Temperature	157°C
Pressure (total)	1-7 MPa
Methanol feed	42.2 mol/kg cat/hr
He (+N_2 trace)	776.4 mol/kg cat/hr
Zr_2/SO_4^{2-} weight	0.40 g

Figure 54 presents the space time yield of dimethyl ether (DME). It is clear that increasing the methanol pressure favored an increase in the dimethylether (DME) formation rate. The productivity of DME was in general higher when no competition with isobutanol was present. Upon returning to the original partial pressure of methanol, only minor deactivation of the catalyst was seen.

E. Pressure Dependence of Isobutanol Dehydration

The effect of pressure on the dehydration of isobutanol over ZrO_2/SO_4^{2-} in the absence of methanol was investigated. The following experimental conditions were used:

Temperature	157°C
Pressure (total)	0.1-3.04 MPa (1-30 atm)
Isobutanol feed	21.1 mol/kg catalyst/hr
He (+ N_2 trace) flow	800.7 mol/kg catalyst/hr
Catalyst weight	0.40 g

Figure 55 presents the space time yields of the major products of isobutanol dehydration, mostly isobutene and some *cis*- and *trans*-2-butene, as a function of isobutanol pressure. It is apparent that the isobutene production was strongly dependent on isobutanol pressure. As in the case of the dehydration reaction in the presence of methanol above, the formation of isobutene decreased with increasing alcohol pressure.

F. Dehydration of Isobutanol Only Over ZrO_2/SO_4^{2-}

The activity and selectivity of dehydrating isobutanol over the ZrO_2/SO_4^{2-} catalyst in the absence of methanol was investigated further. The activity and selectivity of the

Figure 54. Space time yields of products as a function of methanol pressure over the ZrO_2/SO_4^{2-} catalyst at 157°C, in the absence of isobutanol.

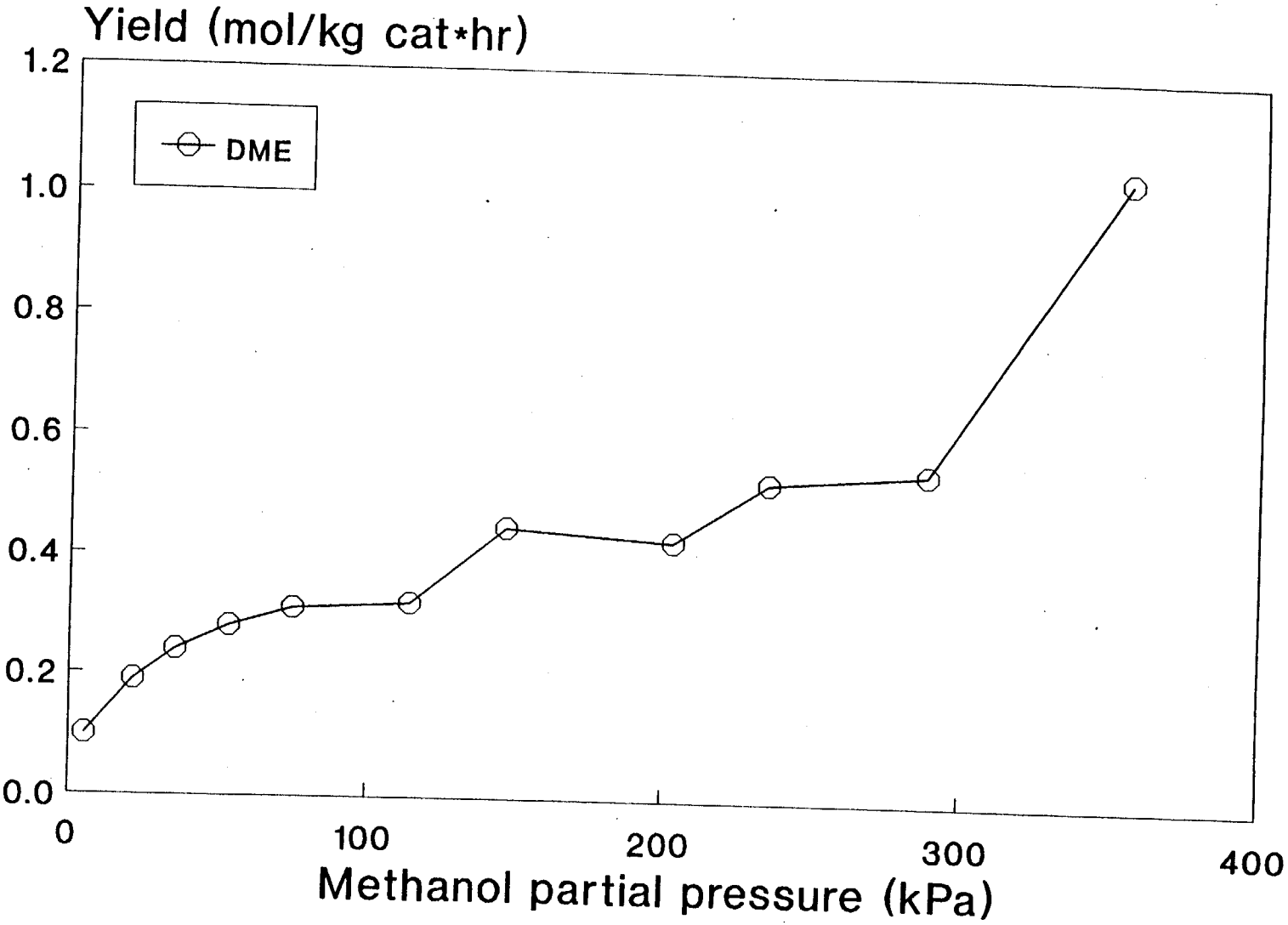
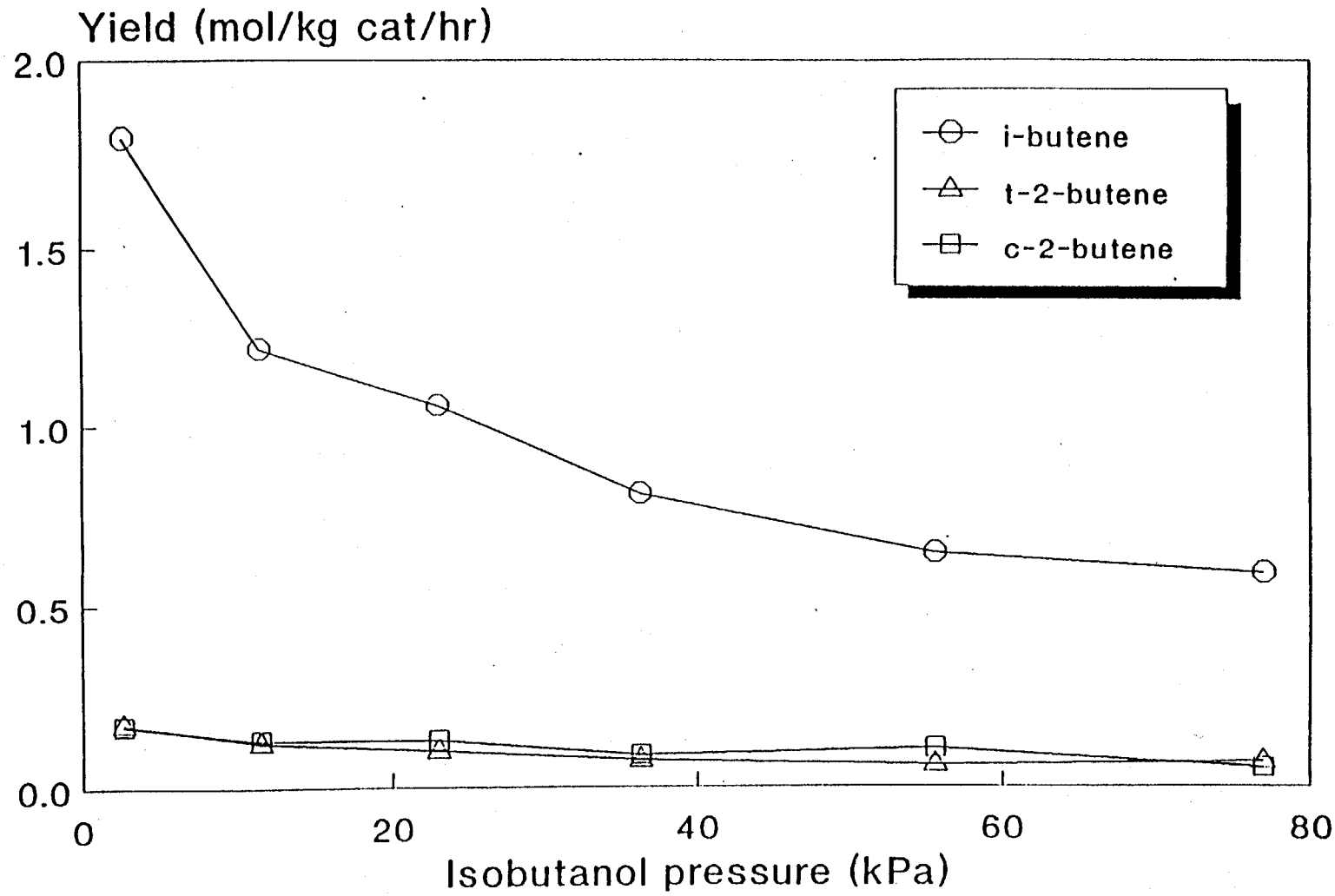


