

and 2.10. The main products observed before the addition of isobutylene were methanol and C₁-to-C₃ hydrocarbons. There was no measurable change in the rate of formation of C₁ and C₂ hydrocarbons with addition of isobutylene.

The added isobutylene, besides reacting with methanol to form MTBE, hydrogenated to isobutane and dimerized. Figure 2.11 and 2.12 show the conversion and selectivity of added isobutylene to various hydrocarbon products as a function of time. As can be seen, both conversion and selectivity of isobutylene changed considerably with time and reached a steady-state value after 10-12 hours of isobutylene addition. Figure 2.13 shows the effect of reaction temperature on the rate of isobutylene conversion to different products over the physical mixture of Li₄/Pd/S₂ + ZSM-5. The rate of isobutylene hydrogenation and the C₃-C₇ hydrocarbon formation increased with an increase in reaction temperature. On the other hand, the opposite trend was noted for the rate of dimer formation which decreased with an increase in reaction temperature.

(c) Formation of MTBE

The rates of MTBE formation after 2 hours of isobutylene addition over the three catalyst/zeolite mixtures followed the order: {Li₄/Pd/S₂ + ZSM-5} > {Li₄/Pd/S₂ + LZ210-12} > {Li₁/Pd/S₁ + ZSM-5}. Physical mixtures of Li-Pd/SiO₂ and ZSM-5 had higher resistances to deactivation compared to Li₄/Pd/S₂ + LZ210-12. In the latter case, the rate of MTBE formation kept on decreasing and reached zero after 14 hours of isobutylene addition.

2.4 DISCUSSION

2.4.1 CO hydrogenation

2.4.1.1 Effect of Li Promotion on the CO Hydrogenation Activity of Pd/SiO₂

The observed increase in the rate of methanol formation as a result of Li promotion over Pd/SiO₂ is in good agreement with what has been reported earlier in literature (27,28). This increase has been related to the stabilization of the methanol intermediate in the methanol formation and an increase in Pd dispersion (27,28).

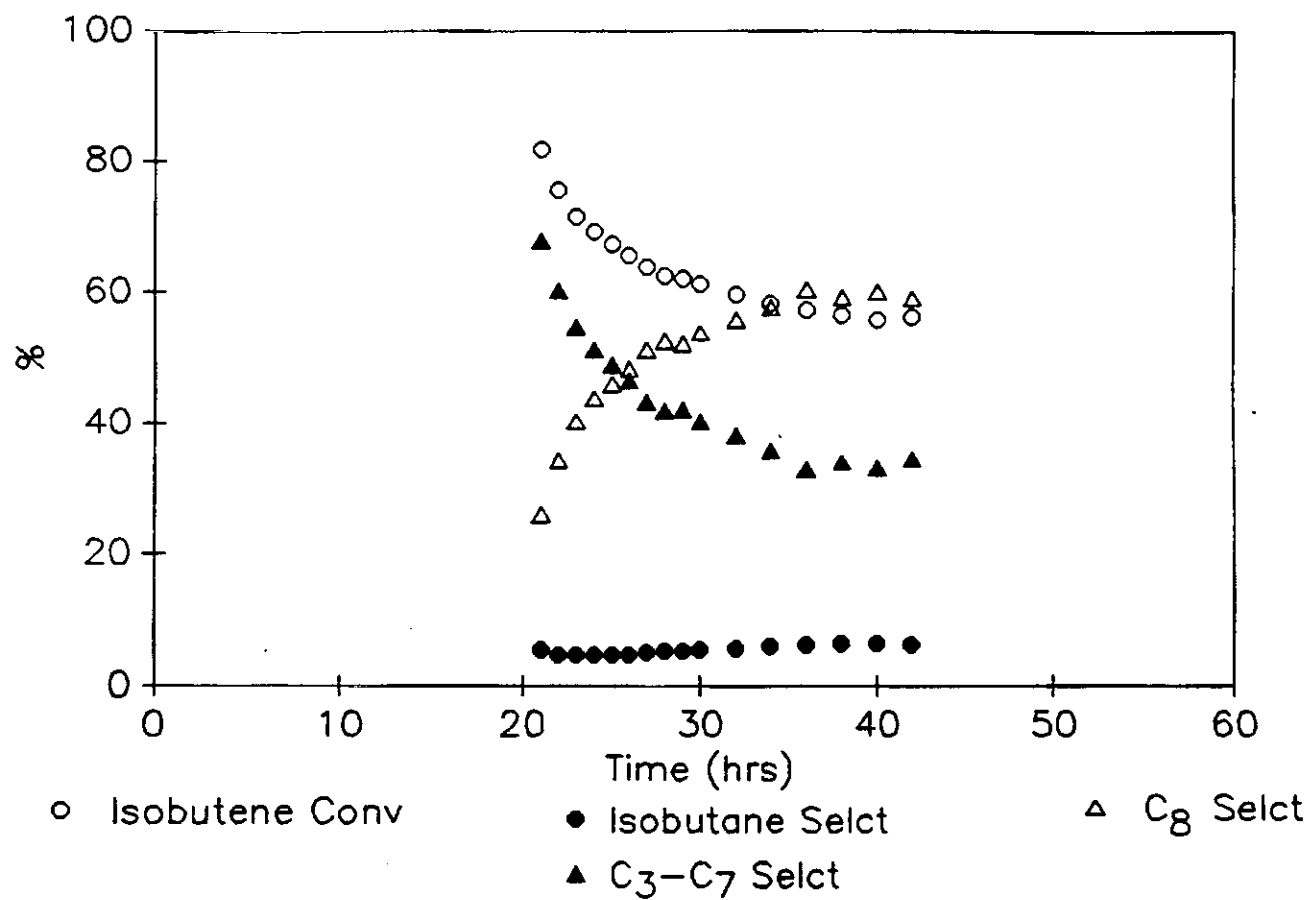


Figure 2.9 Isobutylene conversion and product selectivities over Li₄/Pd/S₂ + ZSM-5.

