

CHAPTER 7

DISCUSSION AND COMPARISON OF EXPERIMENTAL RESULTS

Appendix B summarizes the results of analysis of experimental data for the case of the ternary methanol synthesis catalyst described in Chapter 6, the results of this and an industrial binary catalyst as well as those obtained by W. Tanthapanichakoon for a similar ternary catalyst but with different composition are plotted in Figs 7.1-7.55, so that the effects of reaction pressure, temperature, space velocity and catalyst type on the CO conversion per pass, product selectivity and product space time yield of methanol and DME may be visualized.

7.1 Discussion of Experimental for Catalyst No.1

Here catalyst no.1 means the ternary methanol synthesis catalyst composed of Cu : Zn : Cr = 31 : 38 : 10. To investigate the effects of temperature, pressure, and space velocity on methanol synthesis with this catalyst, experiments were carried out under the conditions summarized in Table 7.1. The catalyst powder was pelletized to obtain a density of 2 gm/cm^3 and then screened between meshes # 16 and 30. An amount of 1.5 ml of the screened catalyst was packed in the tubular reactor for methanol synthesis from a synthesis gas containing $\text{CO} : \text{H}_2 = 1 : 2$.

Table 7.1 Summary of Experimental Conditions for Catalyst No.1

(Cu : Zn : Cr = 31 : 38 : 10)

Pressure (atg)	Space Velocity (hr^{-1})	Temperature Range ($^{\circ}\text{C}$)
20	2000	200-300
	4000	200-300
	8000	200-300
	16000	200-300
30	2000	200-300
	4000	200-300
	8000	200-300
	16000	200-300
40	2000	200-300
	4000	200-300
	8000	200-300
	16000	200-300

Total CO Conversion

Figs 7.1-7.12 show that total conversion of CO(%) smoothly increased with temperature and especially with pressure. At high temperature and high pressure, intermolecular distance of reactants (CO and H₂) was closer and the reactants were more activated than at low temperature and low pressure. Hence it was much easier for the reaction to proceed. The same can be said of other reactions. Total conversion of CO decreased against increasing space velocity, because at a higher space velocity there was less time for CO and H₂ to react.

Methanol Selectivity

Theoretically, besides methanol, CO and H₂ could react to form other products, as indicated in Table 2.11. We see that the formation of paraffinic hydrocarbons (reactions 1-3, 8 in Table 2.11) was favored thermodynamically over the methanol reaction at all temperatures and that high pressures should have the greatest favorable effect on reactions 4-7 and 9. Therefore an appropriate catalyst should be selected for methanol synthesis. Figs 7.1-7.12 were the results obtained using a prepared catalyst, with mole ratios of CuO : ZnO : Cr₂O₃ = 31:38:5. They indicated that methanol selectivity increased with pressure mostly in the range of 200-240°C, and beyond that temperature it began to decrease. If the temperature was below 200°C, methanol was rarely synthesized. Therefore, the optimal temperature range of highest methanol selectivity for this catalyst was between 220-250°C. That methanol selectivity would decrease against temperature above 250°C was in line with thermodynamic equilibrium, namely,

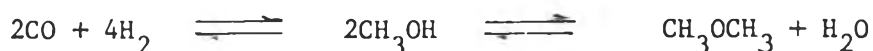
$$X_{\text{CH}_3\text{OH}} = \frac{K (X_{\text{CO}}) (X_{\text{H}_2})^2 P^2}{K_y}$$

While K_y increased with temperature and decreased against pressure, K decreased exponentially with temperature. Therefore the equilibrium yield of methanol, $X_{\text{CH}_3\text{OH}}$, and methanol selectivity should increase with increasing pressure but decrease rapidly against temperature. The same conclusion might be obtained by applying Le Chatelier's rule to the synthesis reaction, which is highly exothermic (see Table 2.11) and is accompanied by a contraction in volume three moles of reacting gases result in one mole of product.

Figs 7.13-7.19 indicated that the space time yield (STY) of methanol generally increased with temperature, pressure and with space velocity between 2000-8000 hr^{-1} . However, STY of methanol decreased for space velocity above 8000 hr^{-1} because the yield and selectivity of methanol were decreased.

DME Selectivity

Figs 7.1-7.12 show that DME selectivity might vary with temperature and pressure in a similar manner to methanol. The main reason was that according to equation 5 of table 2.11 DME was produced by the dehydration of methanol :

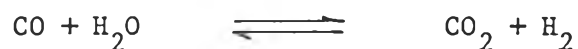


With respect to space velocity, DME selectivity decreased against space velocity because at a high space velocity, there was not enough time for methanol to dehydrate further to become DME.

Figs 7.20-7.26 indicated that the space time yield of DME increased with temperature at fixed pressure.

CO₂ Selectivity

Figs 7.1-7.12 show that selectivity of CO₂ increased with increasing temperature but against decreasing space velocity. The influence of pressure was not remarkable. It was surmised that CO₂ came mainly from the following reaction



If so, then the yield of CO₂ should depend on the availability of H₂O and the concentration of CO. It was observed that when little H₂O was detected, the concentration of CO₂ would be high, and vice versa. At high temperatures, total CO conversion as well as CO₂ selectivity was found to be higher. With respect to space velocity, it was the same as CH₃OH, DME selectivity and CO conversion that at higher space velocity it was not enough time for CO to hydrate with H₂O to occur CO₂ further, so less CO₂ was obtained at higher space velocity.

Hydrocarbons Selectivity

Only light saturated hydrocarbons from our methanol synthesis, such as CH₄, C₂H₆, and C₃H₈, could be detected. As mentioned earlier, the methanation reaction is favored thermodynamically over the methanol synthesis reaction. So are the formation of higher paraffins. However, the rates of formation of higher paraffins are slower than that of methane, because of the increasing number of moles

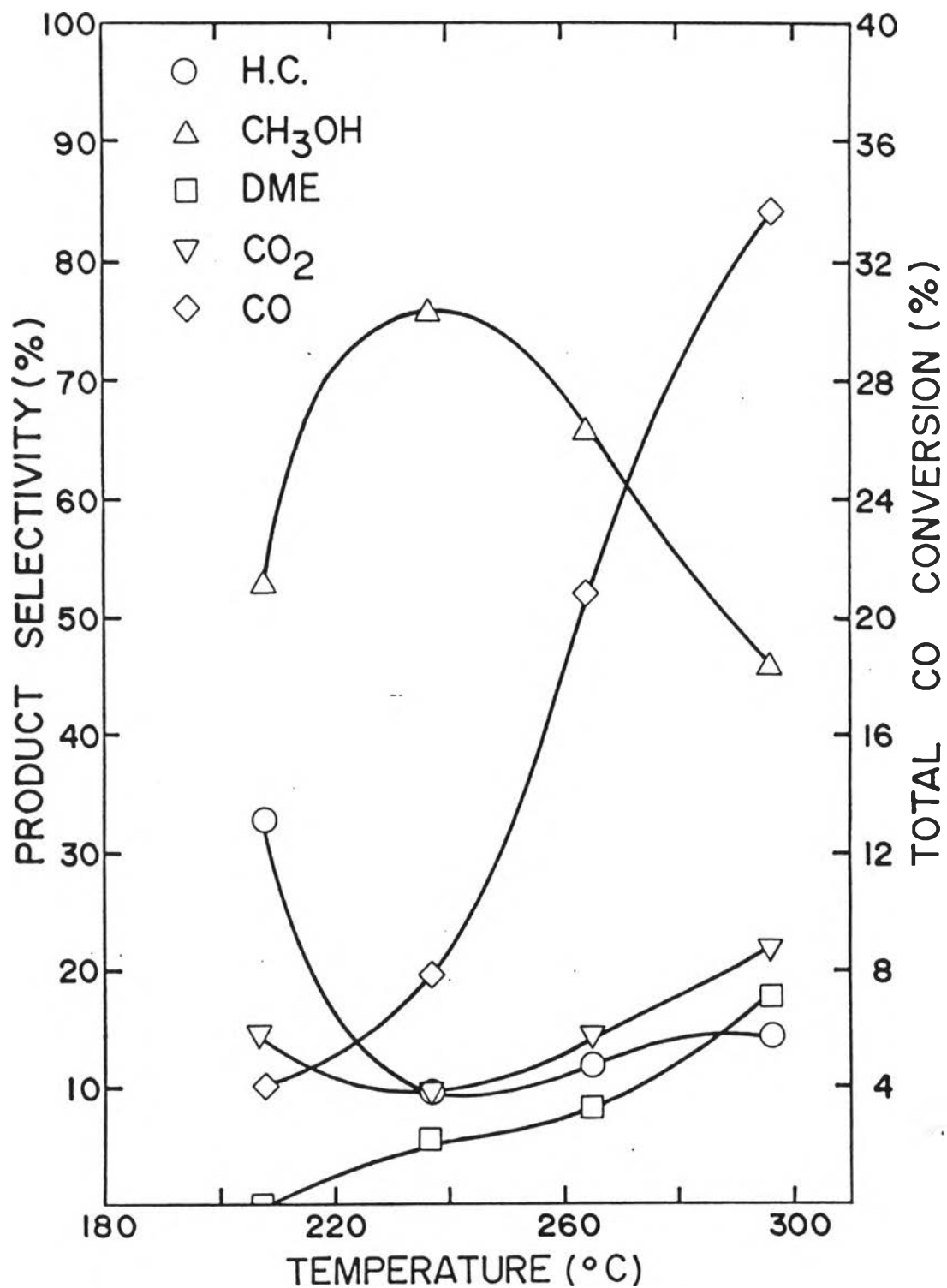


Figure 7.1 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 40 atg, 2,000 hr⁻¹) of Catalyst no.1

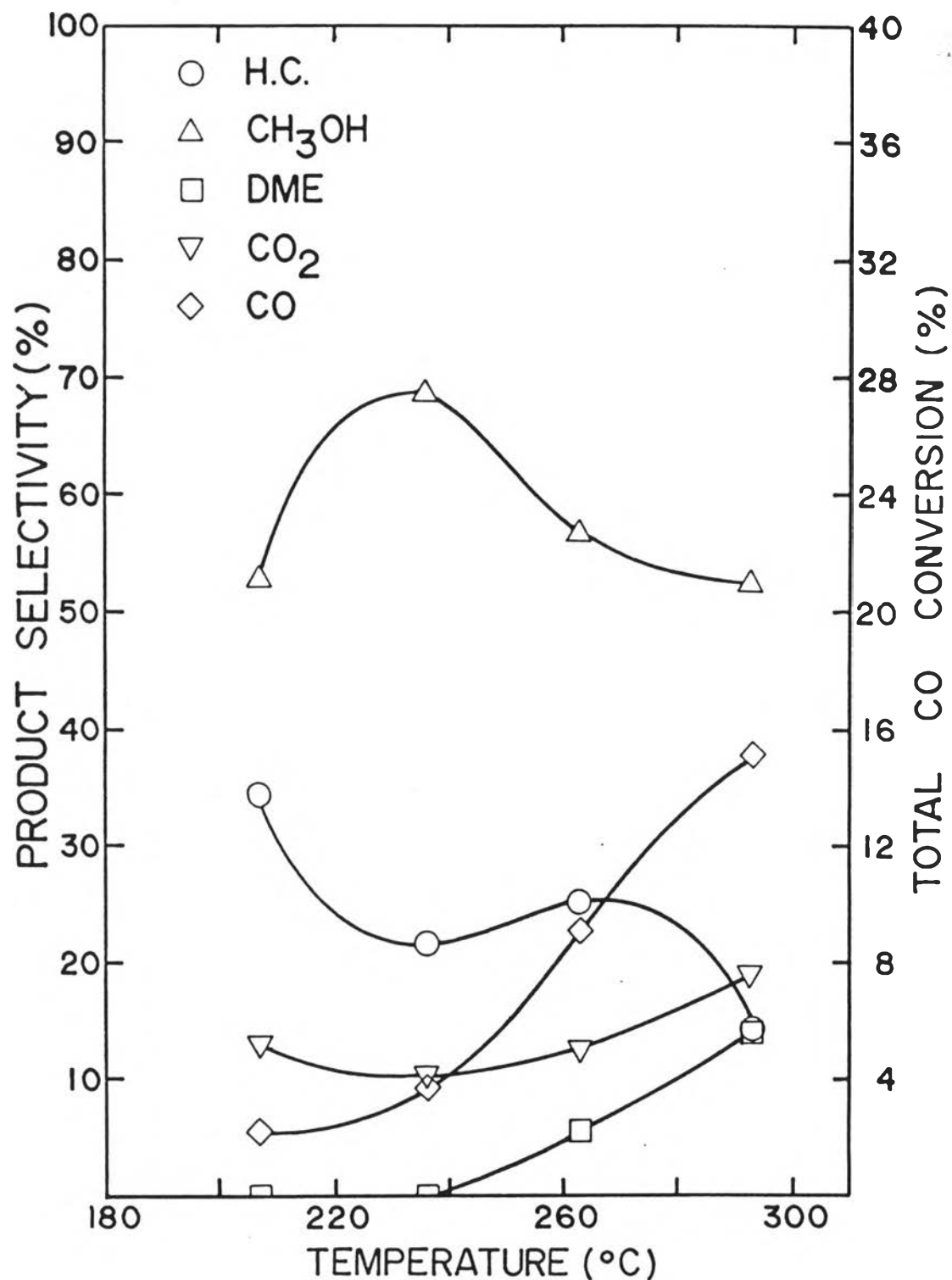


Figure 7.2 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 40 atg, 4000 hr⁻¹) of Catalyst no.1

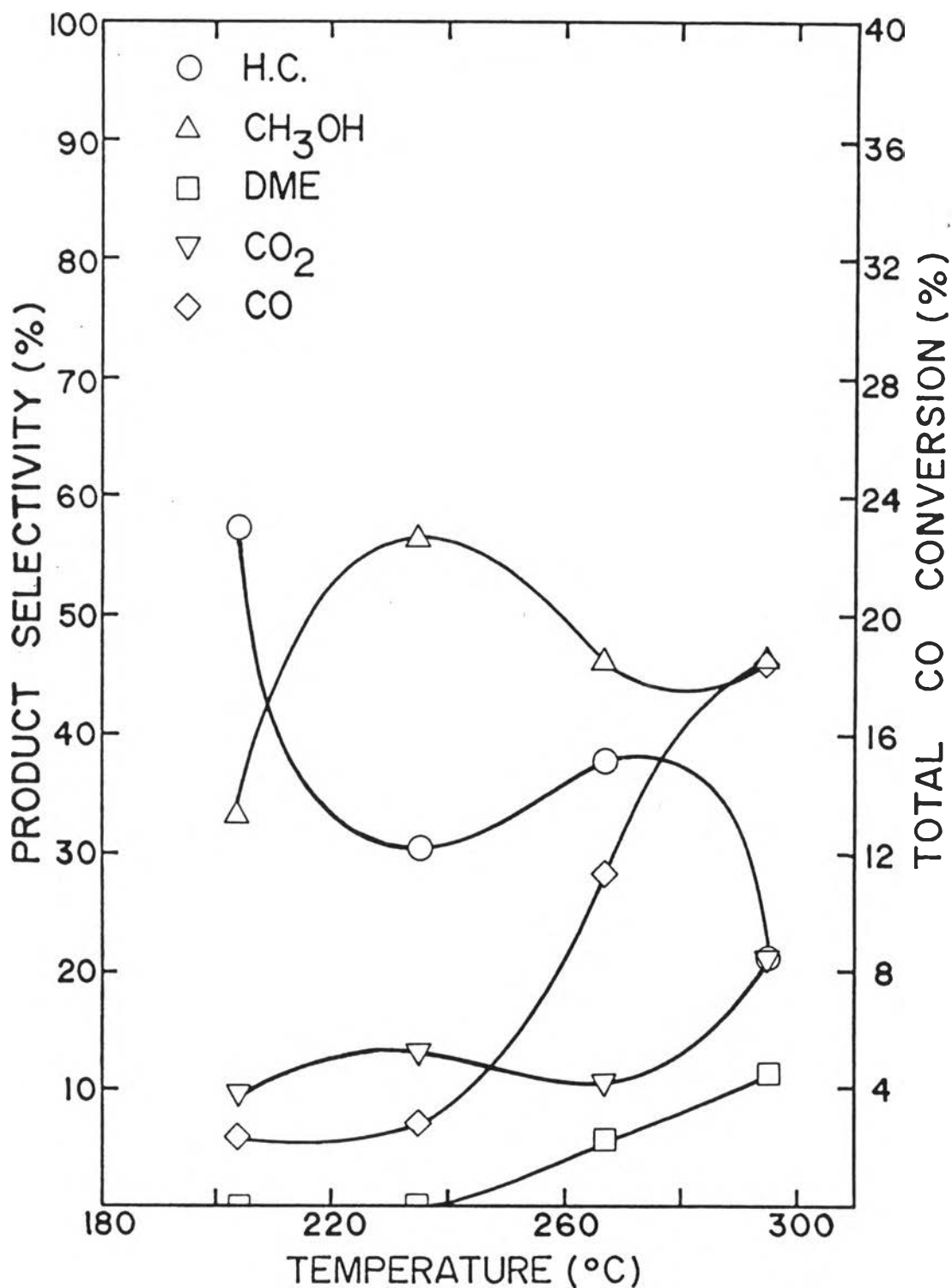


Figure 7.3 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 40.atg, 8000 hr⁻¹) of Catalyst no.1

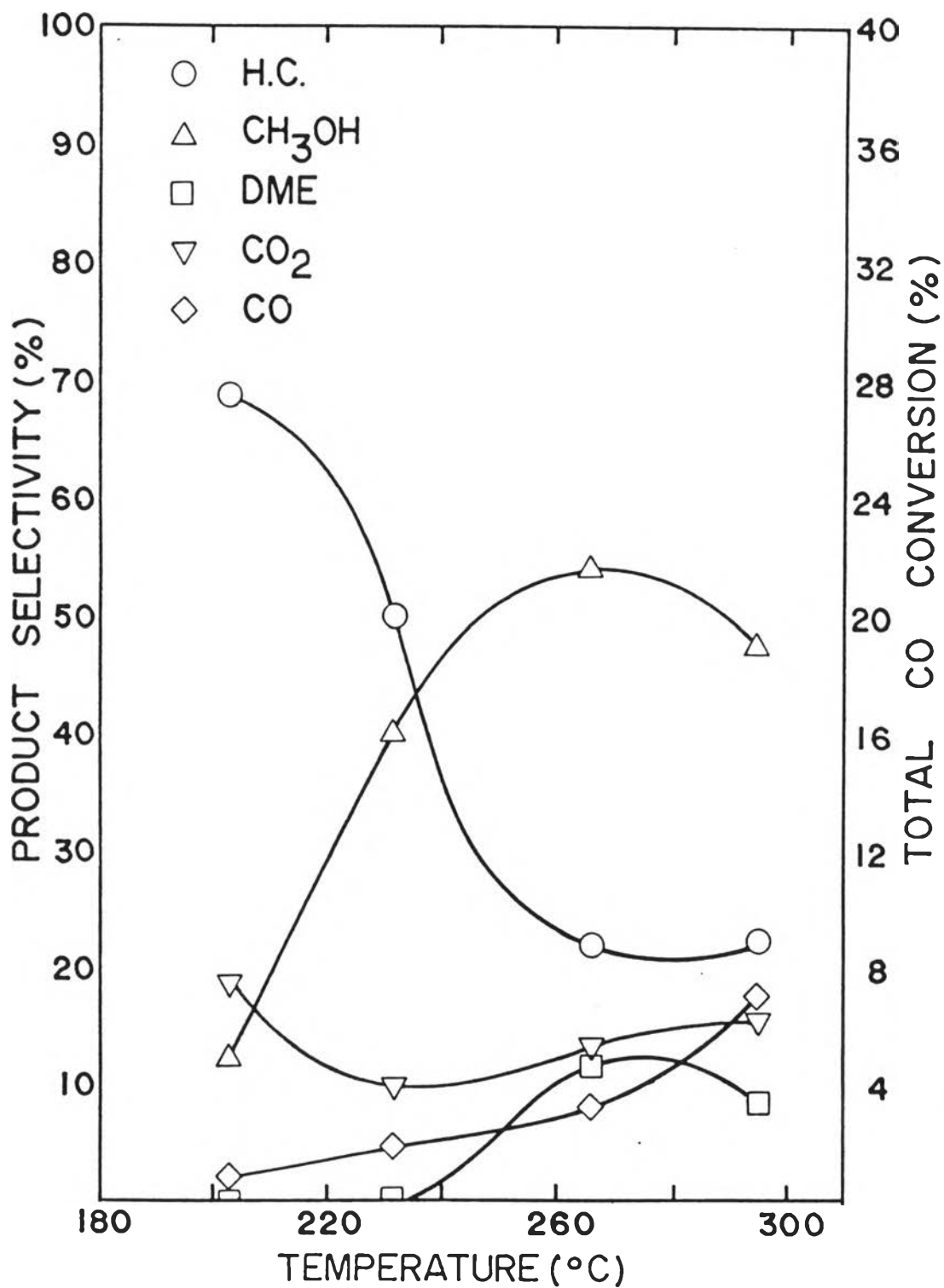


Figure 7.4 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 40 atg, 16000 hr⁻¹) of Catalyst no.1

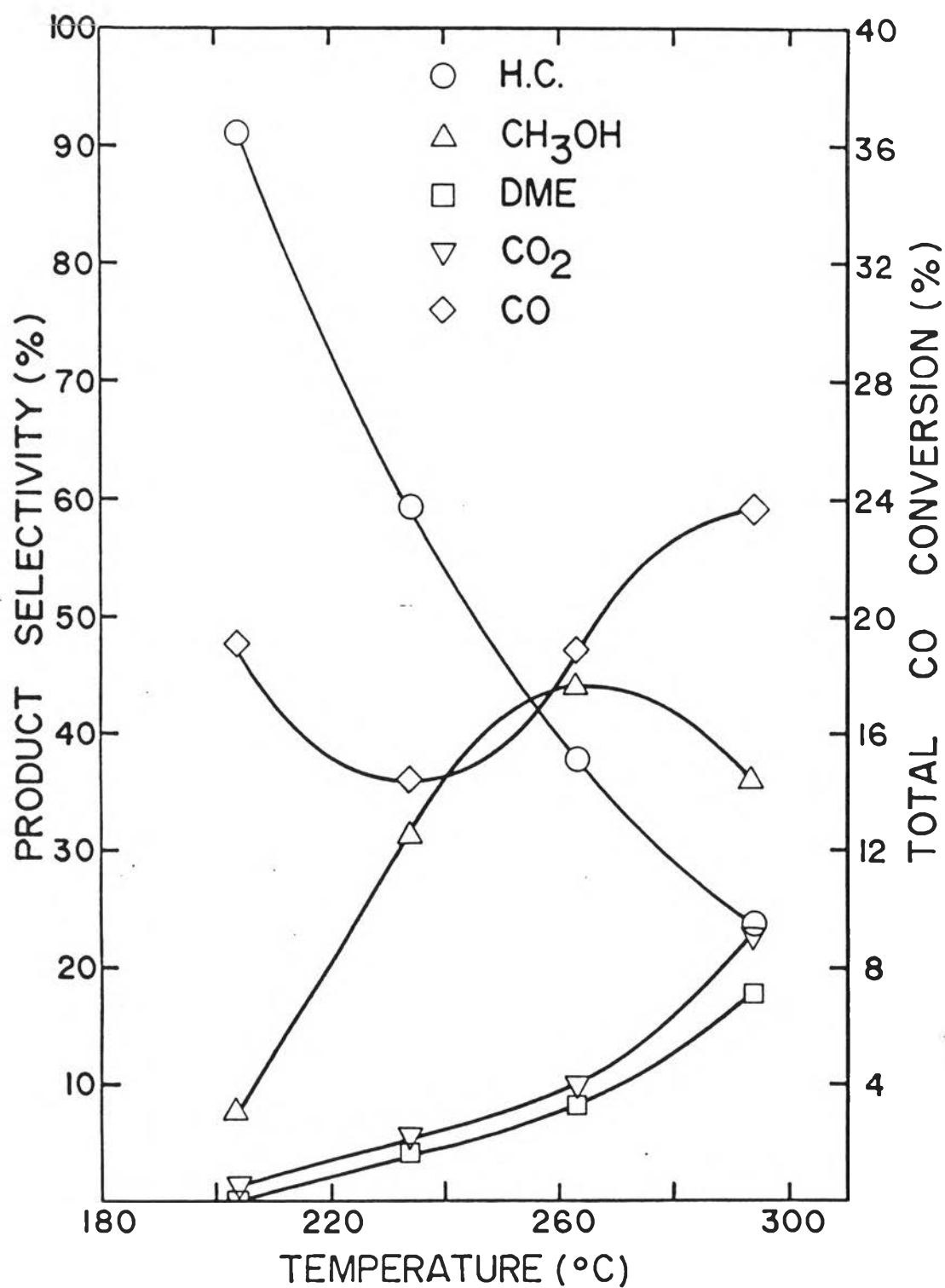


Figure 7.5 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 30 atg, 2000 hr⁻¹) of Catalyst no.1

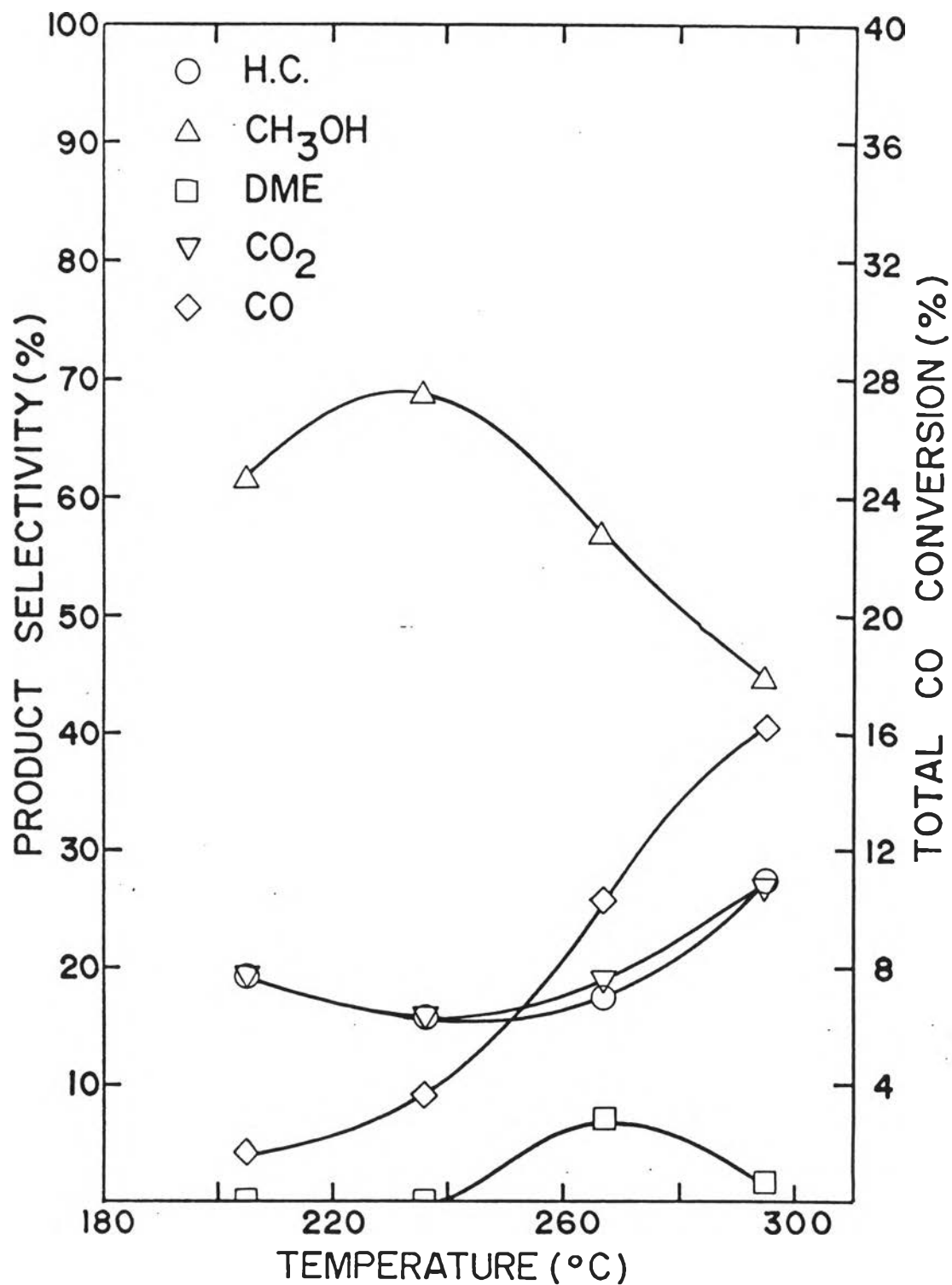


Figure 7.6 Effect of Temperature (200–300°C) on Total CO Conversion and Product Selectivities (at 30 atg, 4000 hr⁻¹) of Catalyst no.1