Figure 55. Space time yields of products as a function of isobutanol pressure over the ZrO_2/SO_4^{2-} catalyst at 157°C at 0.1-3.04 MPa, in the absence of isobutanol.



catalysts for isobutanol dehydration were obtained with respect to reaction temperature and reactant space velocity.

The ZrO_2/SO_4^{2-} catalyst calcined to 620°C was placed in the reactor and the following reaction conditions were utilized during the course of the investigation:

Temperature	125, 135, 150, 175, 200, 225°C
Pressure	0.1 MPa
Isobutanol feed	1.69-20.28 mol/kg catalyst/hr
He + N_2 flow	18.78 mol/kg catalyst/hr
Catalyst weight	5.0 g.

The isobutanol space velocity of 1.69 mol/(kg cat. hr) was used in an initial temperature dependence study from 125 to 175°C. At the temperature of 200°C, the isobutanol flow rate was raised sequentially to 6.76, 13.52, and 20.28 mol/(kg cat. hr). A final test was performed at 225°C using 20.28 mol/(kg cat. hr) of isobutanol. Testing was carried out for several hours at each point of temperature and space velocity. The only major products observed with the on-line GC analysis were isobutene, *trans*-2-butene, and *cis*-2-butene, while trace amounts of octenes and C_8 ethers were seen. At higher reaction temperatures, methanol and other products believed to be cracking products of isobutanol were seen, as was also observed for isobutanol dehydration over H-mordenite.

The yields of the major products under these conditions are presented in Figures 56A-56C. It can be seen that the predominant product was isobutene in each case and that high activity was achieved at 175°C while maintaining the high selectivity to isobutene (Figure 56A). As the temperature was increased from 125°C to 175°C, the total isobutanol conversion progressively increased from 13 to 85 mol% while the isobutene selectivity varied from 86 to 79 mol%. Increasing the space velocity of the isobutanol (Figure 56B) increased the yield of isobutene while also maintaining the isobutene selectivity at 80-81 mol%. The highest productivity of isobutene of 11.35 mol/(kg cat. hr) was obtained at 225°C and a flow

Figure 56a. Space time yields of products for the dehydration of isobutanol only over the ZrO_2/SO_4^{2-} catalyst as a function of temperature.

