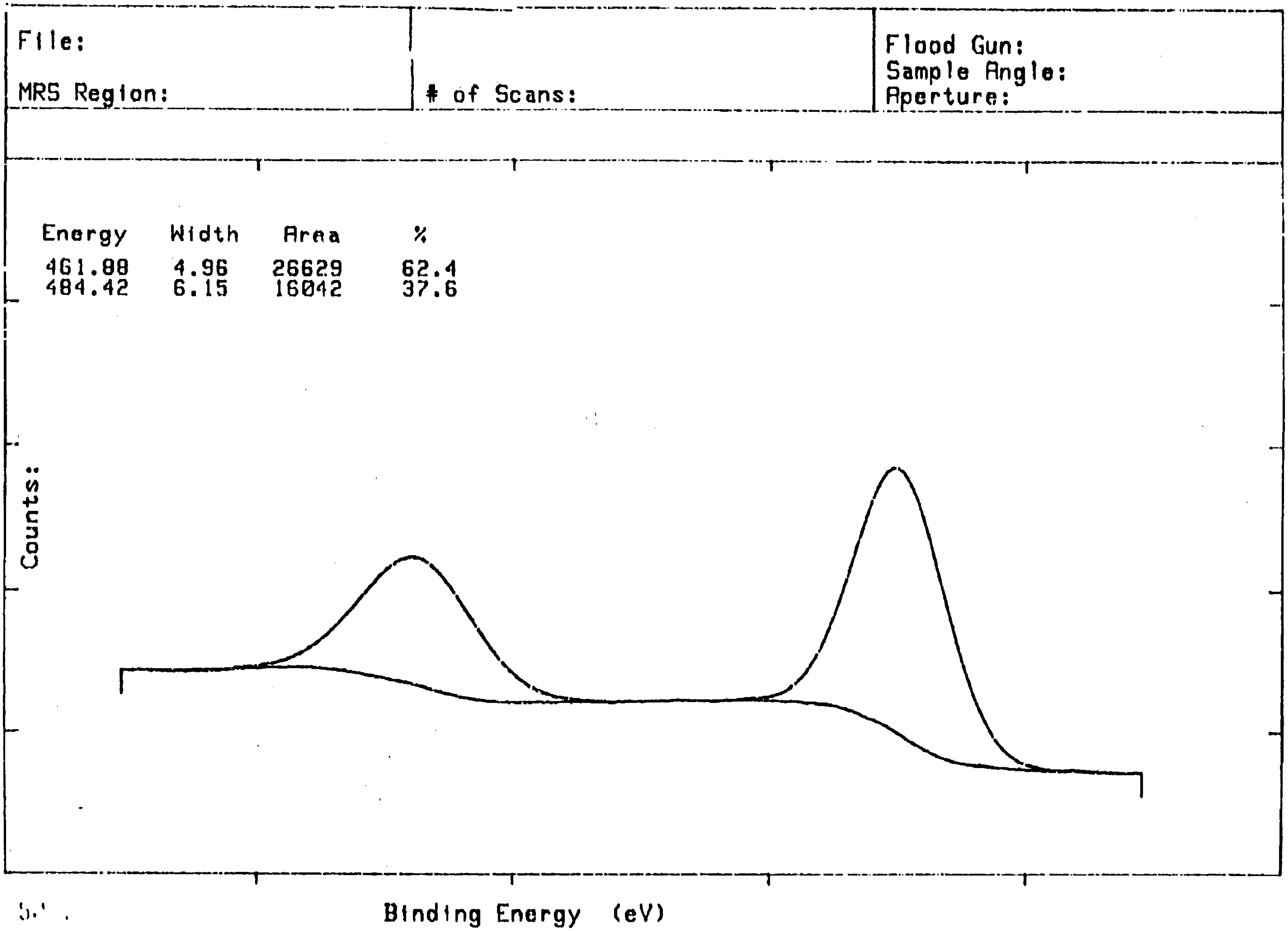
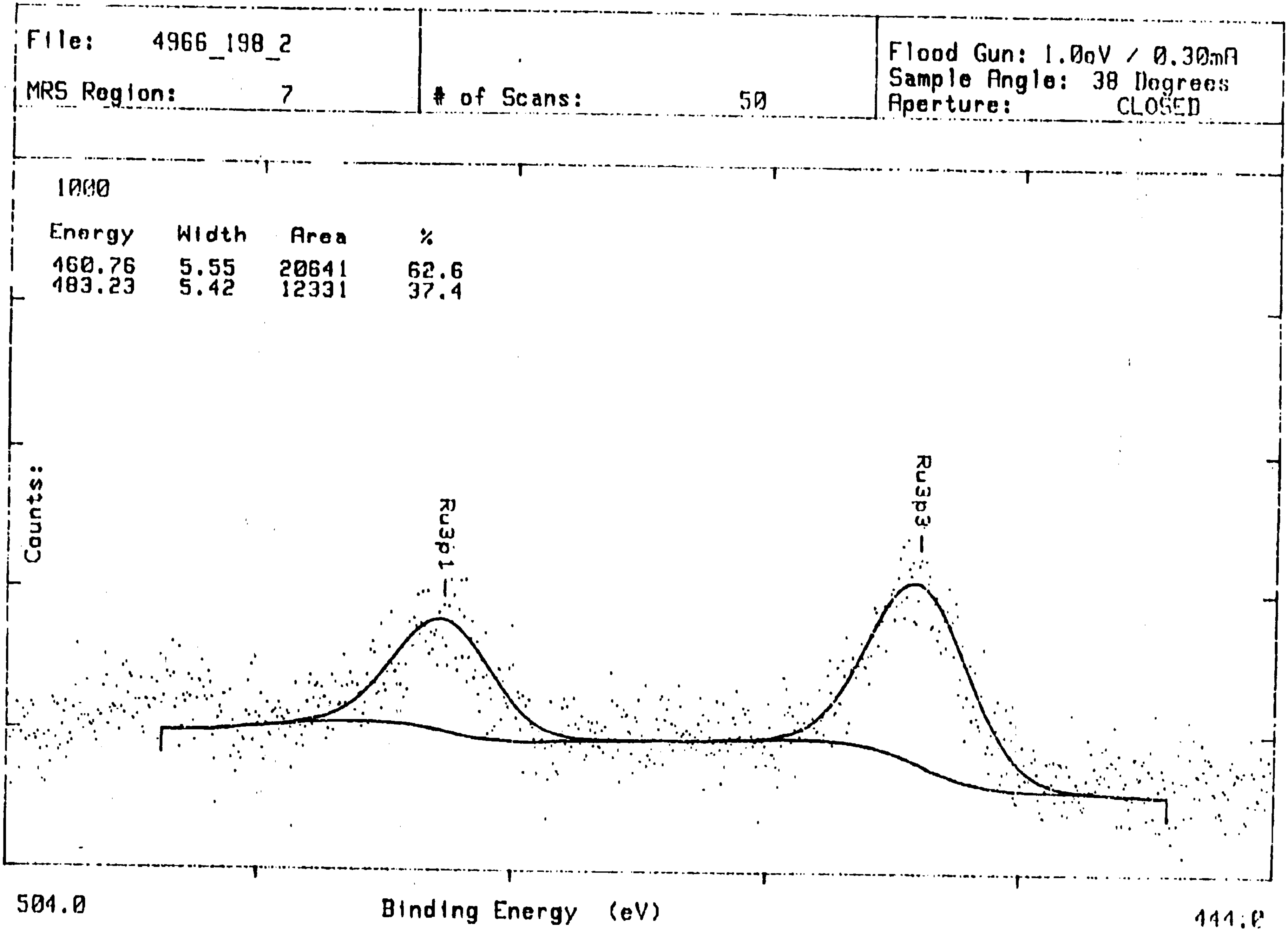