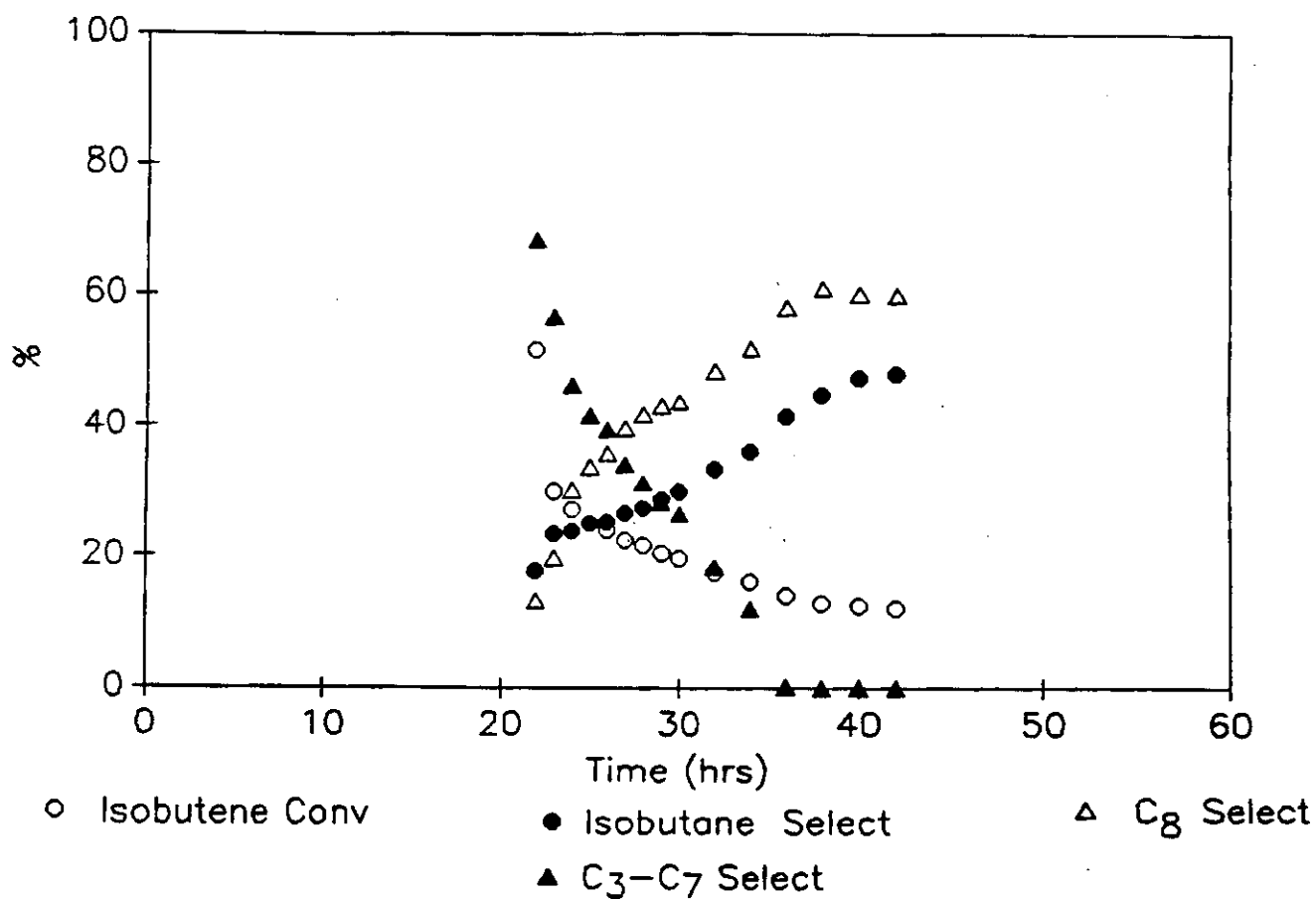


Figure 2.10 Isobutylene conversion and product selectivities over Li₄/Pd/S₂ + LZ210-12.