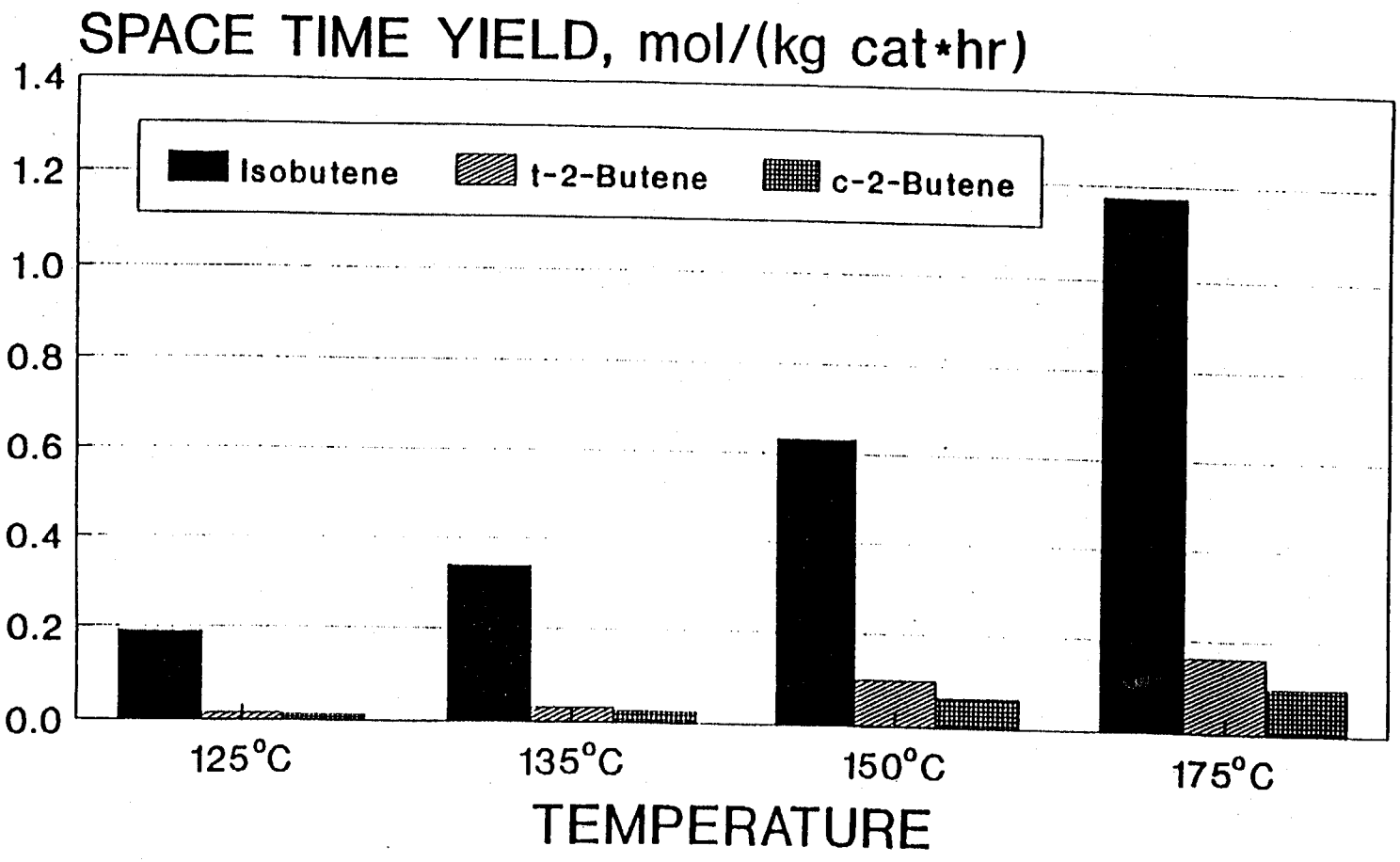


Figure 56b. Space time yields of products for the dehydration of isobutanol only over the ZrO_2/SO_4^{2-} catalyst as a function of gas hourly space velocity at 200°C.