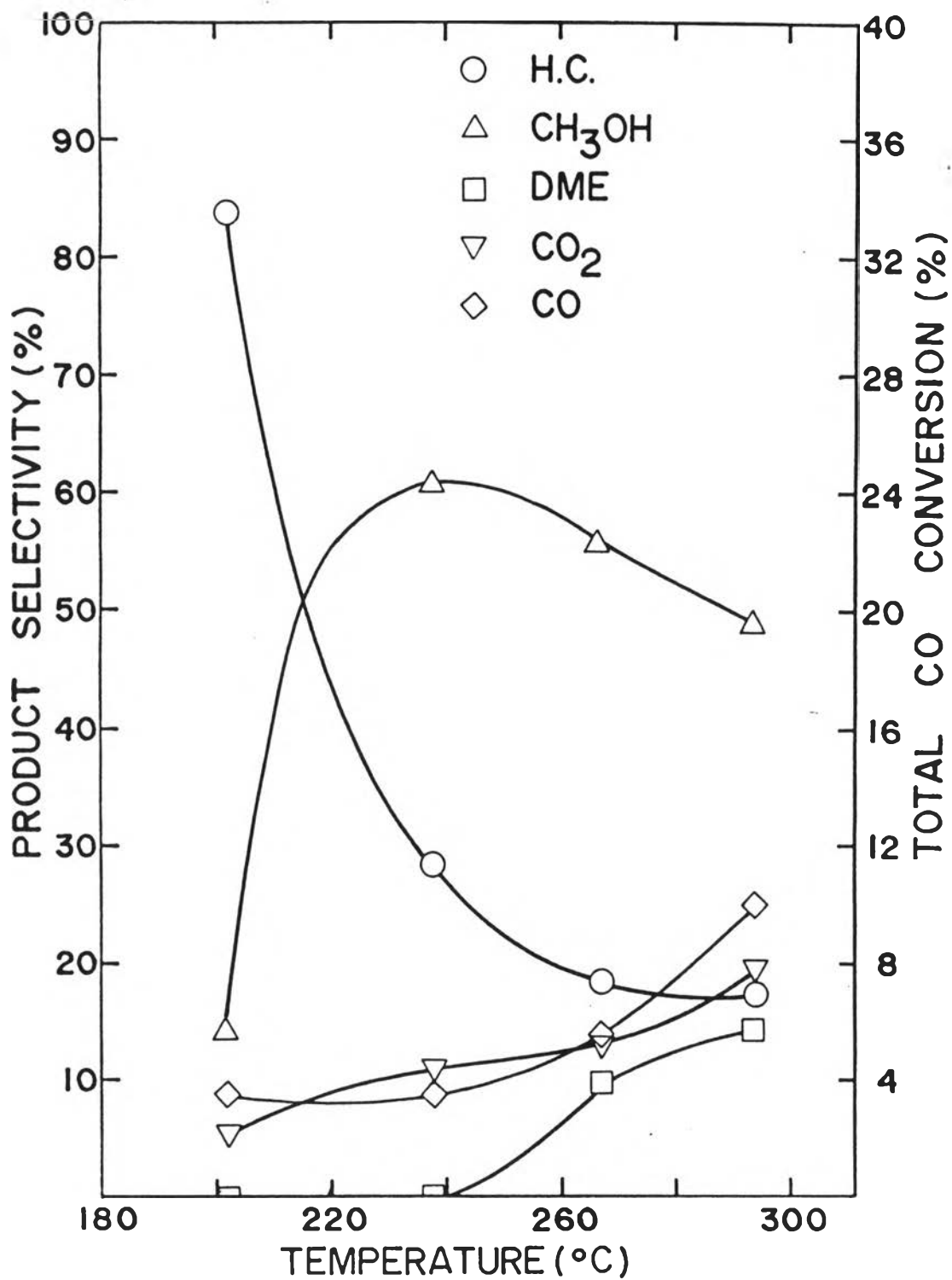


Figure 7.7 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 30 atg, 8000 hr⁻¹) of Catalyst no.1

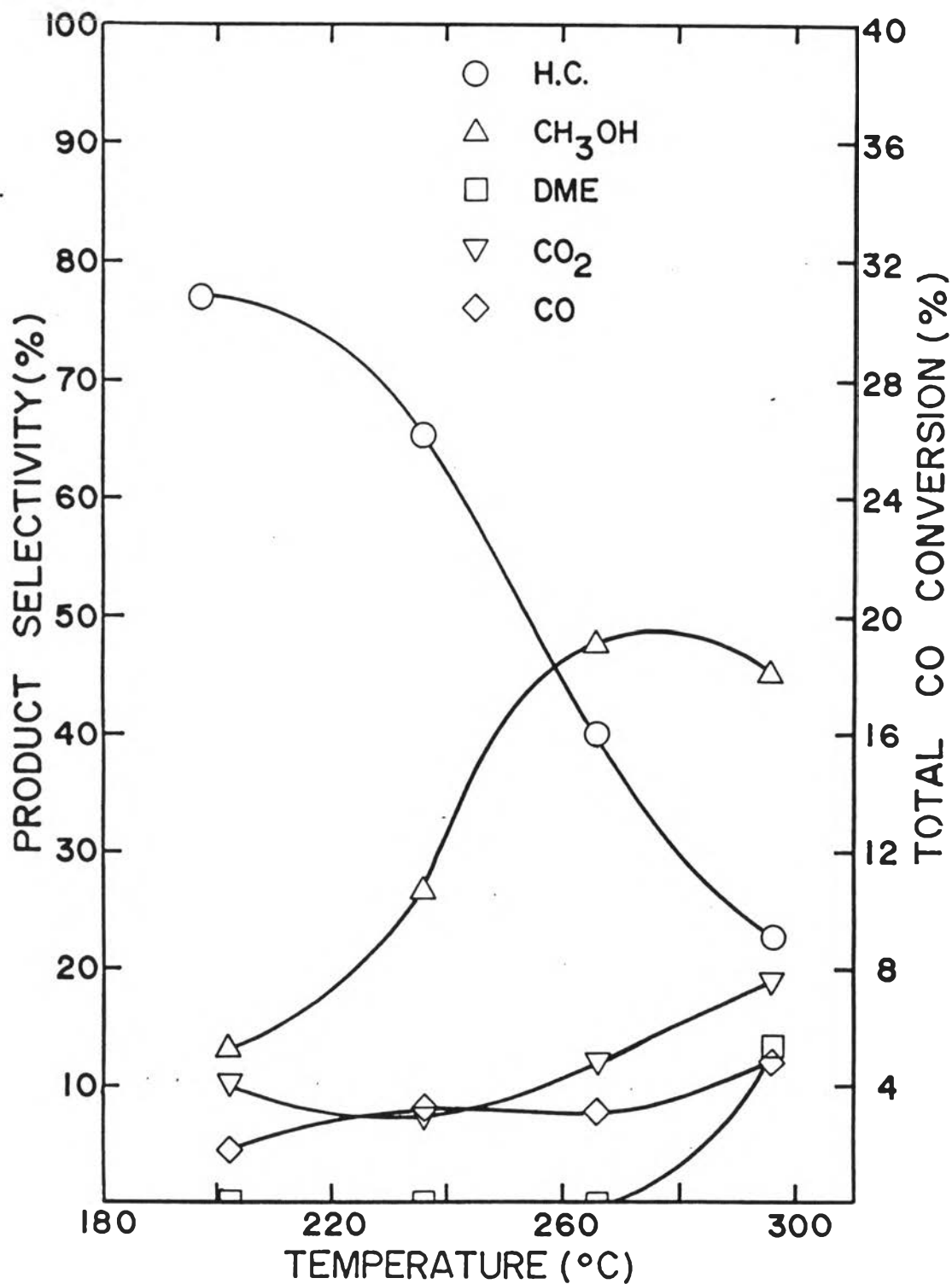


Figure 7.8 Effect of Temperature (200–300°C) on Total CO Conversion and Product Selectivities (at 30 atg, 16000 hr⁻¹) of Catalyst no.1

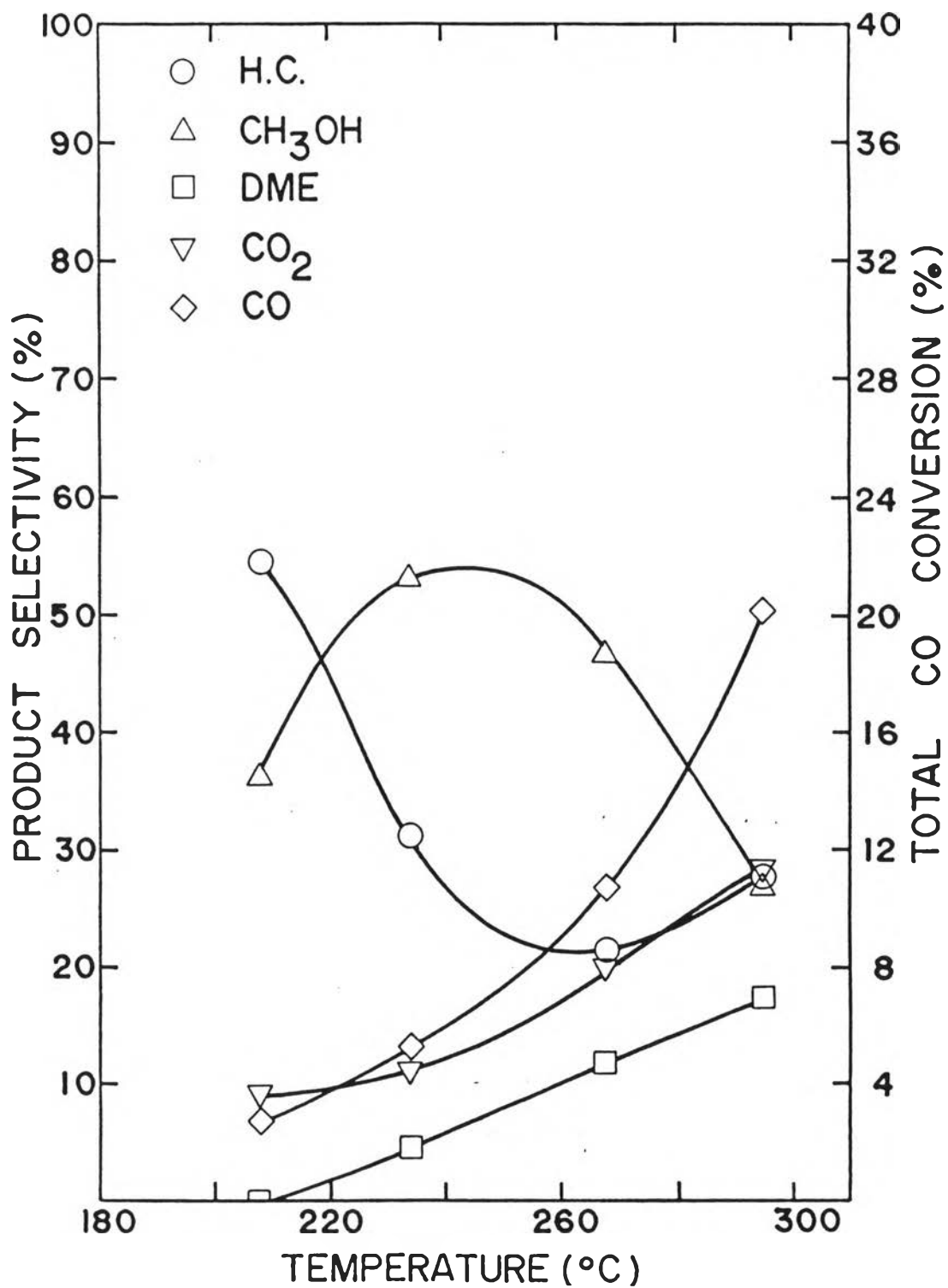


Figure 7.9 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 20 atg, 2000 hr⁻¹) of Catalyst no.1

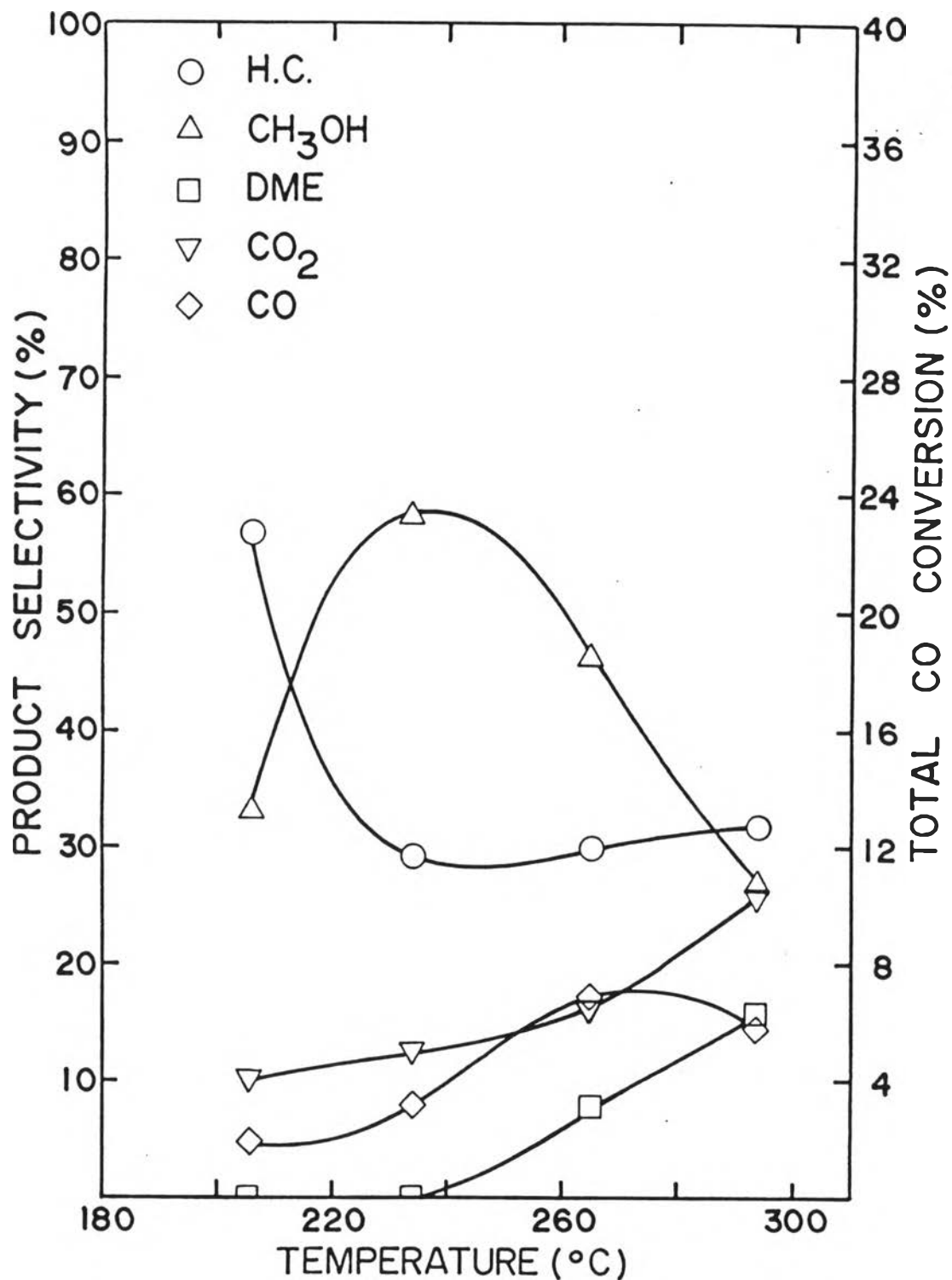


Figure 7.10 Effect of Temperature (200–300°C) on Total CO Conversion and Product Selectivities (at 20 atg, 4000 hr⁻¹) of Catalyst no.1

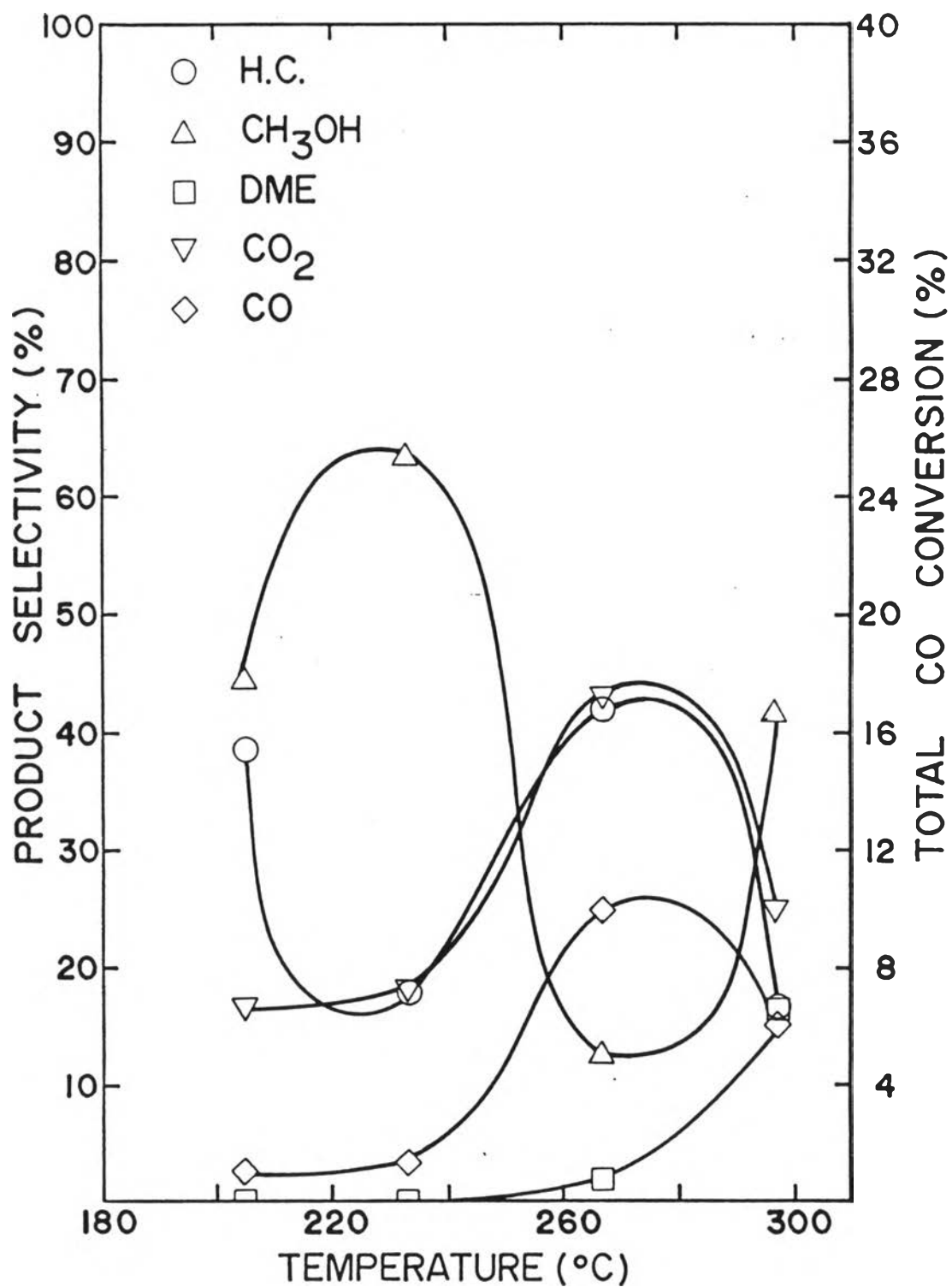


Figure 7.11 Effect of Temperature (200–300°C) on Total CO Conversion and Product Selectivities (at 20 atg, 8000 hr⁻¹) of Catalyst no.1

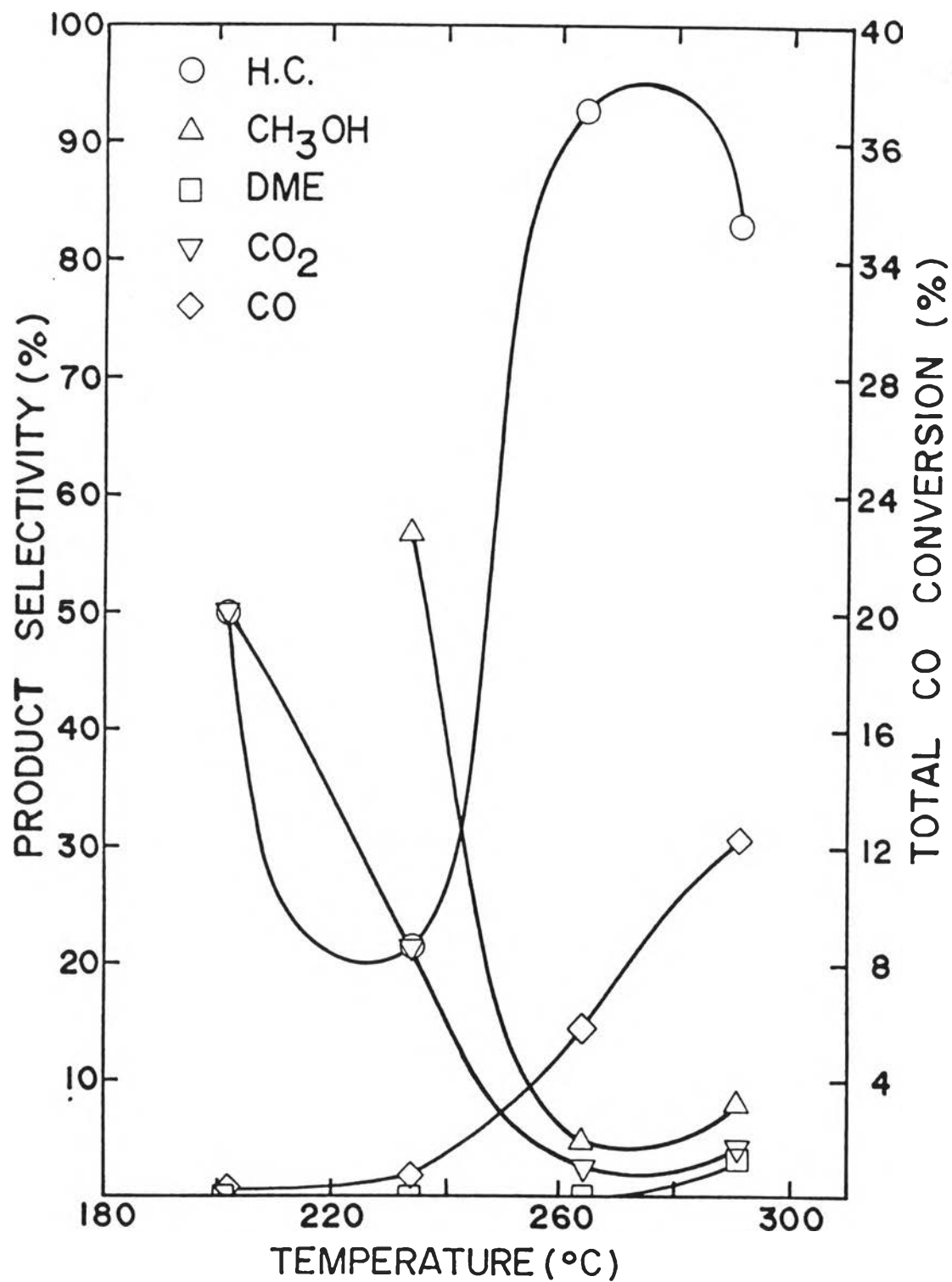


Figure 7.12 Effect of Temperature (200-300°C) on Total CO Conversion and Product Selectivities (at 20 atg, 16000 hr⁻¹) of Catalyst no.1

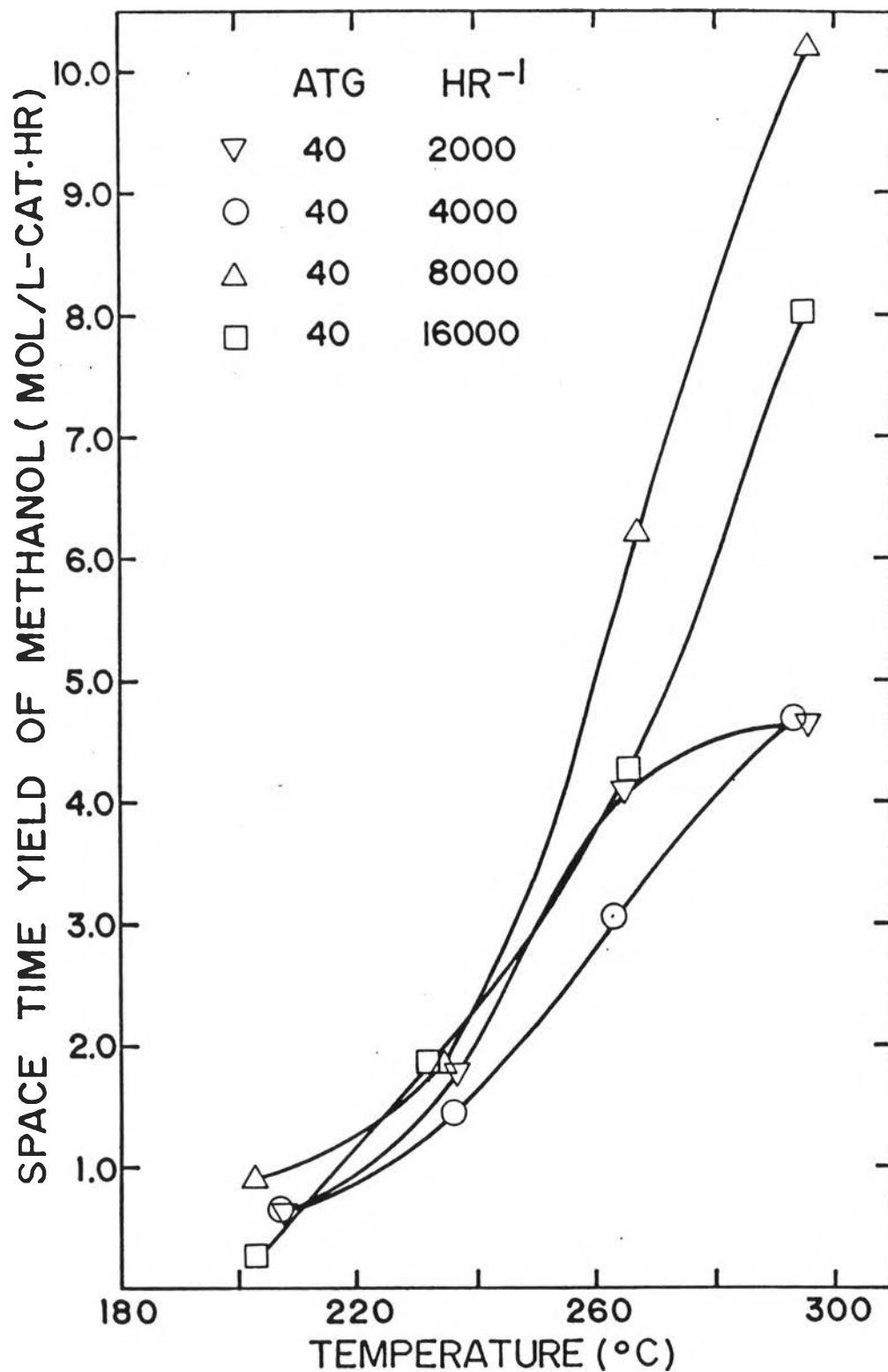


Figure 7.13 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of MeOH (at 40 atg) of Catalyst No.1

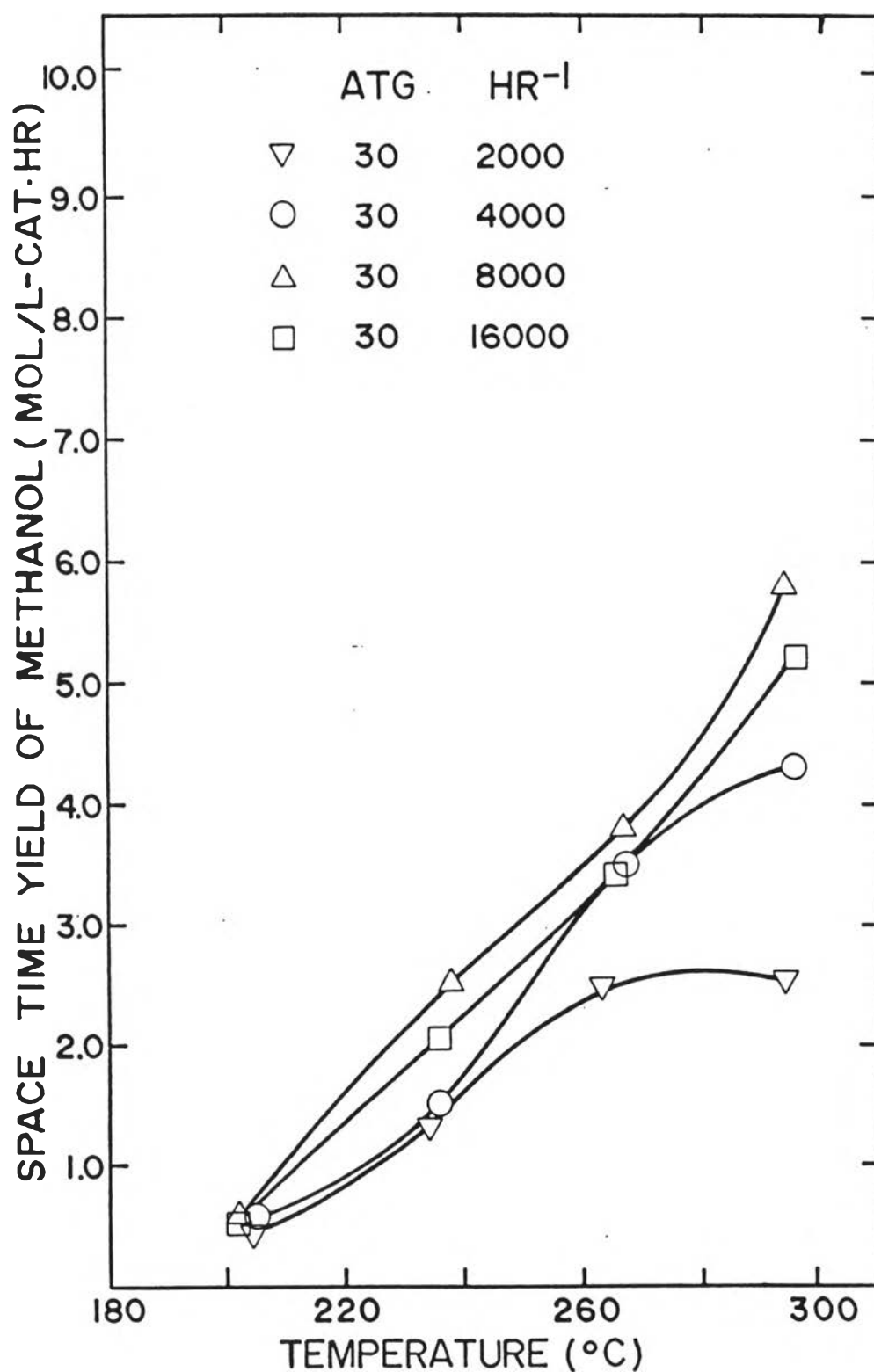


Figure 7.14 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of MeOH (at 30 atg) of Catalyst No.1