Figure 5-306: XPS Spectrum Around the Ru 3_p Region for the Modified Ruthenium Catalyst 4966-180

Energy	Width	Area	%
461.88	4.96	26629	62.4
484.42	6.15	16042	37.6

Figure 5-307: XPS Spectrum Around the Ru 3_p Region for the Unmodified Ruthenium Catalyst 4966-198



File: 4966_198_2

MRS Region: 7

# of Scans: 50

Flood Gun: 1.0eV / 0.30mA

Sample Angle: 38 Degrees

Aperture: CLOSED

Energy	Width	Area	%
460.76	5.55	20641	62.6
483.23	5.42	12331	37.4

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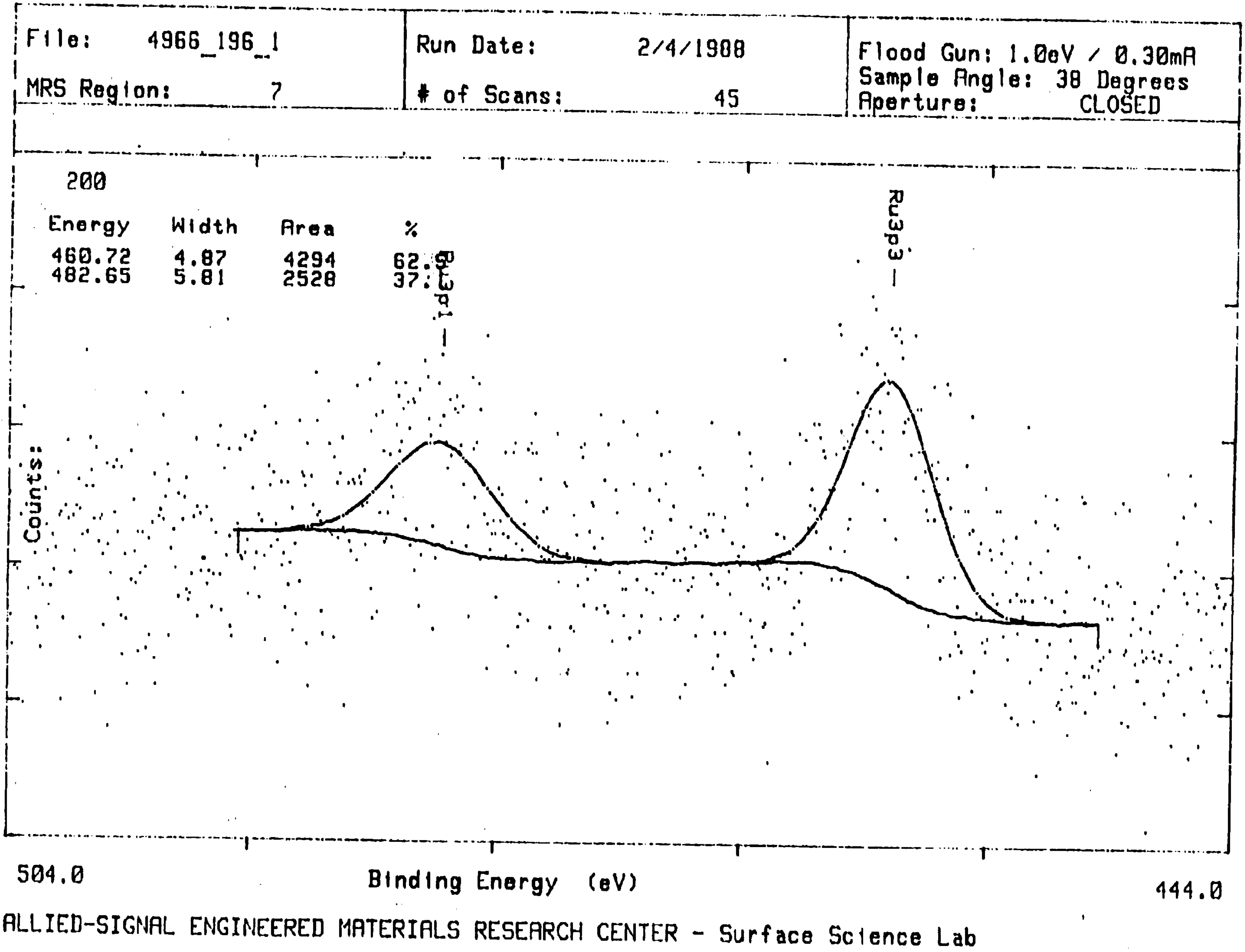
Figure 5-308. XPS Spectrum Around the Ru 3p Region for the Modified Ruthenium Catalyst 4966-196



File: 4966_196_1
MRS Region: 7
Run Date: 2/4/1988
# of Scans: 45
Flood Gun: 1.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

200

Energy	Width	Area	%
460.72	4.87	4294	62.9
482.65	5.81	2528	37.[illegible]

