at 90°C, except for the H-mordenite catalyst that is active and selective for methanol dehydration to DME. Higher temperatures are needed for significant alcohol dehydration with inorganic catalysts. In general, the organic polymeric catalysts are unstable at these higher temperatures, i.e. 120-140°C.

The yields of DME observed for the inorganic catalysts followed the order H-mordenite $>$ montmorillonite $\approx$ SiO_2/Al_2O_3 $\approx$ ZrO_2/SO_4^{2-} $>$ γ-Al_2O_3. The relative order of space time yields of isobutene production followed the order ZrO_2/SO_4^{2-} $>$ SiO_2/Al_2O_3 $>$ montmorillonite $>$ H-mordenite $\approx$ γ-Al_2O_3. The selectivity behavior of the H-ZSM-5 zeolite catalyst was very strongly dependent on the reaction temperature. Probably, the most important finding of the inorganic catalyst testing is the remarkable selectivity properties of H-mordenite and ZrO_2/SO_4^{2-}. The ability of these catalysts to selectively dehydrate either methanol or isobutanol in a mixture containing both alcohols was unexpected. Even at near total conversion of one of the alcohols, the other alcohol remains essentially unconverted. The use of ZrO_2/SO_4^{2-} may lead to a new process where methanol/isobutanol streams, the major products of higher alcohol synthesis over alkali/Cu/ZnO catalysts, can be selectively dehydrated to methanol/isobutene streams that are the current feedstocks for industrial MTBE production.

C. Dehydration of Alcohols Over Silica and Zirconia Supported PW_{12} Heteropolyacid NO_2O_5, and $Fe/Mn/ZrO_2/SO_4^{2-}$ Catalysts

Supported heteropolyacids are used as heterogenous catalysts in several industrial applications. They are reported to possess strong acidic character, as well as unique selectivity characteristics. The activities and selectivities of silica-supported and zirconia-supported phosphotungstic acid, designated herein as PW_{12}/SiO_2 and PW_{12}/ZrO_2, for the standard reaction of a 1/1 molar MeOH/i-BuOH mixture were investigated. In addition, niobic acid ($Nb_2O_5.xH_2O$) and iron-and manganese-doped sulfate modified zirconia catalysts were tested for catalytic activity.

The <u>silica-supported phosphotungstic acid catalyst</u> was prepared using $H_3PW_{12}O_{40}$, obtained from Fisher Scientific, Co. This compound is also sometimes referred to by others as tungstophosphoric acid or 12-polytungstophosphoric acid. Silica gel was obtained from Davison and had the following properties: Davisil grade 646, 35-60 mesh, surface area = 300 m^2/g, pore volume = 1.15 cm^3/g, and 150 Å pore size. An aqueous solution consisting of 5 g of phosphotungstic acid in 23 ml of distilled water was prepared. A 20 g portion of the silica was impregnated with this solution, with constant mixing, to make a 20% loading of phosphotungstic acid by weight. The impregnated silica, PW_{12}/SiO_2, was placed in a 100°C oven overnight. A sample of this material calcined to 200°C was also prepared. These calcination temperatures were chosen because they are below the decomposition range reported for heteropolyacids.

The <u>zirconia-supported phosphotungstic acid catalyst</u>, designated herein as PW_{12}/ZrO_2, was prepared in a similar manner. An aqueous solution consisting of 1.68 g of phosphotungstic acid in 5.5 ml of distilled water was prepared, and 6.72g of Zr(OH), prepared from hydrolyzed $ZrOCl_2{\cdot}8H_2O$, was impregnated with this solution, with constant mixing, to make a 20% loading of phosphotungstic acid by weight. The impregnated zirconium hydroxide, $PW_{12}/Zr(OH)_4$, was placed in a 100°C oven overnight and then calcined to 300°C for 3 hr.

"Niobic acid", actually hydrated niobium oxide ($Nb_2O_5{\cdot}xH_2O$), was calcined at 200°C for 2 hr. A literature report indicates that high surface area and strong acidity are maintained only with low calcination temperatures such as this (42).

Recently, an iron and manganese doped sulfate-modified zirconia catalyst

($Fe/Mn/ZrO_2/SO_4^{2-}$) has been reported to possess stronger and more populous acid sites than ZrO_2/SO_4^{2-} (43). This catalyst was also reported to be many times more active for the low temperature isomerization of butane.

The $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst was prepared according to the method described in Ref. 31. This involved first dissolving 73 g of $ZrOCl_2 \cdot 8H_2O$ in *ca.* 100 ml of distilled water. About 700 ml of aqueous ammonia was added, and the solution was stirred for 2 hr. The $Zr(OH)_4$ formed was filtered and washed with distilled water until free of chloride ion. This solid was put in an oven at 100°C overnight to dry. The solution used to impregnate the $Zr(OH)_4$ consisted of 1.133 g $(NH_4)_2SO_4$, 2.234 g of $Fe(NO_3)_3 \cdot 9H_2O$, and 0.658 g of a 51 wt% solution of $Mn(NO_3)_2$. These salts were dissolved in distilled water to make 26.5 ml of a solution that was used to impregnate 25 g of $Zr(OH)_4$. The impregnated catalyst was dried in a 110°C oven overnight followed by calcination at 620°C for 3 hr. The catalyst preparation was designed to give 1.5% Fe, 0.5% Mn, and 4.0% SO_4^{2-} by weight supported on ZrO_2.

Catalytic Testing Results

The samples were diluted with Pyrex beads, charged to the reactor, and tested using the following reaction conditions:

Temperature	90, 125, 150, 175°C, (also 200 and 225°C)
Pressure	0.1 MPa
Methanol feed	1.72 mol/kg catalyst/hr
Isobutanol feed	1.72 mol/kg catalyst/hr
He + N_2 flow	16.0 mol/kg catalyst/hr
Catalyst weight	5.0 g

The results, presented as the space time yields of the major products as a function of reaction temperature, are given in Figures 29 and 30 for the catalysts prepared at the 100 and 200°C calcination temperatures of PW_{12}/SiO_2. The results are identical for the two

Figure 29. Space time yields of products over the PW_{12}/SiO_2 catalyst calcined at 100°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