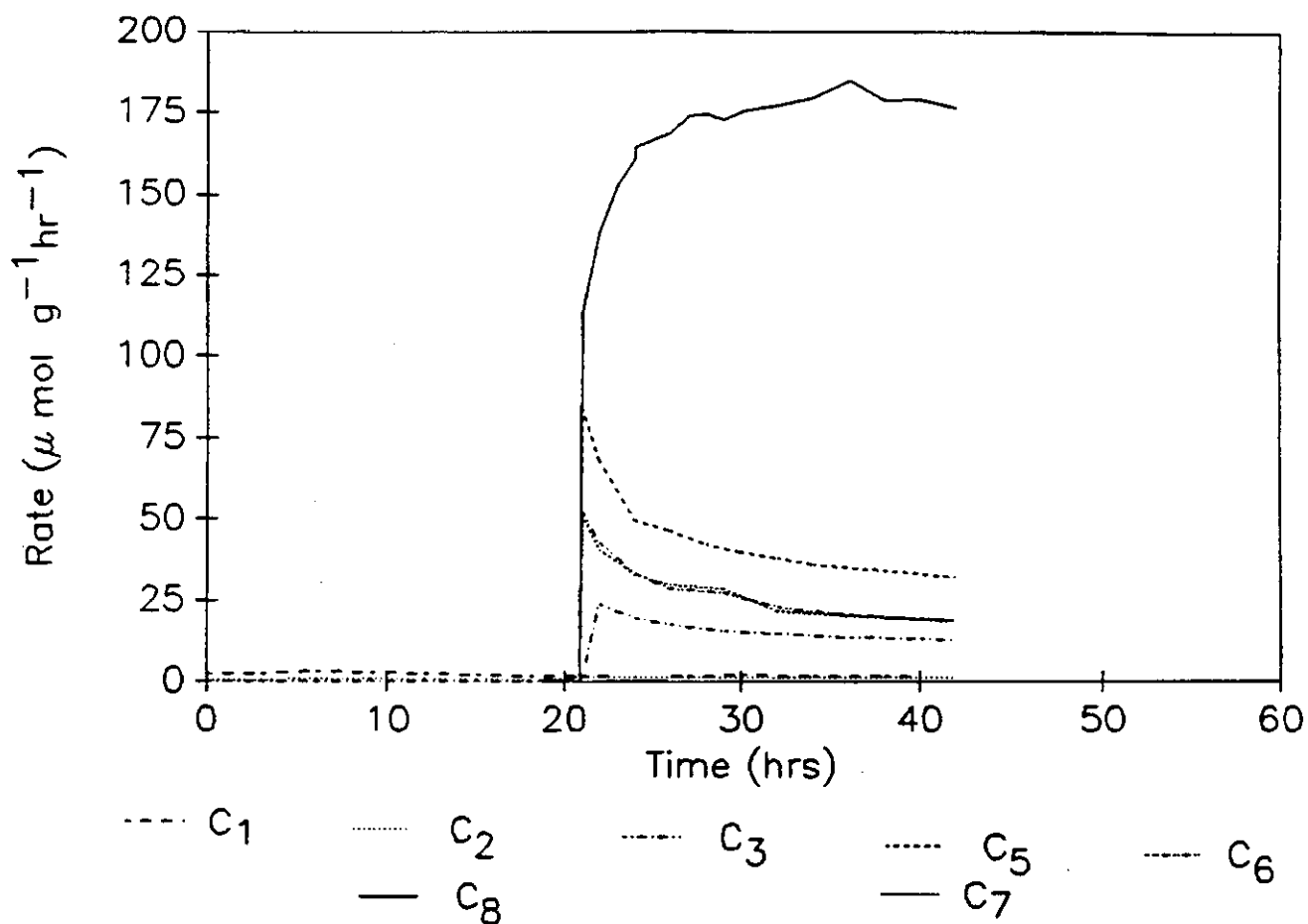


Figure 2.11 Rate of elution of various hydrocarbons during CO hydrogenation in the absence and presence of isobutylene over Li₄/Pd/S₂ + ZSM-5. Break in curves indicate the introduction of isobutylene.

2.4.1.2 CO Hydrogenation over Composite Catalysts

The rate of methanol elution from composite catalysts was lower than the rate of methanol formation over the metal catalyst alone. This is probably related to the fact that methanol can be reacted to other hydrocarbons over the acidic zeolite catalysts. Table 2.8 shows a comparison of the rates of formation of each product over Li1/Pd/S2 and a physical mixture with ZSM-5. In addition to the formation of aromatics on the composite catalyst, the rates of formation of C₂-C₆ were higher than on the Li1/Pd/S2 alone. Although no aromatics were observed for the other two composite catalysts ({Li4/Pd/S2 + ZSM-5} and {Li4/Pd/S2 + LZ210-12}), similar increases in the rate of C₂-C₃ hydrocarbon formation were also noticed to a less significant extent.

2.4.2 Addition of Isobutylene during CO Hydrogenation

2.4.2.1 Pd/SiO₂ and Li-Pd/SiO₂

(a) Formation of Methanol

The decrease in the rate of methanol formation with the addition of isobutylene over Pd/S2 and Li1/Pd/S2 can largely be attributed to the presence of adsorbed isobutylene on the methanol synthesis site. Large amounts of adsorbed isobutylene under synthesis conditions acts as a surface-hydrogen scavengers which in turn affects the overall rate of CO conversion. A minor contributing factor can be the participation of the isobutylene in the hydrocarbon synthesis by reacting with C₁-intermediates which are also responsible for methanol synthesis, thereby reducing the surface concentration of these intermediates and hence the rate of methanol formation.

(b) Formation of MTBE.

Despite a significant decrease in the rate of isobutylene hydrogenation with the Li promotion of the Pd/SiO₂ catalysts, no MTBE was formed with the addition of isobutylene during CO hydrogenation on any of the Li-Pd/SiO₂ catalysts. This suggests that MTBE cannot be formed directly on metal sites from methanol precursors and that MTBE formation requires the presence of acid sites.