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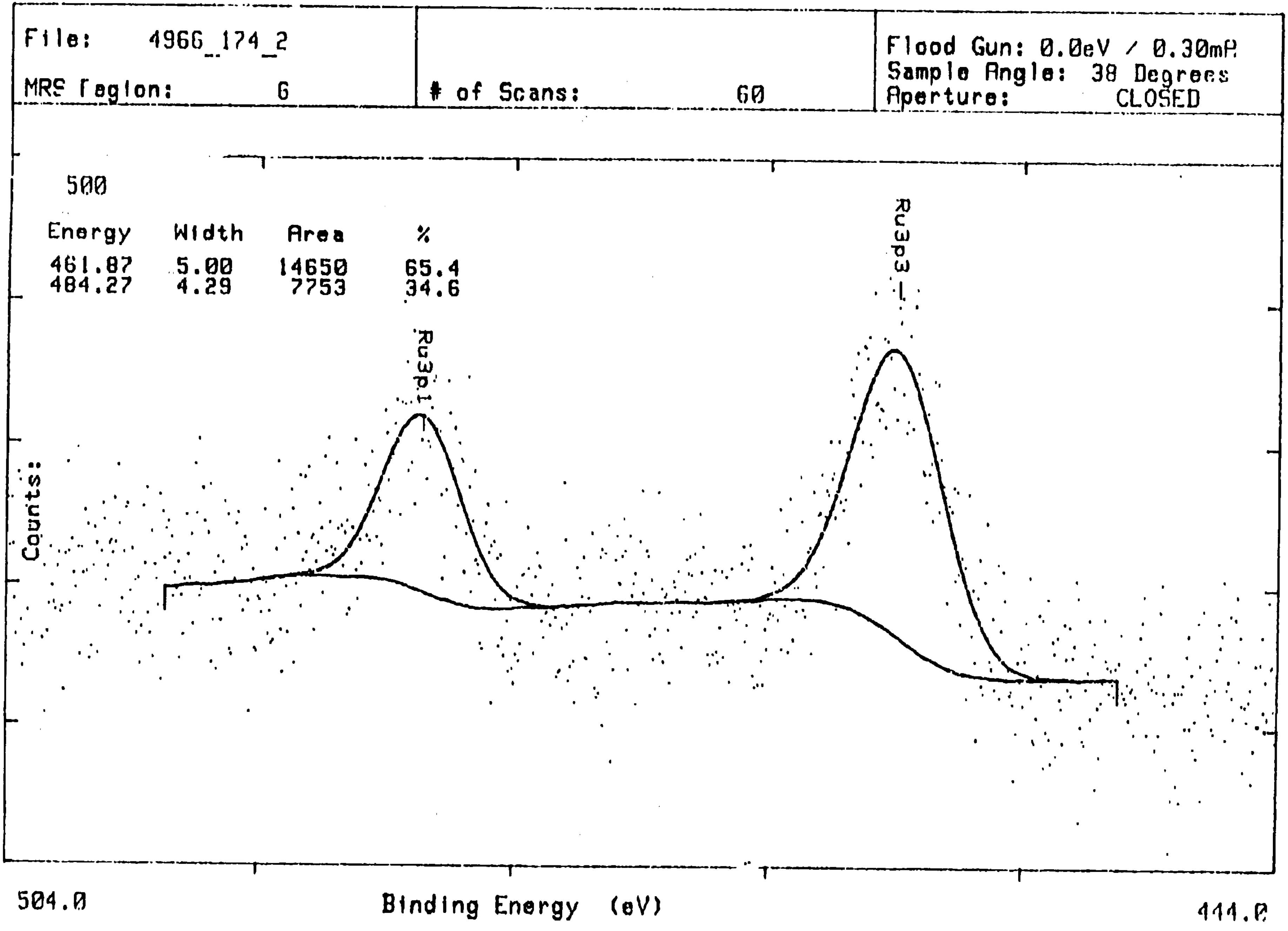
Figure 5-309. XPS Spectrum Around the Ru 3p Region for the Ir-Modified Ruthenium Catalyst 4966-174



It is important to note that all fresh catalysts described above were rereduced *in situ* with 350 torr H_2 at 200°C for 1 hour prior to the XPS measurements. A measurement without the *in situ* reduction step with the unmodified ruthenium Catalyst 4966-198 resulted in a Ru $3p_{3/2}$ binding energy of 462.56 eV, compared to 461.22 eV for the *in situ* reduced catalyst (Figure 5-310).

The unmodified ruthenium Catalyst 4966-198 showed a higher ruthenium surface concentration relative to the modified Catalyst 4966-180. This result is consistent with the higher CO adsorption on the unmodified catalyst.

5.3.5.2 Characterization of Used Catalysts

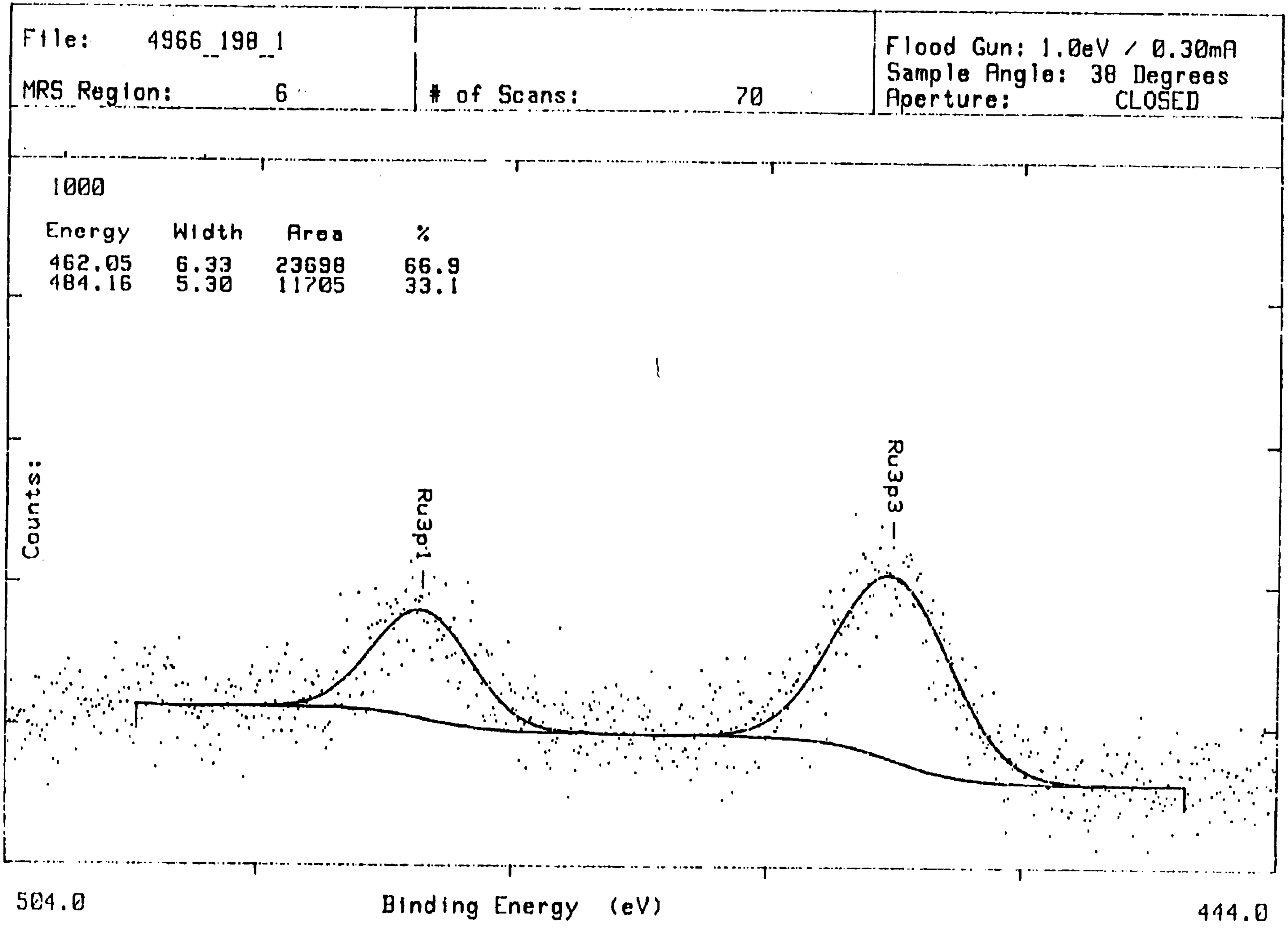
5.3.5.2.1 STEM Examination

Most of the retained Fischer-Tropsch products were removed from used catalysts by soxhlet extractions prior to STEM examination.

STEM examination of the unmodified ruthenium Catalyst 4966-198 did not show any noticeable change in the ruthenium particle size which remained 4-6 nm after 825 hours of testing in Run 47 (Figures 5-311 and 5-312). The STEM micrographs for the modified ruthenium Catalyst 4966-180 after 1700 hours of testing in Run 47 are shown in Figures 5-313 through 5-319.