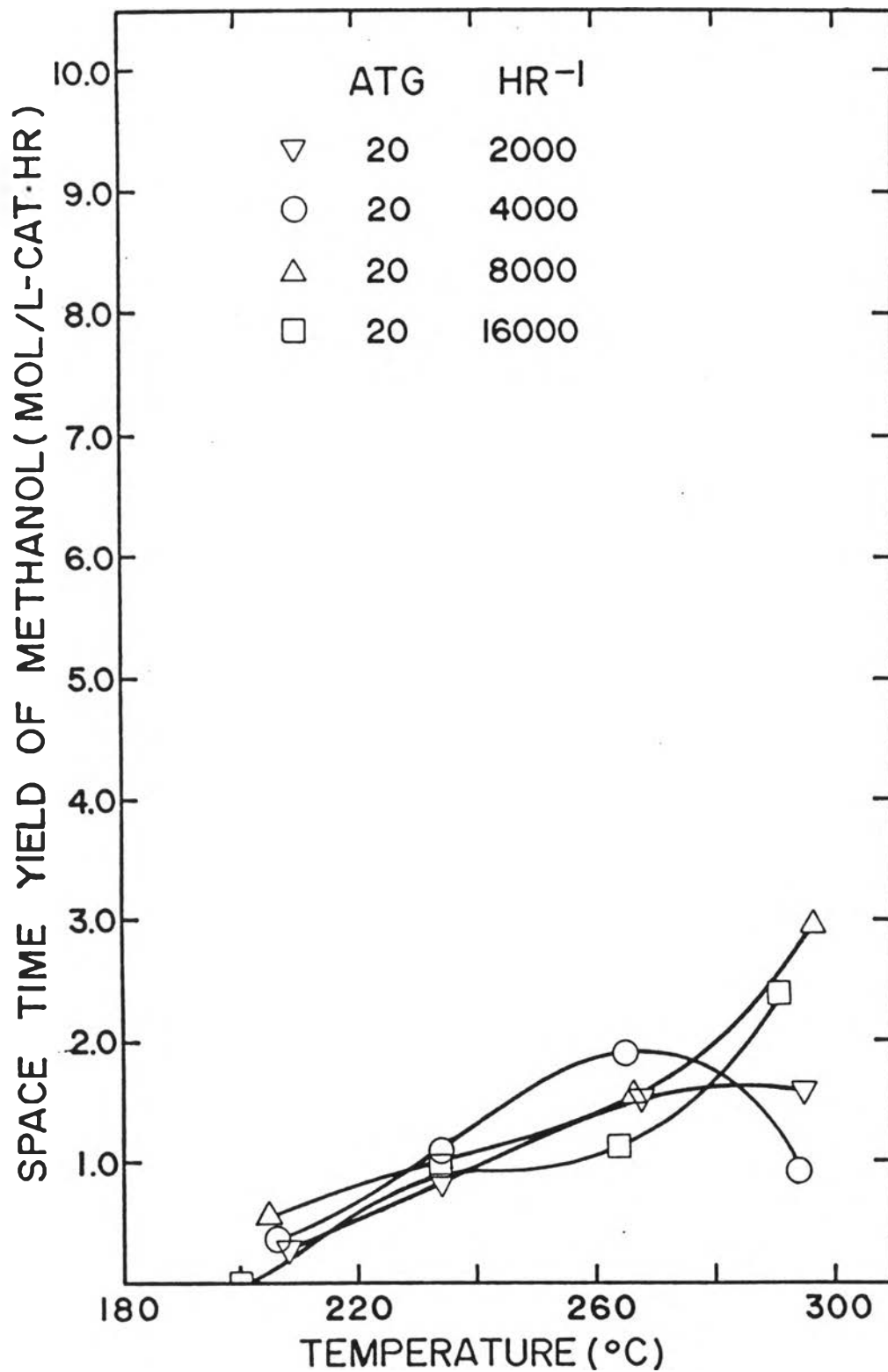


Figure 7.15 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of MeOH (at 20 atg) of Catalyst No.1

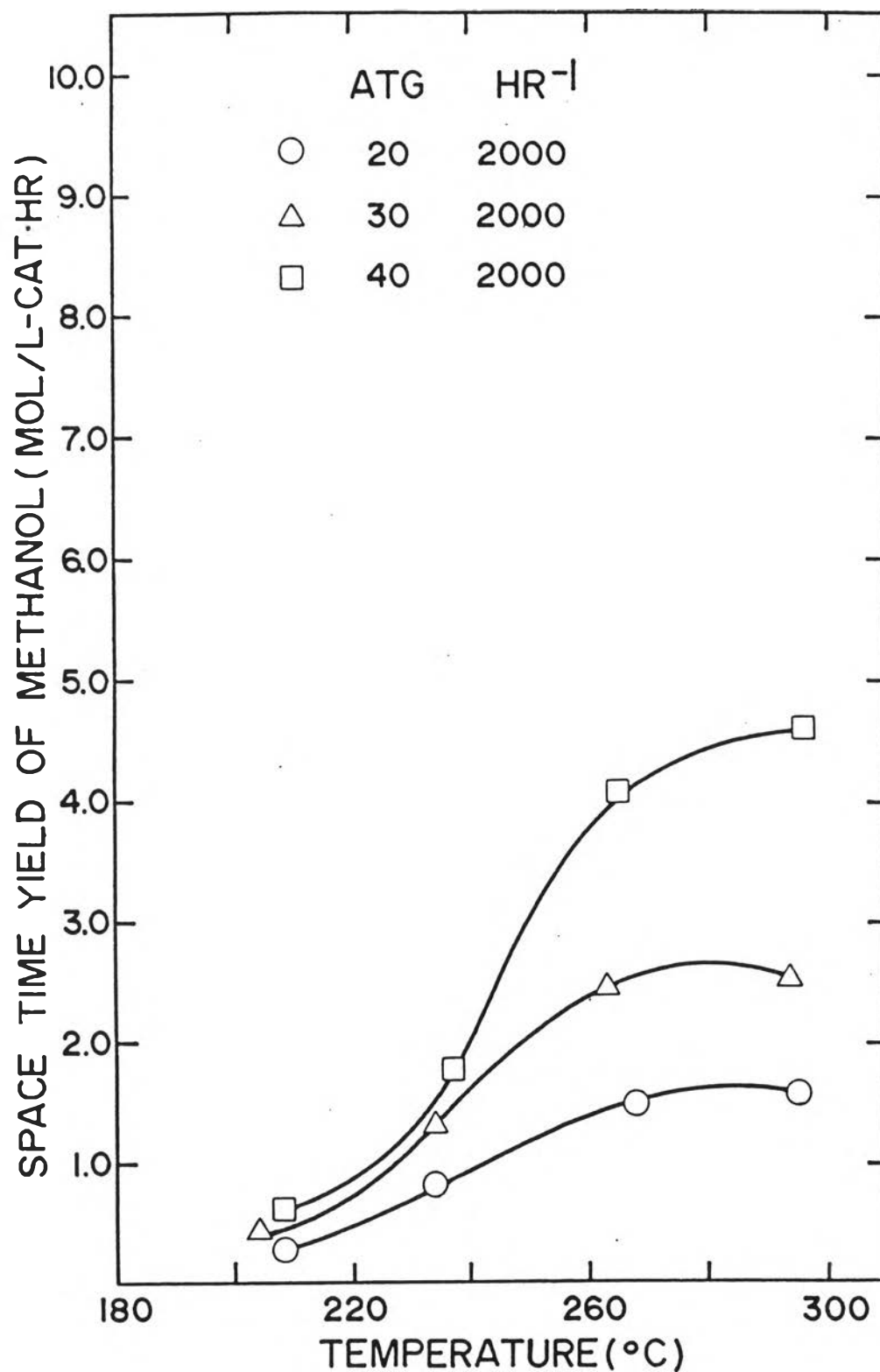


Figure 7.16 Effect of Temperature (200–300°C) and Pressure (20–40 atg) on Space Time Yield of MeOH (at 2000 hr⁻¹) of Catalyst No.1

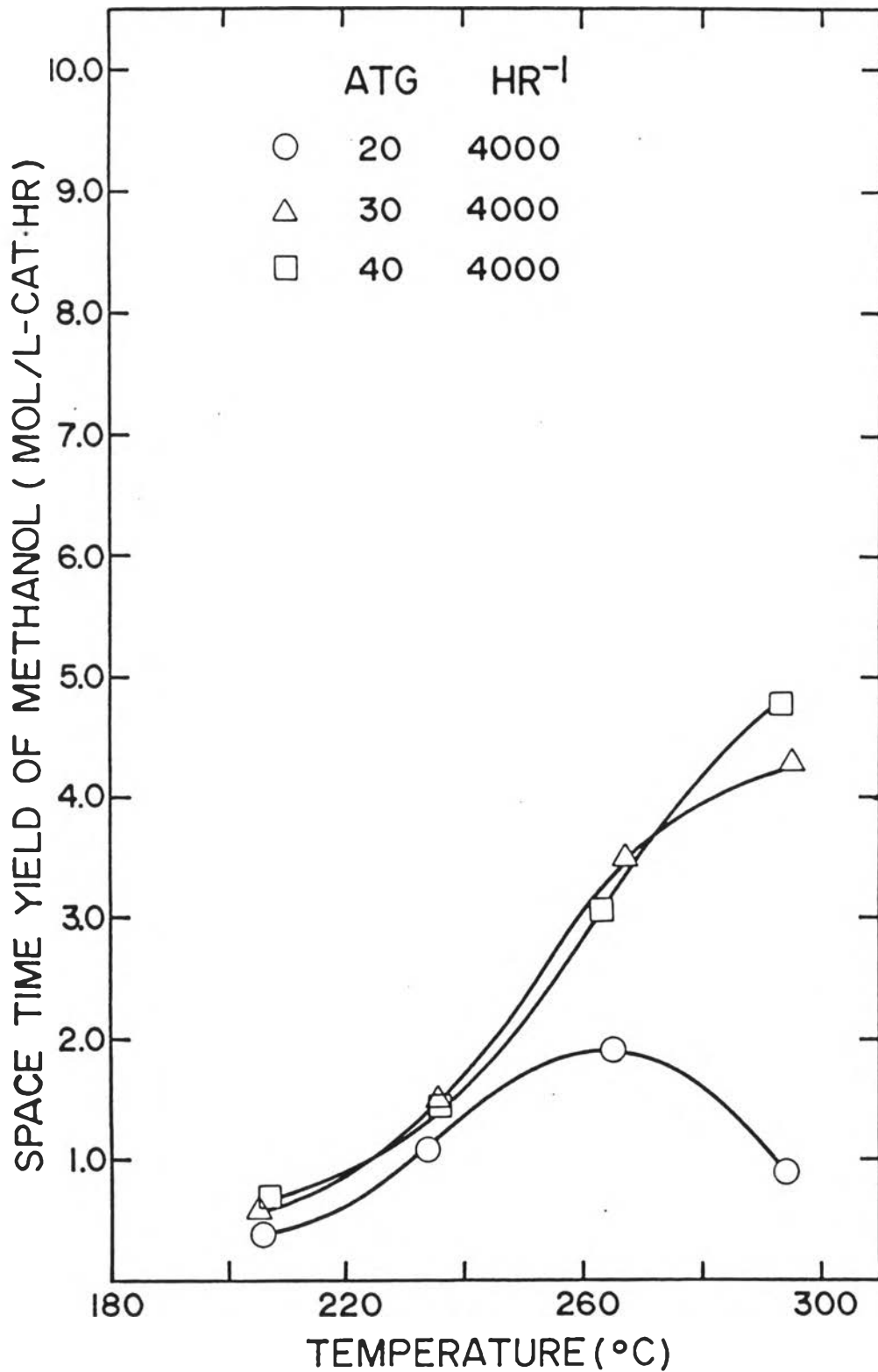


Figure 7.17 Effect of Temperature (200–300°C) and Pressure (20–40 atg) on Space Time Yield of MeOH (at 4000 hr⁻¹) of Catalyst No.1

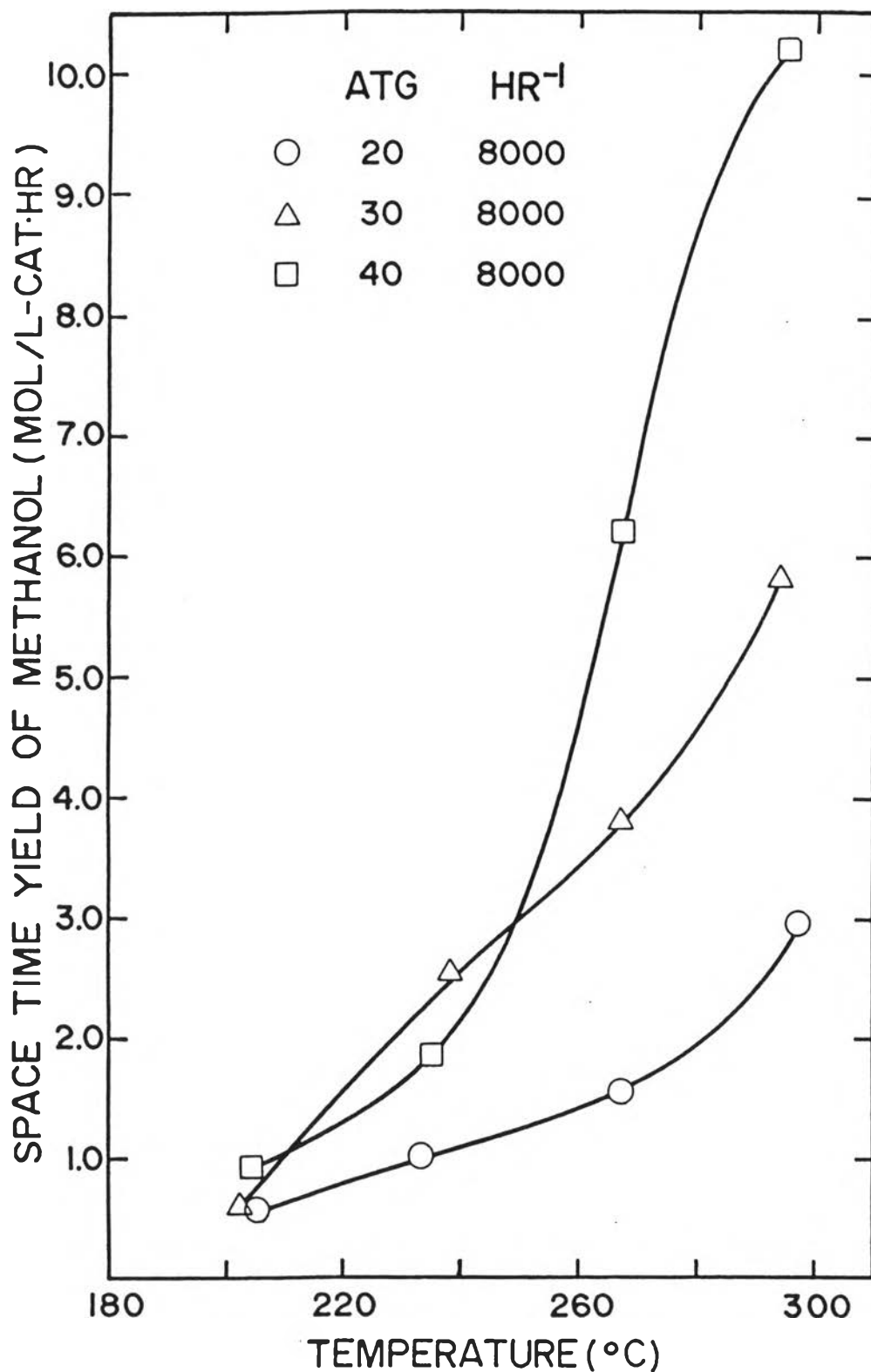


Figure 7.18 Effect of Temperature (200-300°C) and Pressure (20-40 atg) on Space Time Yield of MeOH (at 8000 hr⁻¹) of Catalyst No.1

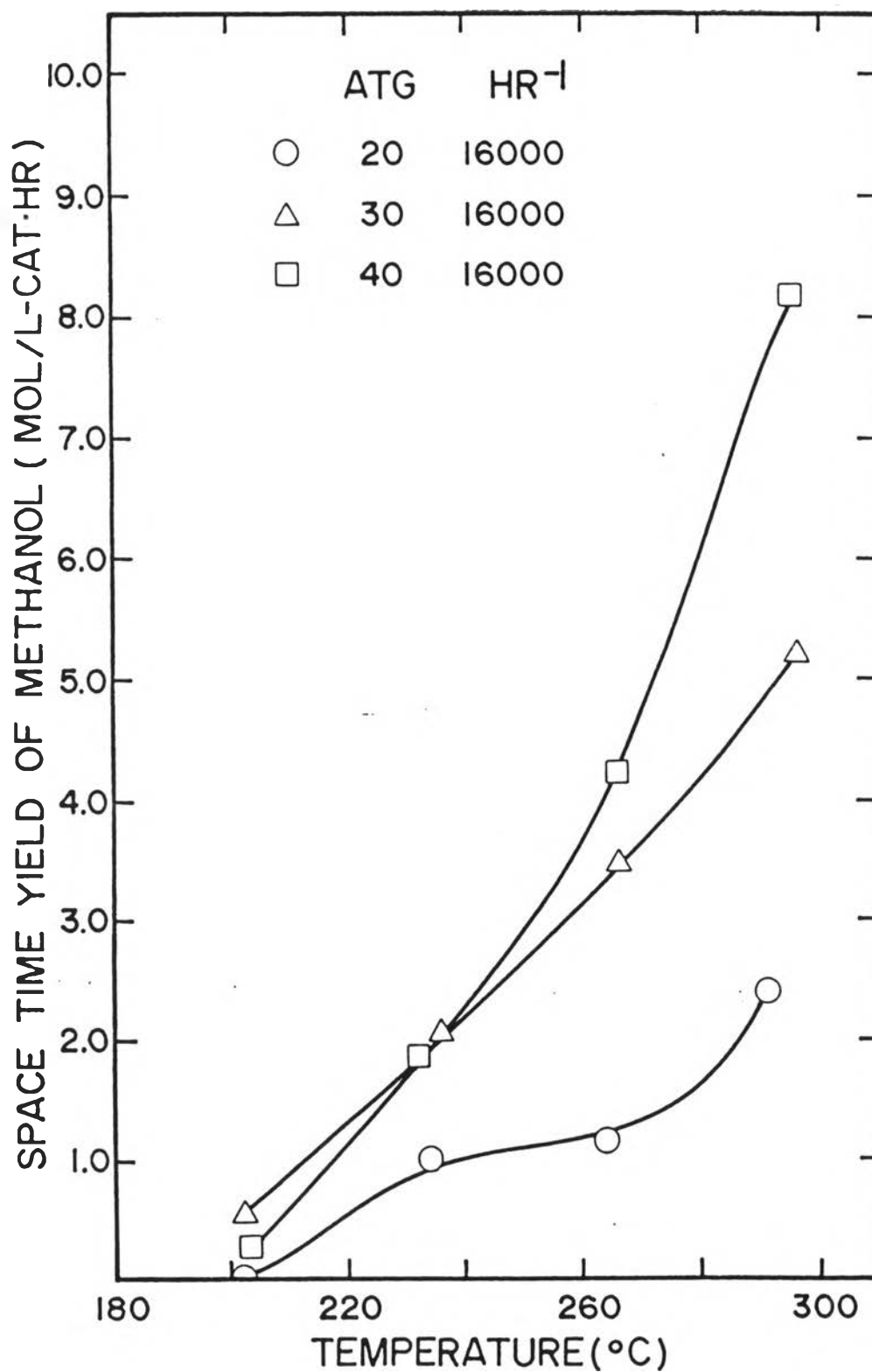


Figure 7.19 Effect of Temperature (200-300°C) and Pressure (20-40 atg) on Space Time Yield of MeOH (at 16000 hr⁻¹) of Catalyst No.1

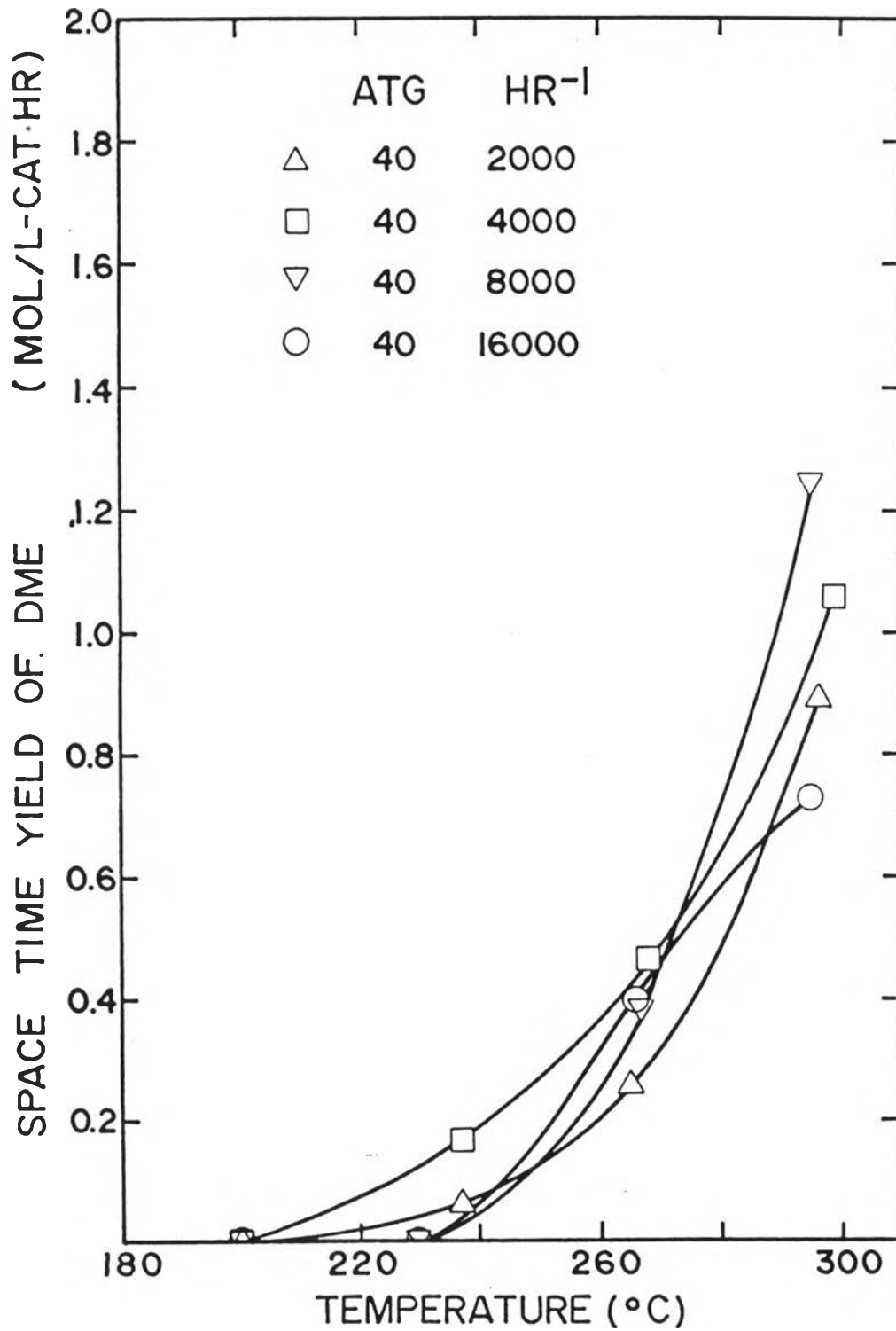


Figure 7.20 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of DME (at 40 atg) of Catalyst No.1

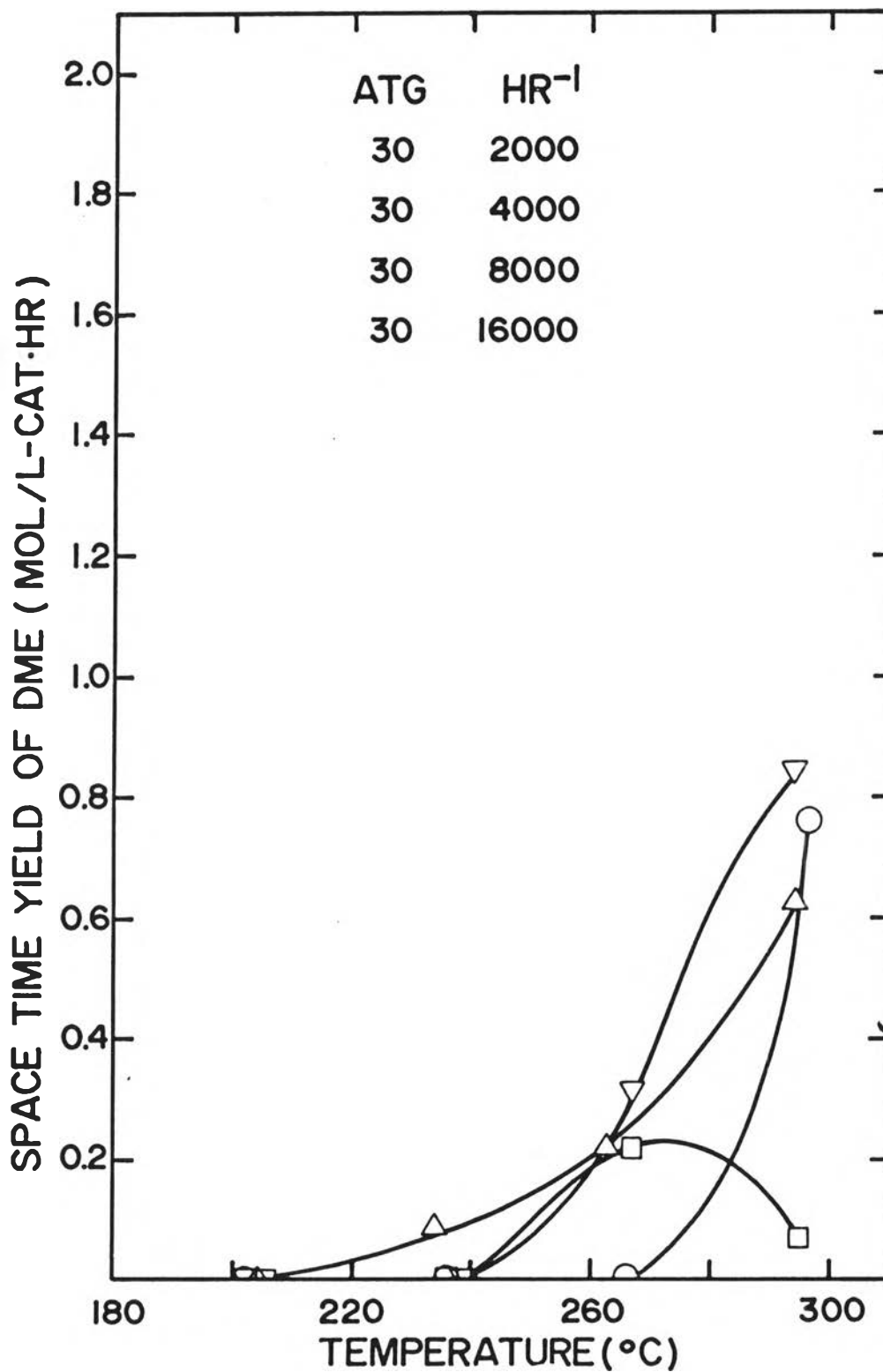


Figure 7.21 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of DME (at 30 atg) of Catalyst No.1

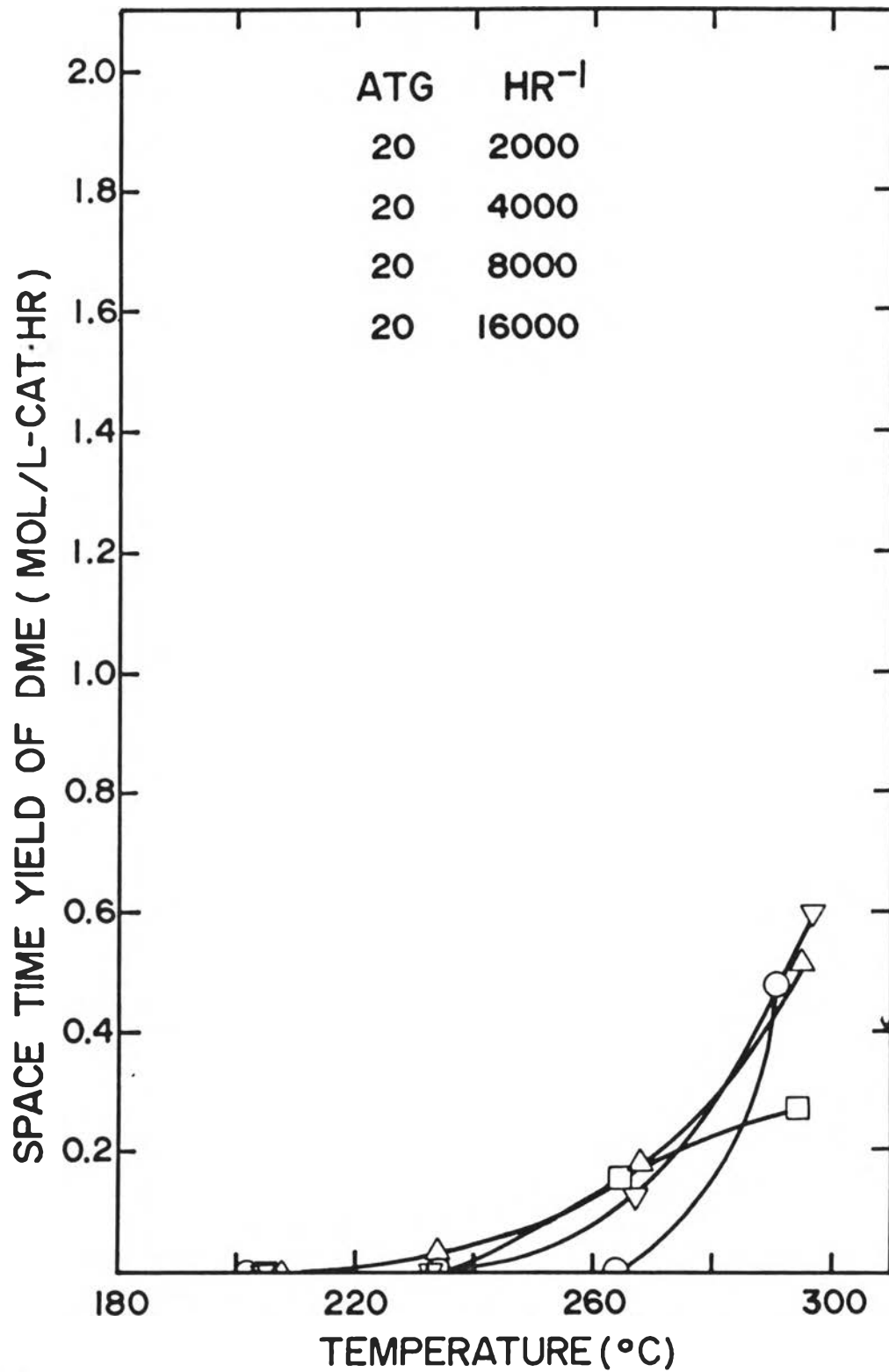


Figure 7.22 Effect of Temperature (200-300°C) and Space Velocity (2000 - 16000 hr⁻¹) on Space Time Yield of DME (at 20 atg) of Catalyst No.1