2.4.2.2 Composite Catalysts

(a) Formation of Methanol

The initial increase in the rate of methanol elution with the addition of isobutylene may be attributed to the competition of various molecular species for the zeolitic sites. The added isobutylene can displace methanol, formed over the Li-Pd/SiO₂, resulting in an apparent increase in the rate of methanol formation. The rapid decrease in the rate of methanol elution was likely the result of deactivation of the Li-Pd/SiO₂. The faster rate of deactivation of methanol synthesis activity with the addition of isobutylene to the composite catalyst as compared to that for Li-Pd/SiO₂ was most likely due to the formation of heavy polymeric surface species known to be the precursor of coke on the zeolite surface which may have been deposited on the Pd/SiO₂.

(b) Formation of MTBE

Although the methanol synthesis activity of Li1/Pd/S2 was almost 10-fold higher than for Li4/Pd/S2, the rate of MTBE formation over composite catalysts of the latter was much higher than on the composite catalyst of the former. The most likely explanation is the great differences in the hydrogenation activity of the two metal catalysts. It can be speculated that during reaction, when isobutylene reached the composite catalyst bed with the syngas feed, most of it is immediately hydrogenated before significant formation of methanol can occur. This indicates that hydrogenation activity of the metal catalysts plays a crucial role in this reaction scheme.

The higher initial rate (two hours after isobutylene addition) of MTBE formation on {Li4/Pd/S2 + ZSM-5} as compared to on {Li4/Pd/S2 + LZ210-12} can be attributed to the higher resistance of ZSM-5 to deactivation. It should be remembered that CO hydrogenation was carried out for 20 hours over both composite catalysts before the addition of isobutylene was actually started. Methanol produced on the metal catalyst was constantly being converted into heavy aliphatic and aromatic hydrocarbons over the zeolite sites. This reaction alone can contribute to zeolite deactivation. ZSM-5, because of its unique geometrical structure, prevents the oligomerization of hydrocarbons and minimizes the formation of coke on its surface.

2.5 SUMMARY

Addition of isobutylene during CO hydrogenation shows that MTBE formation cannot be carried out on metal sites and likely always requires the presence of acid sites. However, MTBE can be made successfully when acid sites, provided by a zeolite, are present in the vicinity of the methanol synthesis sites. Addition of isobutylene during CO hydrogenation over a composite catalyst consisting of Li-Pd/SiO₂ and a hydrogen-zeolite resulted in the formation of measurable amounts of MTBE. The major byproducts of reaction scheme were isobutane, the dimer of isobutylene, and C₃ to C₇ hydrocarbons, the cracked products of dimer. In general, ZSM-5 was found to be better than LZ210-12 HY zeolite as the acid component of composite catalyst. Li₄/Pd/S₂ was found to be superior to Li₁/Pd/S₂ as the CO hydrogenating component of the composite catalyst.