Approximately 50% of the ruthenium particles remained 4-6 nm, while the rest aglomerated to 15-25 nm size range. During STEM examination, the alumina particles which apparently had pores filled with retained Fischer-Tropsch products could be distinguished from alumina particles which did not have pores filled. The presence of retained products could be detected because they volatilized under the high intensity of the x-ray beam. The ruthenium had not agglomerated on alumina particles which apparently did not have pores filled with products. The ruthenium particles migrated to the exterior of alumina

Figure 5-310. XPS Spectrum Around the Ru 3p Region for the Unmodified Ruthenium Catalyst 4966-198 Without the in situ Rereduction Step



File: 4966_198_1

MRS Region: 6

# of Scans: 70

Flood Gun: 1.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

Energy	Width	Area	%
462.05	6.33	23698	66.9
484.16	5.30	11705	33.1

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STEM Micrographs of Unmodified Ruthenium Catalyst 4966-198 After Use in Run 47

Figure 5-311

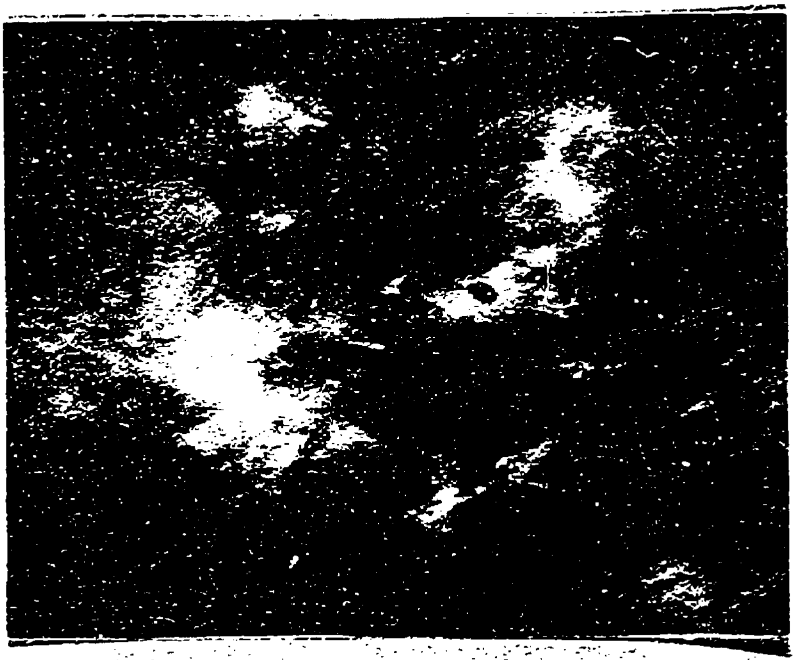


Figure 5-312

STEM Micrographs of Modified Ruthenium Catalyst 4966-180
After 1700 Hour-Test in Run 46

Figure 5-313. Pores Filled with Reaction Products

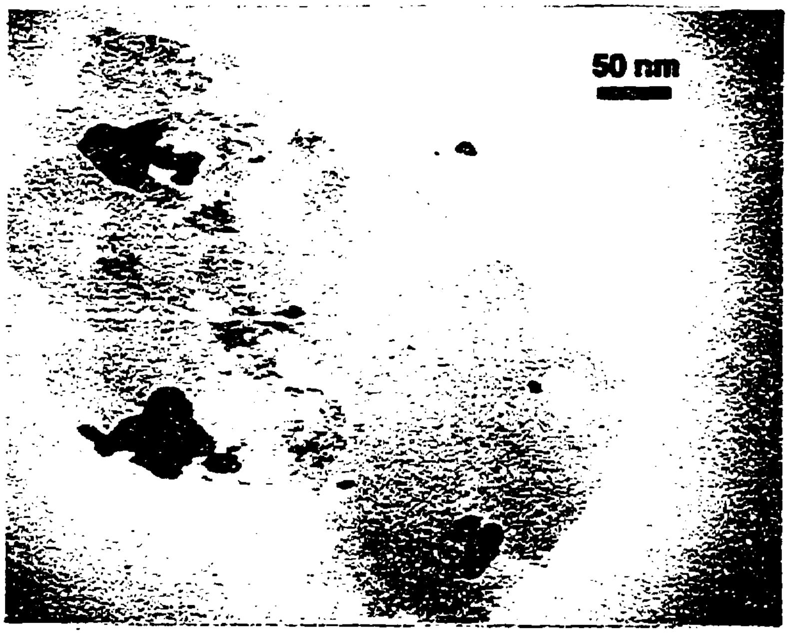


Figure 5-314. Pores Not Filled with Reaction Products

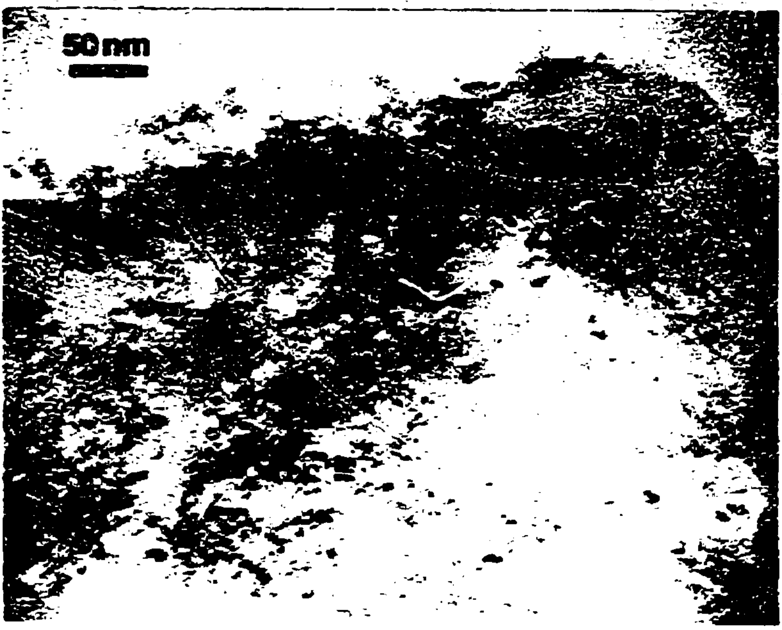
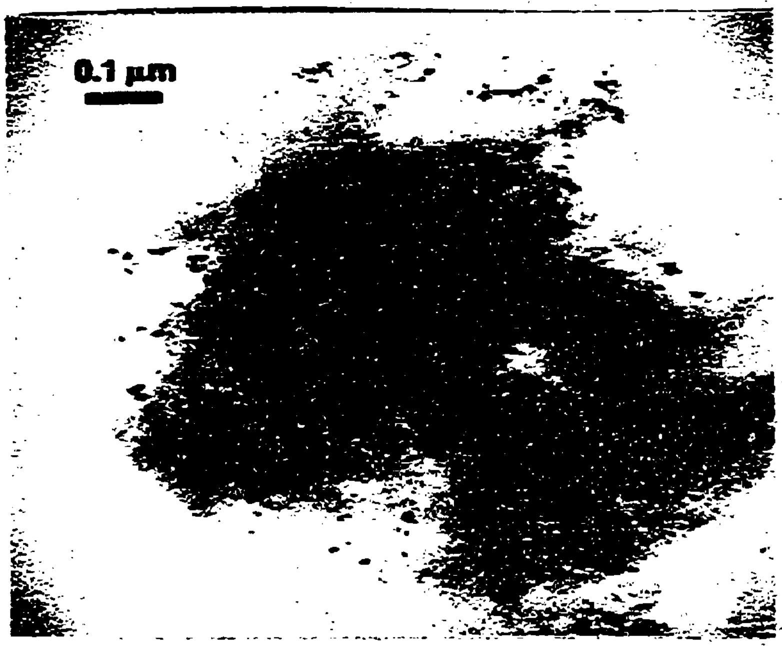