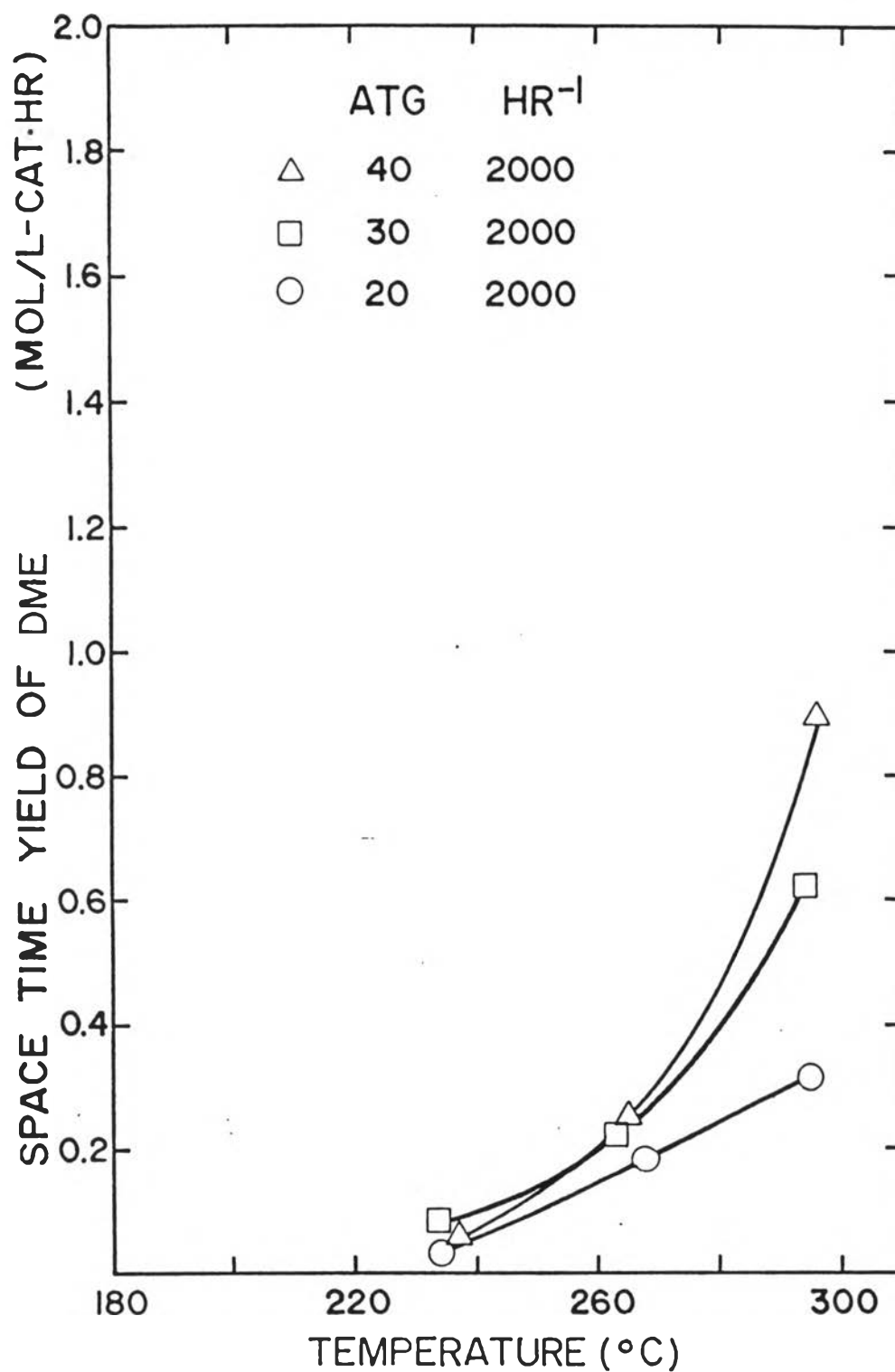


Figure 7.23 Effect of Temperature (200-300°C) and Pressure (20-40 atg) on Space Time Yield of DME (at 2000 hr⁻¹) of Catalyst No.1

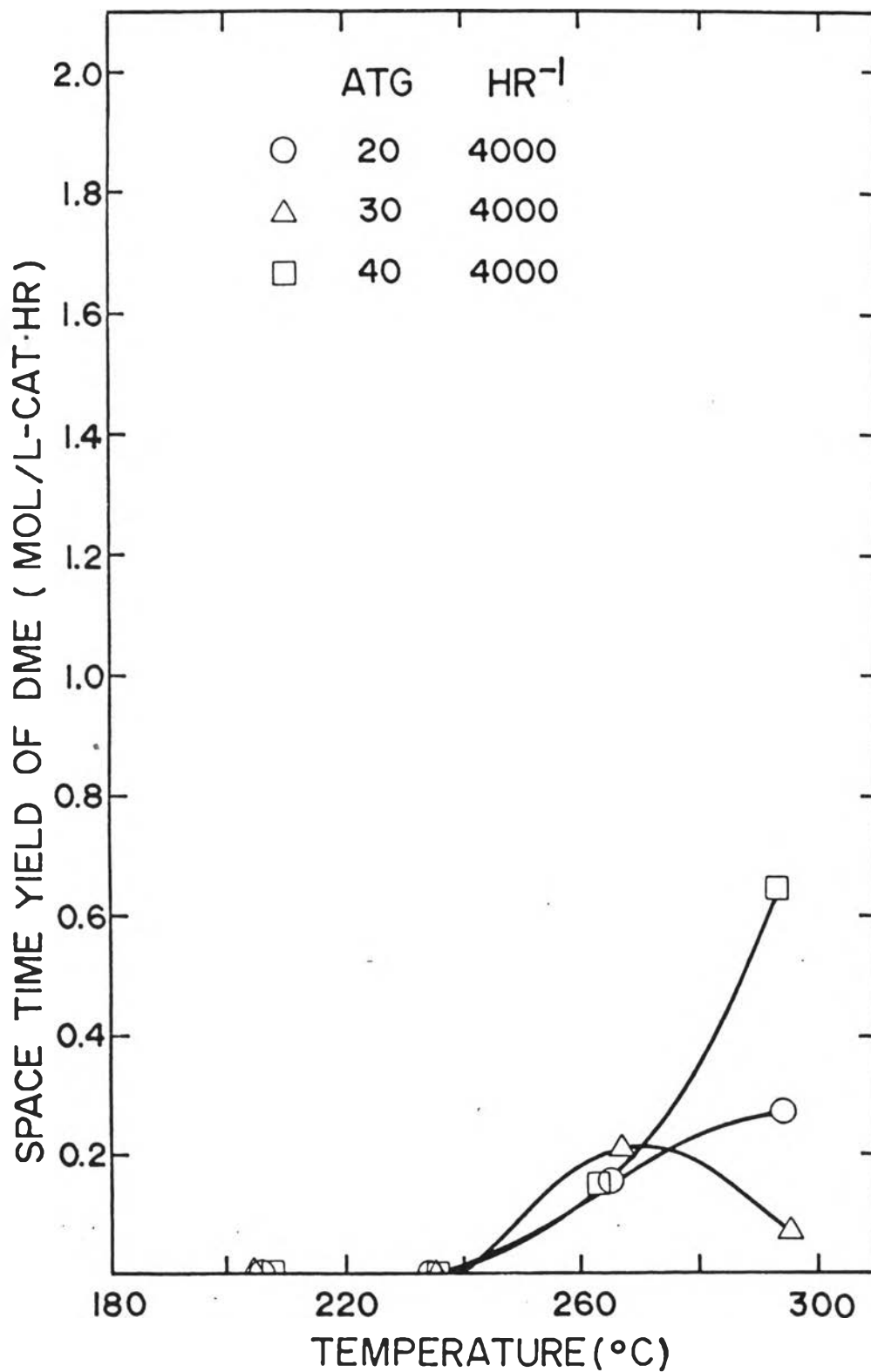


Figure 7.24 Effect of Temperature (200-300 °C) and Pressure (20-40 atg) on Space Time Yield of DME (at 4000 hr⁻¹) of Catalyst No.1

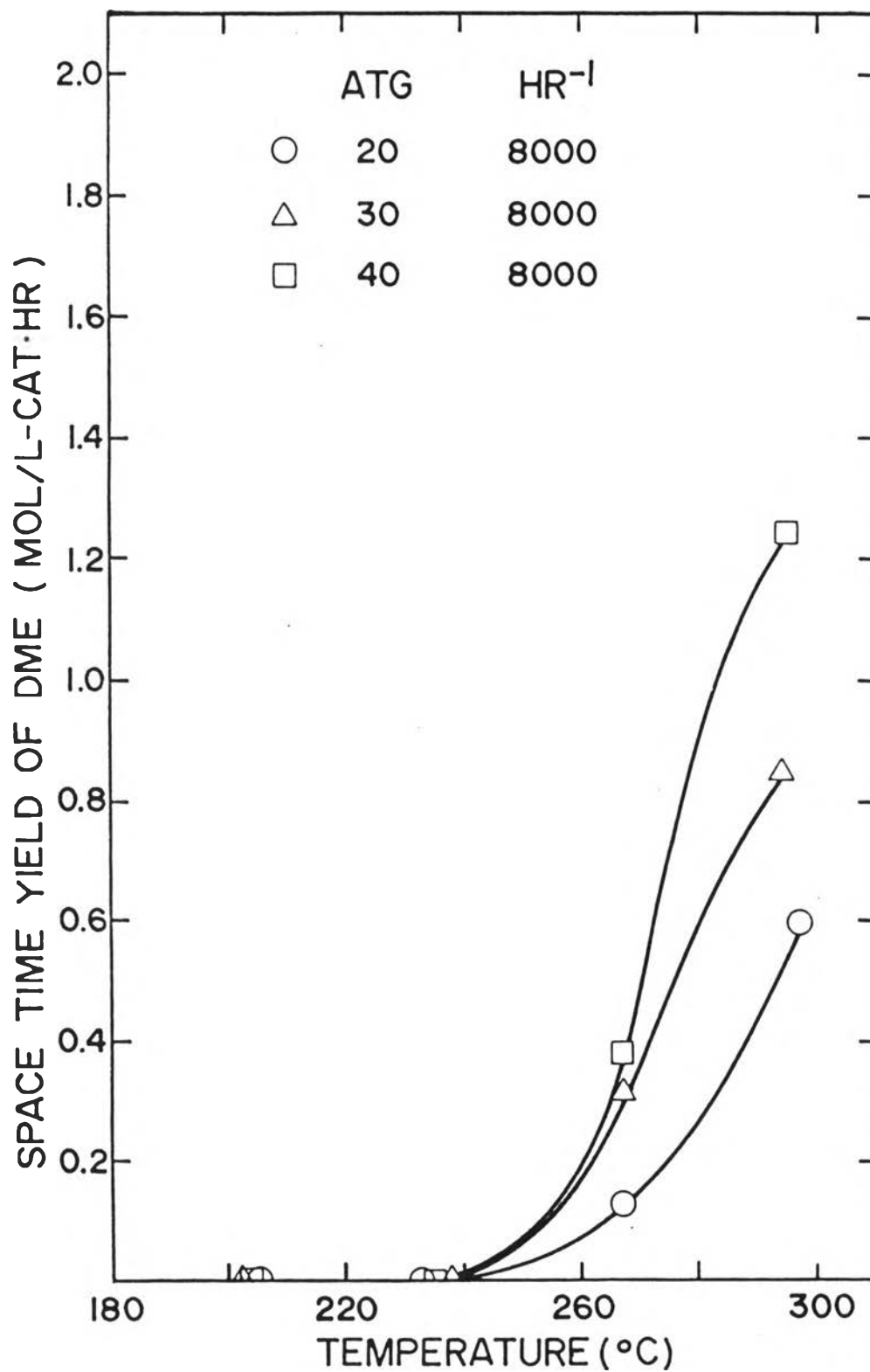


Figure 7.25 Effect of Temperature (200-300°C) and Pressure (20-40 atg) on Space Time Yield of DME (at 8000 hr⁻¹) of Catalyst No.1

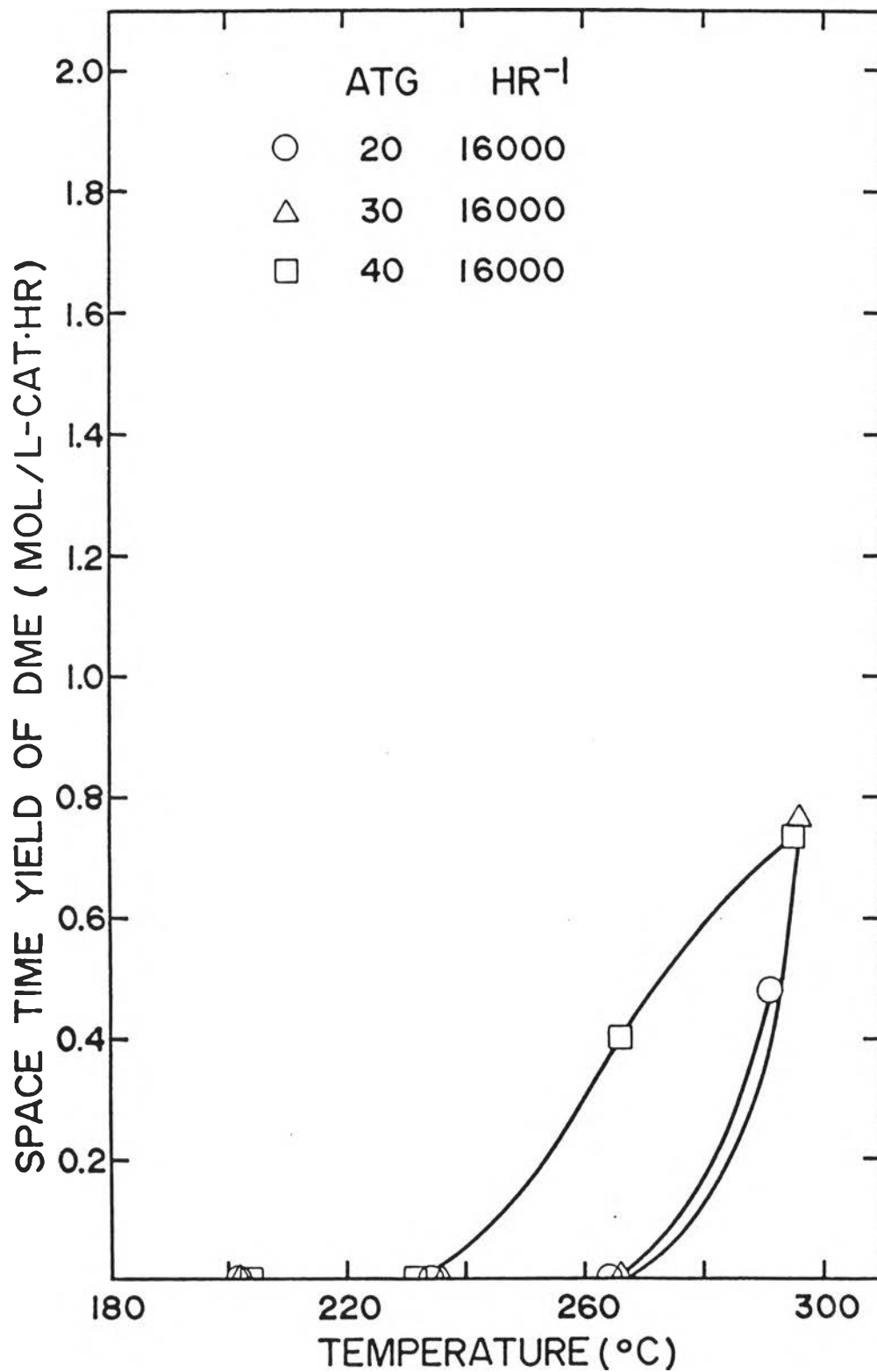


Figure 7.26 Effect of Temperature (200-300°C) and Pressure (20-40 atg) on Space Time Yield of DME (at 16000 hr⁻¹) of Catalyst No.1

participating in the reaction. With proper selection of a catalyst together with good temperature control, it was possible to suppress the formation of methane and other hydrocarbons. From Figures 7.1-7.12 we see that hydrocarbons selectivity generally decreased against increasing pressure. It also decreased in the temperature range of 200-250°C before rising again with temperature. Thus the effect of temperature on hydrocarbons selectivity was contrary to methanol selectivity. Hence, there existed an optimum temperature for methanol selectivity, wherein little hydrocarbons were produced.

Conclusions of Methanol Synthesis Results for Prepared Catalyst No.1

It was found that both temperature and pressure assisted to increase total CO conversion, but at high temperatures (over 250°C) methanol selectivity was quite low. This agreed well with the thermodynamic equilibrium of the methanol synthesis reaction. Since pressure had not much influence on the selectivities of other by-products, the methanol synthesis ought to be operated at a higher pressure (around 80~100) and in the temperature range of 220-250°C.

7.2 Comparison of Experimental Results between Catalyst No.1 and No.2

The catalyst no.1 and no.2 were both ternary catalyst but with different composition of Cu, Zn and Cr

For catalyst no.1 it was Cu : Zn : Cr = 31 : 38 : 10, whereas for catalyst no. 2 it was Cu : Zn : Cr = 2 : 2 : 1. Only experimental results under comparable conditions for catalyst no.1 and no. 2 may be compared, although the general qualitative effects of

pressure, temperature and space velocity will also be compared

Comparison of Total CO Conversion

The qualitative effects of temperature and pressure at fixed space velocity on methanol synthesis were the same for both catalysts. Both temperature and pressure assisted to increase total CO conversion (see Figures 7.1-7.2 and 7.27-7.33). Similarly, total CO conversion decreased with increasing space velocity for both catalysts. Thus, we may conclude that the effects of temperature, pressure and space velocity on total CO conversion qualitatively the same for catalyst no.1 and no.2

Maximum observed total CO conversion for catalyst no.1 was 38% at 40 atg, 268°C, 4000 hr⁻¹ while it was 30% at 30 atg, 300°C, 1900 hr⁻¹ for catalyst no.2 . These were, however, not directly comparable because they belonged to different experimental conditions. Table 7.2 attempts to make some quantitative comparisons under similar experimental conditions. We see that at 30 atg, 300°C and 2000 hr⁻¹, total CO conversion at 24% for catalyst no.1 was only slightly lower than at 27% for catalyst no.2. On the other hand, at 40 atg, 300°C and 2000 hr⁻¹, total CO conversion for catalyst no.1 at 34% was slightly higher than at 30% for catalyst no.2.

Thus we might say that there was not much difference in total CO conversion between the two catalysts at high temperature and high pressure.

At low temperatures (230~260°C), however, catalyst no.1 appears to have a significantly higher total CO conversion than catalyst no.2

Table 7.2 Comparison of Total CO Conversion Between Catalyst No.1 and No.2

Experimental Condition	Total CO Conversion (%)	
	Catalyst No.1	Catalyst No.2
20 atg, 260°C, $\approx 2000 \text{ hr}^{-1}$	9	4
20 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	20	11
30 atg, 230°C, $\approx 2000 \text{ hr}^{-1}$	14	2
30 atg, 300°C, $\approx 200 \text{ hr}^{-1}$	24	27
40 atg, 240°C, $\approx 2000 \text{ hr}^{-1}$	9	3
40 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	34	30

Comparison of Methanol Selectivity and Space Time Yield of Methanol

Methanol selectivity for both catalysts generally increased with increasing pressure. It tended to rise at first with temperature before decreasing as temperature increases further. With respect to space velocity for both catalysts failed to exhibit any regular pattern (see Figures 7.1-7.12 and 7.27-7.33)

Table 7.3 compares methanol selectivity under similar experimental conditions between catalyst no.1 and no. 2, as obtained from figures 7.1-7.33. It is obvious from table 7.3 that catalyst no.1 generally had a significantly higher methanol selectivity than

catalyst no.2 under all comparable experimental conditions.

Table 7.3 Comparison of Methanol Selectivity Between Catalyst No.1 and No.2

Experimental Conditions	Methanol Selectivity	
	Catalyst No.1	Catalyst No.2
20 atg, 260°C, $\approx 2000 \text{ hr}^{-1}$	51	25
20 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	27	7
30 atg, 230°C, $\approx 2000 \text{ hr}^{-1}$	28	25
30 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	37	5
40 atg, 240°C, $\approx 2000 \text{ hr}^{-1}$	76	25
40 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	46	5

In general, space time yield (STY) of methanol for both catalysts increased with both pressure and temperature, except at 20 atg for catalyst no.2 (see Figures 7.13-7.19, and Figures 7.34-7.35). With respect to space velocity, STY of methanol for catalyst no.1 increased as space velocity increased from 2000-8000 hr^{-1} but decreased for space velocity above 8000 hr^{-1} because total CO conversion and methanol selectivity dropped rapidly at very high space velocity. On the other hand, STY of methanol for catalyst no.2 increased all the way with space velocity because its methanol selectivity decreased only slightly with space velocity. (Note that $\text{STY} = \text{space velocity} \times \text{total CO conversion} \times \text{methanol selectivity}$)

Table 7.4 compares the STY of methanol under similar experimental conditions. Obviously, catalyst no.1 had a much higher STY of methanol than catalyst no.2 under comparable conditions.

Table 7.4 Comparison of Space Time Yield of Methanol
Between Catalyst No.1 and No.2

Experimental Conditions	Space Time Yield (mol/l-cat.hr)	
	Catalyst No.1	Catalyst No.2
20 atg, 260°C, $\approx 2000 \text{ hr}^{-1}$	1.4	0.38
20 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	1.6	0.28
30 atg, 230°C, $\approx 2000 \text{ hr}^{-1}$	1.2	0.37
30 atg, 300 C, $\approx 2000 \text{ hr}^{-1}$	2.6	0.48
40 atg, 240°C, $\approx 2000 \text{ hr}^{-1}$	1.4	0.05
40 atg, 300°C, $\approx 2000 \text{ hr}^{-1}$	4.6	0.6

Comparison of CO₂ selectivity

For both catalysts CO₂ selectivity generally increased with temperature in the high range . However, in the low temperature range, some experiments showed CO₂ selectivity to decrease with temperature. Since these were accompanied by increased methanol selectivity, it might be thought that some CO₂ was converted to CH₃OH as in the reaction $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$. With respect to pressure and space velocity, CO₂ selectivity appeared slightly affected for both catalysts.

From table 7.5 we see that catalyst no.1 had a lower CO₂ selectivity than catalyst no.2 under similar experimental conditions

Table 7.4 Comparison of CO_2 Selectivity Between Catalyst No.1 and No.2

Experimental Conditions	CO_2 Selectivity(%)	
	Catalyst No.1	Catalyst No.2
20 atg, 260°C , $\approx 2000 \text{ hr}^{-1}$	17	15
20 atg, 300°C , $\approx 2000 \text{ hr}^{-1}$	28	22
30 atg, 230°C , $\approx 2000 \text{ hr}^{-1}$	5	65
30 atg, 230°C , $\approx 2000 \text{ hr}^{-1}$	22	70
40 atg, 240°C , $\approx 2000 \text{ hr}^{-1}$	10	53
40 atg, 300°C , $\approx 2000 \text{ hr}^{-1}$	22	75

Comparison of Hydrocarbon Selectivity

Hydrocarbon selectivity of catalyst no.1 generally decreased with temperature and pressure. But it was contrary to catalyst no.2. Hydrocarbon selectivity for both catalysts generally increased as space velocity rose (Figures 7.1 - 7.12 and 7.27 - 7.33)

We see from table 7.5 that catalyst no.1 possessed higher hydrocarbon selectivity than catalyst no.2 under comparable conditions but showed lower CO_2 selectivity.

Table 7.6 Comparison of Hydrocarbon Selectivity Between
Catalyst No.1 and No.2

Experimental Conditions	Hydrocarbon Selectivity(%)	
	Catalyst No.1	Catalyst No.2
20 atg, 260°C, 2000 hr ⁻¹	24	5
20 atg, 300°C, 2000 hr ⁻¹	28	10
30 atg, 230°C, 2000 hr ⁻¹	63	2
30 atg, 300°C, 2000 hr ⁻¹	24	3
40 atg, 240°C, 2000 hr ⁻¹	10	3
40 atg, 300°C, 2000 hr ⁻¹	22	4

Comparison of DME selectivity and Space Time Yield of DME

Selectivity and STY of DME for both catalysts generally increased with temperature but were slightly affected by pressure. It might be said that the effect of pressure was not much different between both catalysts (see Figures 7.1-7.33)

With respect to space velocity, DME selectivity for both catalysts normally decreased with space velocity. However, for catalyst no.1 STY of DME increased with space velocity until 8000 hr⁻¹, above which it then decreased. For catalyst no.2 STY of DME generally decreased with space velocity. The reason was that STY of DME depended on both total CO conversion and DME selectivity, but DME selectivity for catalyst no.1 decreased only slightly with space velocity, while that of catalyst no.2 decreased considerably with space velocity.

Table 7.7 shows that catalyst no.1 a lower DME selectivity than catalyst no.2 under comparable conditions. On the other hand, catalyst no.1 generally gave a slightly higher space time yield of DME because its total CO conversion was higher.

Table 7.7 Comparison of DME Selectivity and Space Time Yield of DME
Between Catalyst No. 1 and No.2

Experimental Conditions	DME Selectivity(%)		STY of DME (mol/l-cat.hr ⁻¹)	
	Catalyst No.1	Catalyst No.2	Catalyst No.1	Catalyst No.2
20 atg, 260°C, ≈ 2000 hr ⁻¹	10	45	0.15	0.3
20 atg, 300°C, ≈ 2000 hr ⁻¹	18	52	0.32	0.88
30 atg, 230°C, ≈ 2000 hr ⁻¹	5	8	0.08	0.02
30 atg, 300°C, ≈ 2000 hr ⁻¹	18	15	0.63	0.76
40 atg, 240°C, ≈ 2000 hr ⁻¹	5	15	0.08	0.01
40 atg, 300°C, ≈ 2000 hr ⁻¹	18	11	0.9	0.61

From the above we may conclude that the qualitative effects of temperature, pressure and space velocity on methanol synthesis were quite similar between catalyst no.1 and no.2, except at very high space velocity (over 8000 hr⁻¹). More specifically, catalyst no.1 generally yielded less by-products (except hydrocarbons) than catalyst no.2, and thus synthesized more methanol.

Both catalysts were same of the ternary type comprising Cu, ZnO and Cr₂O₃ and were prepared with the same procedure that included mechanical mixing of ZnO and CrO₃, which reportedly had higher activity than catalysts obtained by coprecipitation (K.K. 1982). Their compositions, however, were different, the atomic ratios of Cu : Zn : Cr being 31 : 38 : 10 and 2 : 2 : 1 for catalyst no.1 and no.2, respectively.