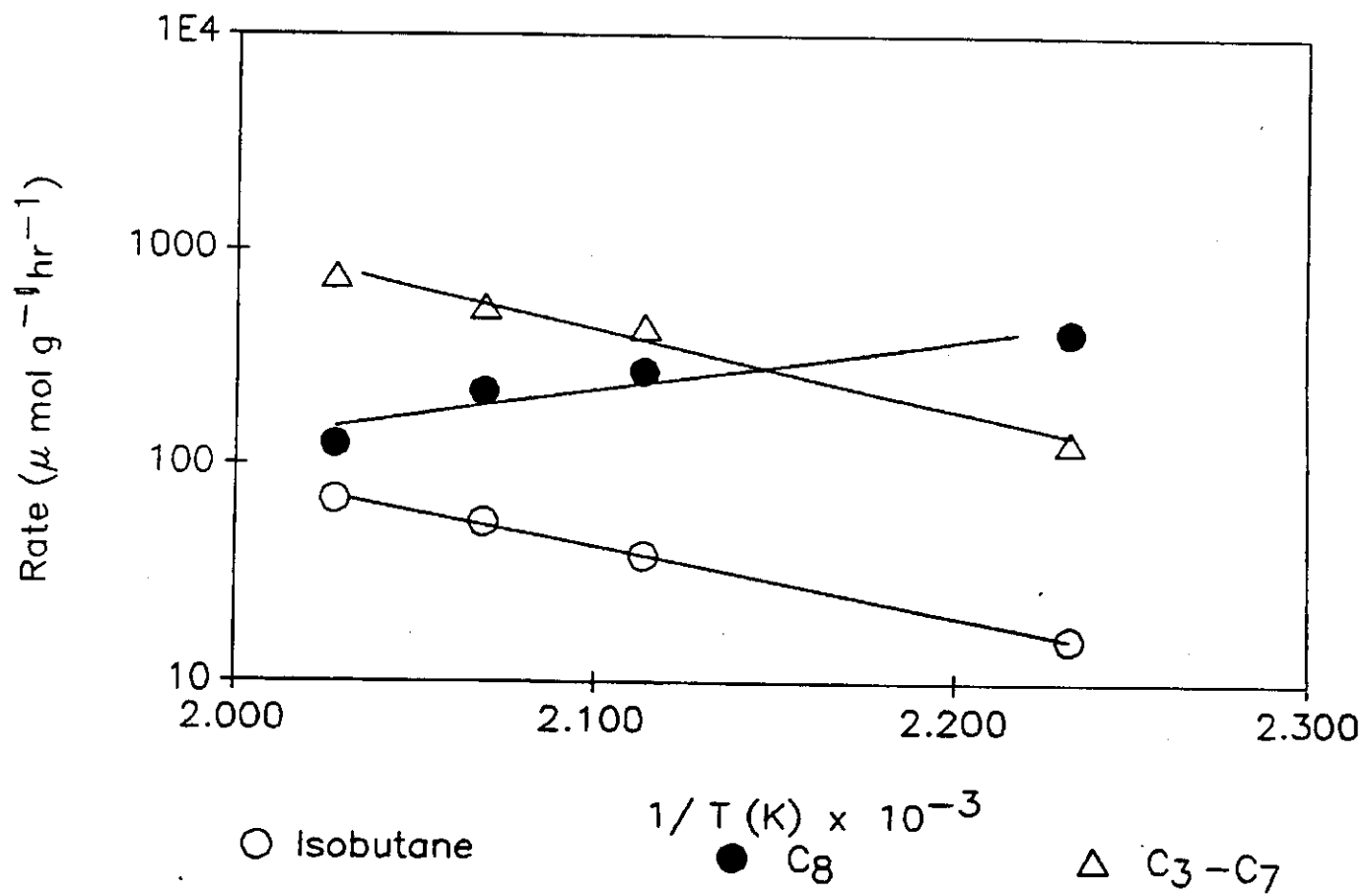


Figure 2.13 Selectivities of isobutylene to various products over Li₄/Pd/S₂ + ZSM-5.

3. SLURRY PHASE MTBE SYNTHESIS

3.1 INTRODUCTION

One primary objective of this project was to evaluate the reactions of interest in a slurry-phase. To this end a laboratory-scale slurry bubble column reactor (SBCR) was designed and constructed. Catalysts and conditions previously identified were used as a basis for this portion of the work.

3.2 EXPERIMENTAL

3.2.1 Reactor

The criteria for the design of the SBCR was described in detail in the First Quarterly Technical Report. The final reactor is schematically depicted in Figure 3.1. It consists of a one-inch internal diameter tube of 36" working length and a 2-inch i.d., 12" long disengaging zone with built-in sight glass. A concentric filter arrangement in the middle of the reaction zone is used for filtering the liquid. The gas distributor consists of a plate with three 1-mm holes equally spaced. The reactor is built in flanged sections.

The system is capable of handling two gas feeds and two liquid feeds. Pre-mixed synthesis gas ($H_2/CO = 0.7$) and a 5% i-butylene/He mixture were used as the reactants. Methanol could be introduced as one of the liquid feeds. The effluent passed through a gas-liquid separator and the gas analyzed by gas chromatography. Liquid products could be collected and analyzed off-line. The dispersing medium consisted of Chevron Synfluid PAO 4, a hydrogenated poly- α -olefin having a molecular weight of ca. 600. Catalysts were pretreated off-line.

Due to cost restrictions, a number of desirable automation features which we identified in the initial design were not included in the final system. Liquid withdrawal and gas sampling into the GC was performed manually. Also, no automatic level control was provided.

The start-up procedure was as follows:

- 1) The reactor was brought to operating temperature overnight. The SBCR and transfer lines were maintained at 100°C and 150°C, respectively. A flow of nitrogen was started to flush the reactor column (about 2 hours).