Figure 5-315

STEM Micrograph of Modified Ruthenium Catalyst 4966-180
After 1700 Hour-Test in Run 46

Alumina Particle with Pores Partially Filled with Products



STEM Micrographs of Modified Ruthenium Catalyst 4966-180 After 1700 Hour-Test in Run 46

Migration of Ruthenium Particles to Exterior of Al_2O_3

Figure 5-316

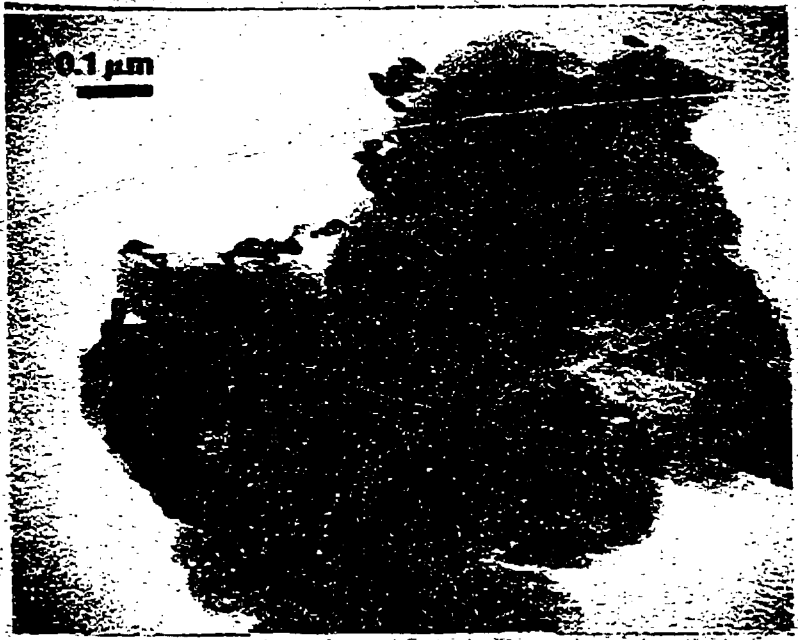


Figure 5-317

STEM Micrographs of Modified Ruthenium Catalyst 4966-180
After 1700 Hour-Test in Run 46

Agglomeration of Ruthenium Particles at the Exterior of Al_2O_3 Particles

Figure 5-318

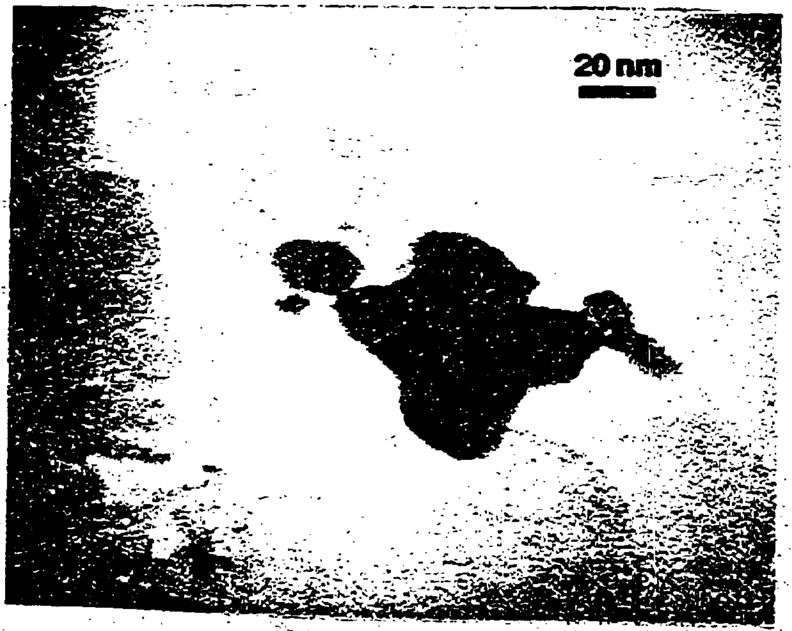
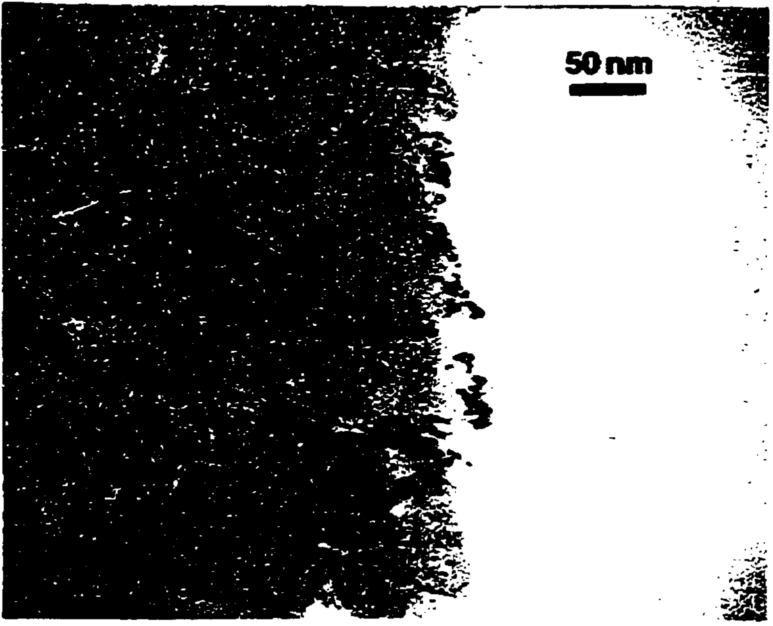


Figure 5-319



particles on alumina particles which apparently had pores filled. Typically, 4 to 6 ruthenium particles merged together to make one larger ruthenium particle.

5.3.5.2.2 XPS Measurements

The spectra around the C 1s region for the new modified ruthenium Catalyst 4966-180 and for the unmodified ruthenium Catalyst 4966-198 tested in Runs 46 and 47, respectively, are shown in Figures 5-320 and 5-321. The used catalysts were soxhlet extracted with cyclohexane in order to remove most of the Fischer-Tropsch wax prior to the XPS measurements. The C 1s binding energies and the per cent carbon on the surface for these two catalysts are summarized in Table 5-54. The Ru $3p_{3/2}$ and the O 1s data for the fresh and used catalysts are also summarized in the same table to help in the interpretation of the results. Finally, the same table also gives data obtained with alumina-titania-supported ruthenium Catalyst 4966-124 tested in Run 39 (Figure 5-322).

Two types of carbon species were identified.