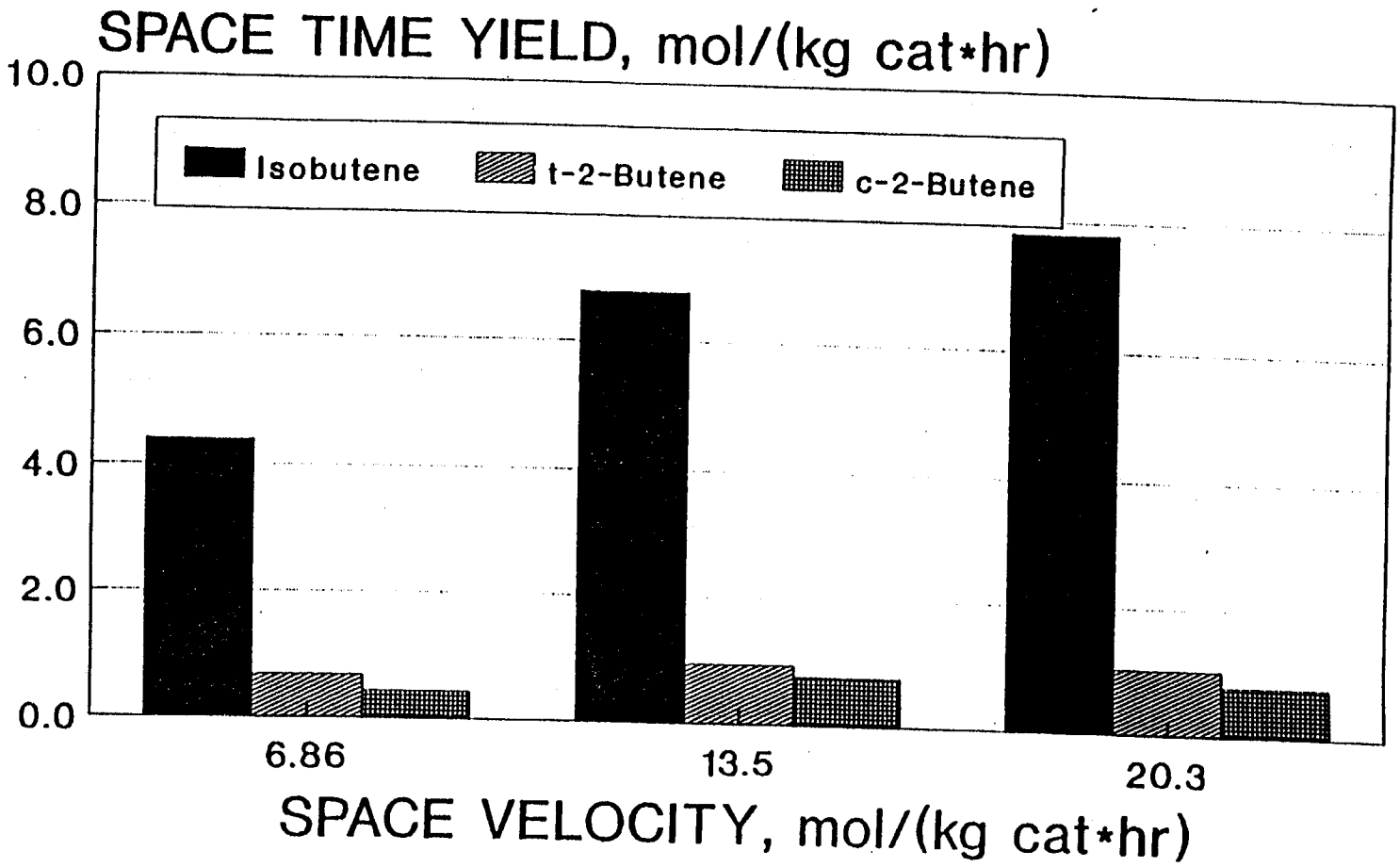
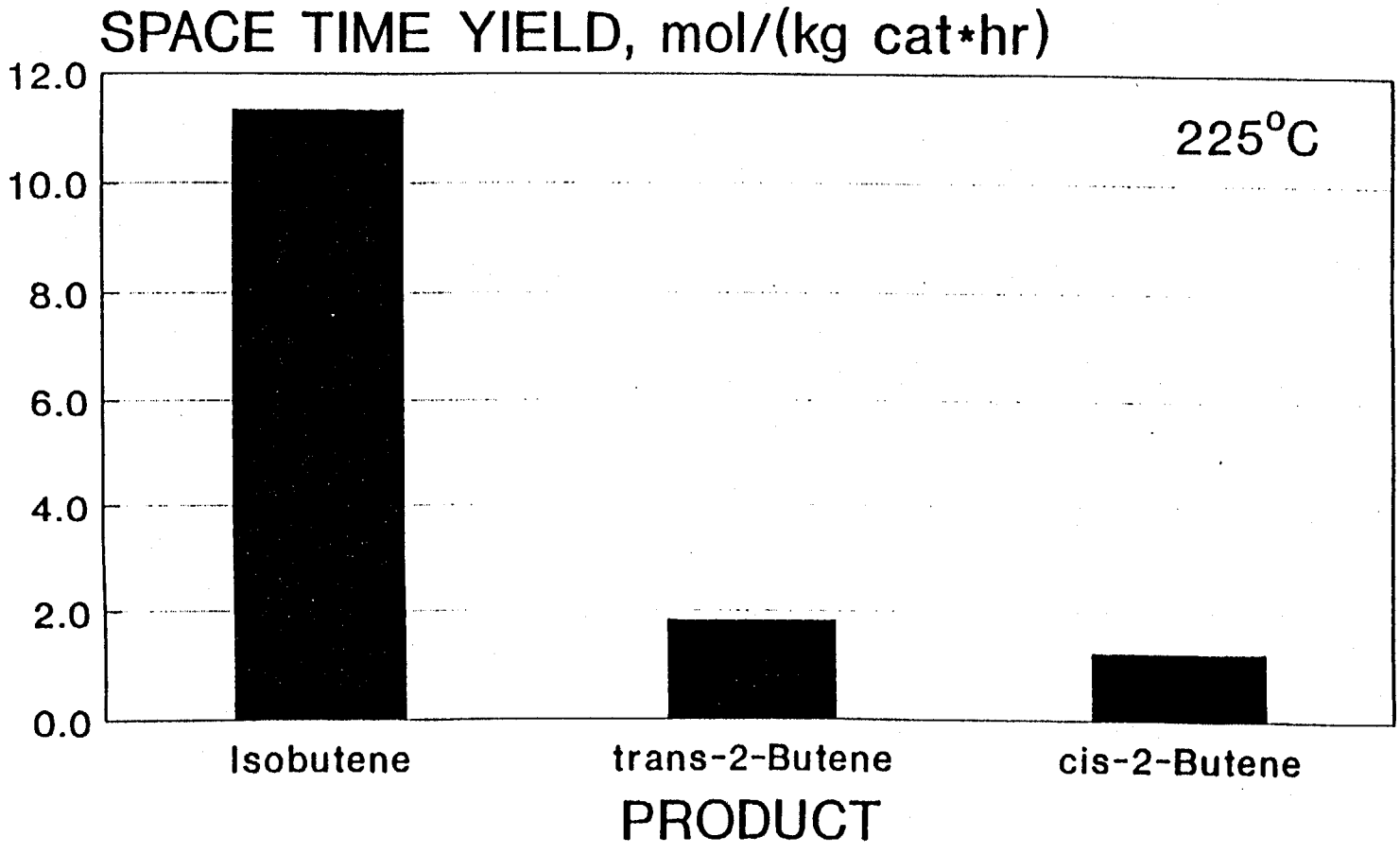


Figure 56c. Space time yields of products for the dehydration of isobutanol only over the ZrO_2/SO_4^{2-} catalyst at 200°C; isobutanol feed = 20.69 mol/kg cat/hr.



rate of 20.28 mol isobutanol/(kg cat. hr), as shown in Figure 56C. In this case, the selectivity of isobutene among the butenes at this high productivity was 79%. This space time yield can be compared with the highest reported value of isobutanol production from synthesis gas, which is claimed to be 10 mol/(kg cat. hr) (50). Thus, the dehydration of isobutanol to isobutene would not be a limiting step in an overall process of converting synthesis gas to MTBE.