Going back to the section on selection of methanol synthesis catalysts, we see that Cu and Zn are metals not far to the right of the boundary marked on the periodic table 2.5. They guided the hydrogenation of CO to methanol because their oxides chemisorbed CO with only moderate strength, just sufficient to perturb the CO molecule to enable it to react with hydrogen. On the other hand, Cr_2O_3 caused dissociated chemisorption of CO and tended to break CO or any of the intermediates into fragments. So Cr_2O_3 was not quite appropriate as methanol synthesis catalyst. In the past, it was found that pure CuO or ZnO catalyst induced less methanol yield than a mixed catalyst of CuO and ZnO simply because the presence of ZnO induced the amorphous state of copper, which was observed in the most active methanol synthesis (K.K. 1982). From a practical point of view, a good catalyst should possess high activity, high selectivity and finally good resistance toward aging. The presence of Cr_2O_3 (beyond a definite Cr_2O_3 concentration limit) helped to hinder the recrystallization of ZnO. Formerly very high methanol yields had been obtained with catalyst containing 20-30% Cr_2O_3 . Recently the methanol industry has witnessed and successfully employed some active and resistant catalysts, which contain Cr_2O_3 in concentrations lower than that formerly classified as "optimum". For example, Montecatini Chemical Co. used a catalyst containing 11% by weight of Cr_2O_3 (which was the same as catalyst no.1, while it was 19% for catalyst no.2)

In fact, catalyst no.1 and no.2 had the same atomic ratios of Cu and Zn. So it might be said that it was difference in Cr_2O_3 that contributed to the different results. As mentioned earlier Cr_2O_3 caused dissociated chemisorption CO and tended to break CO and any of the intermediates of methanol into fragments, thus resulting in more by-products, which were evident from the experi-

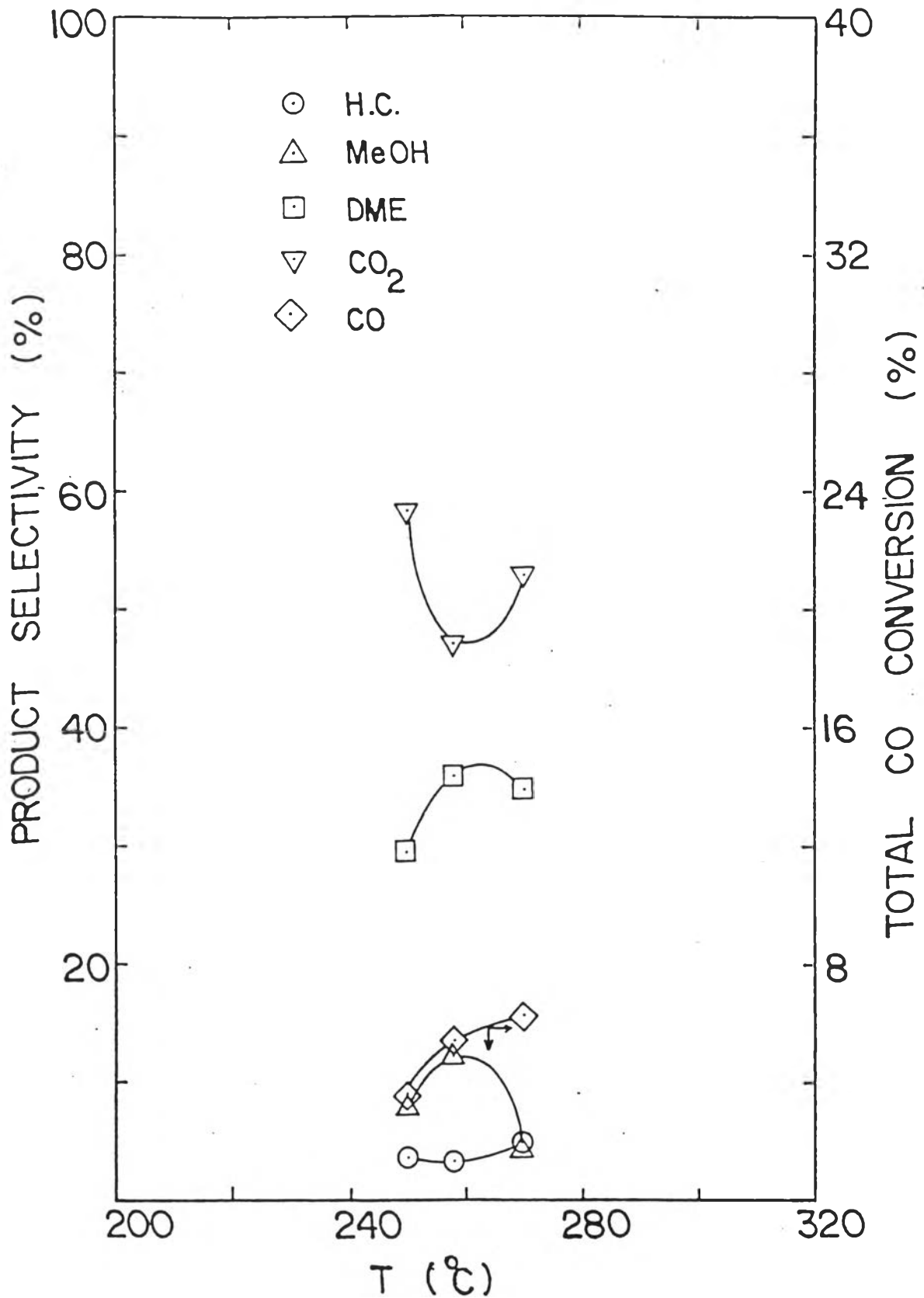


Figure 7.27 Effect of Temperature on Total CO Conversion and Product Selectivities (at 20 atg, 1200 hr^{-1}) of Catalyst No.2

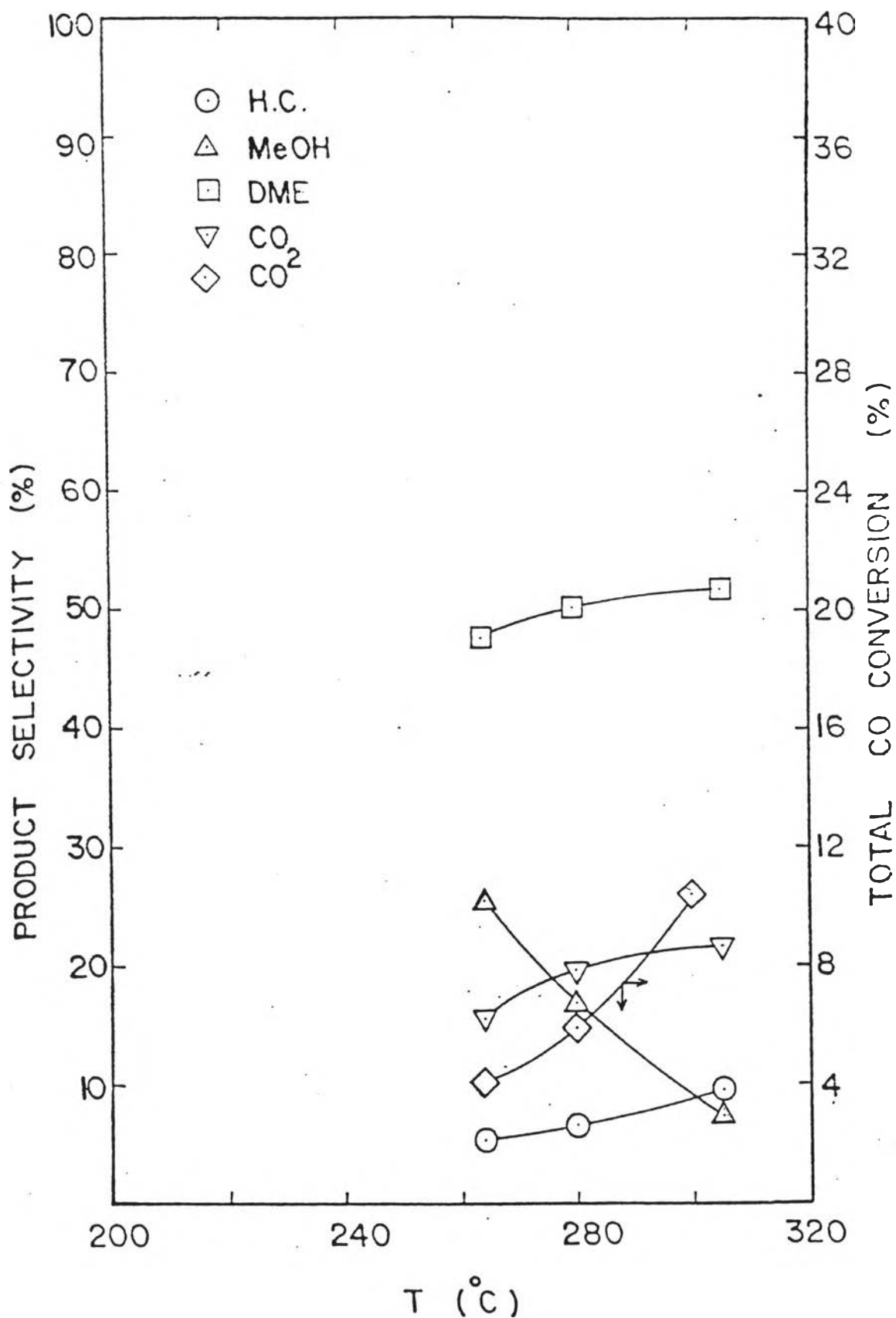


Figure 7.28 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 20 atg, 2400 hr^{-1}) of Catalyst No.2

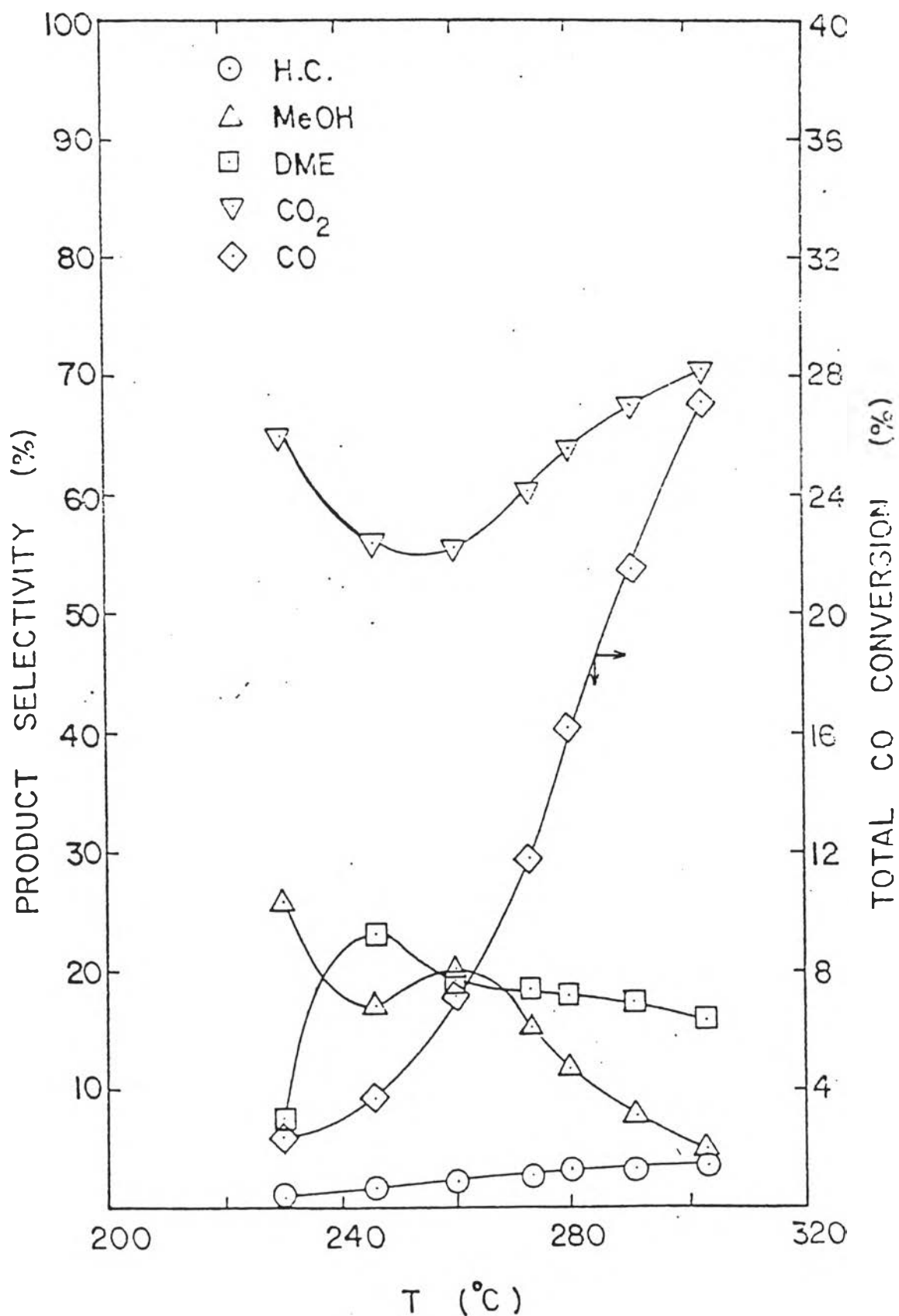


Figure 7.29 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 30 atg, 1900 hr⁻¹) of Catalyst No.2

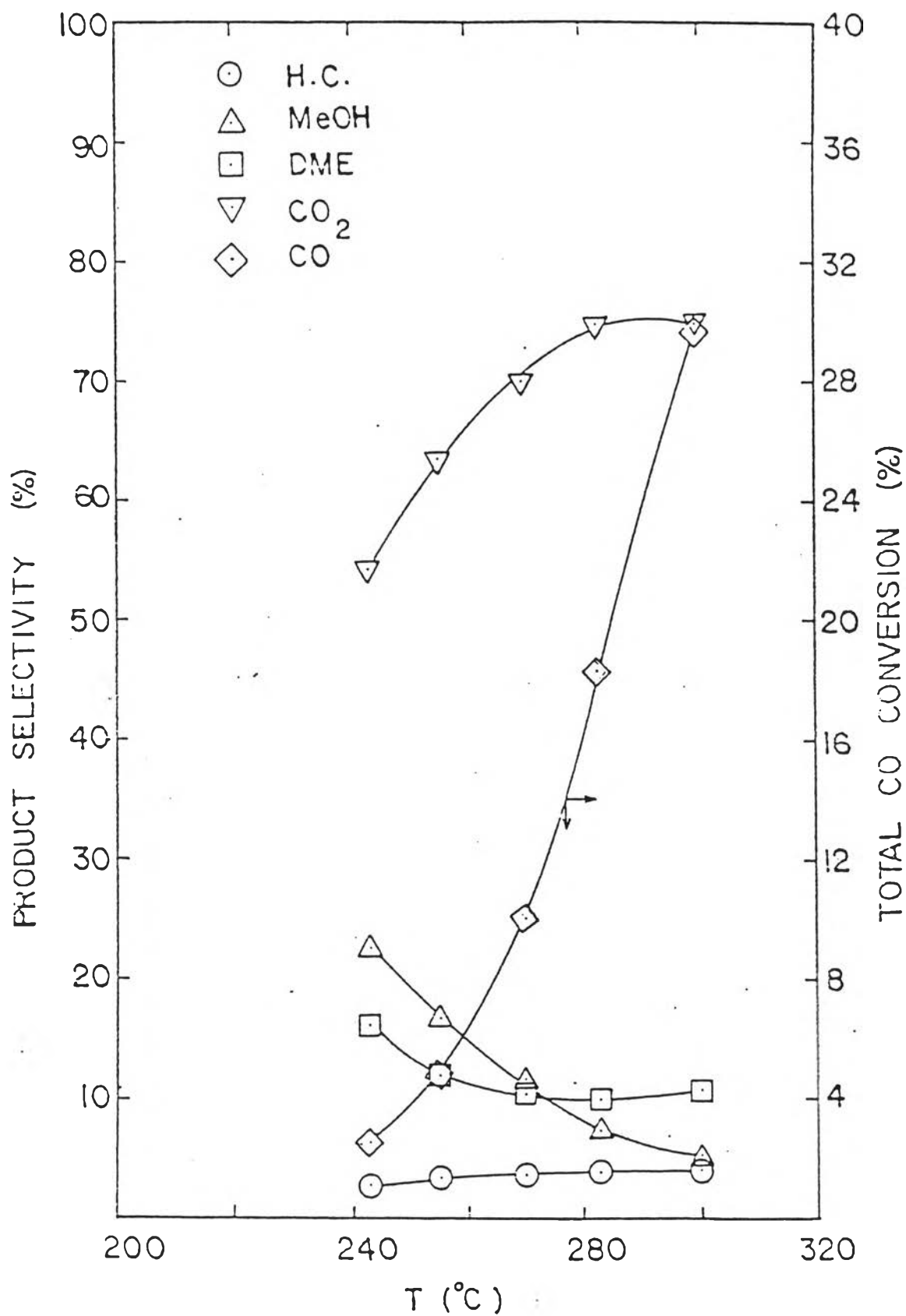


Figure 7.30 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 40 atg , 2400 hr⁻¹) of Catalyst No.2

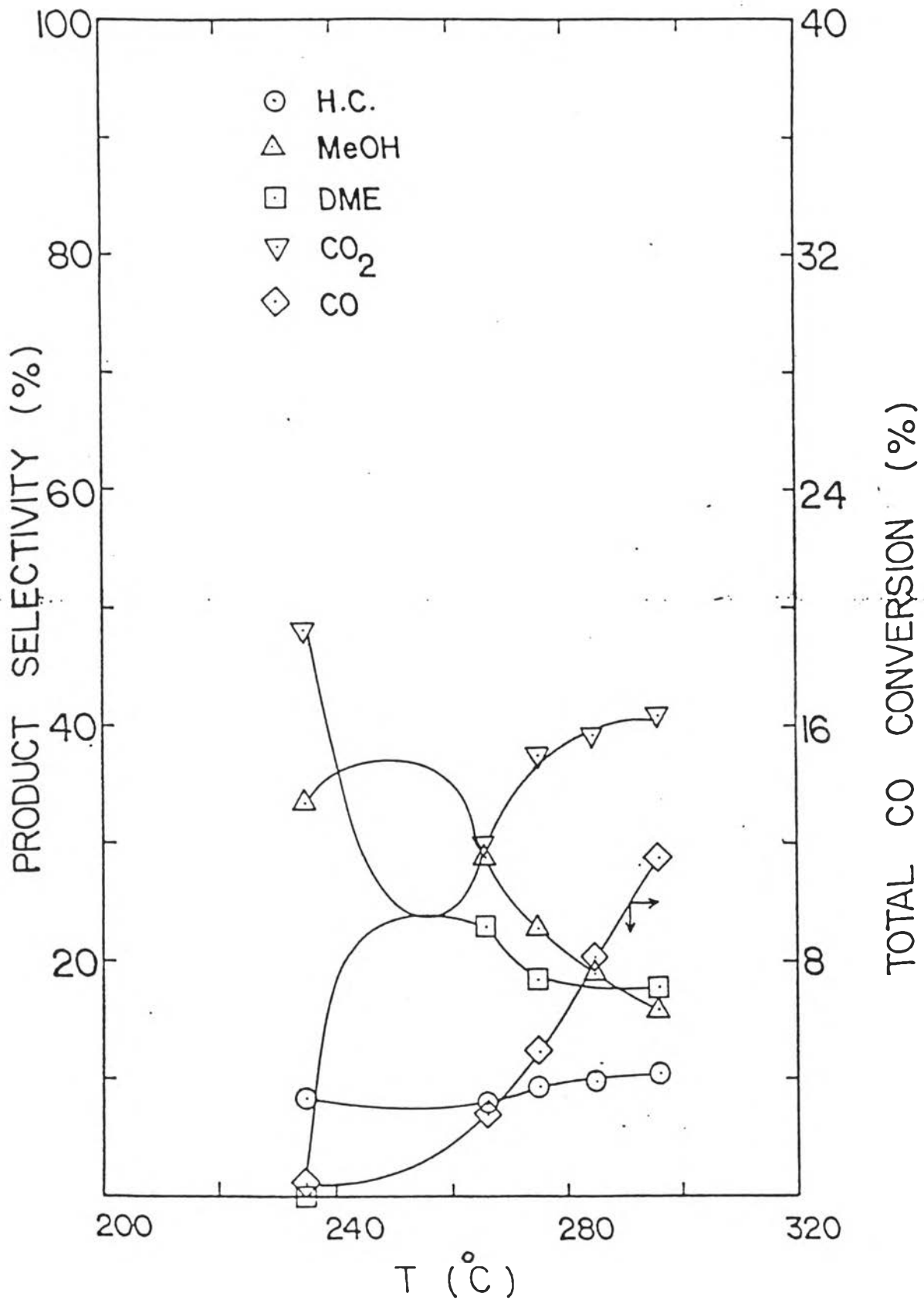


Figure 7.31 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 50 atg , 3500 hr⁻¹) of Catalyst No.2

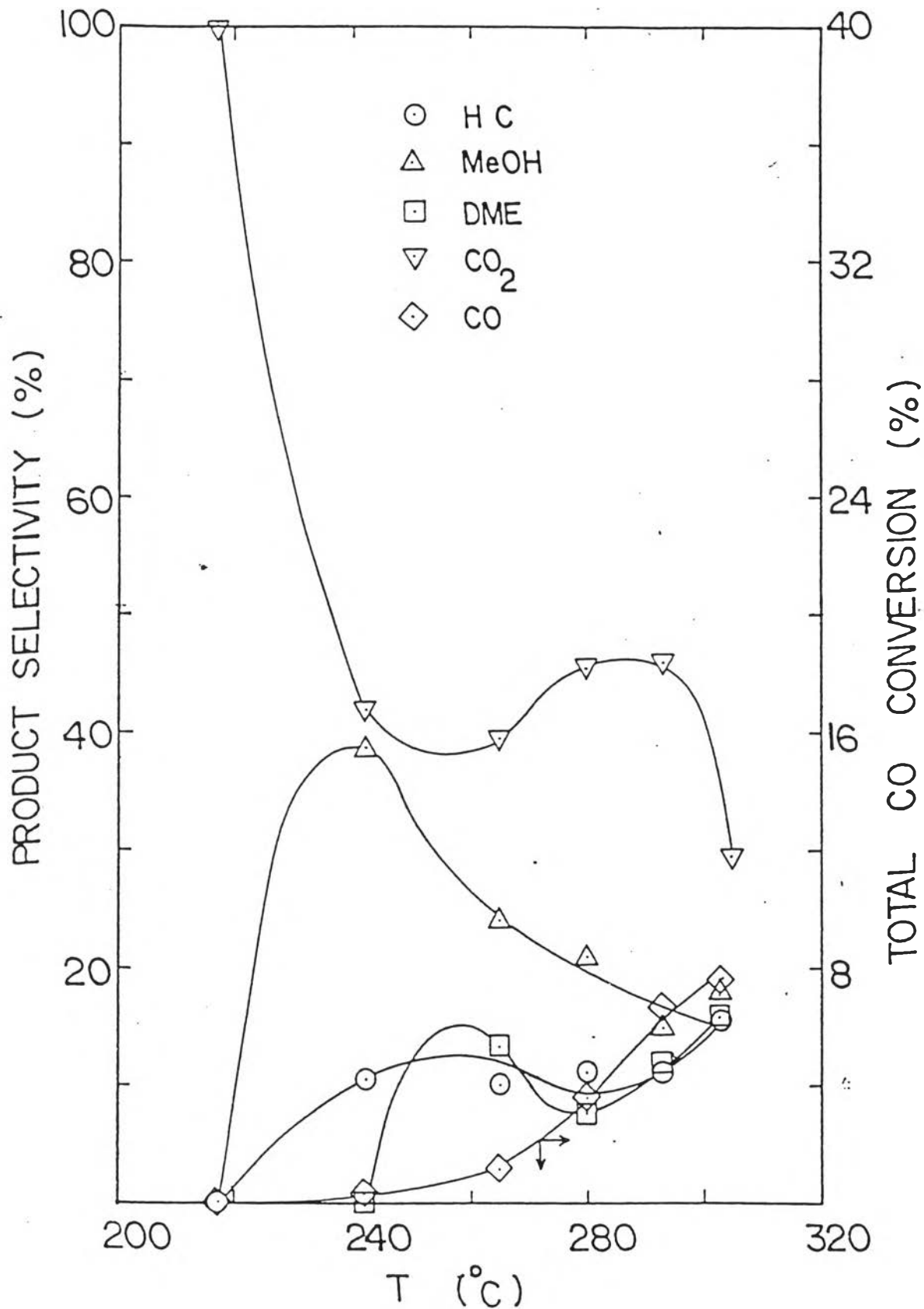


Figure 7.32 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 50 atg , 7900 hr⁻¹) of Catalyst No.2

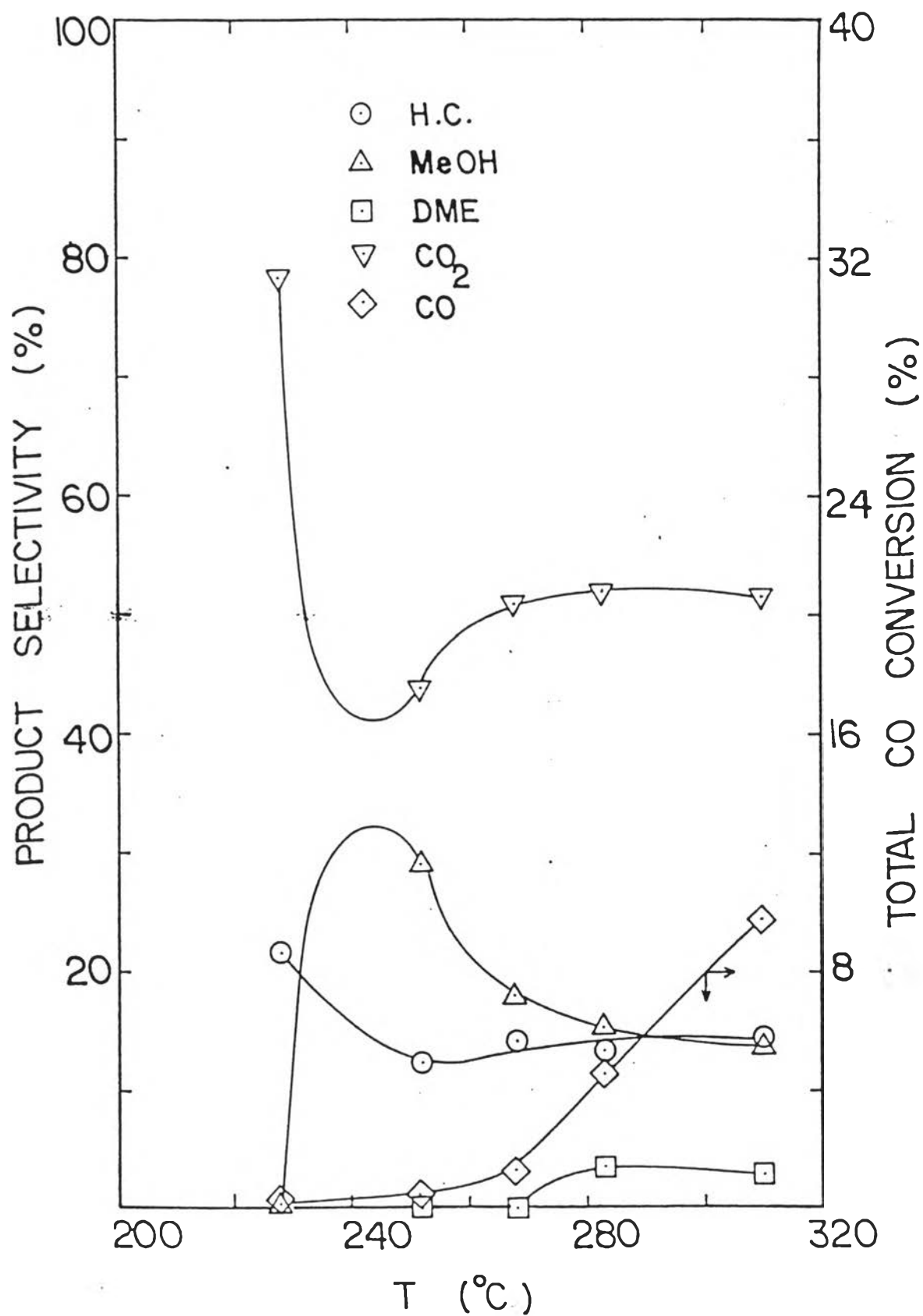


Figure 7.33 Effect of Temperature on Total CO Conversion and Product Selectivities of (at 50 atg, 15100 hr^{-1}) of Catalyst No.2

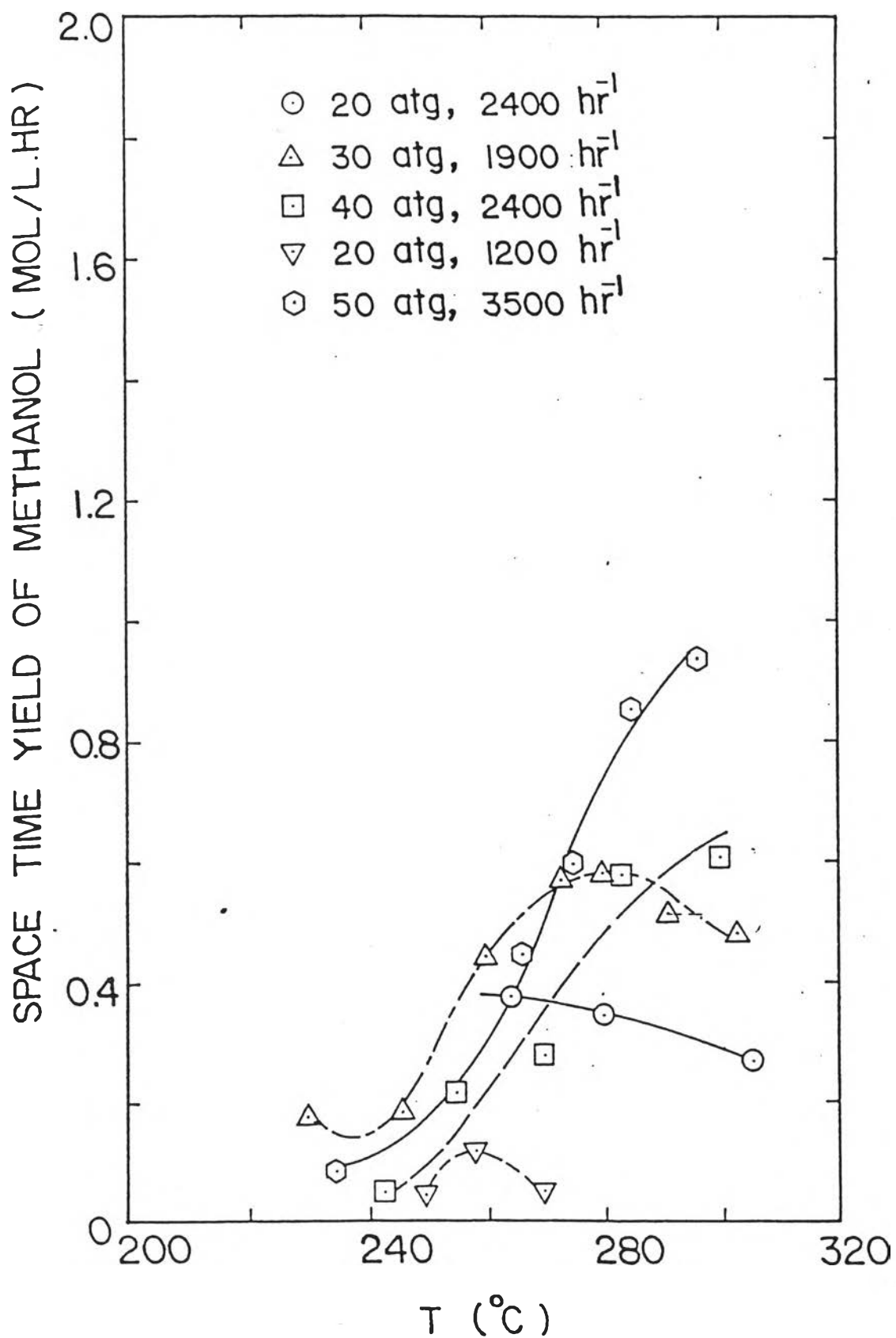


Figure 7.34 Effect of Temperature (200–300°C), Pressure (20–50 atg) and Space Velocity (2400–3500 hr⁻¹) on Space Time Yield of MeOH of Catalyst No.2