The C 1s binding energy of 284.70 eV for the used modified ruthenium Catalyst 4966-180, and 284.79 eV for the used unmodified Catalyst 4966-198 matched with the expected carbon binding energy in a hydrocarbon-type molecule. Based on XPS, this carbon amounted to about 17% (atomic) of the surface for the new modified ruthenium Catalyst 4966-180 after 1700 hours of testing. More carbon was detected (22%) on the surface of the unmodified ruthenium Catalyst 4966-198 after 825 hours of testing. It is not presently clear whether this carbon species is chemically bound to the catalyst surface or is part of the unremoved wax that fills the catalyst pores during reaction.

The C 1s binding energies of 288.82 eV and 288.92 eV in the used catalysts matched the expected carbon binding energy for carbon attached to oxygen, as in some organic molecules. However, it is possible that this carbon may be actually bound to the oxygen on the alumina support. The modified ruthenium catalyst had more of this type of carbon relative to the unmodified catalyst.

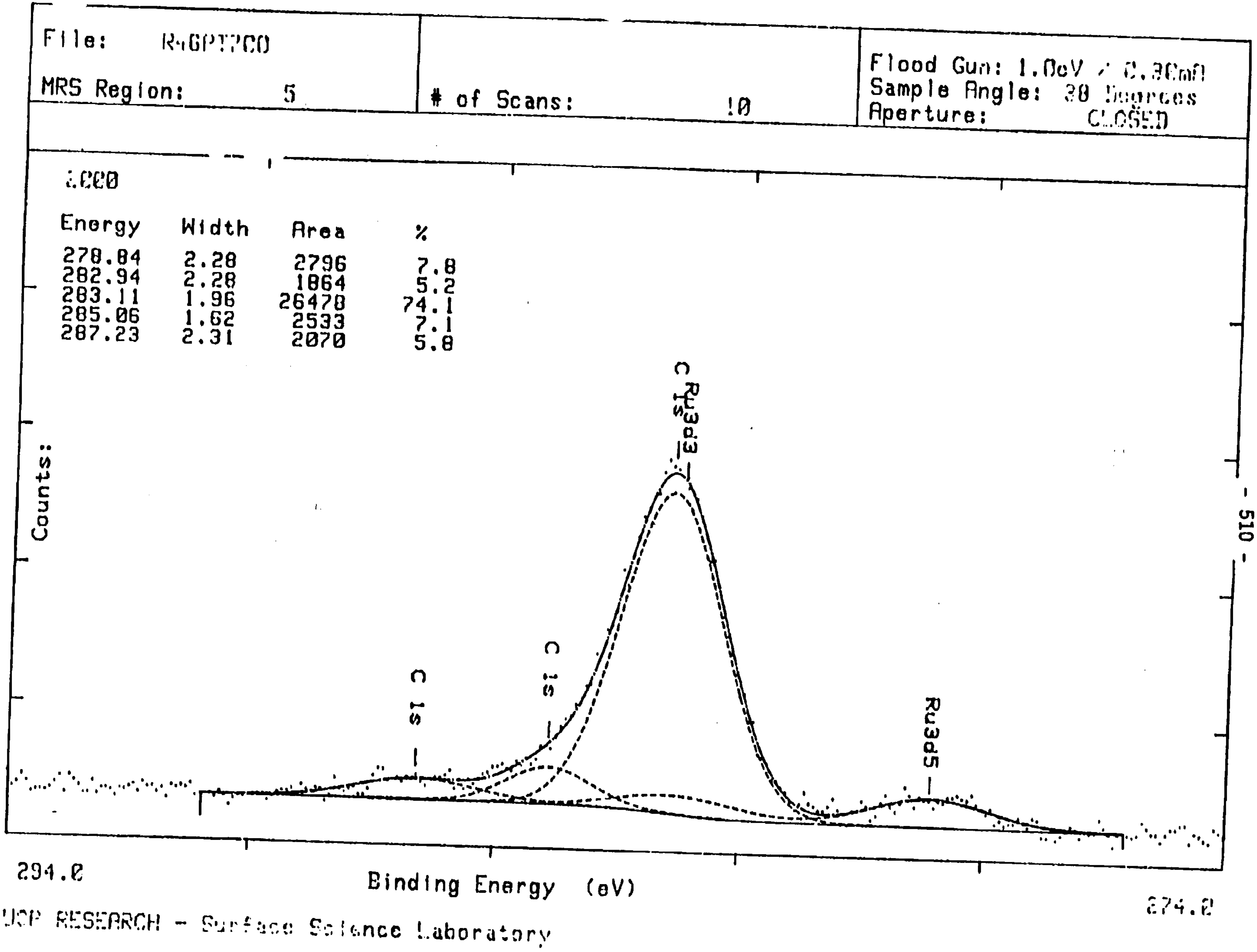
Table 5-54

XPS Measurements on Used Ruthenium Catalysts

	New Modified Ruthenium Catalyst 4966-180 on Al_2O_3		Unmodified Ruthenium Catalyst 4966-198 on Al_2O_3		Ruthenium Catalyst 4966-124 on Al_2O_3-TiO_2	
	Binding Energy, eV	Surface Composition, atomic %	Binding Energy, eV	Surface Composition, atomic %	Binding Energy, eV	Surface Composition, atomic %
C 1s (used catalysis)	284.70 (284.60) 286.65 (286.59) 288.82 (288.04)	16.99 (11.39) 1.63 (0.45) 1.33 (1.03)	284.79 286.54 288.92	22.24 2.34 0.93	284.53 286.19	14.13 1.11
0 1s (used catalysts)	531.46 (530.48) 534.66 (531.85) (533.72)	53.90 (22.88) 0.70 (33.22) (1.94)	531.12 533.14	45.10 3.58	530.99 533.21	50.56 3.72
0 1s (fresh catalysts)	530.92 533.11	55.94 4.78	530.87 533.28	55.84 3.21		
Ru $3p_{3/2}$ (used catalysts)	461.54 (461.25)	0.18 (0.18)	461.90	0.07		
Ru $3p_{3/2}$ (fresh catalysts)	461.32	0.27	461.22	0.35		

Numbers in parentheses after toluene and methylene chloride/methanol extraction.