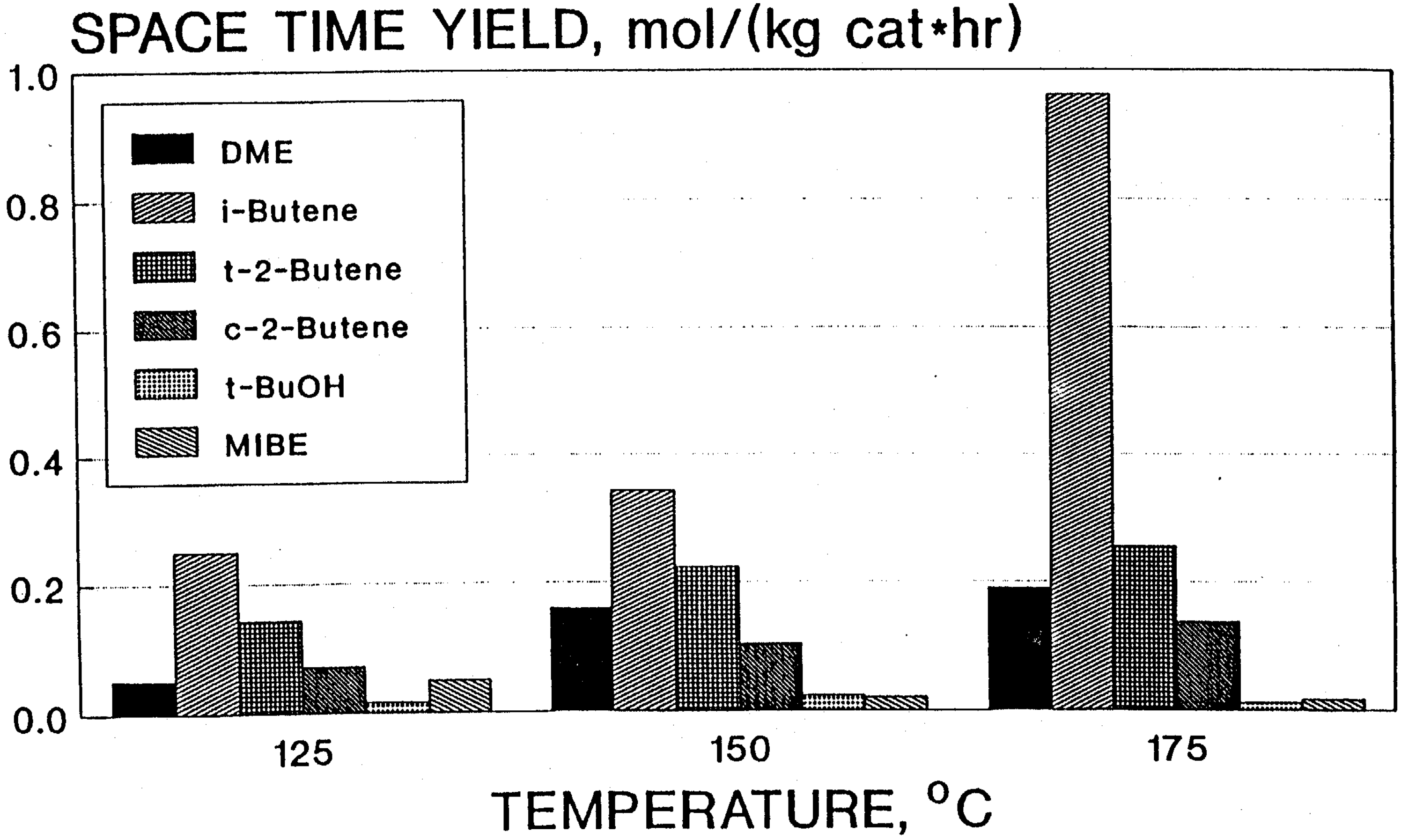
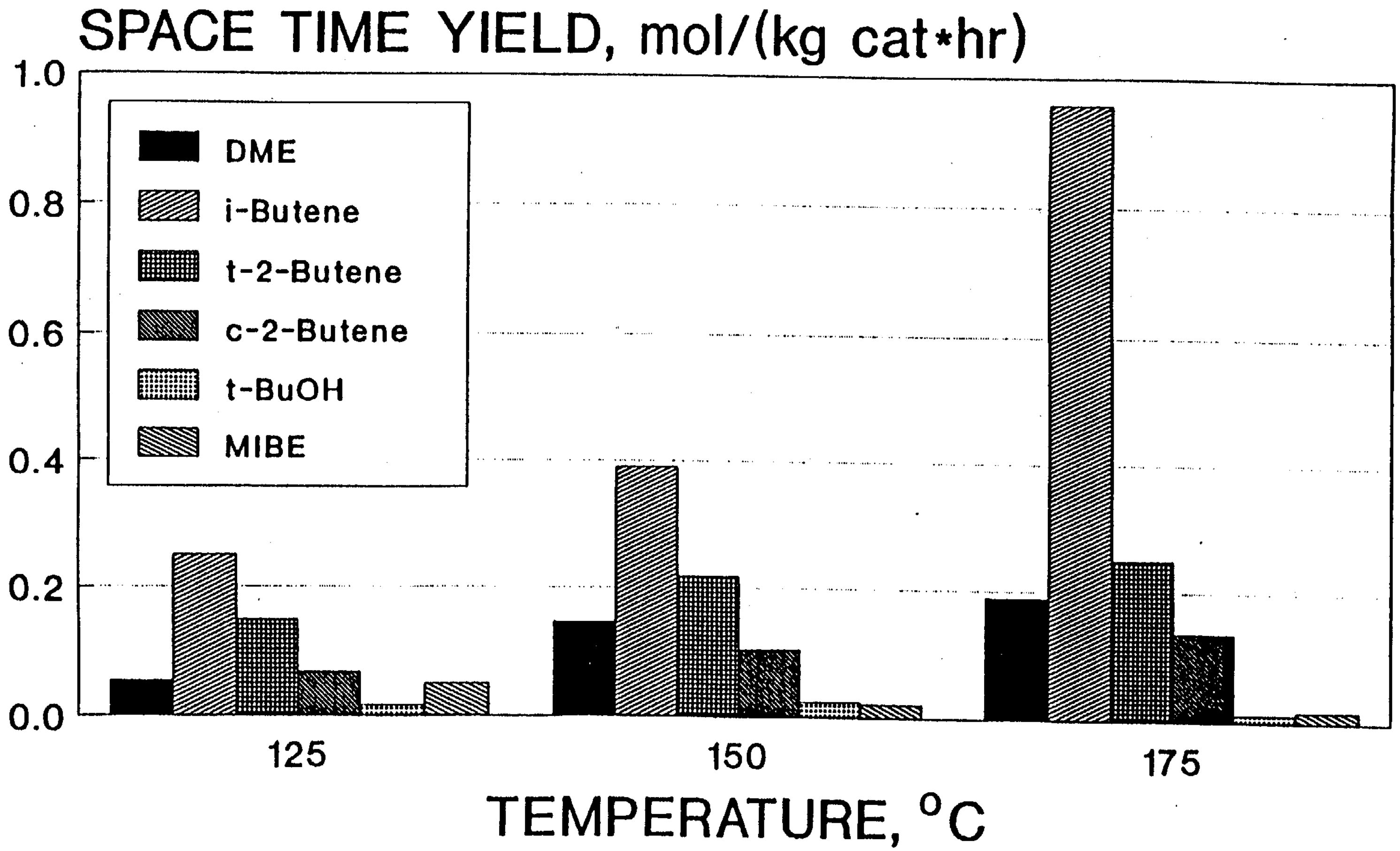


Figure 30. Space time yields of products over the PW_{12}/SiO_2 catalyst calcined at 200°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.



catalyst samples. No activity was found at a reaction temperature of 90°C. The activity and selectivity of PW_{12}/SiO_2 was comparable with the silica-alumina catalyst tested previously, with isobutene being the most selective product at 175°C. However, the ZrO_2/SO_4^{2-} catalyst remains as the most active and selective of all catalysts in the standard test screenings for the reaction of the MeOH/i-BuOH mixture. The presence of t-BuOH (cf. Figures 29 and 30) indicates that some of the isobutene product had been hydrated over this catalyst.

The zirconia-supported heteropolyacid catalyst, PW_{12}/ZrO_2, exhibited low activity and poor selectivity, as indicated in Figures 31-33, relative to other catalysts tested previously. This is especially true with respect to the SO_4^{2-}/ZrO_2-based catalyst. As shown in Figure 31, isobutene is the principal product formed with a space time yield of 0.254 $mol*kg^{-1}*hr^{-1}$, while the rate of production of DME was 0.147 $mol*kg^{-1}*hr^{-1}$. This means that more methanol was converted to DME than the quantity of isobutanol that was converted to isobutene. However, based on the quantities of products formed, the molar selectivities were 29.2% DME, 50.5% isobutene, 8.5% *trans*-2-butene, 8.0% *cis*-2-butene, and 3.8% MIBE.

The overall conversions at 175°C corresponded to 20.7 mol% conversion of isobutanol to products and 18.2 mol% of methanol to products. The %yields are shown in Figure 32, and these are based on the conversion levels of the reactants. For comparison purposes, the %yields are shown in Figure 33 on the basis of product molar composition, where the only difference between Figures 32 and 33 are in the values of DME since DME contains two methyl groups, as already discussed. Earlier, it had been found that pure ZrO_2 was totally inactive for these reactions. Therefore, the activity of the PW_{12}/ZrO_2 catalyst can be attributed to the presence of the phosphotungstic acid ($H_3PW_{12}O_{40}$).

Figure 31. Space time yields of products over the PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