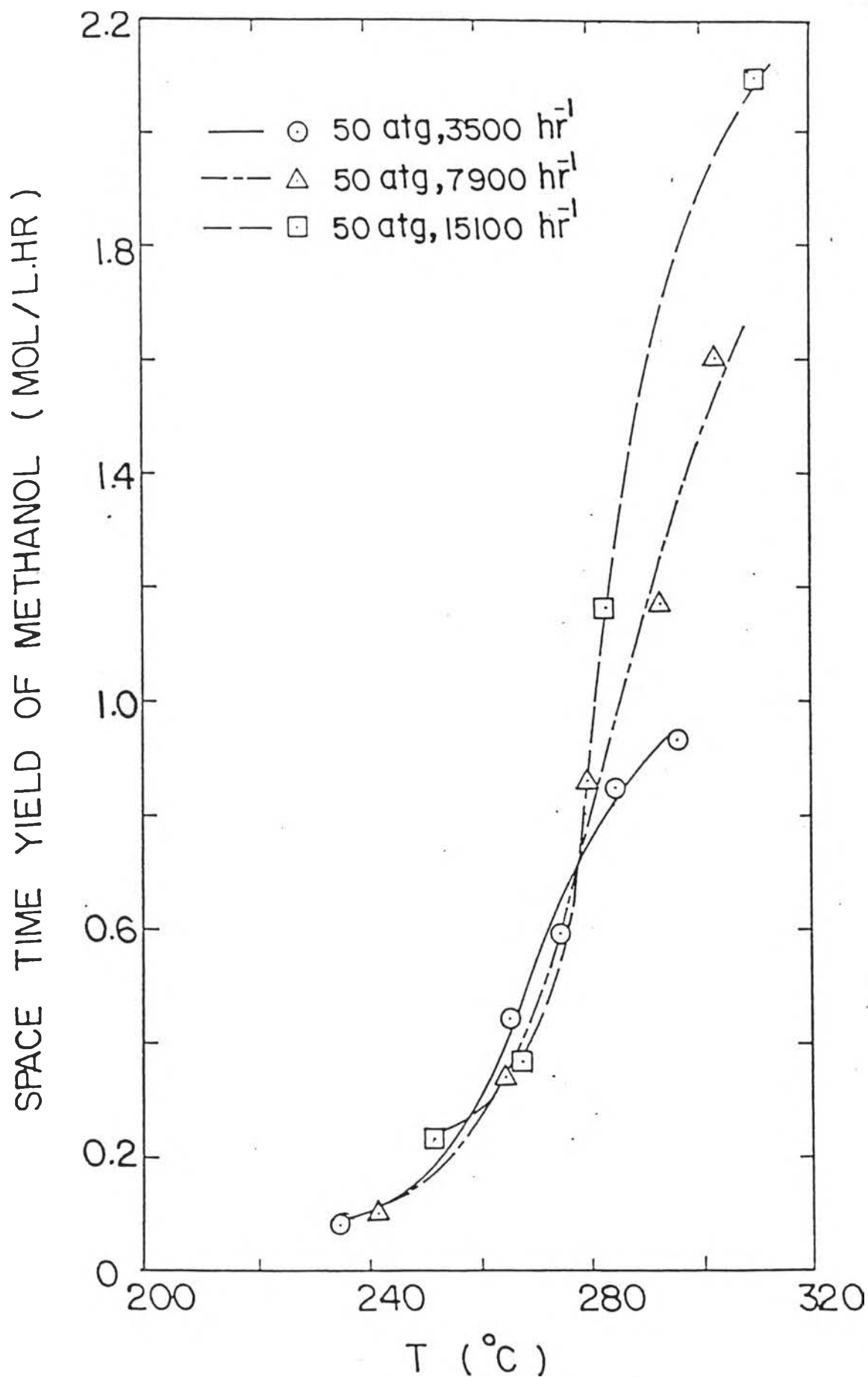


Figure 7.35 Effect of Temperature (200-300°C) and Space Velocity (3500-15100 hr⁻¹) on Space Time Yield of MeOH of Catalyst No.2

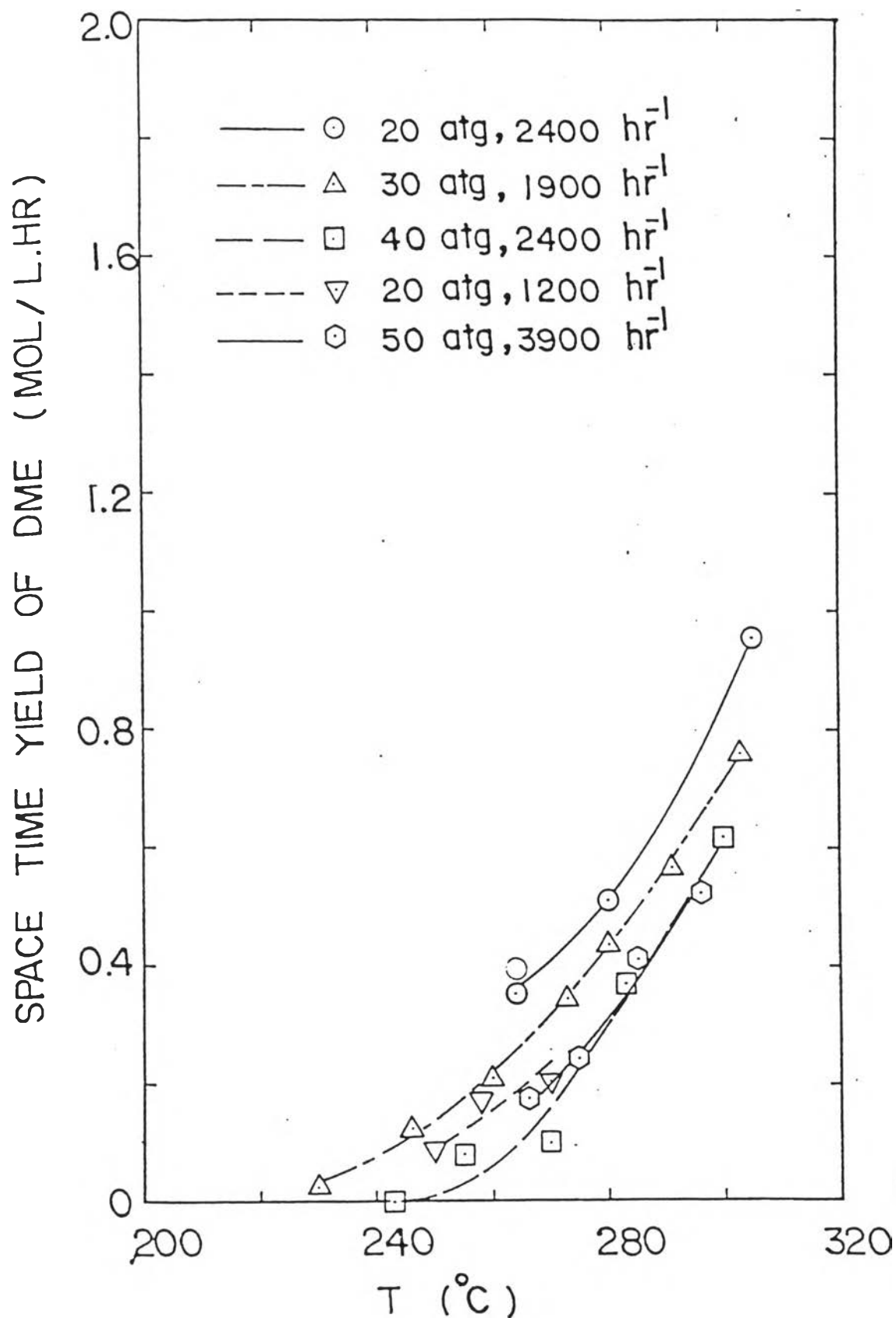


Figure 7.36 Effect of Temperature (200–300°C), Pressure (20–50 atg) and Space Velocity (2400–3900 hr⁻¹) on Space Time Yield of DME of Catalyst No.2

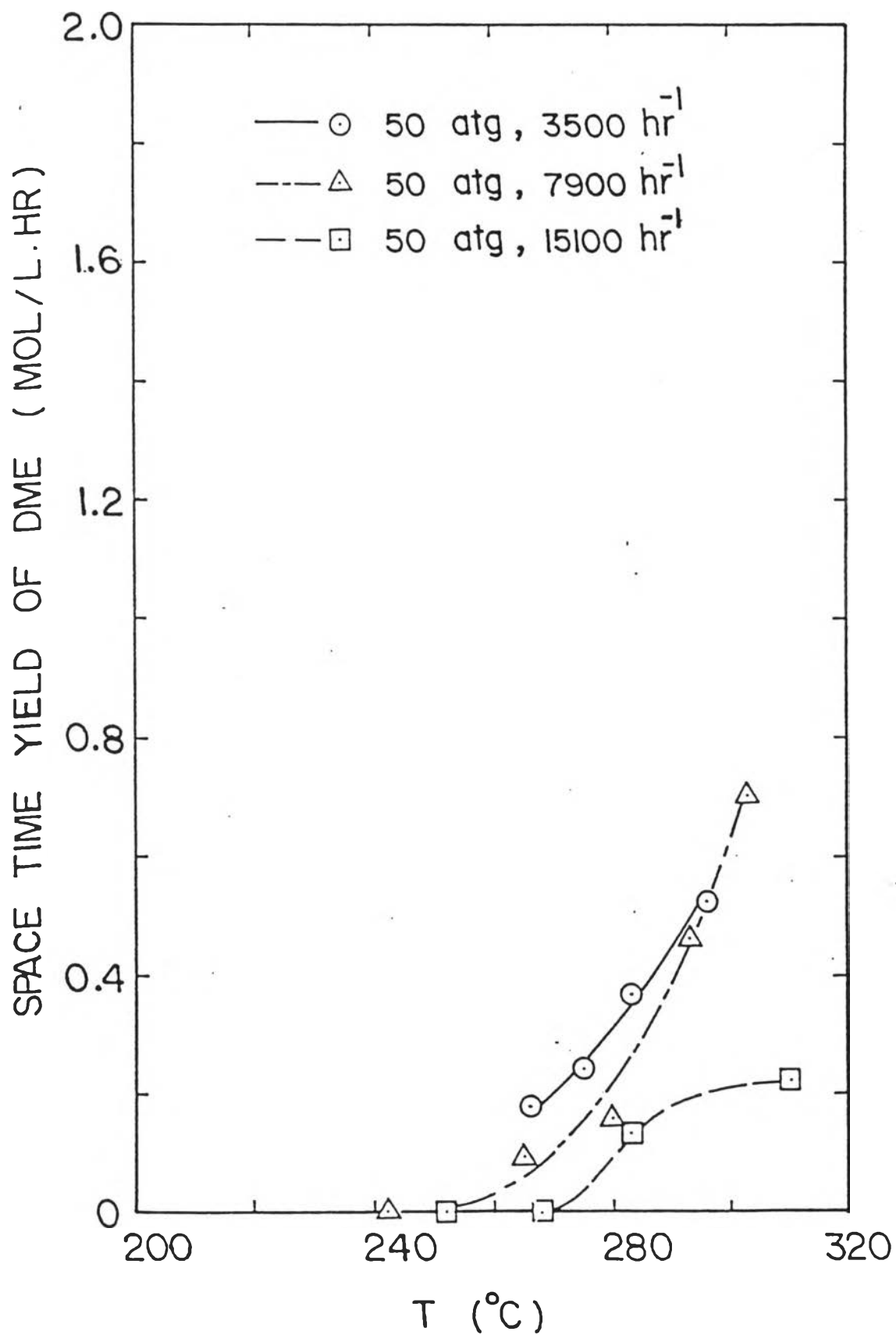


Figure 7.37 Effect of Temperature (200–300°C) and Space Velocity (3500–15100 hr⁻¹) on Space Time Yield of DME of Catalyst No.2

mental results of catalyst no.2 So it was not surprising that catalyst no.1 which contained a smaller amount of Cr_2O_3 was found to perform better than catalyst no.2. However, it is doubtful whether the concentration of Cr_2O_3 may be reduced below 11 wt%

Because of the difference in Cr_2O_3 the "optimum" conditions of methanol synthesis for the two catalysts appeared to be slightly different in the present study. To maximize methanol selectivity for catalyst no.1 synthesis should be carried at a high pressure but low space velocity within the range of 200-250°C. For catalyst no.2 the optimum conditions for methanol selectivity was similar to those of catalyst no.1 except that the temperature range was 220-260°C with respect to STY of methanol, the optimum conditions for catalyst no.1 called for a high pressure, high temperature and space velocity around 8,000 hr^{-1} . Catalyst no.2 also required a high pressure and temperature but with space velocity as high as 16,000 hr^{-1} .

7.3 Qualitative Comparison of Experimental Results among Catalysts No.1, No.2 and No.3

Since catalyst no.1 and no.2 were of the same ternary type with an only difference in Cr_2O_3 concentration, they exhibited similar effects of temperature, pressure and space velocity on methanol synthesis. Thus it suffices to compare either of them to catalyst no.3. Here we choose to compare mainly catalysts no.1 and no.3.

Catalyst no.3 was an industrial binary catalyst obtained from the Catalysts Chemicals Inc., Far East. It composed of zinc and chromium oxides with $\text{Zn/Cr} = 1.8-2.2$. The recommended process conditions were pressure = 300 kg_f/cm^2 , temperature = 300-400°C, and space velocity = around 30,000 hr^{-1} . Because of pressure limitation in the present experimental apparatus, all synthesis experiments were carried out at relatively low pressure (20-40 atg) over

a wide range of space velocity (1600-16000 hr⁻¹). The temperature range, however, was the same as recommended (300-400°C). The difference in temperature between catalyst no.1 and no.3 allowed us to make only qualitative comparison.

Comparison of Total CO Conversion Between Catalysts No.1

and No.3

Total CO conversion for catalyst no.1 generally increased with pressure and temperature but decreased as space velocity increased (see Figures 7.1-7.12). For catalyst no.3, however, total CO conversion remained more or less with respect to pressure and temperature (see Figures 7.37-7.50)

With respect to space velocity, total CO conversion for both catalysts tended to decrease as space velocity increased, but the effect of space velocity for catalyst no.3 was rather slight.

In general catalyst no.3 was found to give a much higher total CO conversion (mostly in the range 60-80%) than catalysts no.1 and no.2 (mostly in range 10-30%), though it had a much lower methanol selectivity.

Comparison of Methanol Selectivity and STY of Methanol Bet-

ween Catalysts No.1 and No.3

Methanol selectivity for catalyst no.1 generally increased with pressure and up to a certain point with temperature. However it was not much affected by space velocity (see Figures 7.1-7.12). Since methanol selectivity for catalyst no.3 was usually very low (see Figures 7.37-7.50), it was hard to tell the effects of temperature, pressure and space velocity from these experimental results. From some simulation results (S.L., 1984) based on Natta's

work on a similar binary catalyst , these results indicated that as pressure and/or space velocity increased methanol selectivity was enhanced. At the same time, the optimum temperature for methanol selectivity also shifted to a higher value. In any case, we may conclude that the qualitative effects of pressure, temperature and selectivity on methanol were similar for the two catalysts.

When the observed values of methanol selectivity were compared among catalyst no 1, no 2 and 3 it was found that catalyst no. 3 usually performed the worst. The positive effect of pressure on STY of methanol was the same for all three catalysts (see Figures 7.13-7.19, 7.34-7.35 and 7.50-7.55). With respect to space velocity, catalyst no. 2 and no. 3 both exhibited a positive effect on the STY of methanol. For catalyst no. 1 the STY of methanol increased with space velocity up to 8000 hr^{-1} , above which it instead decreased. The STY of methanol for catalysts no. 1 and no. 2 increased with temperature but catalyst no. 3 showed no regular effect of temperature in STY.

Comparison of observed value of STY of methanol revealed that catalyst no. 1 had a much higher STY than catalyst no. 3 at the same pressure and space velocity (Note that the temperature ranges were different). Except at 30 atg, catalyst no. 2 also had a slightly higher STY than catalyst 3

Comparison of CO₂ Selectivity

CO₂ selectivity for all three catalysts tended to increase with temperature. Pressure tended to have a slightly positive while space velocity, a slightly negative effect on CO₂ selectivity, especially for catalysts no. 1 and no. 3.

Observed values of CO₂ selectivity for catalyst no.3 generally were higher than those for catalyst no.1 but lower than those for catalyst no.2 (see Figures 7.1-7.12, 7.27-7.33 and 7.27-7.49). The typical CO₂ selectivity was 30-40% for catalyst no.3, was 10-20% for catalyst no.1, and 50-70% for catalyst no.2.

Comparison of Hydrocarbon Selectivity

The general effects of pressure and temperature on hydrocarbon selectivity of catalyst no.1,2, and 3 were rather different. Hydrocarbon selectivity for catalysts no.1 and no.3 tended to decrease against pressure except at 40 atg for catalyst no.3. On the other, pressure only slight effect on hydrocarbon selectivity for catalyst no.2 (see Figures 7.1-7.12, 7.27-7.33 and 7.37-7.49). With respect to temperature, hydrocarbon selectivity generally decreased against temperature for catalyst no.1 and increased slightly with temperature for catalyst no.2. For catalyst no.3 hydrocarbon selectivity usually increased until it reached a peak at a certain temperature, above which it then decreased.

Observed values of hydrocarbon selectivity for catalyst no.2 were less than those of the others. The values were in the range 10-20% for catalyst no.2, while in the range 50-60% for the other two and as high as 70-90% in some cases. At low temperatures catalyst no.1 generally gave a higher hydrocarbon selectivity than catalyst no.3 and vice versa at high temperature.

Comparison of DME Selectivity

Catalyst no.3 had negligible DME selectivity, except at two conditions (40 atg, 1600 hr⁻¹ and 30 atg, 2385 hr⁻¹) possibly

because it gave very low methanol yield. Therefore, it was not possible to compare any further with the other catalysts.

In summary, we might conclude that catalyst no.2 gave a much higher CO_2 selectivity than the others, and that catalyst no.3 gave on the average the same hydrocarbon selectivity as catalyst no.1 but a much higher selectivity than catalyst no.2. On the other hand catalyst no.1 gave a higher methanol selectivity than catalyst no.2 and catalyst no.3, though the comparison with catalyst no.3 might not be meaningful because the temperature range were different.

It should be noted that catalyst no.1 and no.2 were ternary catalysts, ($\text{CuO}/\text{ZnO}/\text{Cr}_2\text{O}_3$), with different concentration of Cr_2O_3 , whereas catalyst no.3 was binary catalyst, (Zn and chromium oxides), whose atomic ratios of Zn and Cr was equal to that of catalyst no.2 (about 2:1). The experimental results seemed to indicate that the ternary catalysts were better than the binary catalyst.

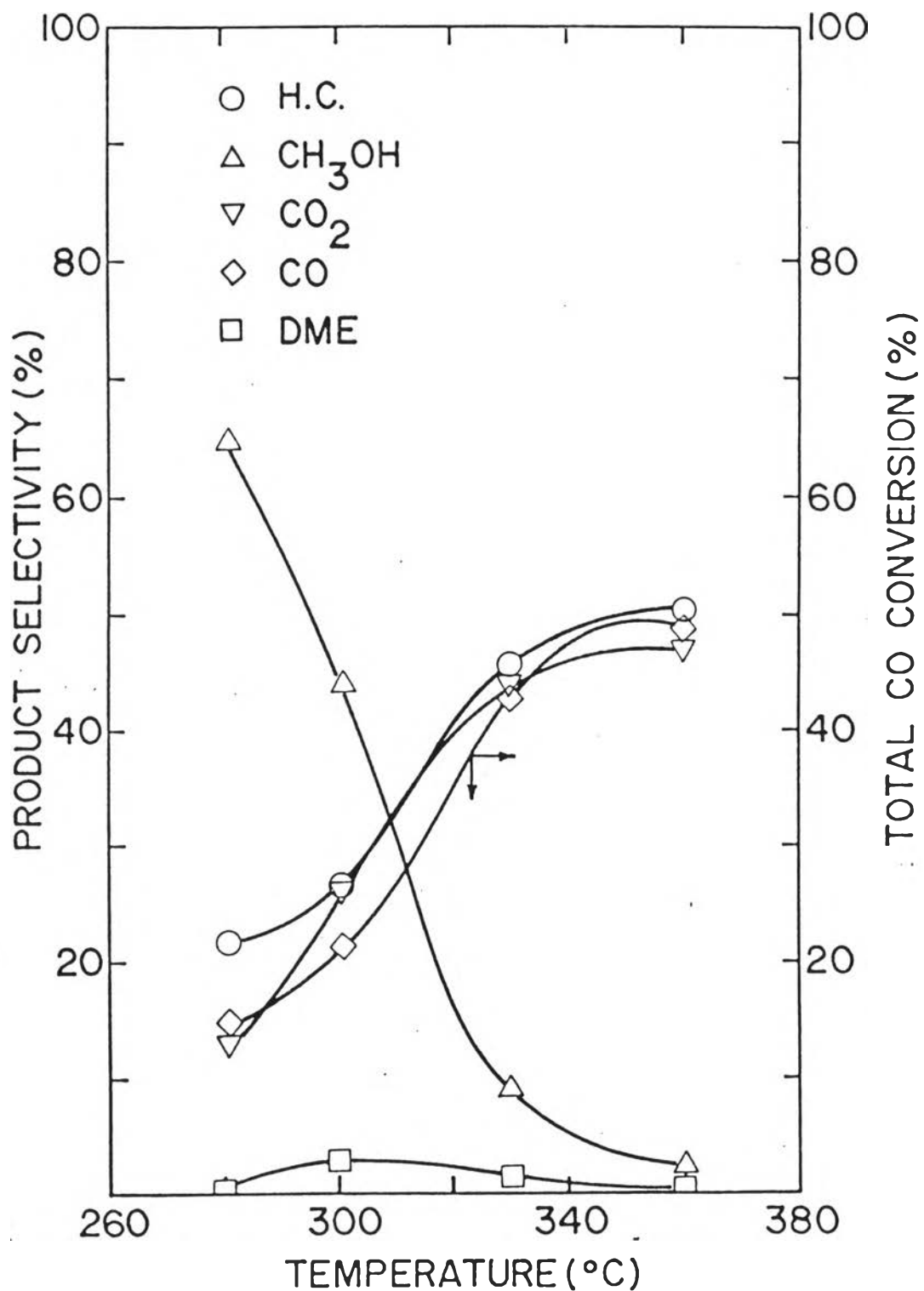


Figure 7.38 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities (at 40 atg, 17000 hr⁻¹) of Catalyst No.3

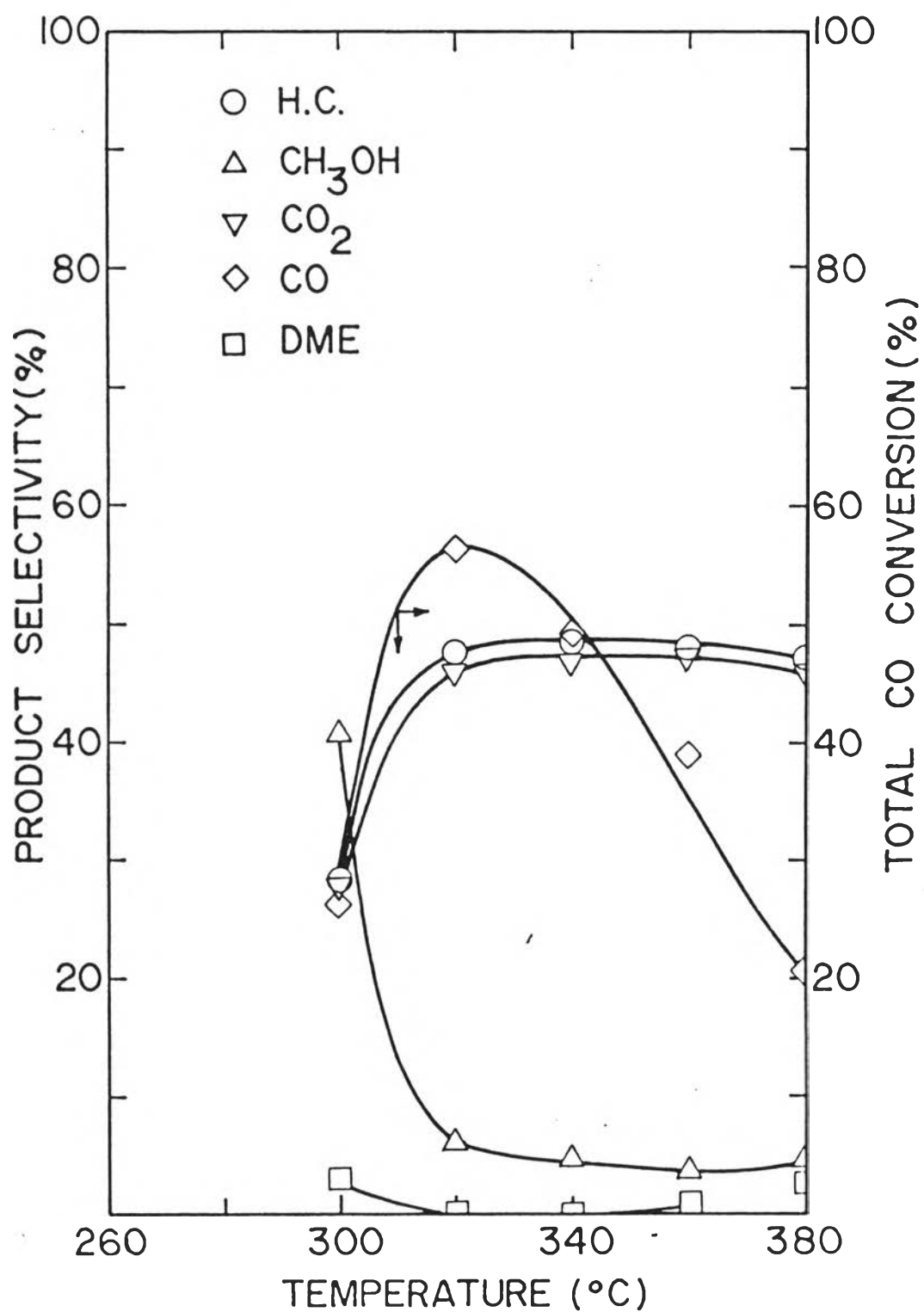


Figure 7.39 Effect of Temperature (300–380°C) on Total CO Conversion and Product Selectivities (at 30 atg, 2400 hr⁻¹) of Catalyst No.3

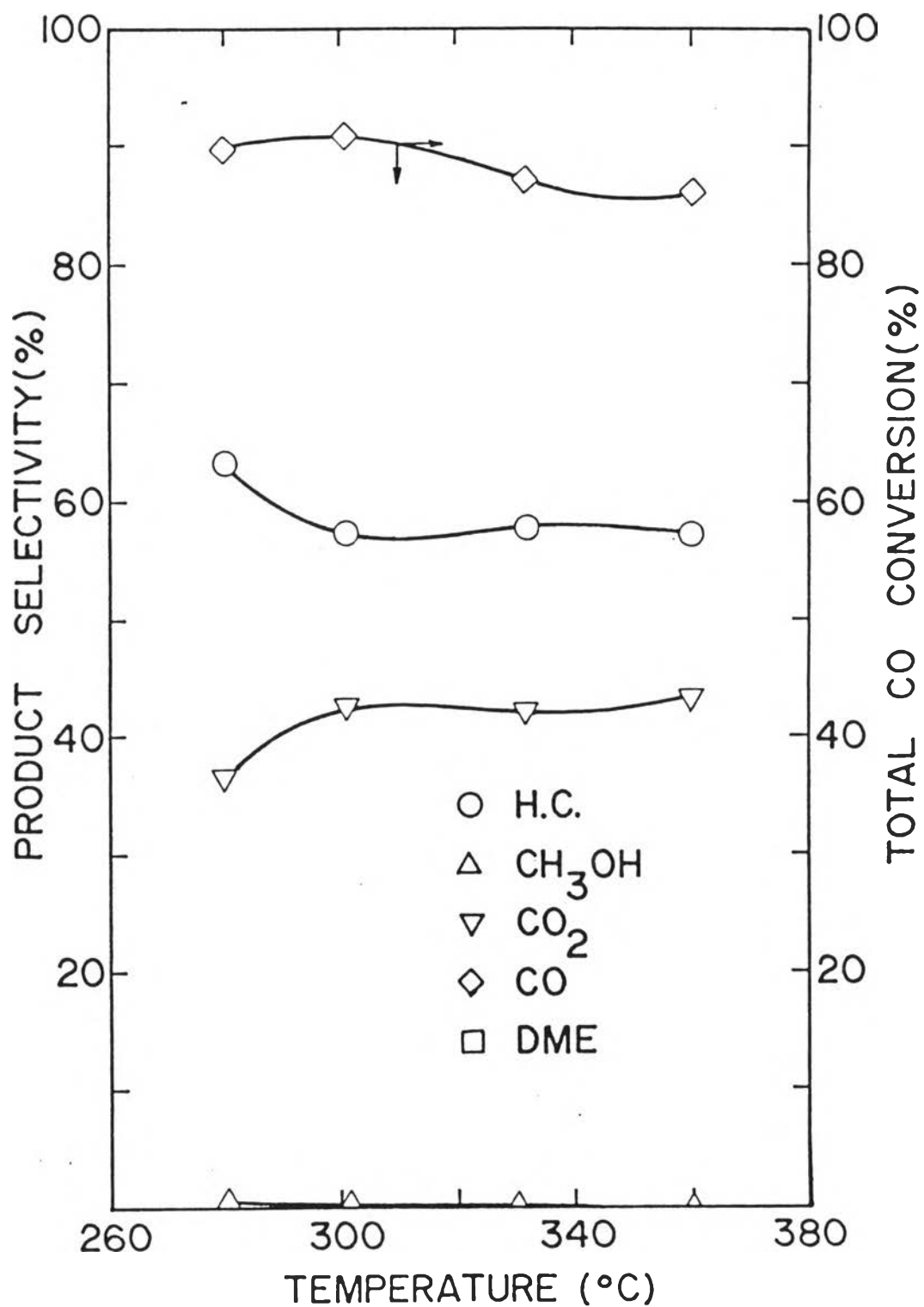


Figure 7.40 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities (at 20 atg, 1600 hr⁻¹) of Catalyst No.3