Figure 5-320. XPS Spectrum Around the C 1s Region for the Modified Ruthenium Catalyst 4966-180 Tested in Run 46



File: R4GPT7CO

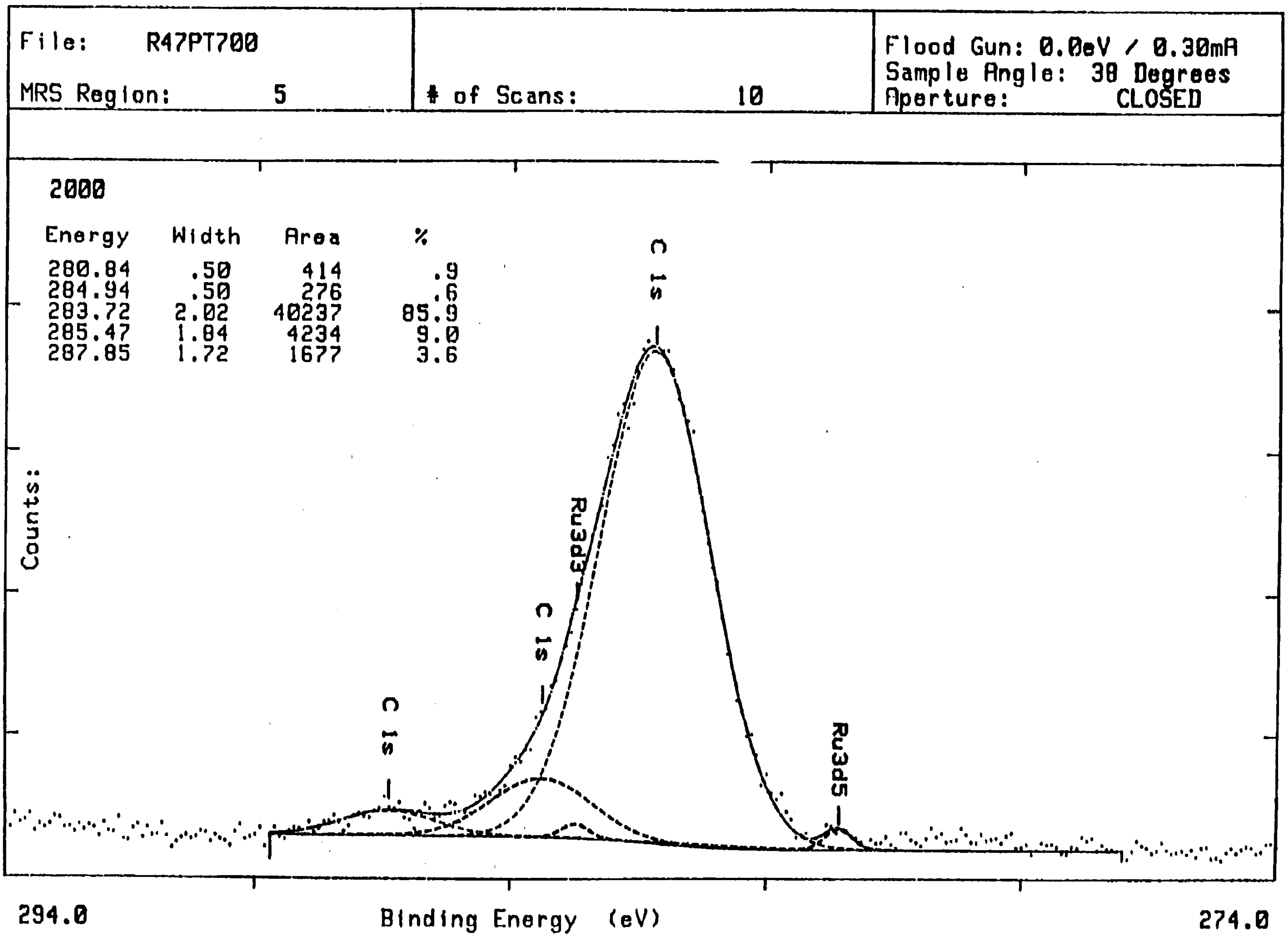
MRS Region: 5

# of Scans: 10

Flood Gun: 1.0eV / 0.30mA
Sample Angle: 30 Degrees
Aperture: CLOSED

Energy	Width	Area	%
278.84	2.28	2796	7.8
282.94	2.28	1864	5.2
283.11	1.96	26478	74.1
285.06	1.62	2533	7.1
287.23	2.31	2070	5.8

Figure 5-321. XPS Spectrum Around the C 1s Region for the Unmodified Ruthenium Catalyst 4966-198 Tested in Run 47



File: R47PT700
MRS Region: 5
# of Scans: 10
Flood Gun: 0.0eV / 0.30mA
Sample Angle: 30 Degrees
Aperture: CLOSED

2000

Energy	Width	Area	%
280.84	.50	414	.9
284.94	.50	276	.6
283.72	2.02	40237	85.9
285.47	1.84	4234	9.0
287.85	1.72	1677	3.6

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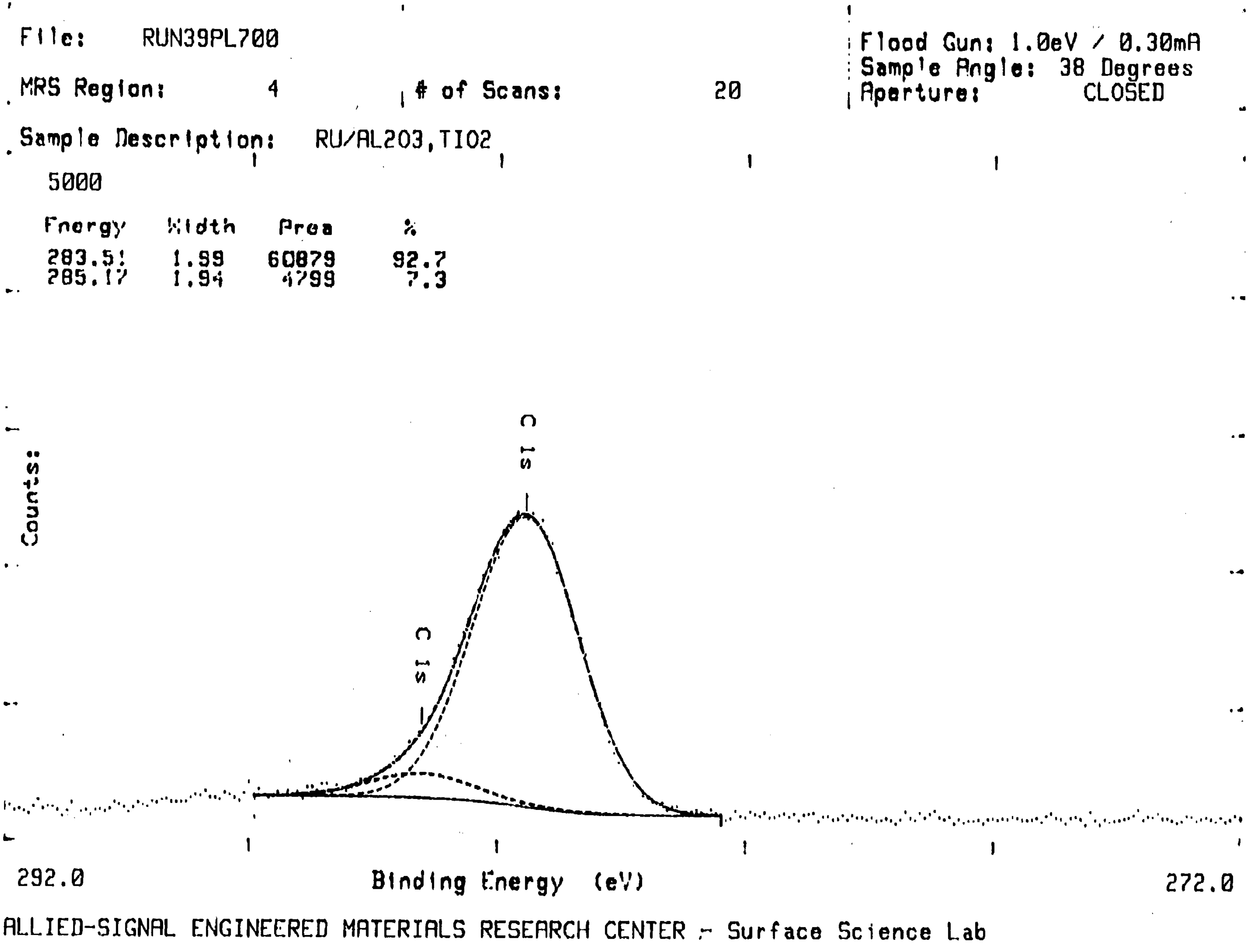
Figure 5-322. XPS Spectrum Around the C 1s Region for the Al_2O_3-TiO_2 Supported Ruthenium Catalyst 4966-124 Tested in Run 39