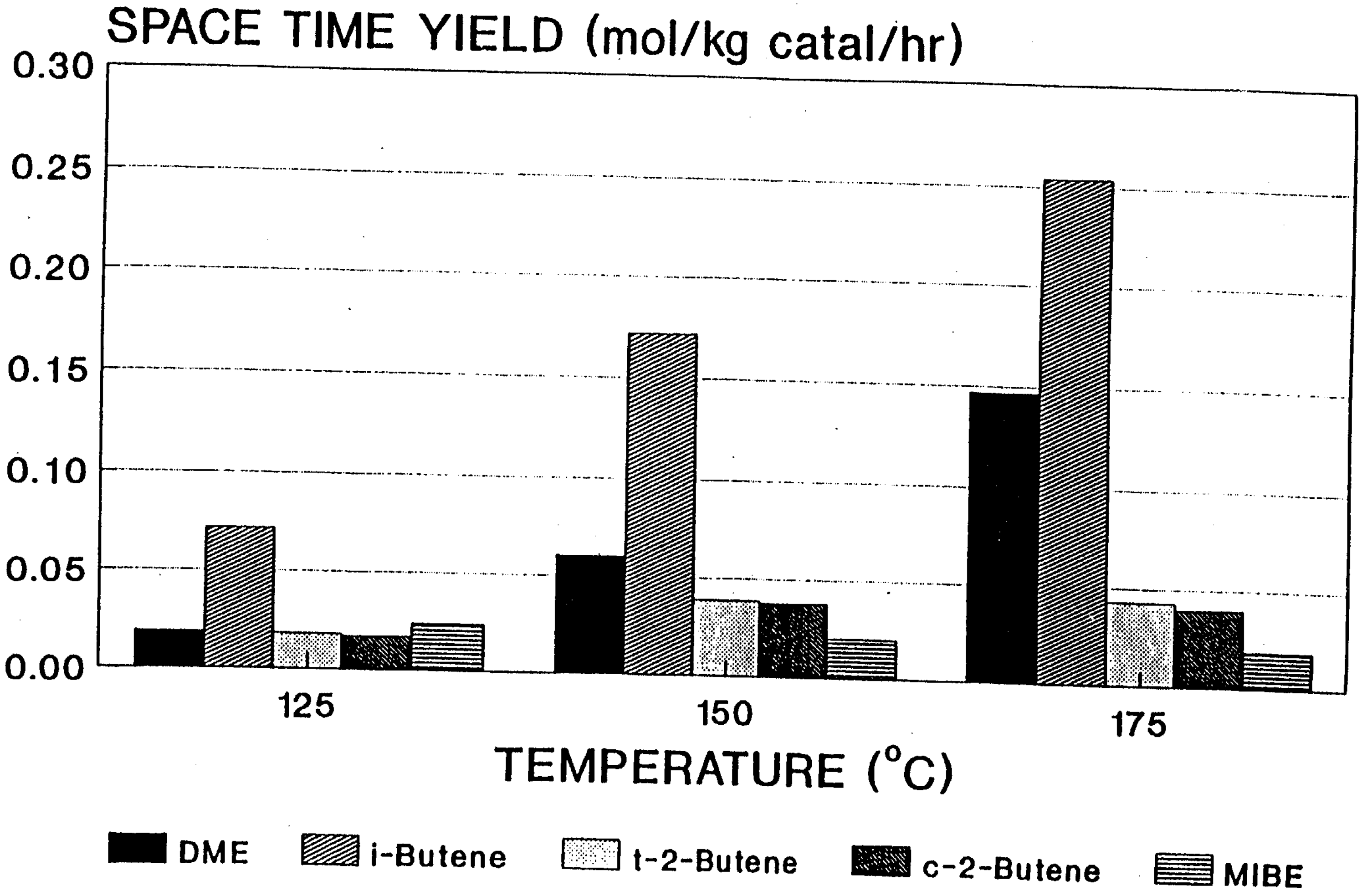


Figure 32. Percent yields of products (based on reactant conversions) over the PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

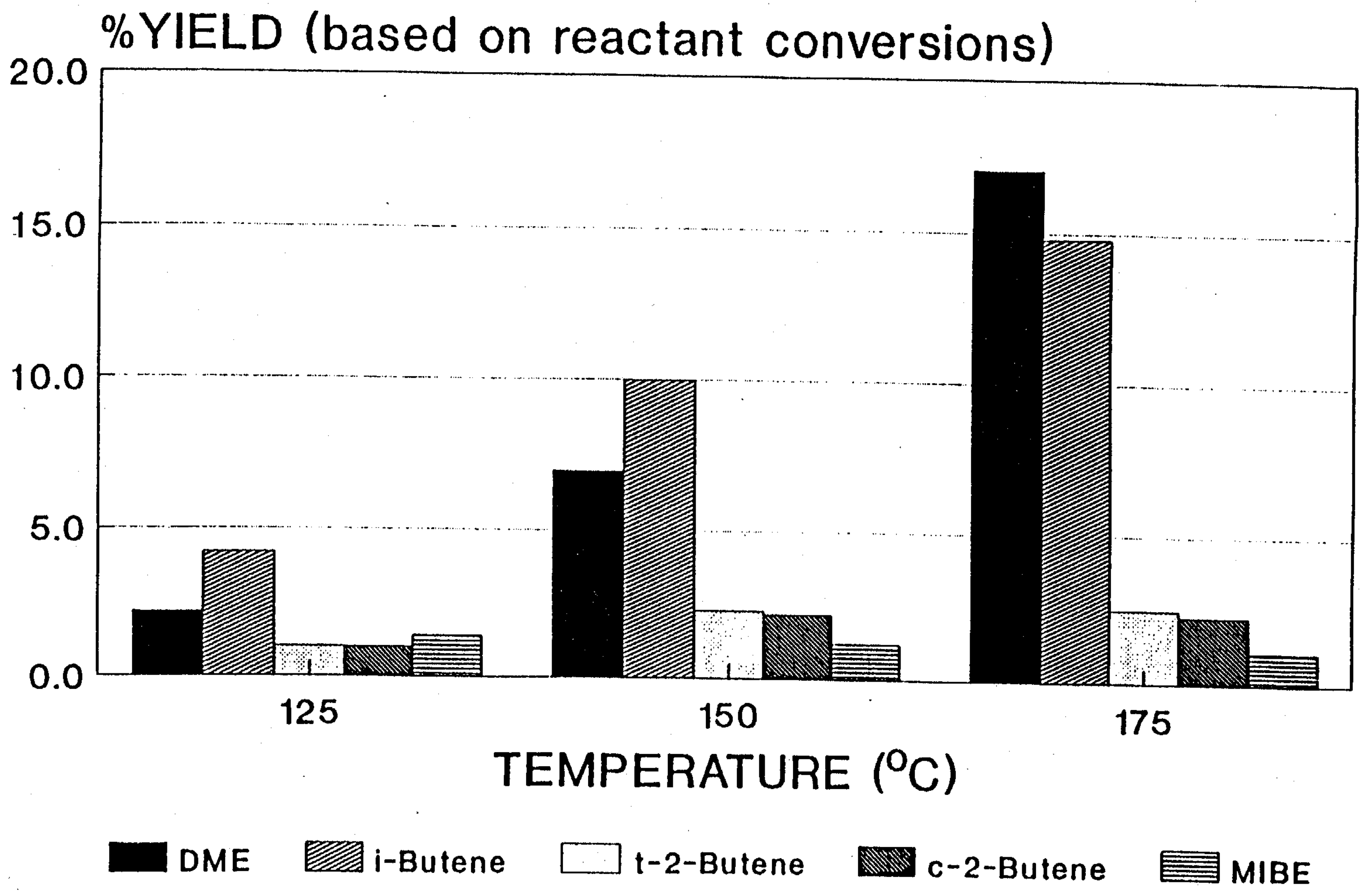
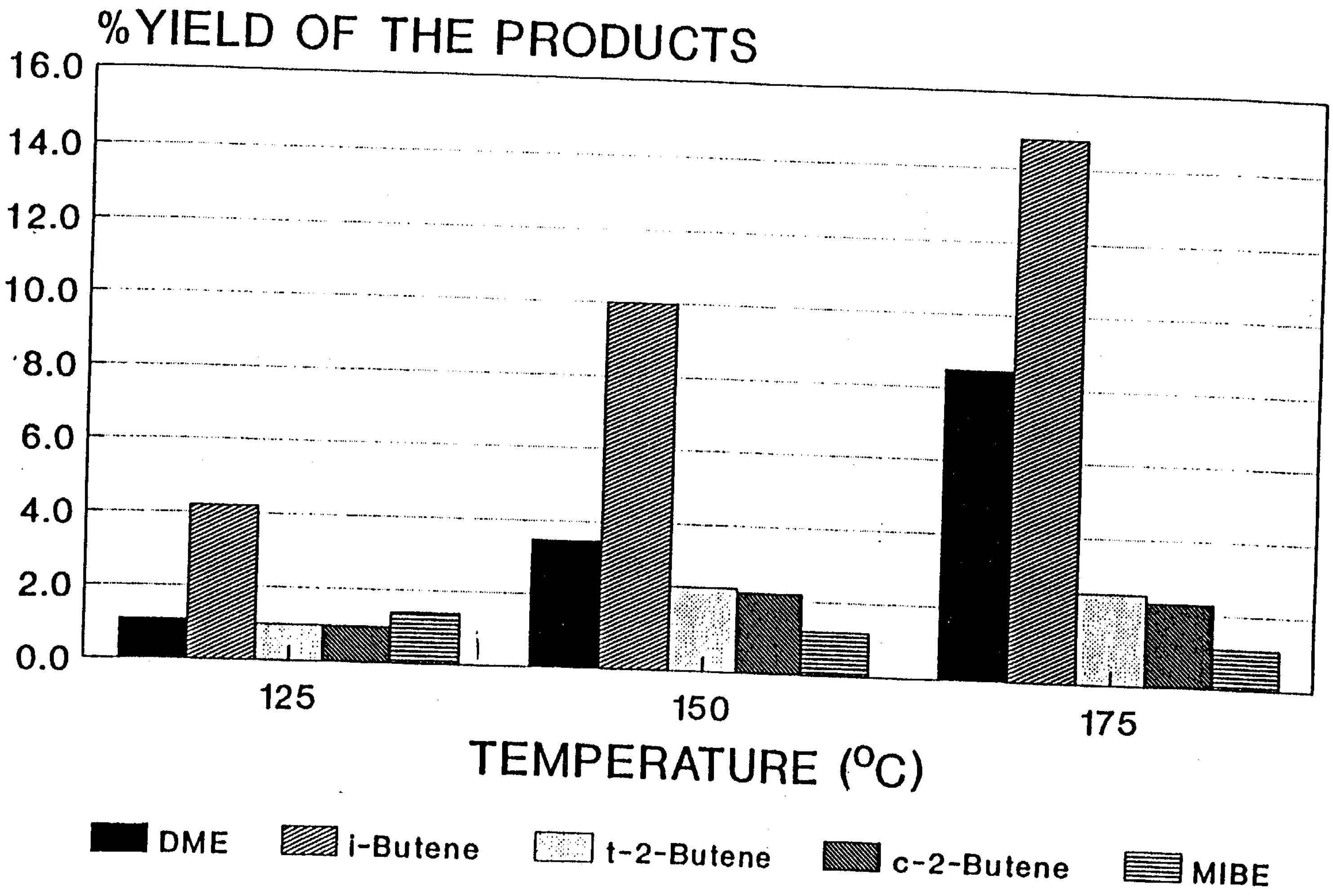