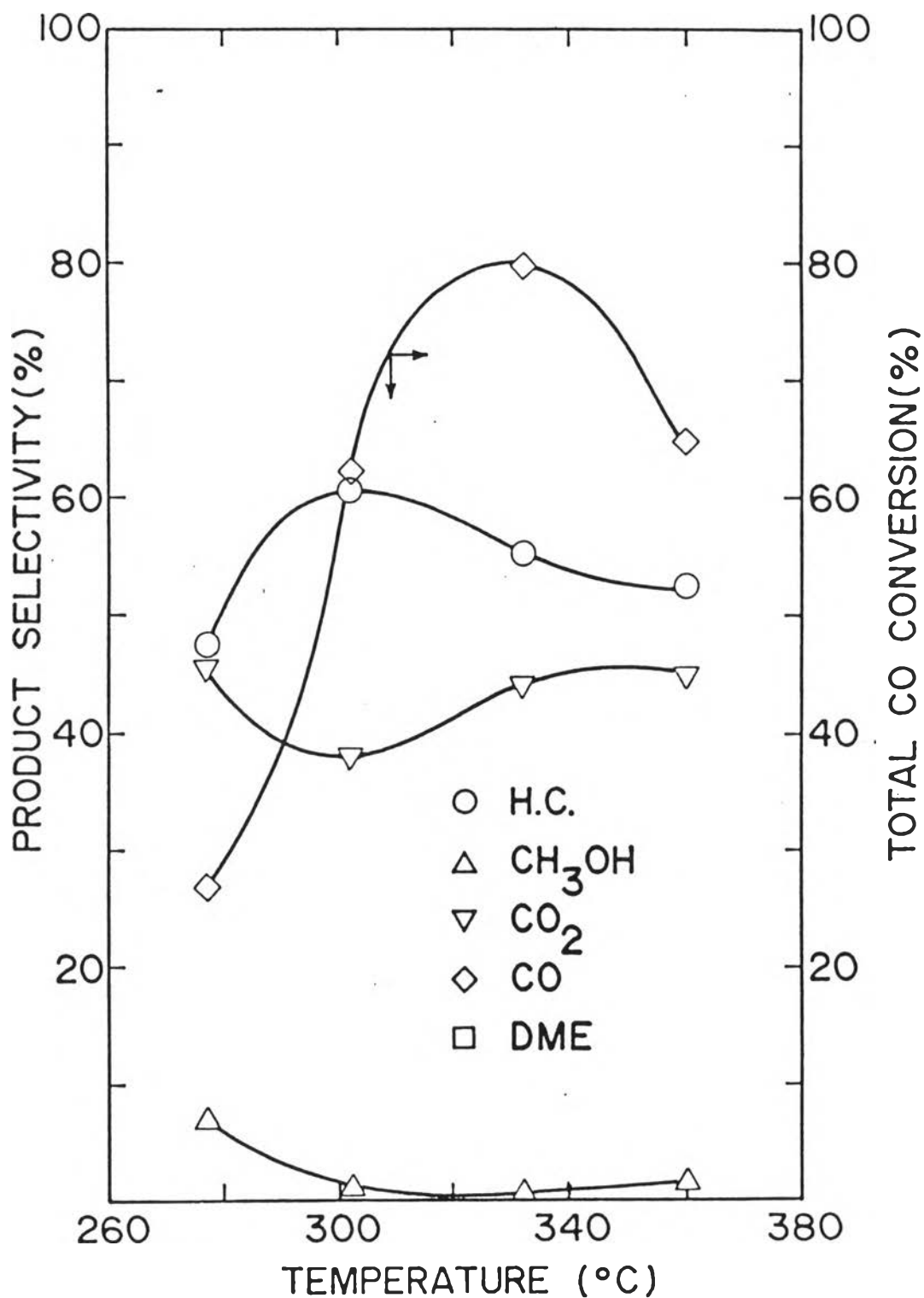


Figure 7.41 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities (at 40 atg, 3900 hr⁻¹) of Catalyst No.3

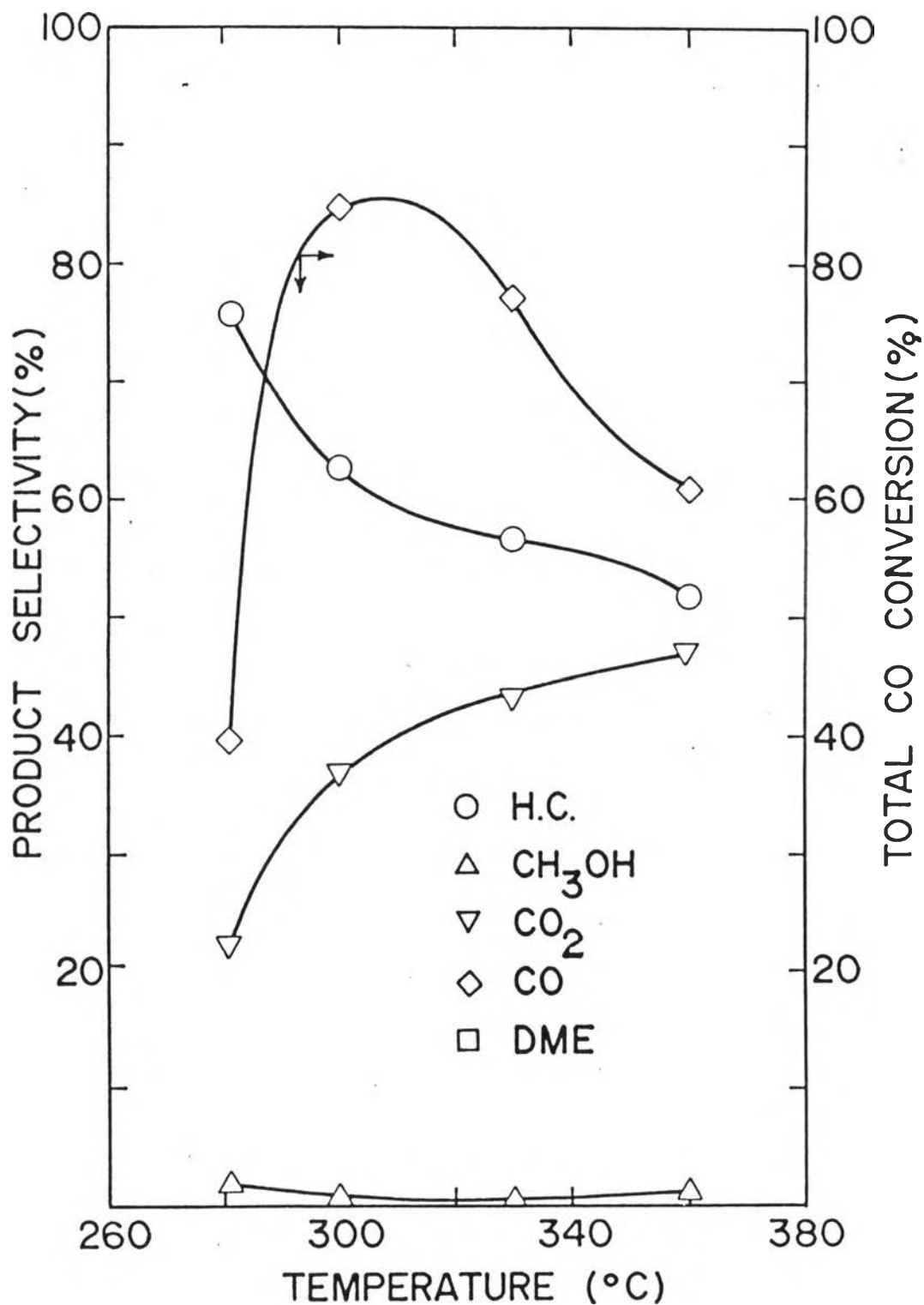


Figure 7.42 Effect of Temperature (280-360 °C) on Total CO Conversion and Product Selectivities at 30 atg, 3500 hr⁻¹ of Catalyst No.3

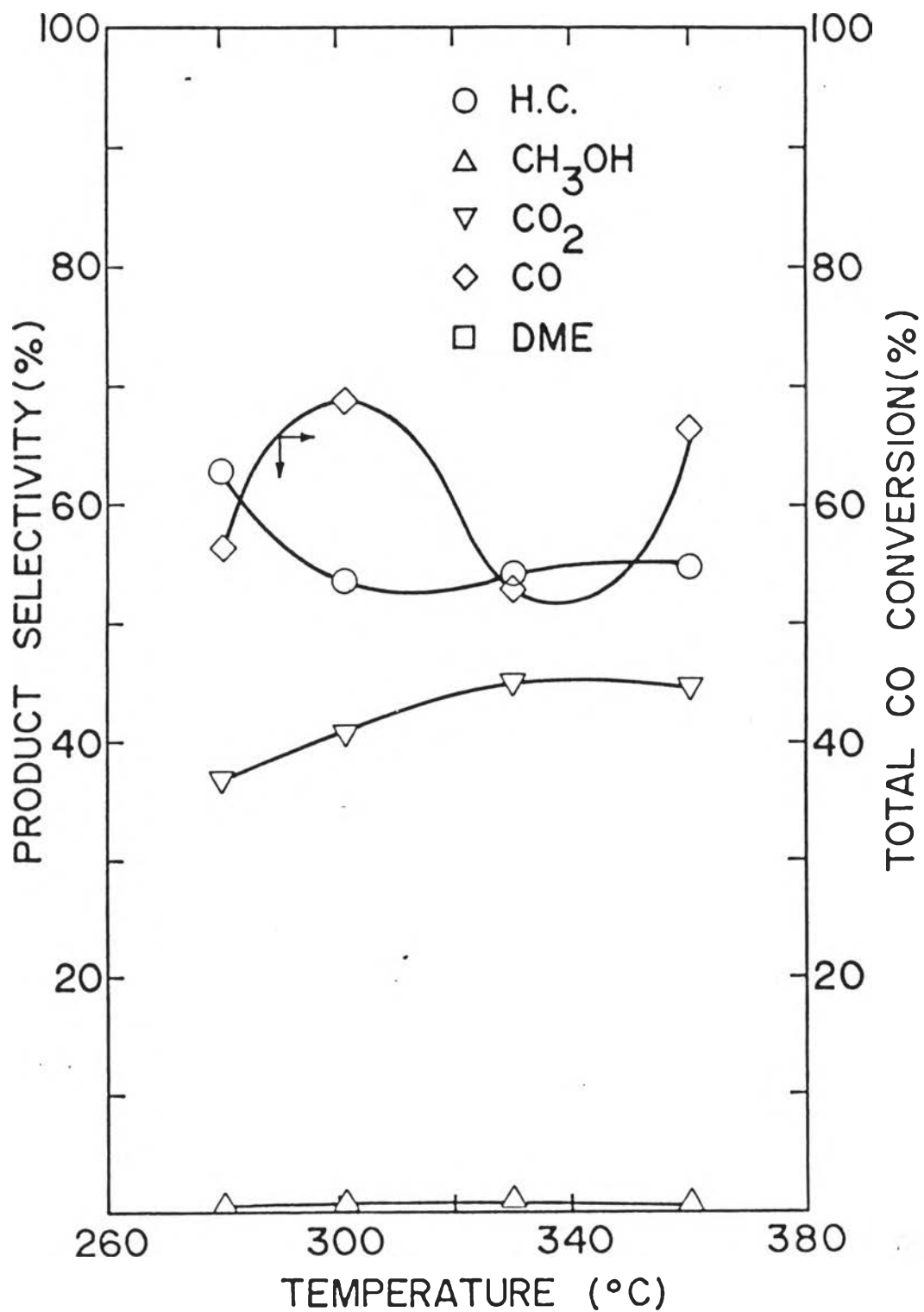


Figure 7.43 Effect of Temperature (280-360°C) on Total Co Conversion and Product Selectivities at 20 atg, 3700 hr⁻¹ of Catalyst No.3

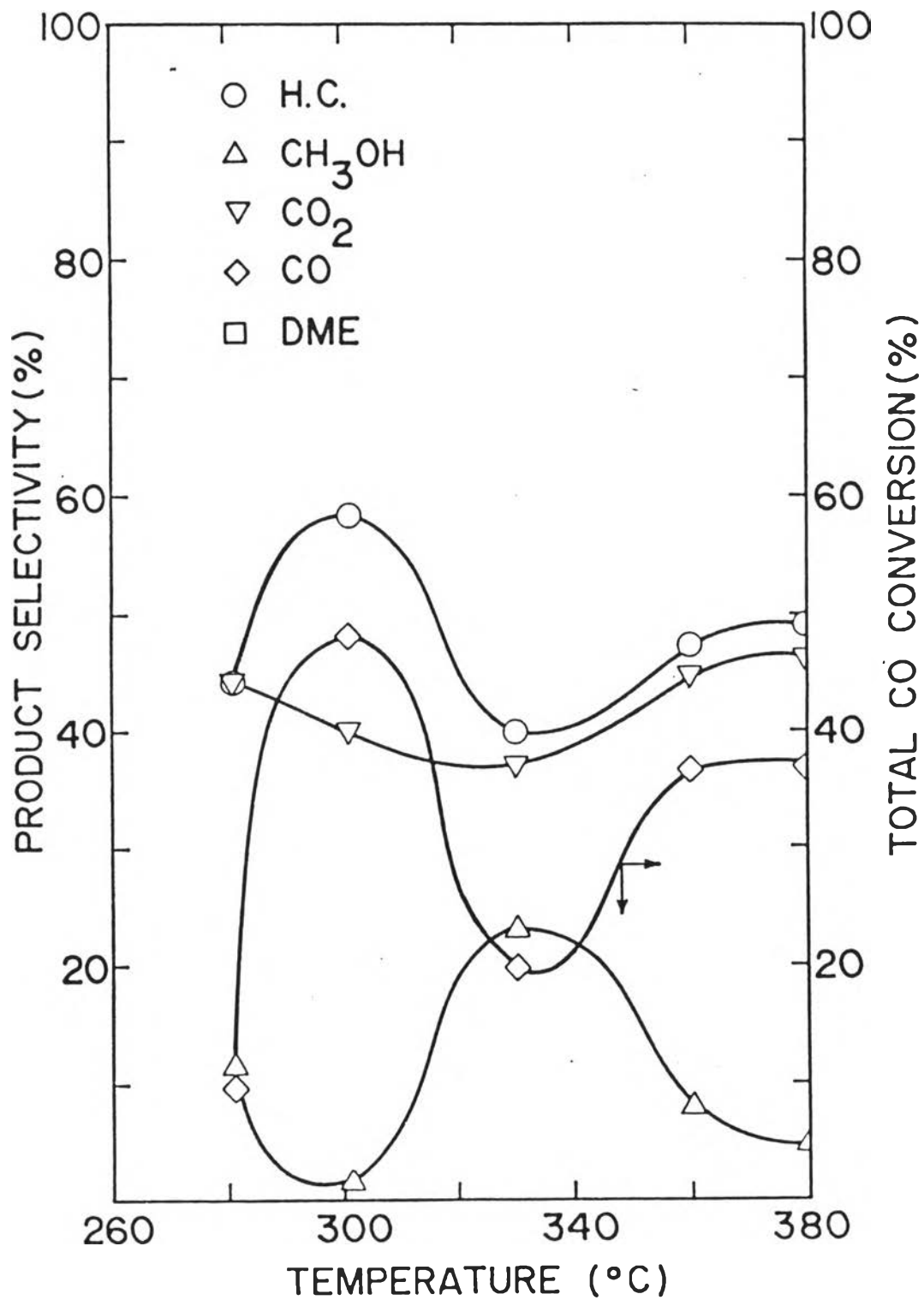


Figure 7.44 Effect of Temperature (280–360°C) on Total CO Conversion and Product Selectivities at 40 atg, 7000 hr⁻¹ of Catalyst No.3

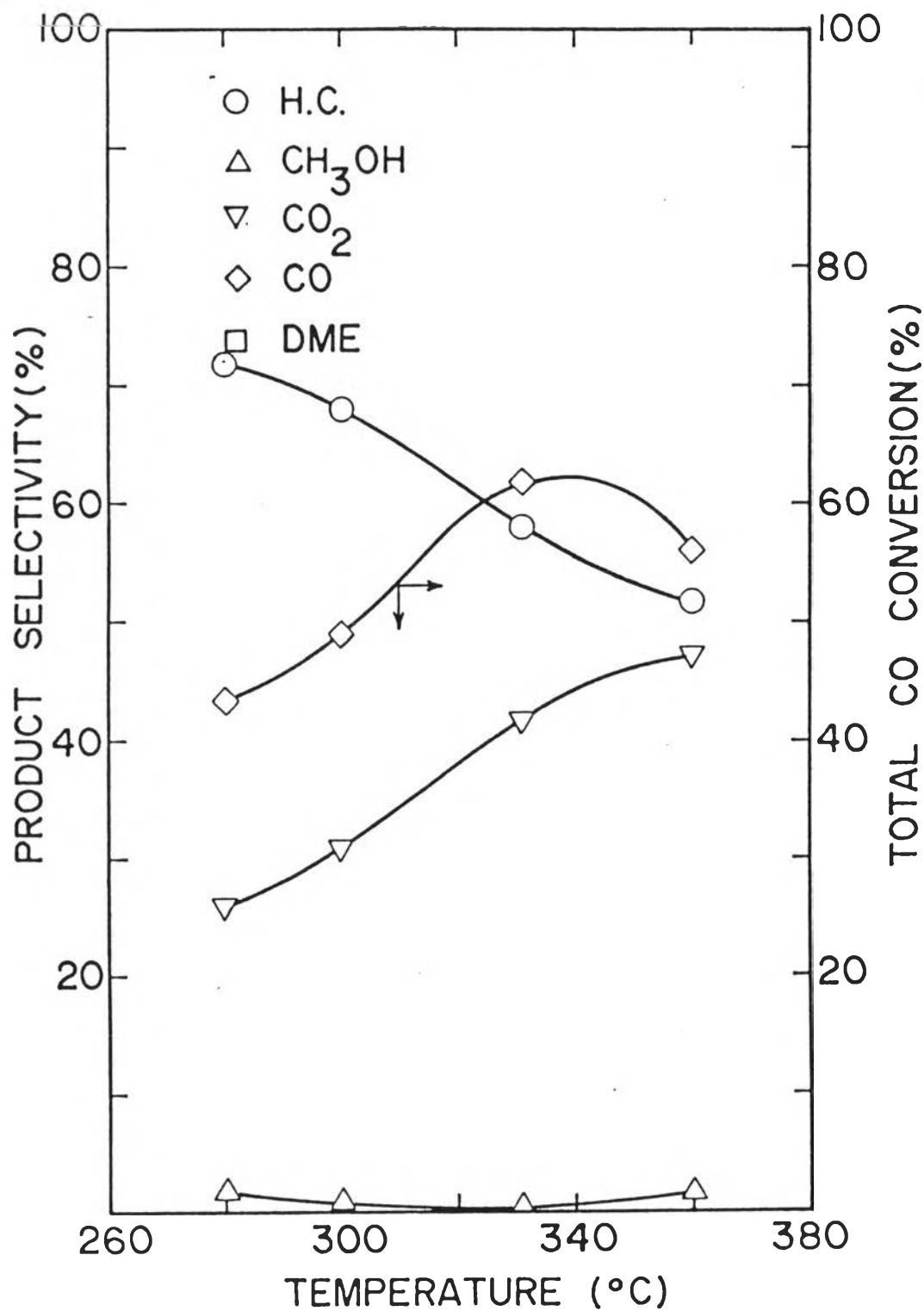


Figure 7.45 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities at 30 atg, 6700 hr⁻¹ of Catalyst No.3

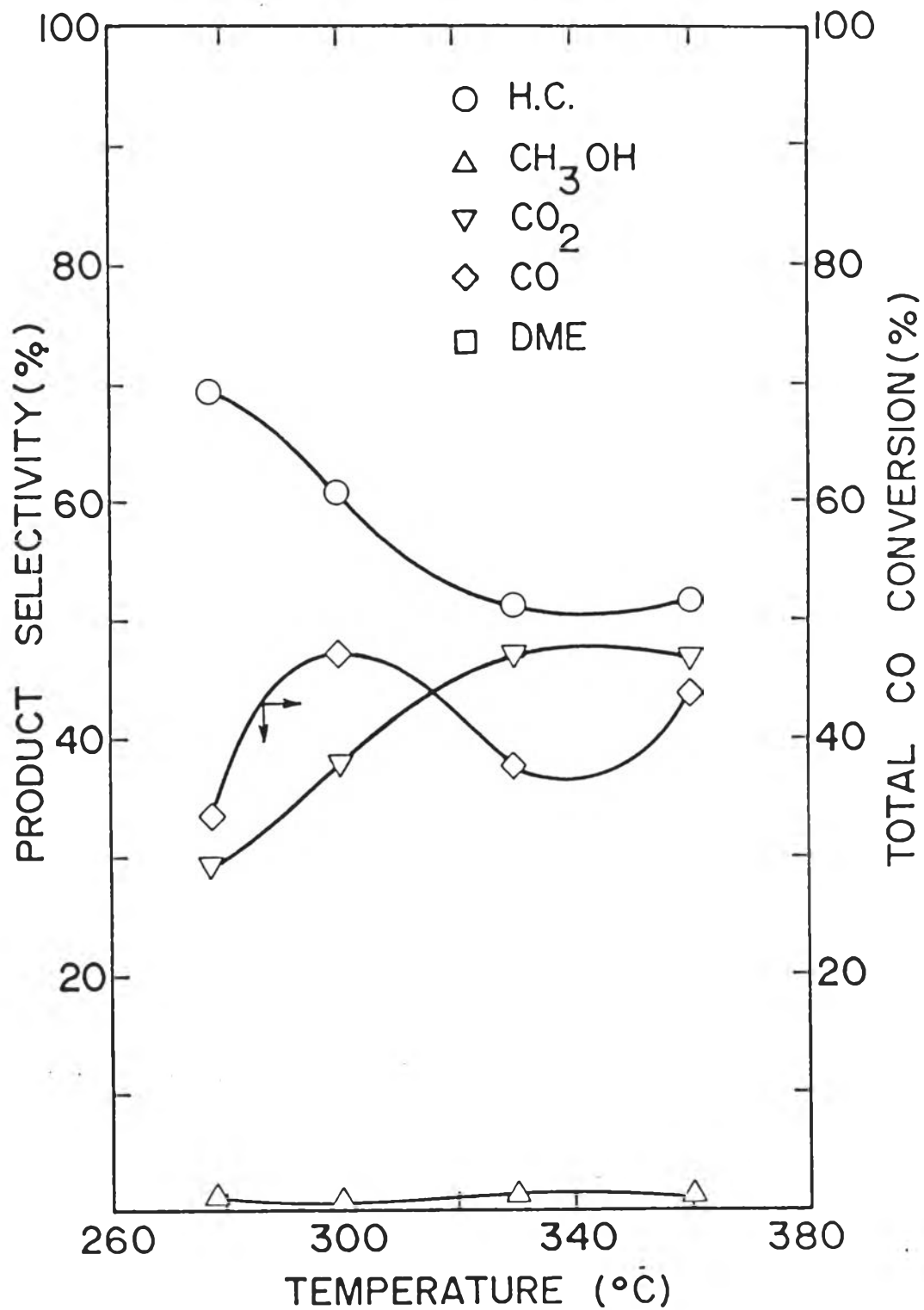


Figure 7.46 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities at 20 atg, 6000 hr⁻¹ of Catalyst No.3

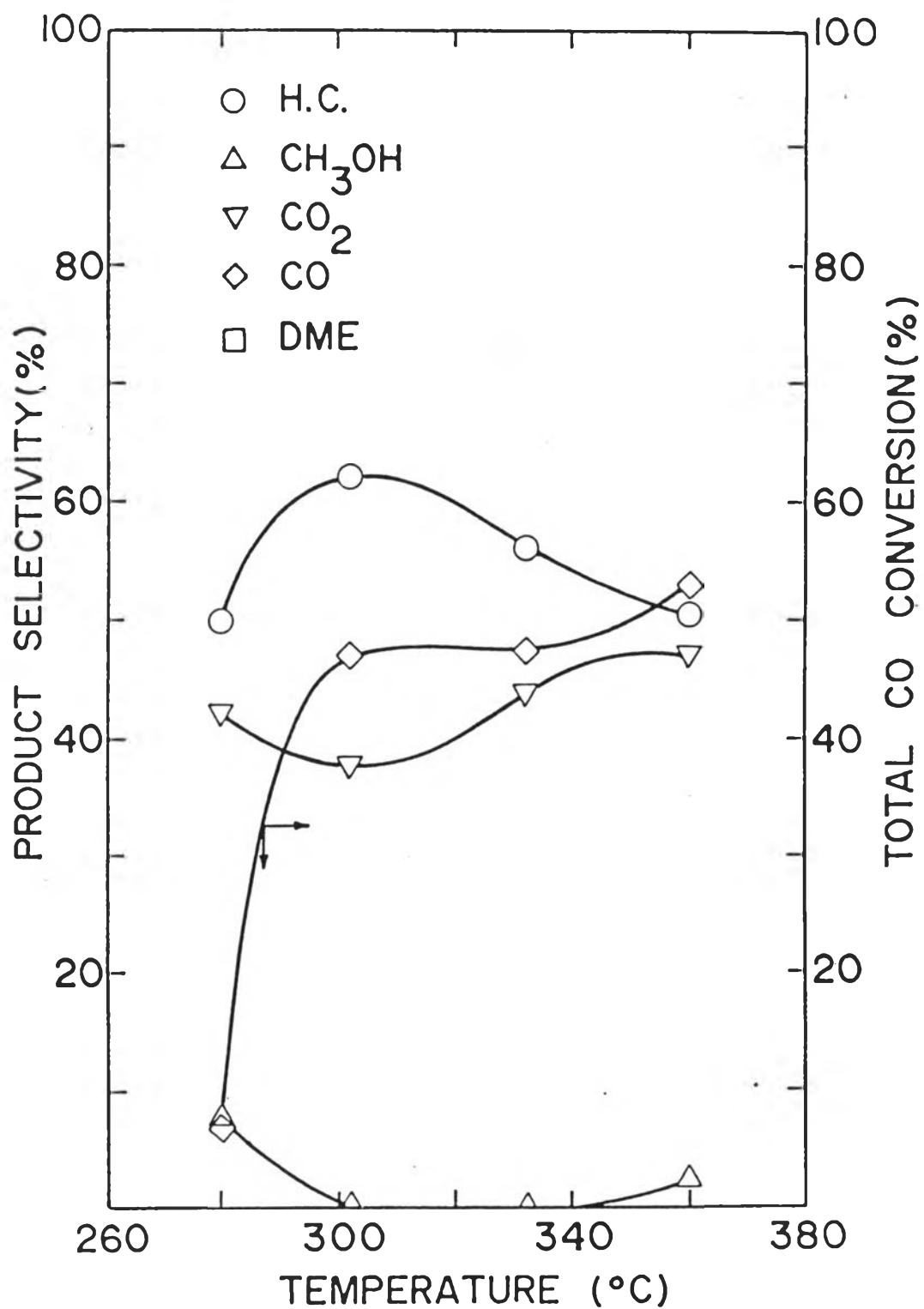


Figure 7.47 Effect of Temperature (230–360°C) on Total CO Conversion and Product Selectivities at 40 atg, 16000 hr⁻¹ of Catalyst No.3

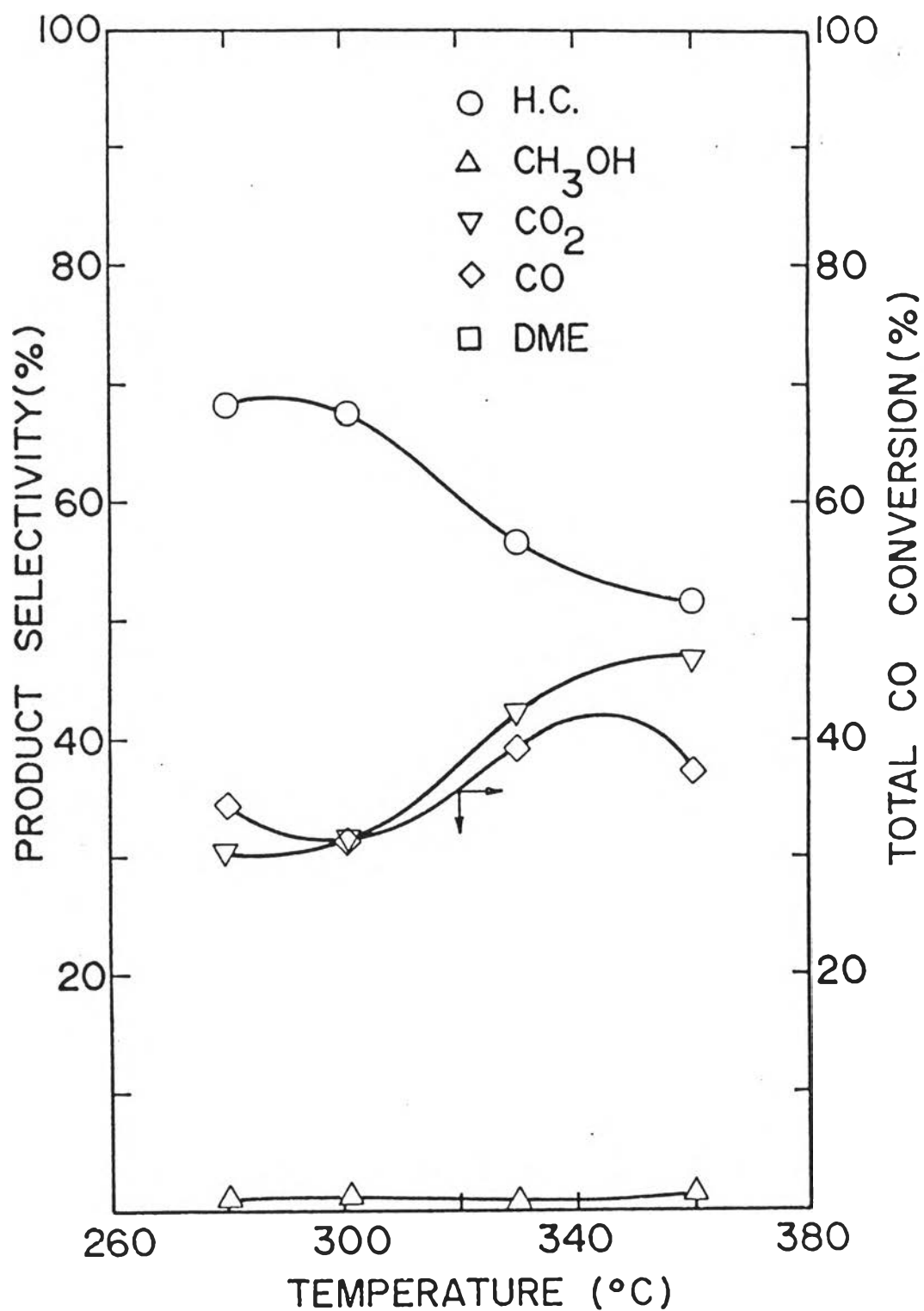


Figure 7.48 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities at 30 atg, 13000 hr⁻¹ of Catalyst No.3