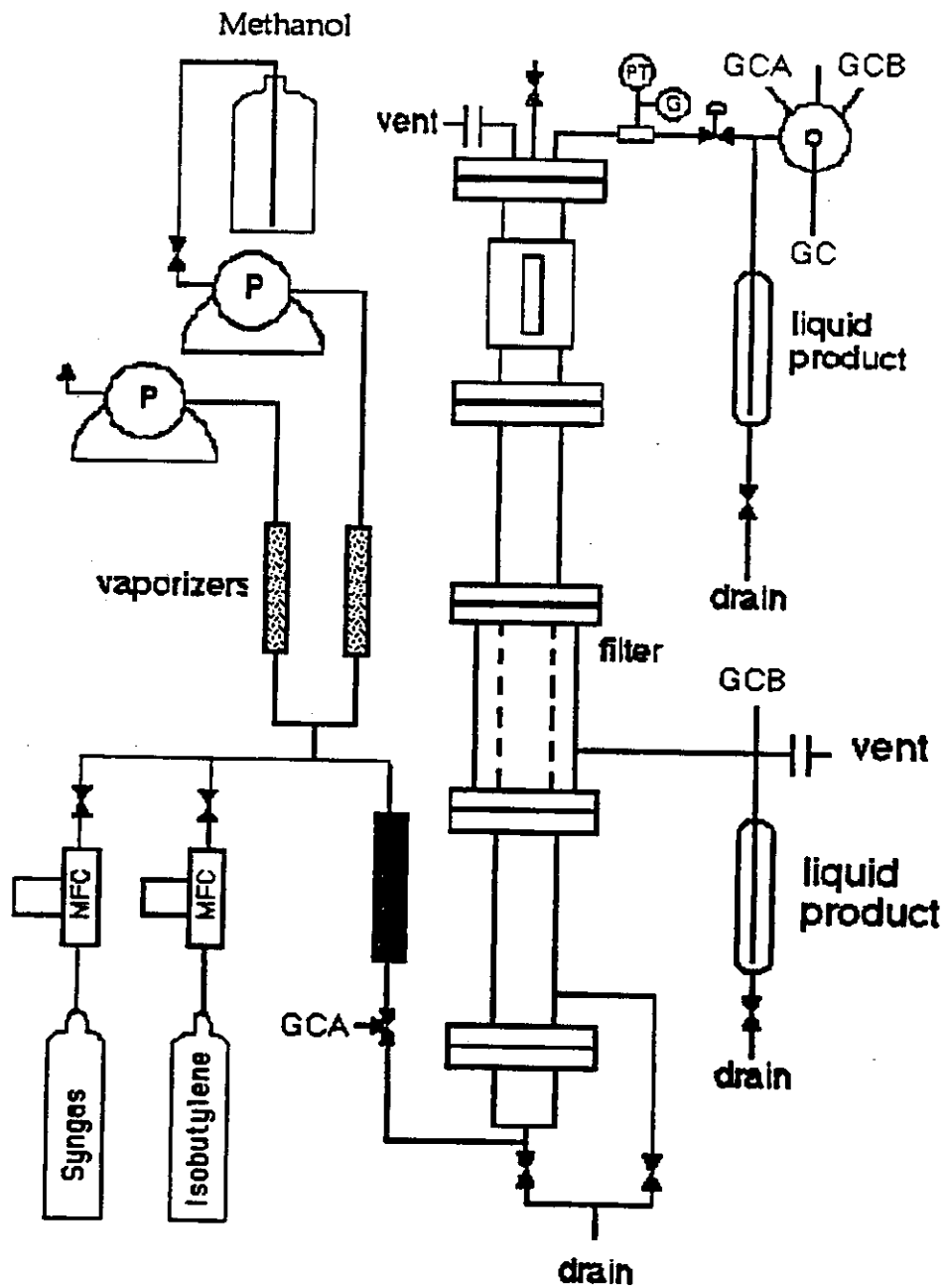


Figure 3.1 Schematic diagram of SBCR.

- 2) Meanwhile, the Synfluid was heated to operating temperature in a separate in-line vessel prior to introduction into the SBCR. It was introduced into the reactor using nitrogen pressure.
- 3) After the temperatures stabilized (about 2.5 hours) the catalyst was loaded and the feeds were started.

3.2.2 MTBE Synthesis from Methanol and Isobutylene

Two catalysts were evaluated: an H-Y zeolite (UOP LZ210-12), and an H-ZSM-5 (Mobil). These catalysts are described in Section 1. The catalysts had been crushed and sieved to 30-100 μm . A 20% catalyst loading (weight of catalyst/weight of liquid) was used. The following feed flow rates were used:

Nitrogen:	1.13 SL/min
5% i-butylene in He:	90 Scc/min
methanol:	0.11 mL/min

This corresponded to a methanol/i-butylene=6.0 and a linear gas velocity of 2.1 cm/sec. The reaction was studied at 100°C and approximately 1.5 bar. The effluent was analyzed periodically during the run by on-line gas chromatography.

3.2.3 MTBE Synthesis from Syngas and Isobutylene

Two catalyst systems were evaluated: a 1:10 mixture of LZ210-12 and a promoted Pd catalyst similar to Li1/Pd/S1 (see Section 2), and a Pd-H-Y which was described in the Eighth and Ninth Technical Reports. The catalysts were sized to 30-100 μm . A 20% catalyst loading (weight of catalyst/weight of liquid) was used. The following feed flow rates were used:

Syngas:	2 SL/min
5% i-butylene in He:	90 Scc/min

The reaction was studied at 200°C and 5 bar. The reaction was started using only syngas. The isobutylene was introduced after approximately 3 hours on-stream. Gas products were analyzed periodically using on-line gas chromatography.

3.3 Results and Discussion

3.3.2 MTBE Synthesis from Methanol and Isobutylene

3.3.2.1 H-Y Catalyst

Two similar runs were conducted. Results from Run #2 are summarized in Figures 3.2 through 3.4 in which various parameters are summarized as a function of time. These Figures are each divided into four time periods. Period I represents analyses taken prior to the introduction of the catalyst. Period II represents analyses taken after introduction of the catalyst. In Period III the i-butylene was cut-off. The i-butylene was restored in Period IV.

Figure 3.2 shows the stability of the feed as a function of time. After approximately one hour, the methanol/i-butylene ratio stabilized and remained fairly constant at 6 except for Period III when the i-butylene was shut-off. Figure 3.3 shows the i-butylene conversion as a function of time. An induction period of over one hour was noted before measurable conversion was obtained. It can also be noted that the reaction rate decreased rapidly, reaching negligible conversion after only 7 hours on-stream. The main products observed in the reaction were MTBE, the i-butylene dimer, and a broad GC peak at long elution times which corresponds to i-butylene oligomers, possibly a C₁₂ hydrocarbon. We have observed these heavies during gas-phase reaction at low methanol/i-butylene ratios.

Figure 3.4 summarizes the carbon selectivities observed towards the main products. During Period IV, the main products observed were the heavy hydrocarbons, with selectivity for MTBE being less than 3-5%. The only time that high MTBE selectivity was noted was during period III, when the i-butylene feed was shut-off. It should be noted that even though during period III there was no i-butylene being fed, i-butylene retained in the reactor continued to elute (see Figure 3.2), along with product MTBE.