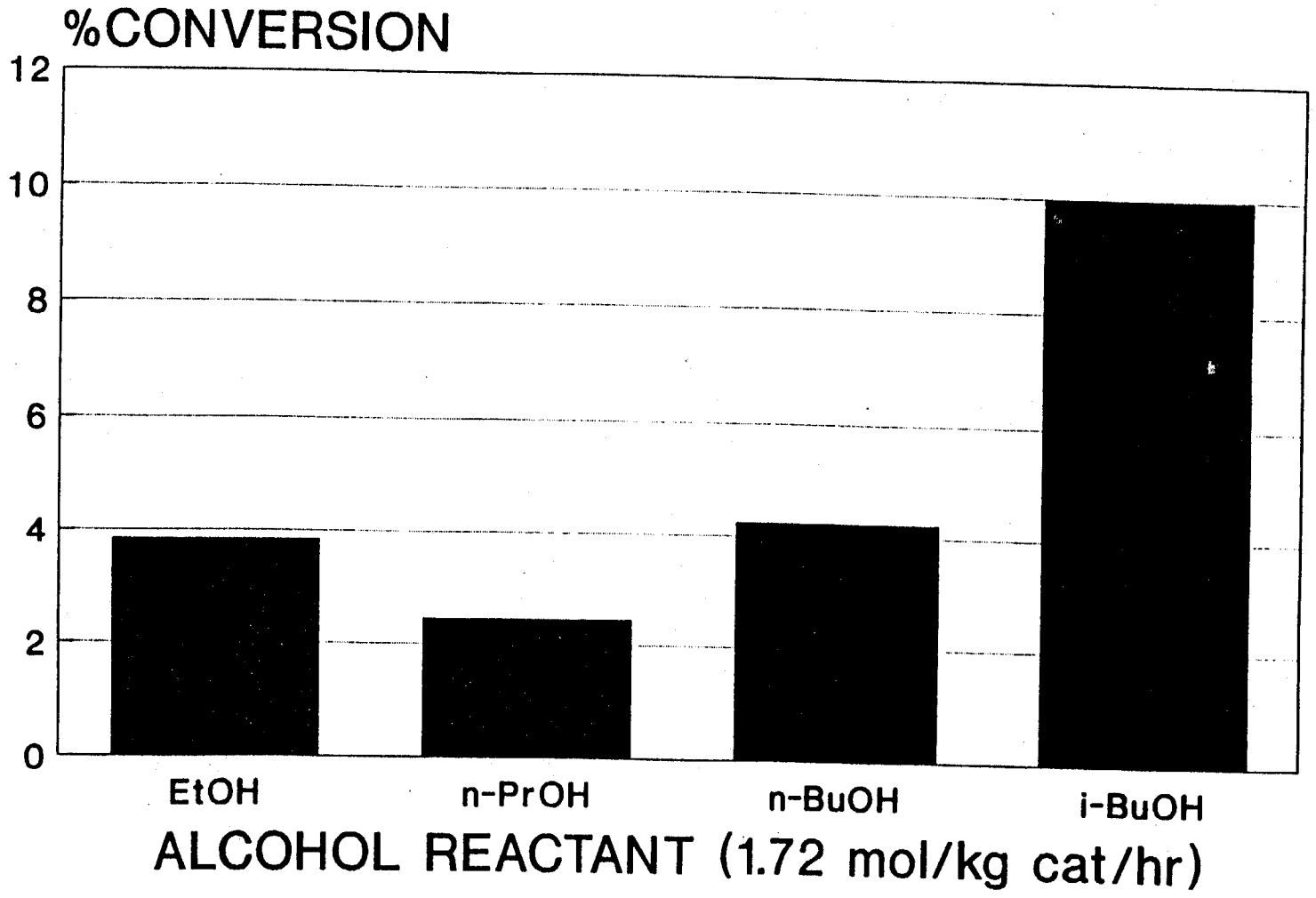
G. Dehydration of Primary Alcohols Over the ZrO_2/SO_4^{2-} Catalyst

In order to compare the ability of the 1% SO_4^{2-}/ZrO_2 catalyst to dehydrate linear alcohols with the dehydration of isobutanol to isobutene, a series of alcohols was individually passed over the catalyst under the usual standard reaction conditions that include an alcohol feed rate of 1.72 mol/kg catal/hr. In this series, the dehydration behavior of isobutanol can be compared with those of the linear primary C_2-C_4 alcohols, i.e. ethanol, n-propanol, and n-butanol. The conversion levels obtained at 157°C are shown in Figure 57. It is evident that the highest activity was shown by the isobutanol reactant and that an appreciably greater quantity of isobutanol was converted to isobutene than observed for the conversion of n-butanol to 1-butene. These results indicate that with a mixture of alcohols over this catalyst, the predominant initial reaction will be dehydration of isobutanol to isobutene, which then could subsequently couple with the other alcohols in the reactant mixture.

H. The Effect of Water on Reaction of MeOH/i-BuOH Over ZrO_2/SO_4^{2-}

A major product of any conversion of the methanol/isobutanol mixture over solid acid catalysts is water. The presence of water can influence the type of acid sites present, e.g. it can in principle convert Lewis acid sites into Brönsted acid sites. In addition, water may also retard the reaction, as was reported for alumina earlier in this report. This latter

Figure 57. Conversion of primary alcohols over the ZrO_2/SO_4^{2-} catalyst at 157°C, alcohol feed rate = 1.72 mol/kg cat/hr.



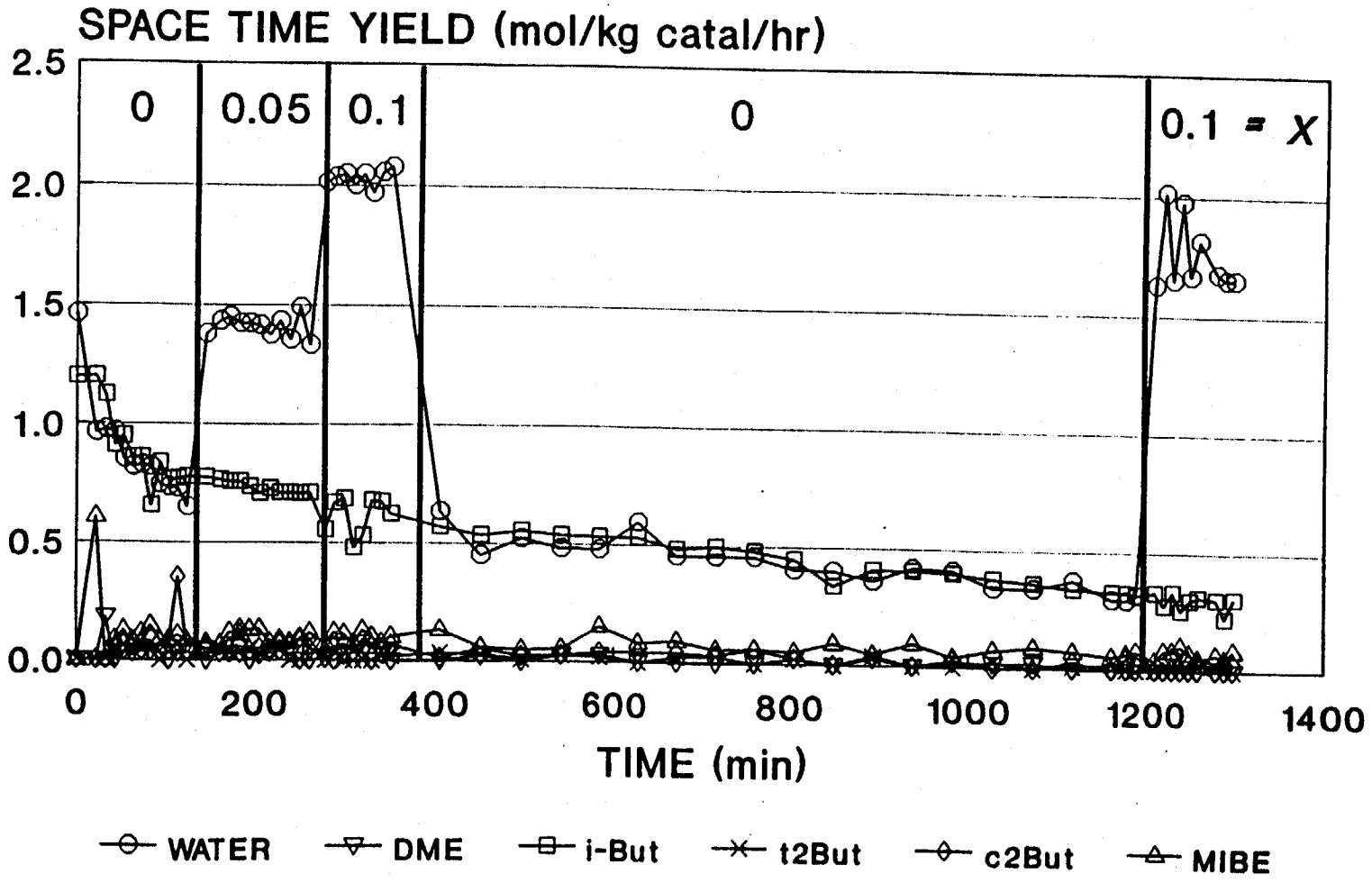
effect may arise from competitive adsorption of water and partial blockage of active sites. In the present experiment, reaction conditions were chosen where a 2/1 mixture of MeOH/i-BuOH was reacted over a 1% SO_4^{2-}/ZrO_2 catalyst at 157°C and 0.1 MPa within the differential regime as described previously. Specifically, the conditions were:

Temperature	157°C
Pressure	0.1 MPa
Water feed	0, 1.08, 2.16 mol/kg catalyst/hr
Methanol feed	43.3 mol/kg catalyst/hr
Isobutanol feed	21.6 mol/kg catalyst/hr
He + N_2 flow	762 mol/kg catalyst/hr
Catalyst weight	0.4 g

The catalyst was first exposed to the dry 2/1 MeOH/i-BuOH mixture, then to a MeOH/i-BuOH/H_2O = 2/1/0.05 mixture, followed by a 2/1/0.1 mixture. The feed was again switched to the dry 2/1 mixture and then back to the 2/1/0.1 MeOH/i-BuOH/H_2O mixture. The results of this experiment are shown in Figure 58. The high gas hourly space velocity (GHSV) of the carrier gas ensured low conversion levels of the reactants, e.g. at 100 hr on stream the conversion of isobutanol to products was about 4 mol% (≈3.7 %yield of isobutene). It can be seen from Figure 58 that the catalyst gradually and steadily deactivated with time on stream. However, the presence or absence of water in the feed under the reaction conditions employed did not affect the productiviry or selectivity of the products, which consisted mainly of isobutene.

Another experiment with a fresh catalyst was carried out wherein the catalyst was first exposed to the water-containing reactant mixture and then to the dry alcohol reactant mixture. No difference in the lack of a water-induced effect from the previous experiment was observed. These results differ from those observed earlier for alumina, where a strong inhibition, *ca.* 30%, in the production of DME, MIBE, and isobutene was noted. Those

Figure 58. Effect of water feed on reaction of methanol/isobutanol = 2/1 over the ZrO_2/SO_4^{2-} catalyst at 157°C and a total pressure of 0.1 MPa.



MeOH/i-BuOH/H_2O = *2/1/x* molar ratio

results with alumina were explained with the knowledge that alumina is known to possess strong acidity only in the form of Lewis acid sites that depend in number and strength on the degree of hydration of the surface. In the case of ZrO_2/SO_4^{2-}, however, Arata (51) has proposed that Lewis acid sites can be converted to strong Brönsted acid sites upon exposure to low partial pressures of water, e.g. 5 torr. In the present investigation, in the "dry" runs where the only water present was that formed as a product of the reaction, the partial pressure of water was less than 1 torr. In the "wet" runs, the partial pressure of water was about 3 torr. Under high conversion conditions, however, the water produced during reaction can reach rather high levels. This test showed that water did not suppress activity nor did it increase activity by creating additional Brönsted sites in the reaction environment utilized in this experiment.

VI. Characterization of the ZrO_2/SO_4^{2-} Catalyst

A. Surface Area of the ZrO_2/SO_4^{2-} Catalyst

The surface areas of the samples were determined by applying the BET/method of analysis at $p/p_o = 0.3$, where p = equilibrium pressure and p_o = the vapor pressure of N_2 at the temperature of the experiment (-196°C). First, the samples were degassed in a helium flow at 250°C, which in general took 30-45 min, depending on the sample size, where the sample weight ranged from 0.03 to 0.3 g. After the degassing procedure was completed, a helium/nitrogen gas mixture was allowed to pass over the sample. Adsorption of nitrogen occurred when the sample container was immersed in liquid nitrogen. The amount of N_2 adsorbed was monitored by measuring the decrease of nitrogen in the helium/nitrogen mixture, as determined by a thermal conductivity detector (TCD). After the adsorption of nitrogen was completed, the liquid nitrogen used for cooling was removed. Upon removal of the coolant, the adsorbed nitrogen started to desorb from the sample. The amount desorbed was also monitored by a TCD.

Calibration of the TCD was performed by injecting a known amount of pure nitrogen gas. It should be noted that this procedure is a single point determination which is not as good as a multipoint determination but usually gives a good approximation of the surface area.

Surface area was determined for non-sulfated zirconia calcined at 620°C and for sulfated zirconia calcined at 100 and 620°C, the results are given in Table 18. The addition of sulfate groups to zirconia dramatically increased the surface area. However, the surface area for sulfated zirconia was strongly dependent on the calcination temperature. Sulfated zirconia has been reported to have a surface area of 65-85 m^2/g (1). Our result, 60.2 m^2/g, is in good agreement. Tanabe et al. also reported that if ammonium sulfate were used as

the sulfate source instead of sulfuric acid, a higher surface area (e. g. ~120 m^2/g) can be obtained (1). The preparation procedure is, however, more complex when ammonium sulfate is used as the sulfate source.