Figure 33. Percent yields of products over the PW_{12}/ZrO_2 catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.



The niobic acid catalyst was essentially inactive at and below 175°C, as shown in Figures 34 and 35. At 200°C, the methanol and isobutanol conversions levels were 9.3 and 10.5%, respectively. When higher temperatures were used, most notably at 225°C, the activity and selectivity approached that seen for the best catalyst tested so far, the ZrO_2/SO_4^{2-} catalyst. At 225°C, as shown in Figure 34, this niobic acid catalyst produced 1.0 $mol*kg^{-1}*hr^{-1}$ of isobutene and only 0.13 $mol*kg^{-1}*hr^{-1}$ of DME. In comparison, the ZrO_2/SO_4^{2-} catalyst produced 1.1 $mol*kg^{-1}*hr^{-1}$ of isobutene and only 0.10 $mol*kg^{-1}*hr^{-1}$ of DME, which was achieved at the lower temperature of 175°C. With the Nb_2O_5 catalyst at 225°C, the reactant conversions were 70.2% isobutanol and 19.6% methanol to products, and Figure 35 shows that the %yields of isobutanol to isobutene and of methanol to DME were 58.7 and 15.5 %, respectively.

The catalytic results for the $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst were similar at the higher reaction temperatures employed to those of the ZrO_2/SO_4^{2-} catalyst. At 175°C, the Fe- and Mn-doped catalyst produced 0.91 $mol*kg^{-1}*hr^{-1}$ of isobutene and 0.03 $mol*kg^{-1}*hr^{-1}$ of DME, as shown in Figure 36. However, at lower temperature, the $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst as prepared here was considerably less active than the ZrO_2/SO_4^{2-} catalyst. For example, at 150°C the yield of isobutene was only 0.24 $mol*kg^{-1}*hr^{-1}$ for $Fe/Mn/ZrO_2/SO_4^{2-}$ compared to 0.61 $mol*kg^{-1}*hr^{-1}$ for ZrO_2/SO_4^{2-}.

This $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst exhibited a greater selectivity in activating isobutanol relative to methanol than the PW_{12}/ZrO_2 catalyst and the $Nb_2O_5 \cdot H_2O$ catalyst. The overall conversion levels for the $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst at 175°C were 61.3% isobutanol to products and 6.2% methanol to products. The %yields for this catalyst are shown in Figure 37. Figures 36 and 37 demonstrate that this catalyst was quite selective for the dehydration of isobutanol to isobutene, specifically 86.6 mol% of the C_4-containing

Figure 34. Space time yields of products over the $Nb_2O_3 \cdot H_2O$ catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

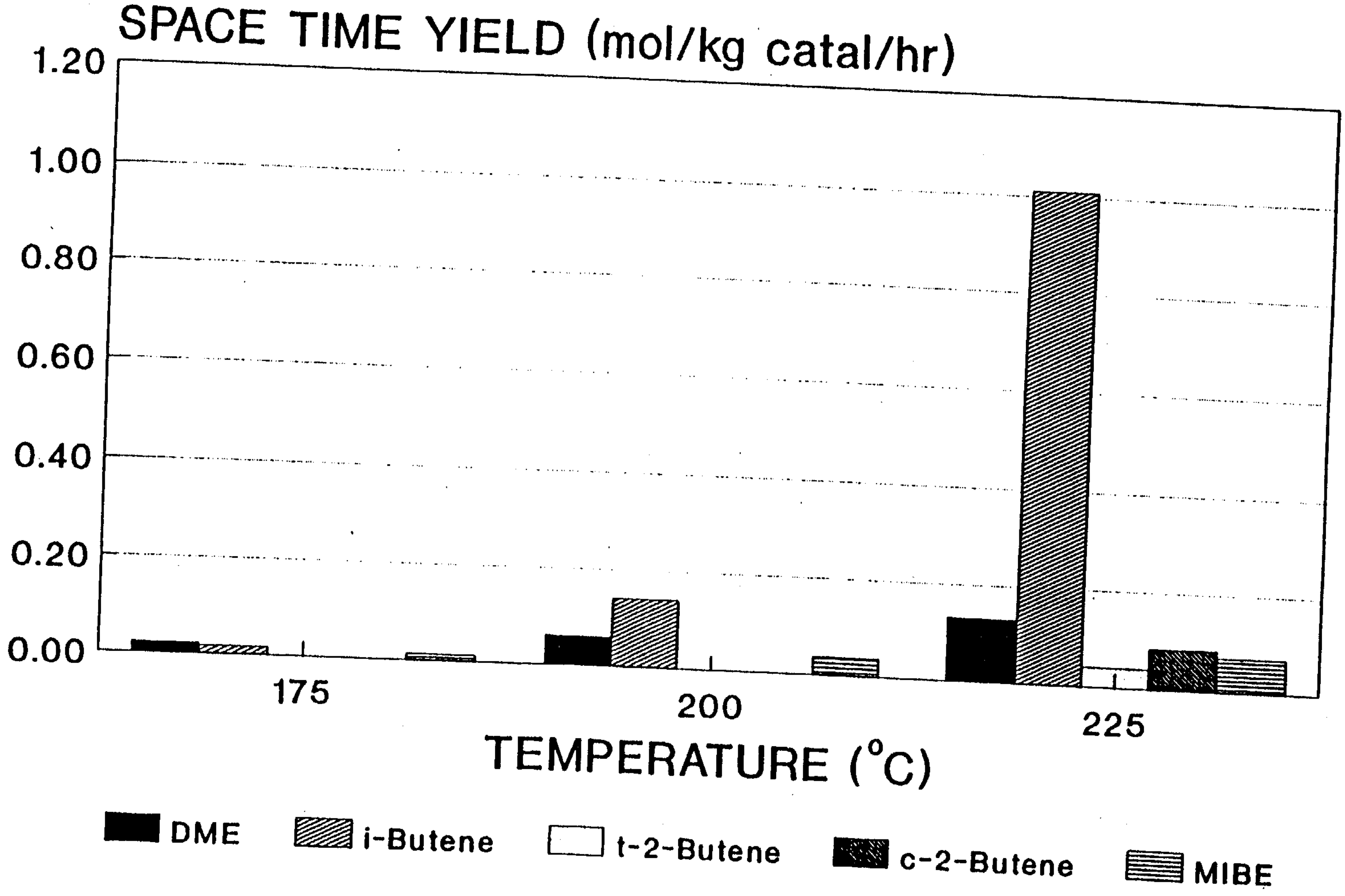


Figure 35. Percent yields of products (based on reactant conversions) over the $Nb_2O_3 \cdot H_2O$ catalyst from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