3.3.2.2 H-ZSM-5 Catalysts

Figures 3.5, 3.6, and 3.7 summarize the results of the reaction in the SBCR using H-ZSM-5 as a catalyst. These Figures are divided into two periods: Period I shows results of analyses taken prior to the introduction of the catalyst, while Period II

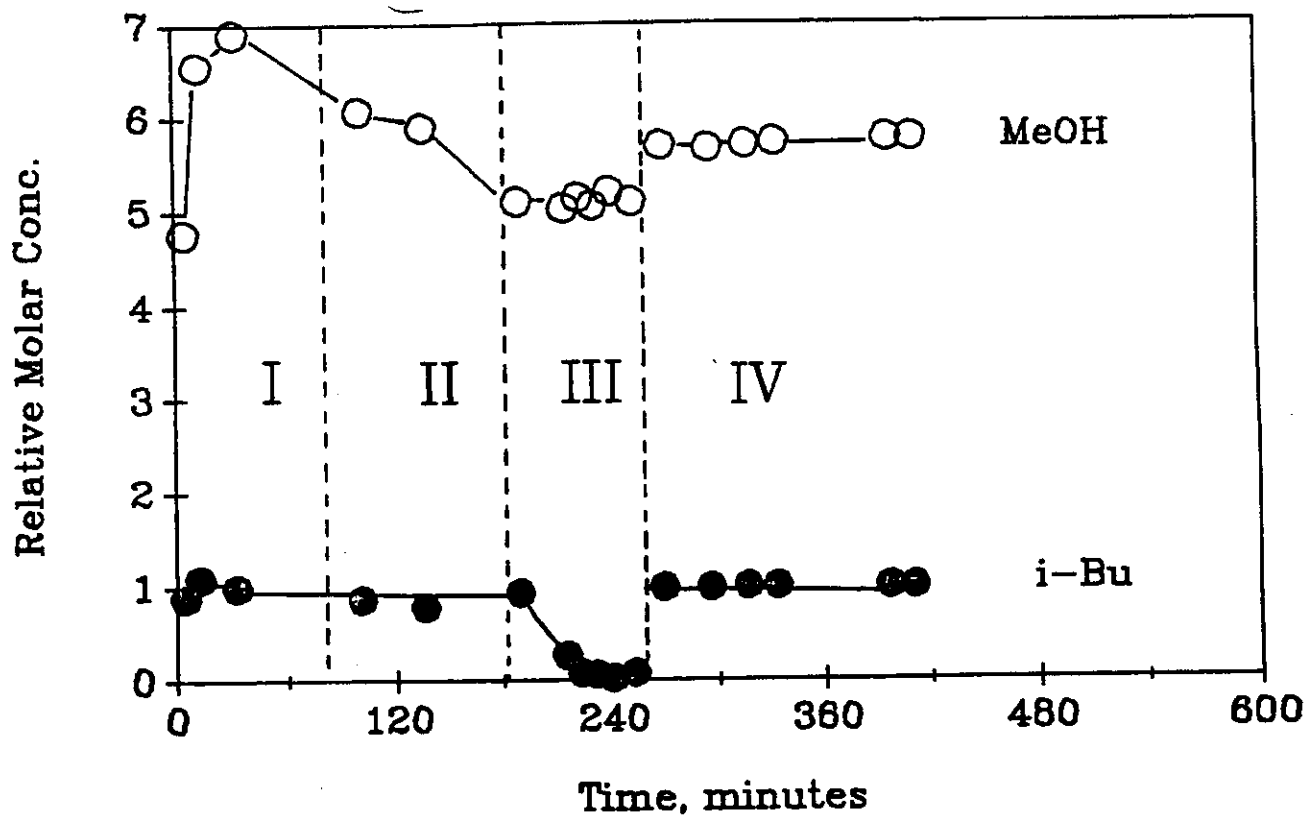


Figure 3.2. Relative molar concentrations of methanol and i-butylene feeds in SBCR. Experimental conditions and meaning of regions I, II, III, and IV are explained in text. Catalyst used was LZ210-12.