Table 18. Surface Areas Determined by Nitrogen Absorption/Desorption

Catalyst	Surface Area (m^2/g)
ZrO_2 (620°C)	<10
ZrO_2/SO_4^{2-} (620°C)	55
ZrO_2/SO_4^{2-} (100°C)	11

The effect of calcination temperature on the surface area of sulfated zirconia was also investigated. It was found that the surface area of the sulfate-modified zirconia decreased as the calcination temperature increased, as shown in Table 19. The reduction in surface area can be attributed to sintering of the catalyst by agglomeration of small particles to form larger particles. The agreement between the BET single point and multipoint methods of analysis is very good. However, the reasons for the much higher values determined by the Langmuir method of data analysis are unknown at this time. The effect of surface area on the catalytic properties of these catalysts, as well as stability of the catalysts under reaction conditions, will be investigated in the successor to this project.

Table 19. Surface Area of the Sulfated Zirconia *vs* Calcination Temperature

Calcination Temp. (°C)	Langmuir (m^2/g)	BET Single Point (m^2/g)	BET Multipoint (m^2/g)
350	379	225	232
455	334	200	205
551	248	146	150
620	181	105	108
720	58	36	37

B. Calculation of the Amount of Sulfur on Sulfated Zirconia

The amount of sulfur on the surface of sulfate modified zirconia has been calculated from data obtained from elemental analysis. The elemental analyses were performed by Galbraith Laboratories, Inc. The results from the two samples that were analyzed were in good agreement, as shown in Table 20. The analytical data from sample number 1 were used to calculate the surface coverage of sulfur on zirconia. Assuming that the zirconia has a body-centered tetragonal structure and that the (100) plane is the surface plane, there would be 5.2×10^{18} ZrO_2/m^2. Assuming that all of the sulfate is on the surface, the amount of sulfur corresponds to 0.55 monolayer.

Table 20. Result of elemental analysis

Sample number	Zirconium (weight %)	Sulfur (weight %)
1	71.33	0.84
2	69.97	0.96

C. Determination of Acidity *via* Aqueous Titration of ZrO_2/SO_4^{2-}

Characterization of the ZrO_2/SO_4^{2-} catalyst included an attempt to determine the number of accessible acid sites in terms of milliequivelents per gram of catalyst, i.e. meq/g. The concentration of sulfur was determined, *via* elemental analysis, to be 0.26 and 0.30 mmol/g for two separate preparations, samples 1 and 2 above. Calcined ZrO_2/SO_4^{2-} is known to possess both Lewis and Brönsted acidic sites. In this study, a suspension of ZrO_2/SO_4^{2-} in water, as well as a Na^+ ion-exchanged sample, were titrated with standard solutions of NaOH to determine the acid content of the catalyst.

A Markson model 88 pH meter was used for determination of pH during the titration

experiments. The NaOH solutions were standardized against known amounts of potassium hydrogen phthalate from Aldrich. In the first experiment, a 2.3095 g sample of ZrO_2/SO_4^{2-} previously calcined to 620°C and containing 0.30/mmol S/g was suspended in *ca.* 40 ml of distilled water. The electrode of the calibrated pH meter was immersed in the aqueous suspension to be titrated. Small volumetric additions from a buret containing 0.07965 N NaOH solution were added to the suspension while recording both the volume of NaOH solution added and the resultant pH of the aqueous suspension. It was noticed that long equilibration times were necessary following NaOH additions, i.e. 1-2 hr. When the titration was close to the neutralization point, i.e. pH of 7, the beaker containing the suspension was covered tightly with parafilm and stirred for three days to equilibrate. Following this period, the titration was continued. In total, 8.17 ml of 0.07965 N NaOH solution were needed to neutralize the suspension with the 2.3095 g sample of ZrO_2/SO_4^{2-}. The following calculation determined the number of acid sites titrated in the experiment:

$$8.17 \text{ ml} \times (0.07965 \text{ meq/ml}) \times (1/2.3095 \text{ g}) = 0.28 \text{ meq/g}.$$

In light of the extensive equilibration times necessary to achieve stable pH readings in the above experiment, an alternative method of acid site determination was utilized. Forni described the method of adding excess NaCl to exchange with H^+ on the surface of catalysts in cases of long equilibration titrations (53). The HCl solution thus formed is easily titrated with base. Approximately 30 ml of a 5% NaCl solution by weight was added to 2.3036 g of ZrO_2/SO_4^{2-}, and this was allowed to stir overnight. The solution was then titrated with 0.1051 N NaOH solution while measuring its pH with the meter. With this method, equilibration was fast, within about a minute at each point. The total volume of 0.1051 N NaOH needed to neutralize the HCl solution was 6.3 ml. The acidity of the ZrO_2/SO_4^{2-} was determined to be:

$$6.30 \text{ ml} \times (0.1051 \text{ meq/ml}) \times (1/2.3036 \text{ g}) = 0.29 \text{ meq/g}.$$

This was approximately the same value as that found for the direct titration of the aqueous suspension. As the concentration of sulfur, existing as SO_4^{2-}, was 0.3o/mmol/g, it appears that there is one Brönsted acid site, under wet conditions, for each sulfate group on the surface. This result indicated that sulfuric acid, which would have two Brönsted protons per sulfate, is not reformed by the addition of water to the catalyst.

D. Catalyst Characterization using X-Ray Photoelectron Spectroscopy (XPS)

Nafion-H was exchanged to its potassium form, designated Nafion-K. To achieve the ion exchange, 10 g of Nafion-H was immersed in 75 ml of 1 M potassium nitrate (KNO_3) and stirred for approximately 45 min. The solution was strongly acidic due to the exchange of H^+ for K^+. A new portion of potassium nitrate was added after the previous was decanted and the catalyst was washed with distilled water. The procedure was repeated until full exchange was reached, as determined by testing the pH of the exchange solution. Four portions of KNO_3 were needed for total exchange of the Nafion-H. Amberlyst-15 was exchanged in the same manner, except ten portions of KNO_3 was required. The higher exchange capacity per weight of Amberlyst-15 *vs.* Nafion-H explains this requirement. Finally, the Nafion-K and K-exchanged Amberlyst-15 were washed in distilled water and allowed to dry overnight at 90°C. XPS measurement of Amberlyst-15, Nafion-H and sulfated zirconia have been conducted to investigate the oxidation state of elements, as well as their relative concentration.