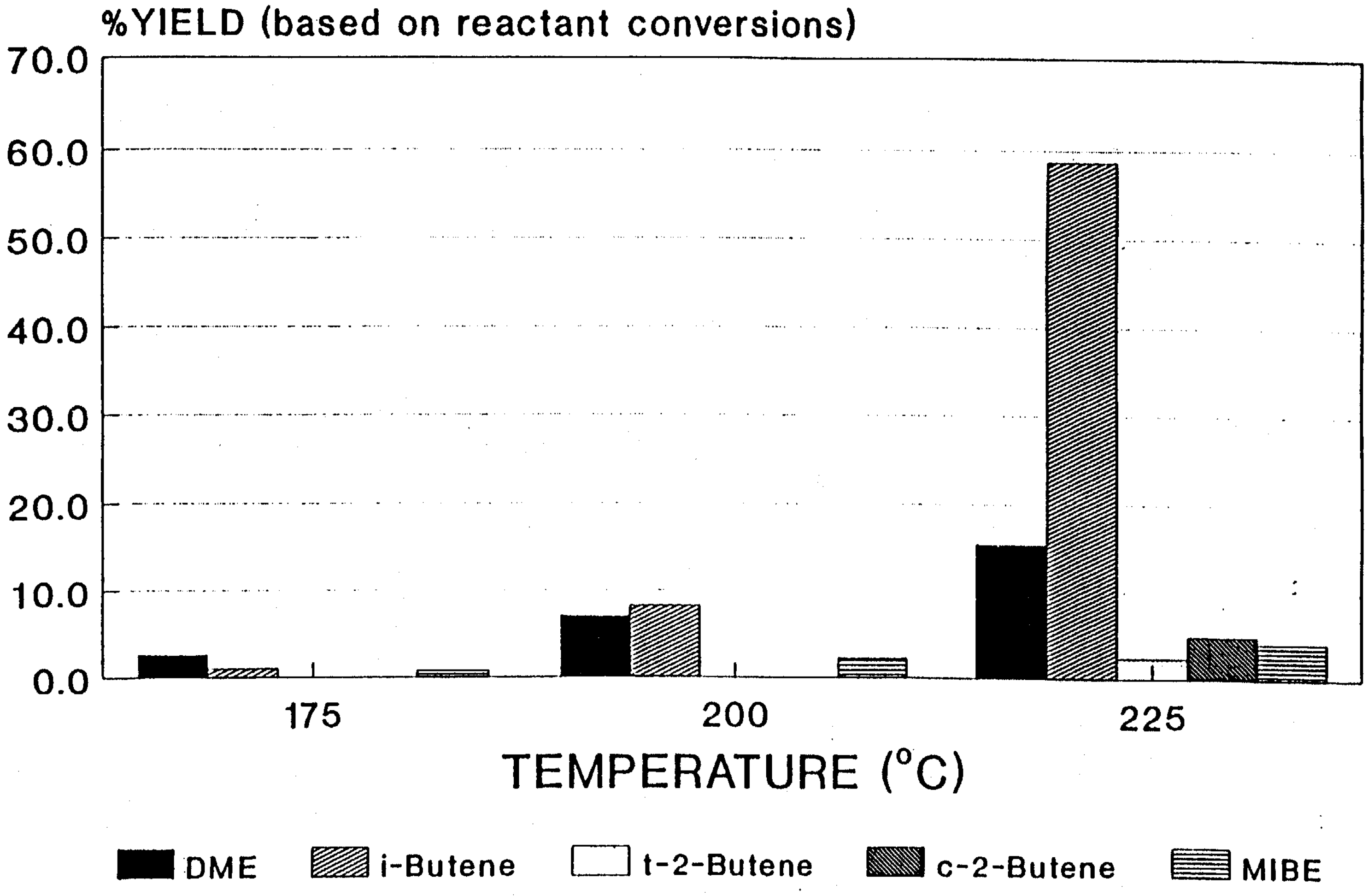


Figure 36. Space time yields of products over the Fe/Mn/ZrO_2/SO_4^{2-} catalyst calcined at 620°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

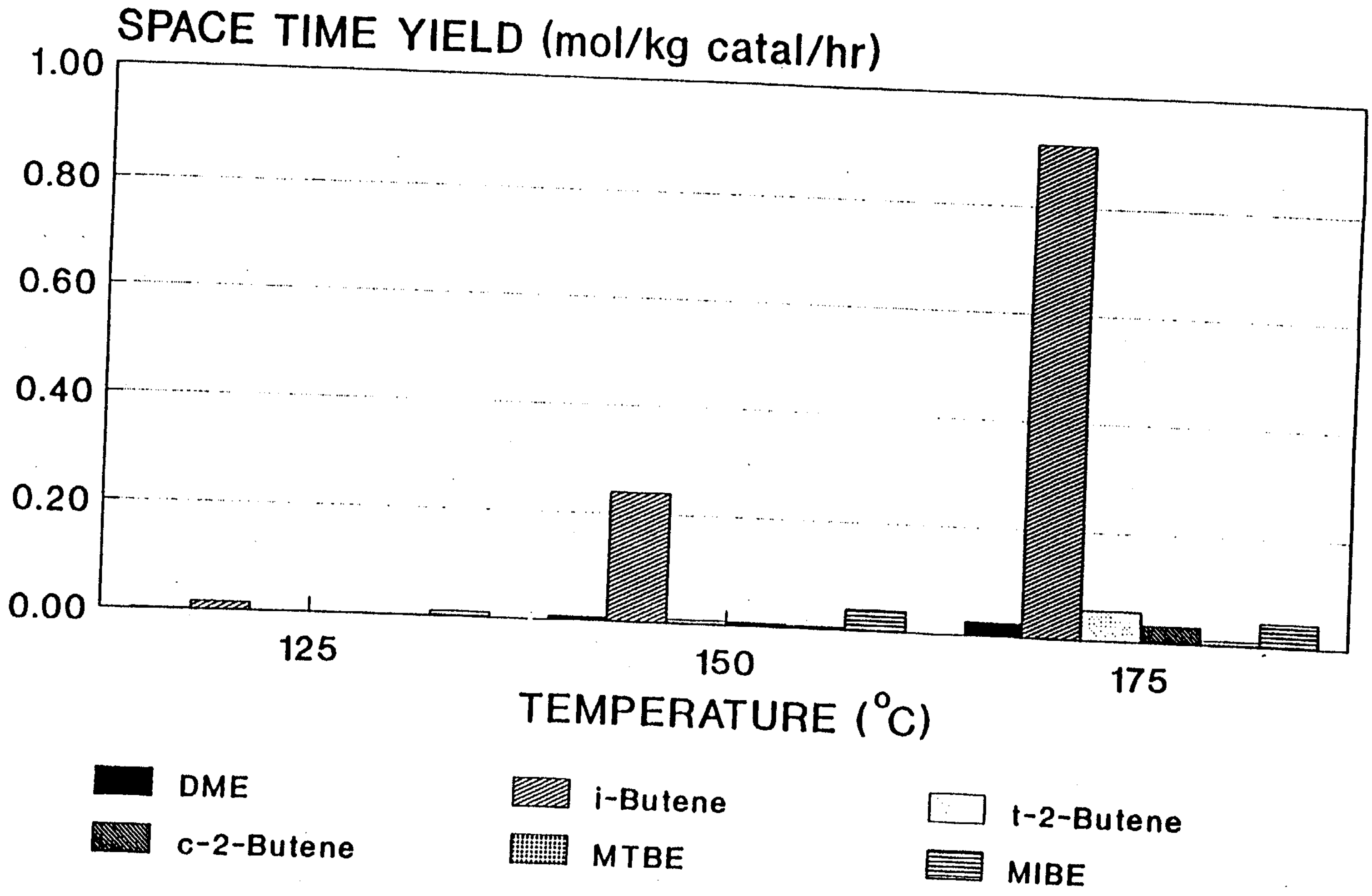
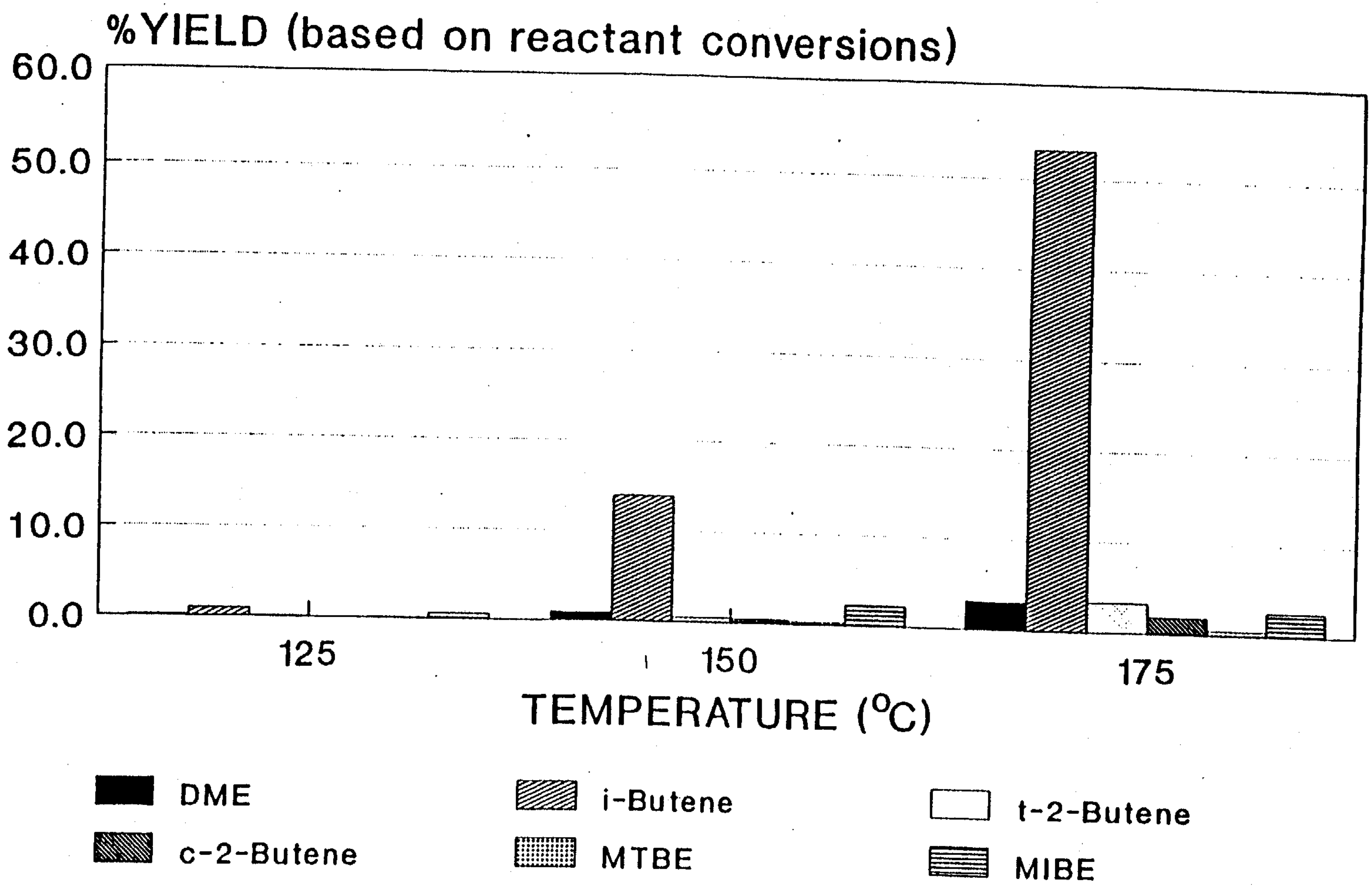