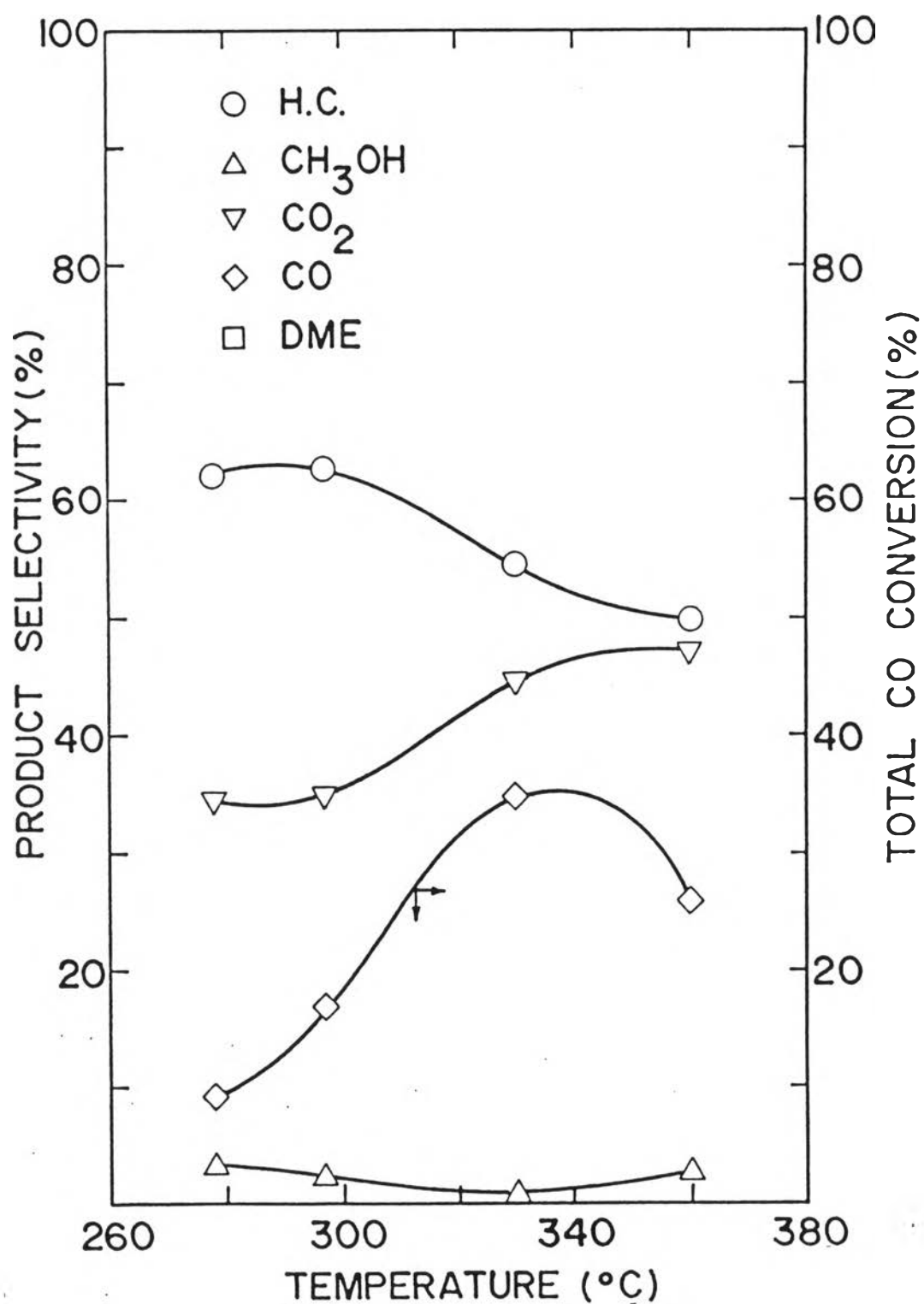


Figure 7.49 Effect of Temperature (280-360°C) on Total CO Conversion and Product Selectivities at 20 atg, 13000 hr⁻¹ of Catalyst No.3

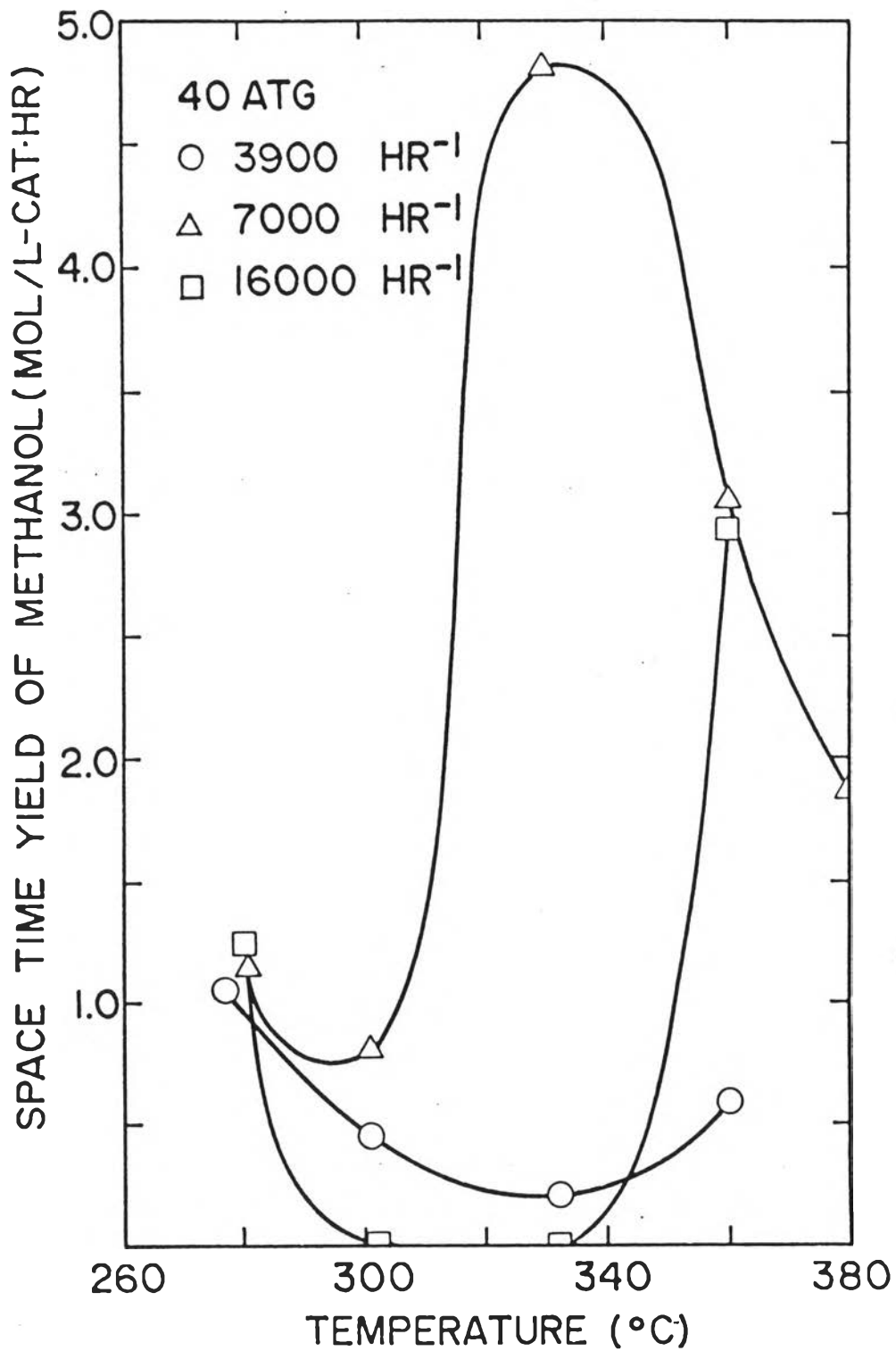


Figure 7.50 Effect of Space Velocity (3900-16000 hr⁻¹) and Temperature (280-380°C) on Space Time Yield of MeOH at 40 atg of Catalyst No.3

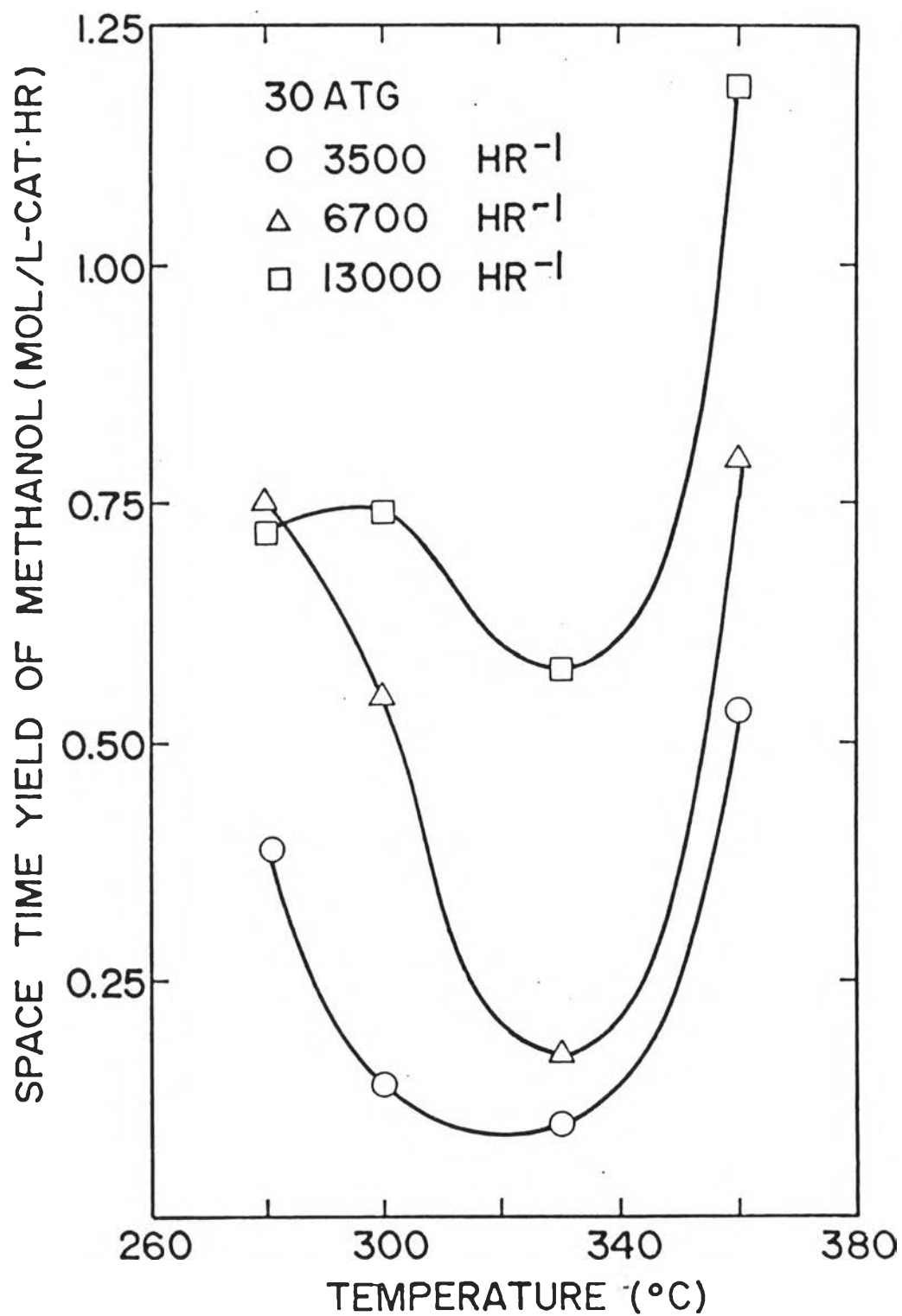


Figure 7.51 Effect of Space Velocity (3500 - 13000 hr⁻¹) and Temperature (280-360°C) on Space Time Yield of MeOH (at 30 atg) of Catalyst No.3

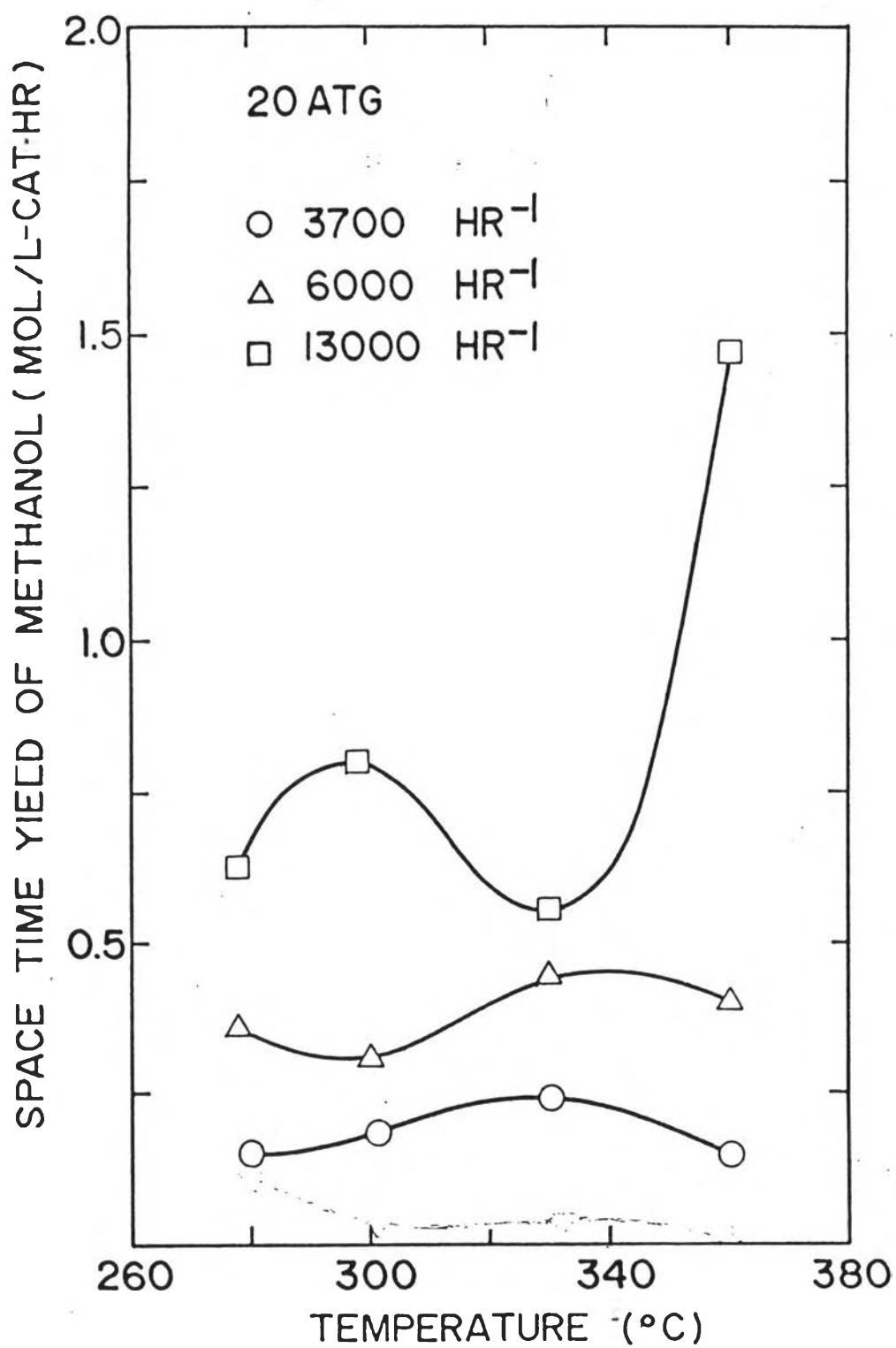


Figure 7.52 Effect of Space Velocity (1600 - 13000 hr⁻¹) and Temperature (280-360°C) on Space Time Yield of MeOH at 20 atg of Catalyst No.3

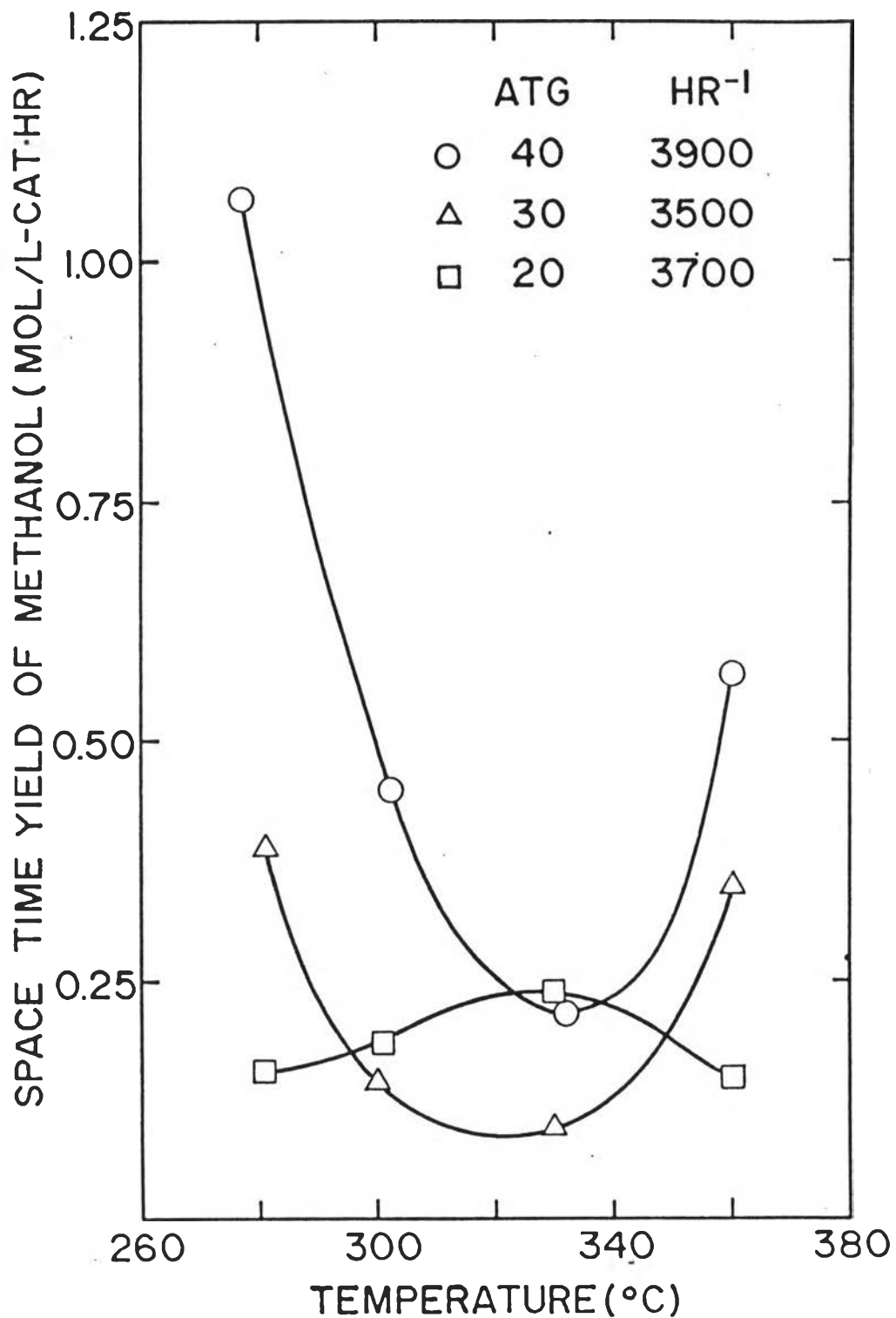


Figure 7.53 Effect of Pressure (20-40 atg) and Temperature (280-380°C) on Space Time Yield of MeOH (3500 - 3900 hr⁻¹) of Catalyst No.3

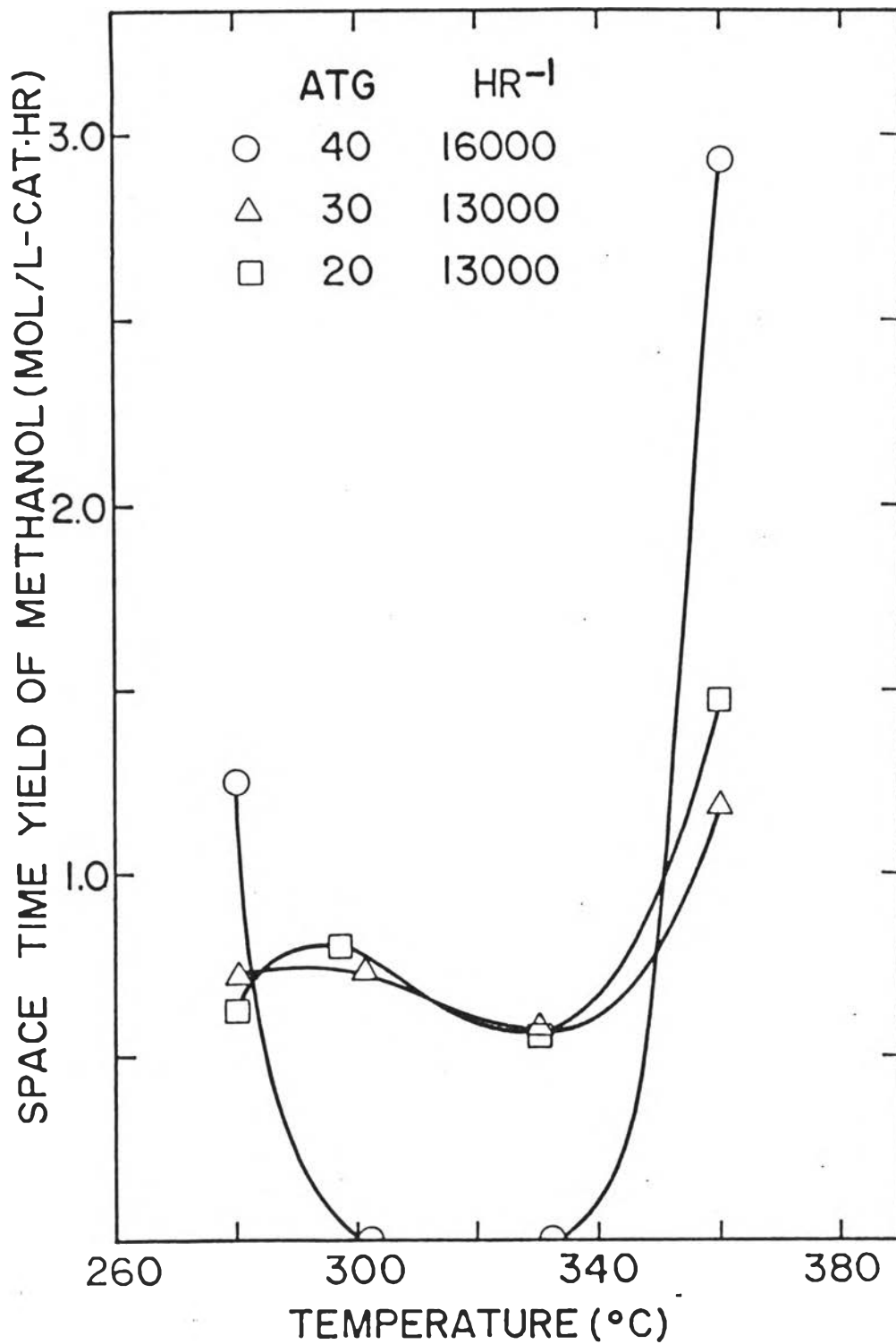


Figure 7.54 Effect of Pressure (20-40 atg) and Temperature (260-380°C) on Space Time Yield of MeOH (13000 - 16000 hr⁻¹) of Catalyst No.3

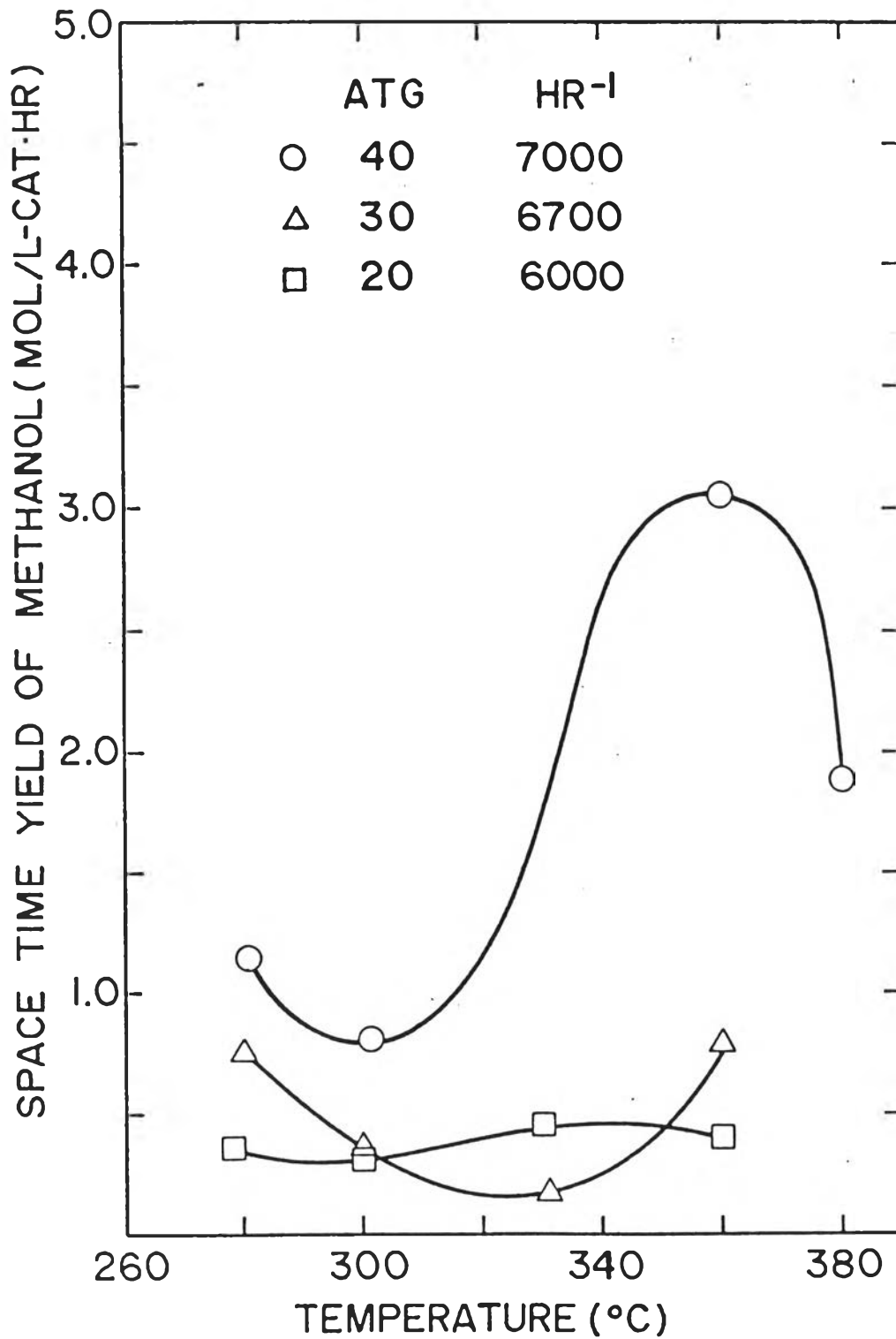


Figure 7.55 Effect of Pressure (20-40 atg) and Temperature (260-360°C) on Space Time Yield of MeOH (6500-7000 hr⁻¹) of Catalyst No.3

CONCLUSIONS

The following conclusions may be drawn from the present work :

1. A ternary methanol synthesis catalyst ($\text{CuO}/\text{ZnO}/\text{Cr}_2\text{O}_3$) with the atomic ratio of $\text{Cu}:\text{Zn}:\text{Cr} = 31:38:10$ was prepared by

a) precipitating $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with NH_4OH to give $[\text{Cu}_2(\text{OH})_3\text{NO}_3]$,

b) mixing mechanically with ZnO and CrO_3 ,

c) calcining at 70°C for 3 hours in an oven and

d) reducing at 220°C for about 45 minutes in a heating furnace under the flow (60ml/min) of a gas mixture with $\text{N}_2:\text{H}_2:\text{CO} = 69:2:1$. The catalyst thus obtained was then pelletized to have a bulk density about 2.7 gm/cc then crushed and screened between mesh # 16 and # 30 for use in methanol synthesis experiments.

2. The experimental apparatus for methanol synthesis, which was mounted within a frame of angular steel, was fabricated using stainless steel Swagelok parts. The maximum design pressure was 50 atg and the maximum design temperature 450°C . The heating furnace was made of refractory brick furnace and temperature control was done using 2 slidaces. Leak-tests at 1,2,5,10 atg with N_2 first and then 10,20,30 40 atg. with H_2 was carried out.

3. In the experiments methanol was synthesized from a pre-mixed gas of CO and H_2 ($\text{CO}:\text{H}_2 = 1:2$). Experiments were carried out

at 20,30 and 40 atg while varying the temperature from 200-300°C and the space velocity from 2000 - 16,000 hr⁻¹. The amount of catalyst packed in $\frac{1}{2}$ " O.D. tubular reactor was 1.5 ml. Analysis of product gases was performed using gas chromatography (Shimadzu GC model 8 AIT (TCD)) equipped with a MS-5A and a porapak T column.

4. From the experimental results done in this study and in other researchers, it may be concluded that the effects of temperature, pressure, space velocity and catalyst type and composition on methanol synthesis were as follows :

4.1 For catalyst no.1, a ternary catalyst of CuO/ZrO/Cr₂O₃ (Cu:Zn:Cr = 31:38:10) total CO conversion generally increased with temperature and pressure but decreased against space velocity. Methanol selectivity increased remarkably with temperature up to optimum temperature (around 250°C) above which it instead decreased. Methanol selectivity also increased with pressure. Space time yield of methanol usually increased with temperature and pressure, and also with space velocity up to around 8000 hr⁻¹, above which it then decreased.

4.2 For catalyst no.2, a similar ternary catalyst of CuO/ZnO/Cr₂O₃ (Cu:Zn:Zr = 2:2:1) total CO conversion usually increased with temperature and pressure but decreased against space velocity. Methanol selectivity generally increased up to an optimum temperature and pressure but decreased against space velocity. Methanol selectivity generally increased up to an optimum temperature (around 240°C), above which it then decreased. Space time yield of methanol was found to increase with temperature , pressure and space velocity in the experiments.

4.3 For catalyst no.3, an industrial binary catalyst of zinc and chromium oxides not only experiments but also a complete simulation study were carried out. It was found that, in general, methanol selectivity increased up to an optimum temperature, whose value shifted higher as pressure and space velocity increased. Above this temperature, methanol selectivity then decreased. Both pressure and space velocity were found to enhance methanol selectivity. The space time yield of methanol also behaved like methanol selectivity under the effects of pressure, temperature and space velocity.

4.4 It was seen that though the effects of temperature, pressure and space velocity on methanol synthesis of triple catalysts were qualitatively rather similar for all three catalysts, their quantitative effects on the yields of main and side products were remarkably different. Catalyst no.1 converted more CO to methanol than catalyst no.2 under the same pressure, temperature and space velocity, and than catalyst no.3 under the same pressure and space velocity but different temperature. Catalyst no.2 and no.3 converted a sizable proportion of CO to CO₂ and in a smaller proportion to hydrocarbons.

4.5 Since catalyst no.2 had a higher proportion of Cr than catalyst no.1 but yielded less methanol, it was concluded that the weight percent of Cr₂O₃ could be as low as 11% for the ternary catalysts of CuO/ZnO/Cr₂O₃.