Amberlyst-15 and potassium exchanged Amberlyst-15 were ground to fine powders that were placed on pieces of silver foil mounted on sample holders. Sulfated zirconia was used as prepared and placed on silver foil as described above. Neither Nafion-H nor

potassium exchanged Nafion-H could be prepared using this technique. Instead, each resin was placed on a piece of aluminum foil covered with silver paint and pressed using a pressure of 18-20 tons for 15 min. to give a smooth continuous surface to analyze.

Amberlyst-15 is a poly(styrene-divinylbenzene) polymer that has been sulfonated with sulfuric acid. The only oxygen atoms present in this copolymer are in the sulfonyl group. XPS data showed that indeed the ratio of oxygen to sulfur was about 3:1 as calculated by using the intensity and sensitivity factors for the elements. Sensitivity factors used for O 1s and S 2p were 2.85 and 1.679, respectively. The potassium exchanged Amberlyst-15 showed a ratio of sulfur to potassium of about 1/1, which confirmed that the resin was 100% exchanged and no acid sites were present. The K 2p lines were used for potassium and the sensitivity factor used was 3.97.

Nafion-H has additional oxygen atoms in ether linkages to the fluorocarbon backbone, and the ratio of oxygen to sulfur was experimentally found to be about 7/1. Potassium exchanged Nafion-H has no catalytic activity as mentioned earlier in this report. The lack of acid sites was confirmed by a ratio of sulfur to potassium of 1/1. It was also determined that the different oxygen atoms in Nafion-H can be distinguished from one another by a slight shift in binding energy.

Sulfated zirconia has at least two different "types" of oxygen, which is demonstrated in Figure 59 as a shoulder on the main oxygen peak. The two maxima within the oxygen peak are about 2 eV apart; although this peak is very broad this follows the pattern described by Arata (51), where the shoulder refers to oxygen in the sulfate group and the peak at lower binding energy corresponds to oxygen of the zirconia. Sulfur was reported to appear at 169.3 eV (51) and that is approximately where the sulfur peak in this sample was observed (Figure 60). This binding energy for sulfur corresponds very well with the binding

Figure 59. XPS of the oxygen 1s region of the ZrO_2/SO_4^{2-} catalyst.

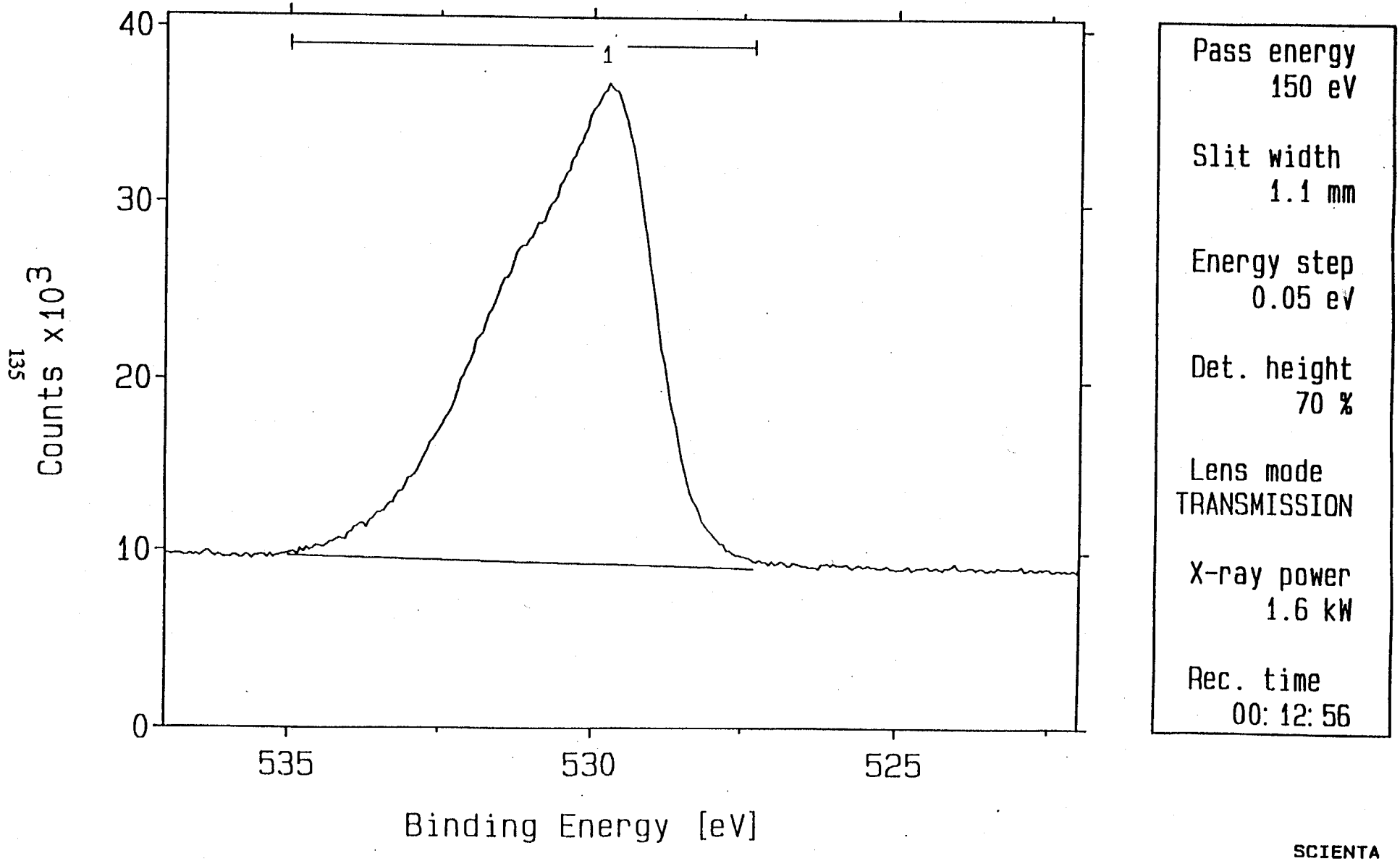


Figure 60. XPS of the sulfur 2p region of the ZrO_2/SO_4^{2-} catalyst.