Figure 37. Percent yields of products (based on reactant conversions) over the Fe/Mn/ZrO_2/SO_4^{2-} catalyst calcined at 620°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.



products was isobutene and 84.4 mol% of all significant products, not including water, was isobutene.

The $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst sample that was tested as described above was calcined at 620°C, although recent literature indicates that a higher calcination temperature might be beneficial for strong acid catalyzed reactions such as isomerization (43,44). Thus, a portion of the impregnated catalyst (prepared by simultaneous aqueous impregnation of $Zr(OH)_4$ with SO_4^{2-}, Mn^{2+}, and Fe^{3+}) that had been dried in a 110°C oven overnight was calcined at 720°C for 3 hr and then tested. As noted previously, the catalyst preparation was designed to give 1.5% Fe, 0.5% Mn, and 4.0% SO_4^{2-} by weight supported on ZrO_2.

The catalytic results are presented in Figure 38 in terms of %yield of the products. Again, it is evident that the predominant product was isobutene and that little of the methanol reactant was converted to products.

The productivity of this catalyst, as expressed in terms of space time yield, is shown in Figure 39 for the reaction temperatures of 125, 150, and 175°C. Low conversion levels are observed at 125 and 150°C, where the mol% conversions of methanol were 0.4 and 2.2%, respectively, while those of isobutanol were 0.7 and 8.9%, respectively. At 175°C, 55.9% of the isobutanol was converted to products, with a selectivity toward isobutene of 88%. In comparison, only 5.0% of the methanol was converted to products at this temperature. These conversions and selectivity were similar to those observed previously for the $Fe/Mn/ZrO_2/SO_4^{2-}$ catalyst calcined to 620°C. Therefore, the temperature of calcination in the range utilized in these studies did not produce a significant effect on the observed activity and selectivity of the catalyst.

Surface areas have been determined for samples of $Fe/Mn/ZrO_2/SO_4^{2-}$, and compairsons were made with niobic acid ($Nb_2O_5.xH_2O$), as well as the 12-phosphotungstic

Figure 38. Percent yields of products (based on reactant conversions) over the Fe/Mn/ZrO_2/SO_4^{2-} catalyst calcined at 720°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.