File: RUN39PL700

MRS Region: 4

\# of Scans: 20

Flood Gun: 1.0eV / 0.30mA

Sample Angle: 38 Degrees

Aperture: CLOSED

Sample Description: RU/AL203,TIO2

Energy	Width	Area	%
283.51	1.99	60879	92.7
285.17	1.94	4799	7.3

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The C 1s binding energy of 286.65 eV and 286.54 eV in the used catalysts matched the expected carbon binding energy for carbon attached to carbon which is bound to oxygen. The unmodified ruthenium catalyst had more of this type of carbon relative to the modified catalyst.

XPS measurements were repeated after the used modified catalyst was soxhlet extracted first with toluene and then with methylene chloride/methanol subsequent to the extraction with cyclohexane. Both the hydrocarbon-type carbon and the carbon apparently bound to oxygen were removed during these extractions.

The C 1s spectra for the used Al_2O_3-TiO_2 supported ruthenium Catalyst 4966-124 was similar to those obtained with Al_2O_3-supported Catalysts 4966-180 and 4966-198. However, the total amount of carbon was less, possibly because of the shorter duration of the run.

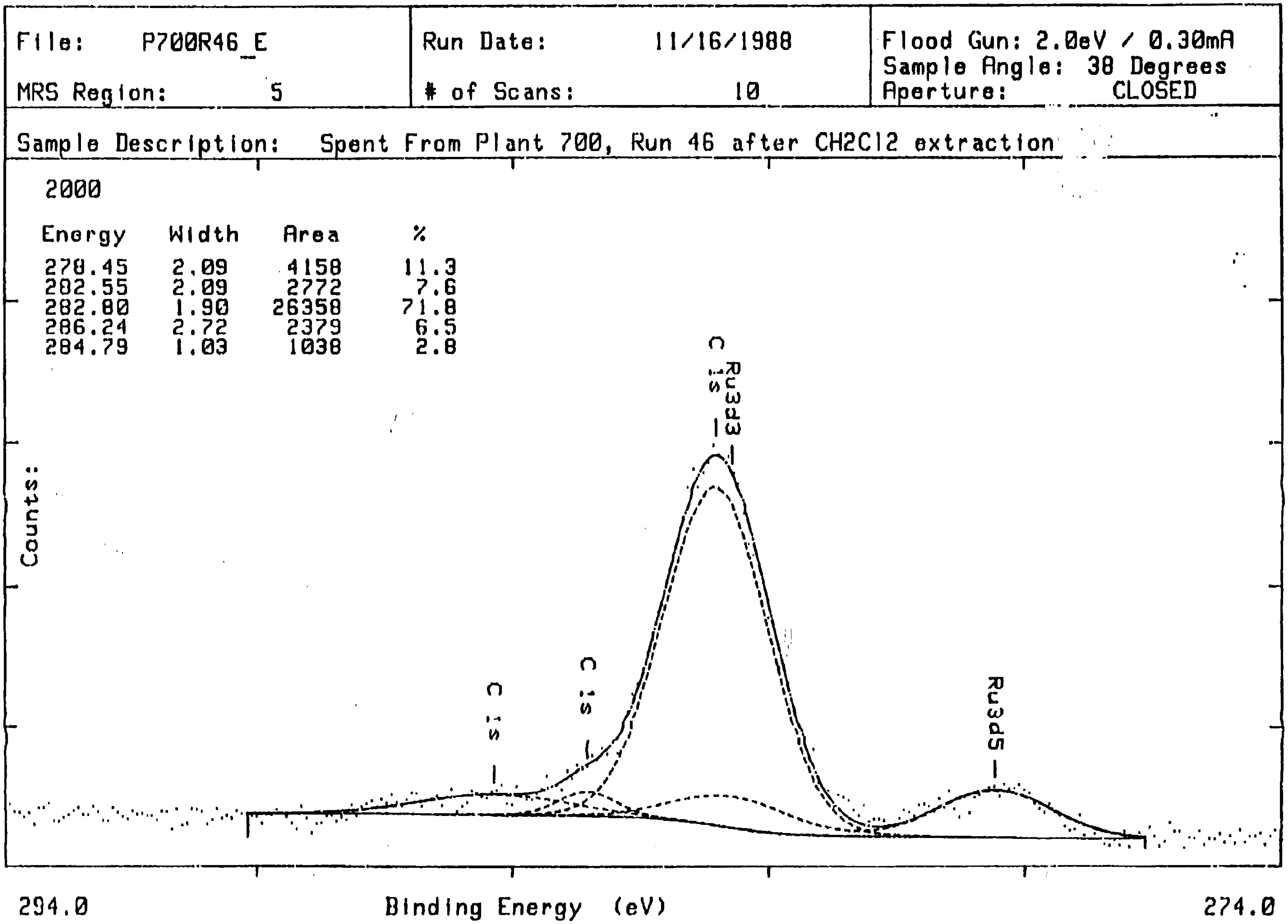
The O 1s binding energy was higher in the used catalysts relative to the fresh catalysts. The significance of this shift is not presently clear. Less oxyen was detected on the surface of the unmodified ruthenium catalyst probably because of the presence of a larger amount of carbon.

The Ru $3p_{3/2}$ binding energies were higher on the used catalysts relative to the fresh catalysts, possibly because of partial oxidation of ruthenium when the used catalysts were exposed to air before the XPS measurements.

The ruthenium surface concentration was 33% less in the used modified Catalyst 4966-180 relative to the fresh catalyst, while the decrease with use was 80% in the unmodified Catalyst 4966-198 Since there was no noticeable ruthenium agglomeration in the unmodified Catalyst 4966-198, the loss of ruthenium signal may be possibly attributed to the deposition of carbon over ruthenium.

There was ruthenium agglomeration in the modified Catalyst 4966-180 during the test. The loss of ruthenium signal from the surface of this catalyst during the test may be partly explained by ruthenium agglomeration. This, then,

Figure 5-322b: XPS Spectrum Around the C 1s Region for the Modified Ruthenium Catalyst 4966-180 Tested in Run 46 After Extraction with Cyclohexane, Toluene, Methylene Chloride/Methanol



File: P700R46_E

MRS Region: 5

Run Date: 11/16/1988

# of Scans: 10

Flood Gun: 2.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

Sample Description: Spent From Plant 700, Run 46 after CH2Cl2 extraction

2000

Energy	Width	Area	%
278.45	2.09	4158	11.3
282.55	2.09	2772	7.6
282.80	1.90	26358	71.8
286.24	2.72	2379	6.5
284.79	1.03	1038	2.8