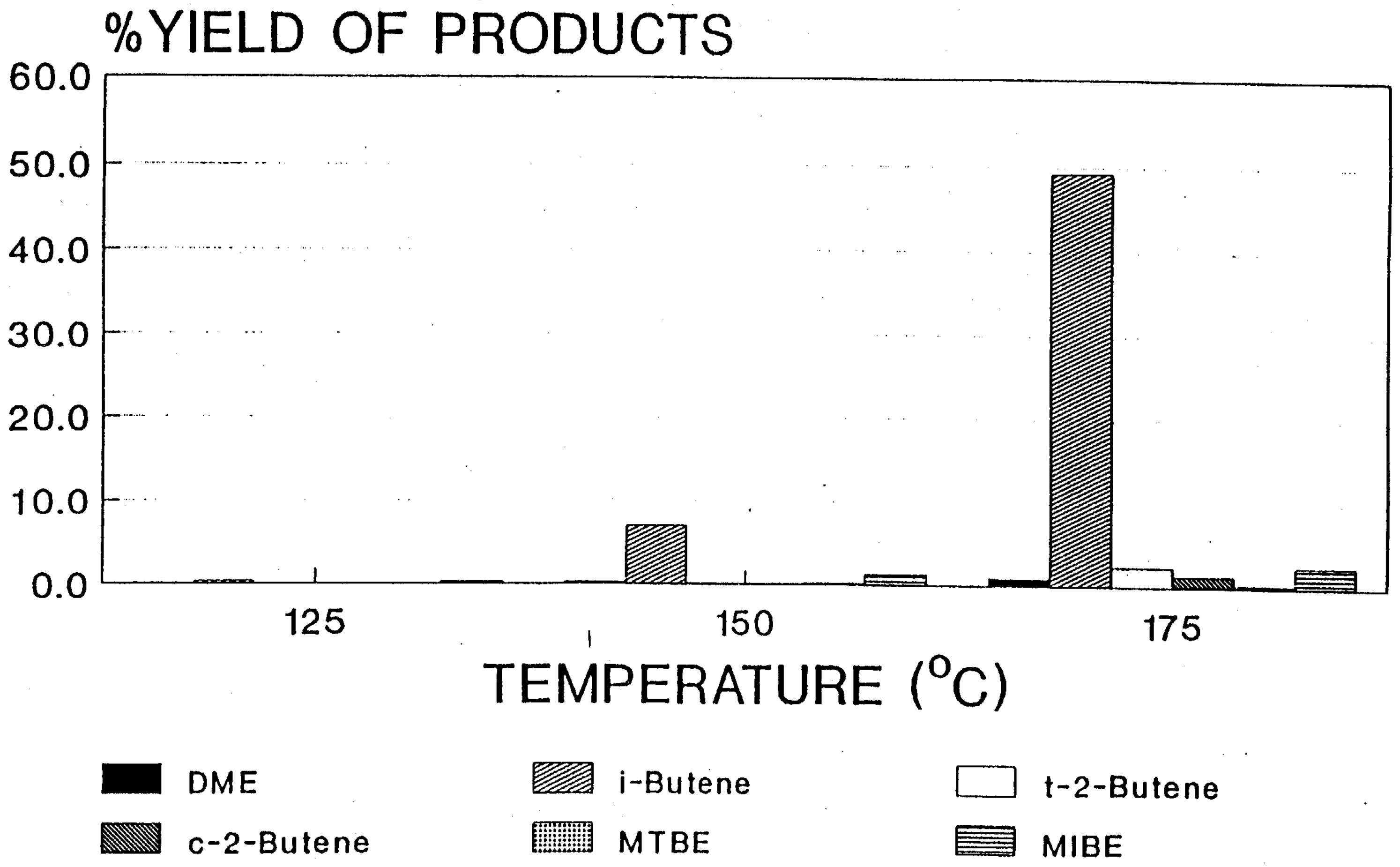
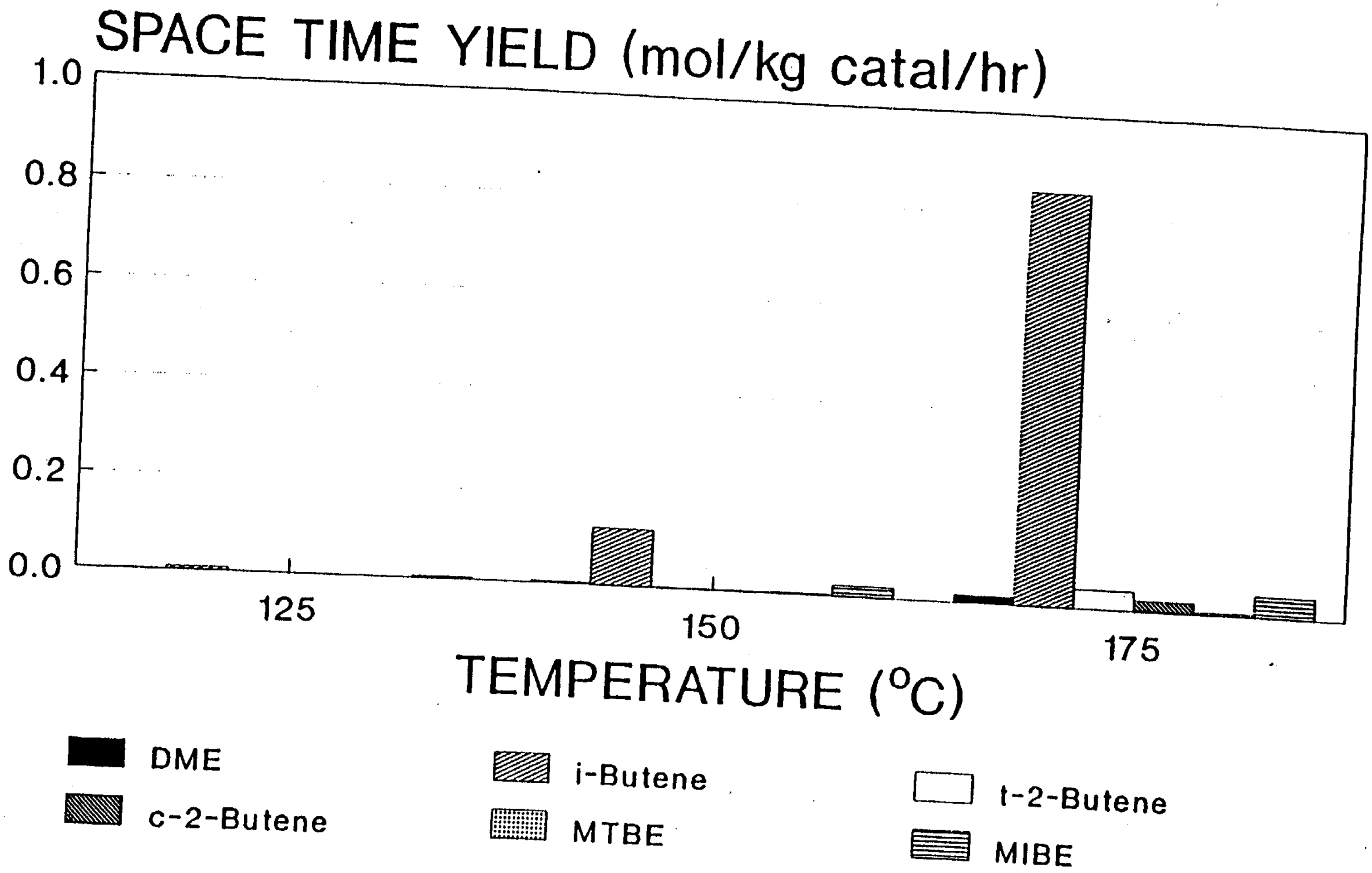


Figure 39. Space time yields of products over the Fe/Mn/ZrO_2/SO_4^{2-} catalyst calcined at 720°C from methanol/isobutanol = 1/1 reactant at 0.1 MPa as a function of temperature.



acid on silica catalyst (PW_{12}/SiO_2) that was prepared and tested. Particular surface areas were determined for $Fe/Mn/ZrO_2/SO_4^{2-}$ samples dried at 100°C and after calcination at 620°C. The uncalcined sample of $Fe/Mn/ZrO_2/SO_4^{2-}$ was degassed at 120°C prior to exposure to N_2 at -196°C, whereas the calcined $Fe/Mn/ZrO_2/SO_4^{2-}$, niobic acid, and phosphotungstic acid on silica (PW_{12}/SiO_2) catalysts were degassed at 300°C. The measured surface areas are given in Table 16. The surface area determined for the calcined $Fe/Mn/ZrO_2/SO_4^{2-}$ sample was in good agreement with the value of 97 m^2/g reported by others (14).

Table 16. Surface Areas

Catalyst	Surface Area (m^2/g)
$Fe/Mn/ZrO_2/SO_4^{2-}$ dried to 100°C	219
$Fe/Mn/ZrO_2/SO_4^{2-}$ calcined to 620°C	83
Niobic Acid	118
(PW_{12}/SiO_2)	218

D. Dehydration of Isobutanol Over H-Mordenite

Dehydration of a methanol and isobutanol mixture gave primarily DME over H-mordenite between 90 and 150°C, as shown in Table 15. The preferential dehydration of methanol was explained in terms of shape selectivity. To investigate if H-mordenite exclusively can dehydrate methanol, a test with only isobutanol as the feed was conducted.

The experiment was carried out at 0.1 MPa at the reaction temperatures of 90, 125, 150, 175, and 185°C, and then the reaction temperature was returned back to 150°C. The isobutanol feed rate was 1.72 mol/kg cat/hr and the He + N_2 flow was maintained at 16.9 mol/kg cat/hr. H-Mordenite was calcined at 400°C for 3 hr, and then a 2.5 g portion was loaded into the reactor for the catalytic test.

As can be seen from Figure 40, the butene product was primarily composed of isobutene, which was also the case for other catalysts such as sulfated zirconia, silica-alumina and montmorillonite, e.g. about one-third of the total quantity of the synthesized butenes consisted of linear butenes. The productivity of butenes was very low at 90°C and at 125°C, which is comparable to the same experiment in the presence of methanol. The dehydration reaction of isobutanol to butenes was facilitated by an increase of the temperature, i.e. higher temperature was needed to activate isobutanol for dehydration. After reaction at 185°C, the system was brought back to 150°C to measure any deactivation of the catalyst. The conversion of isobutanol to butenes decreased from 8.8 to 5.9% over the course of this study.

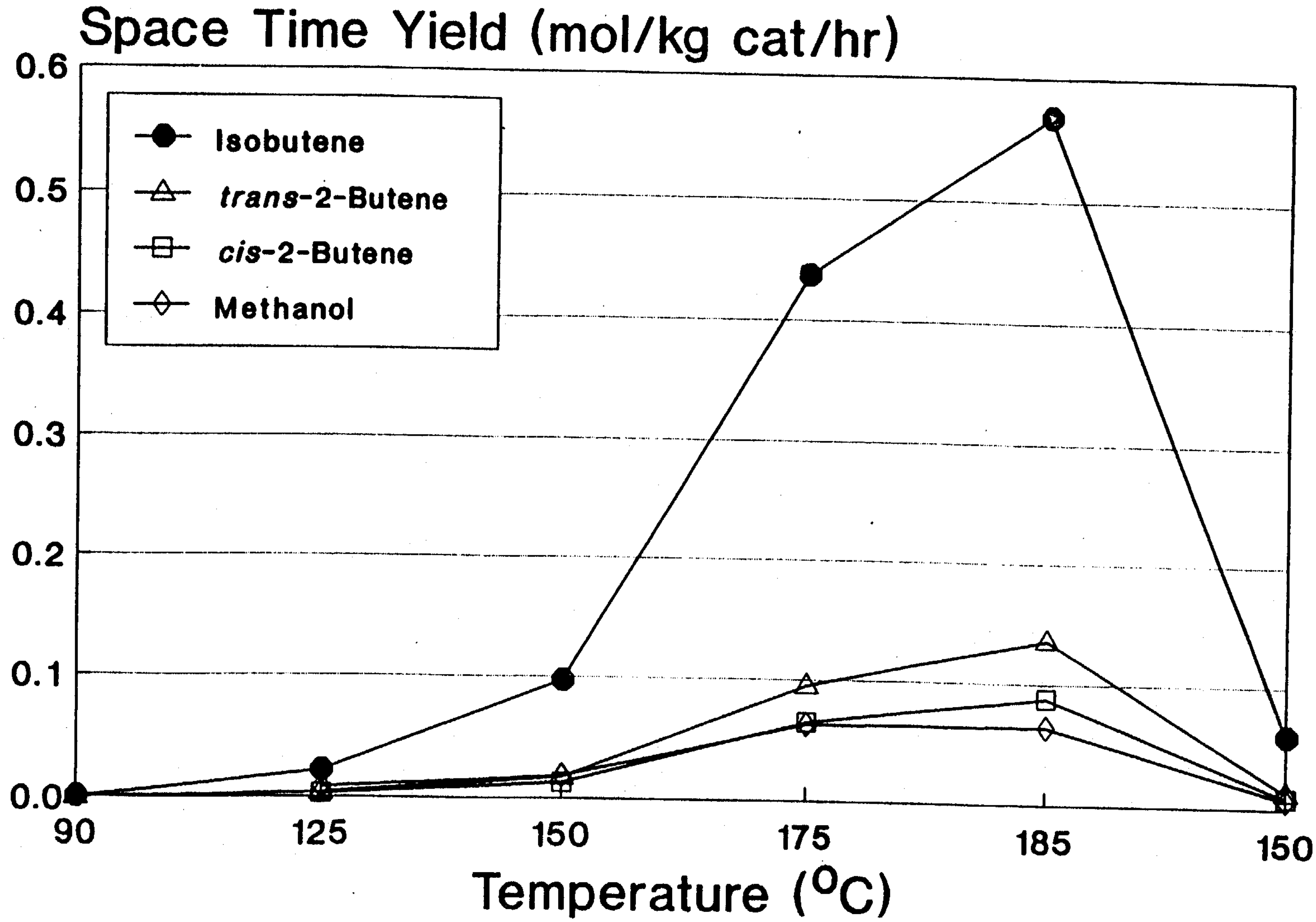
Figure 40 also indicates methanol as a product in this reaction. Methanol was <u>not</u> present in the alcohol feed. The catalyst was not at any point exposed to methanol. In addition to a methanol peak, a new peak was seen in the chromatogram. The new peak has not been unambiguously identified, but comparisons of retention times indicate the possibility of assigning this peak to 1-propanol. The origin of methanol is not known, but the possibility exists that isobutanol or the butenes may crack to C_1 and C_3 fragments giving rise to methanol and propanol following hydration.

E. X-Ray Powder Diffraction of H-Mordenite and H-ZSM-5 Zeolites

Objective

The objective of this experiment was to evaluate the crystallinity of H-ZSM-5 zeolite and H-mordenite before and after the alcohol coupling reaction was carried out to determine if these zeolites were structurally stable under the reaction conditions employed.

Figure 40. The dehydration behavior of isobutanol only over the H-mordenite catalyst as a function of reaction temperature.



The activities and selectivities observed for testing in a tubular downflow reactor with a methanol/isobutanol = 1/1 reactant mixture at ambient pressure and a sequence of temperatures have been previously presented and discussed.

Experimental

The X-ray powder diffraction (XRD) patterns for the two zeolites were obtained on a Phillips APD 3720 Automated X-Ray Powder Diffractometer. Cu K_α radiation with a wavelength of 1.5418 Å was used to obtain the diffraction patterns using the instrument that is located in the Earth and Environmental Sciences Department at Lehigh University. Data were collected in the 2θ scan range from 1 to 60 degrees with a scan rate of 1 degree/min and an angle increment of 0.02 degree. The powdered samples were analyzed in a dry state.

Results

The XRD patterns were obtained for four samples consisting of H-mordenite fresh and after catalytic testing and of H-ZSM-5 zeolite fresh and after catalytic testing. Figure 41 shows the XRD pattern of fresh H-mordenite, and Figure 42 shows the XRD pattern of H-mordenite after reaction. A few of the more intense peaks have been indexed by using ASTM reference cards and tables of data given by Breck (34). Less intense peaks also correspond to the diffraction pattern expected for mordenite. The peaks in Figure 41 are more intense than in Figure 42, which might indicate some amorphous species sorbed on the surface of the used H-mordenite catalyst. This phenomenon is commonly exhibited (45) when analyzing used catalyst samples such as mordenite. As shown in Figure 42, the XRD peaks were in the same positions as those for the fresh catalyst (Figure 41), and all of the peaks were retained after catalytic testing. In addition, no extra peaks are observed in Figure 42 as compared to Figure 41. The crystallite size of the catalyst particles can be determined by using the Sherrer equation for diffraction line broadening (45). The main

Figure 41. XRD pattern of H-mordenite prior to catalytic testing.

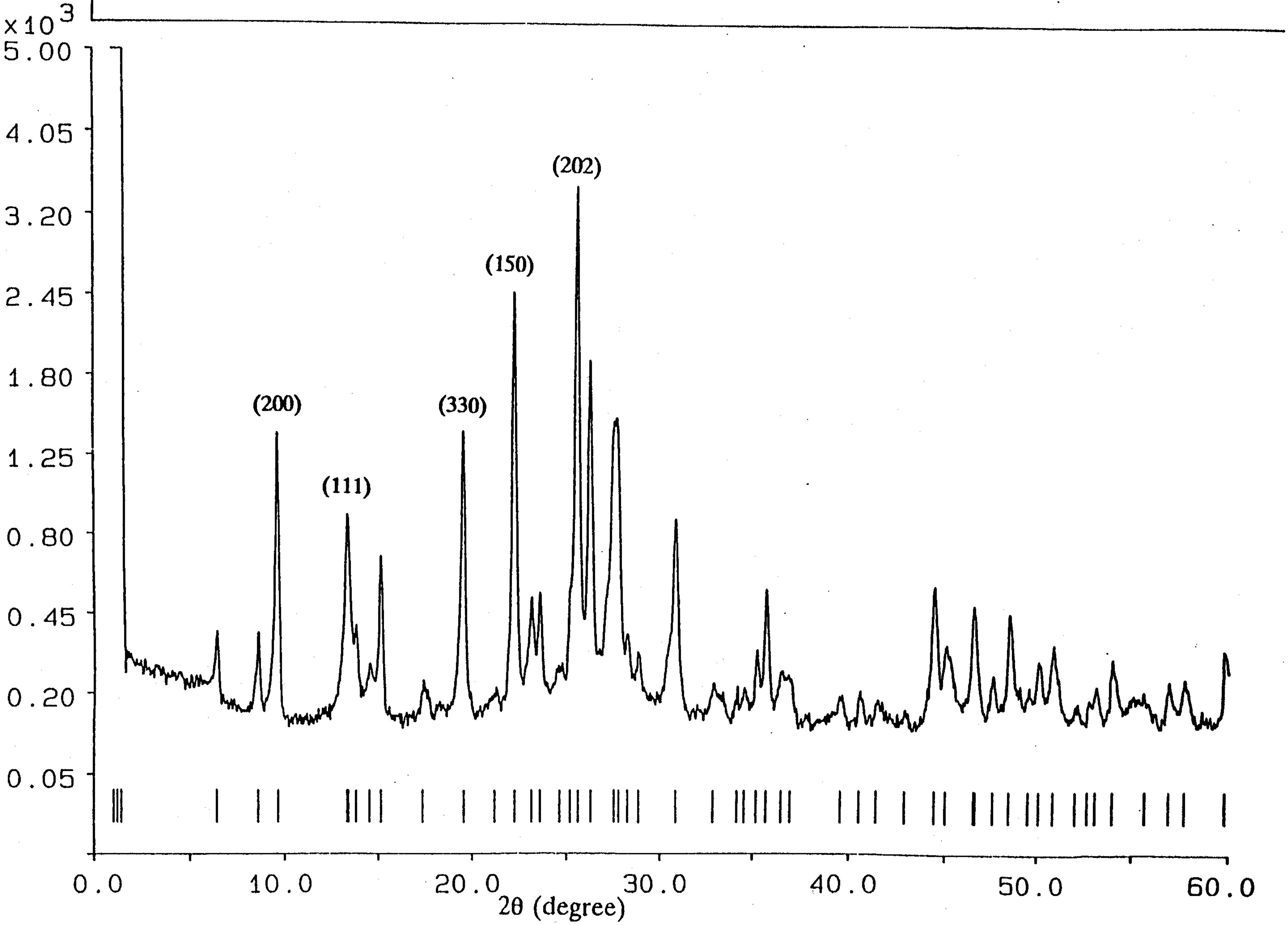


Figure 42. XRD pattern of H-mordenite after catalytic testing.