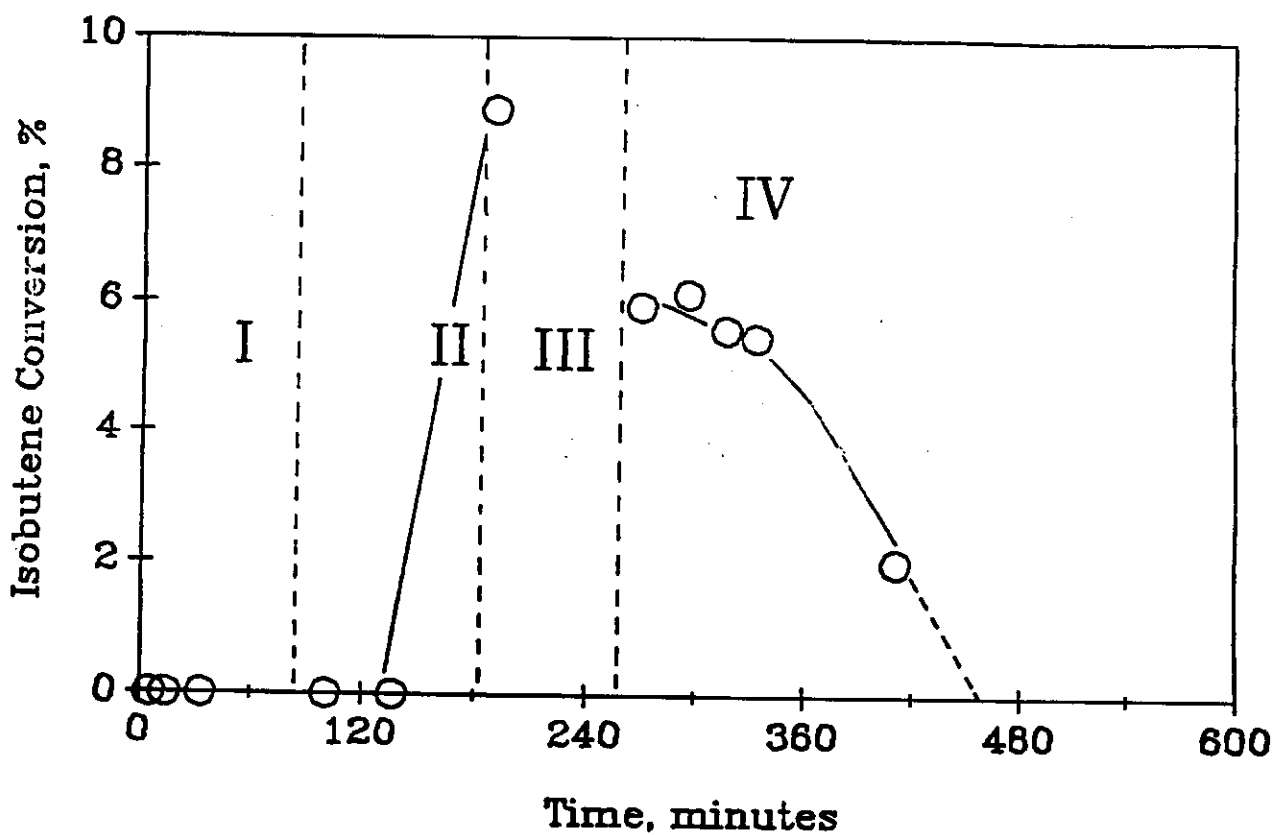


Figure 3.3. Iso-butylene conversion during reaction of methanol and i-butylene in SBCR. Experimental conditions and meaning of regions I, II, III, and IV are explained in text. Catalyst used was LZ210-12.

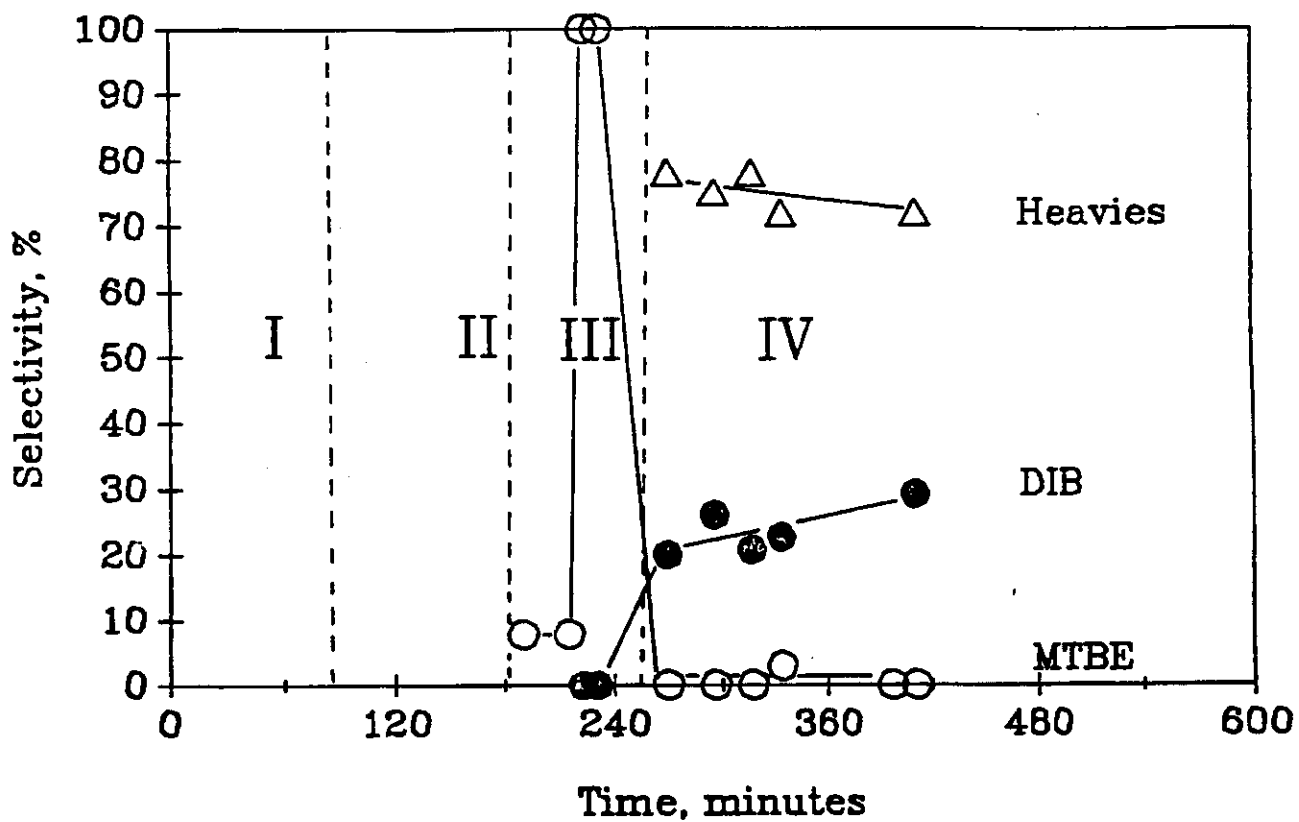


Figure 3.4. Selectivities to major products during reaction of methanol and i-butylene in SBCR. Experimental conditions and meaning of regions I, II, III, and IV are explained in text. Catalyst used was LZ210-12.

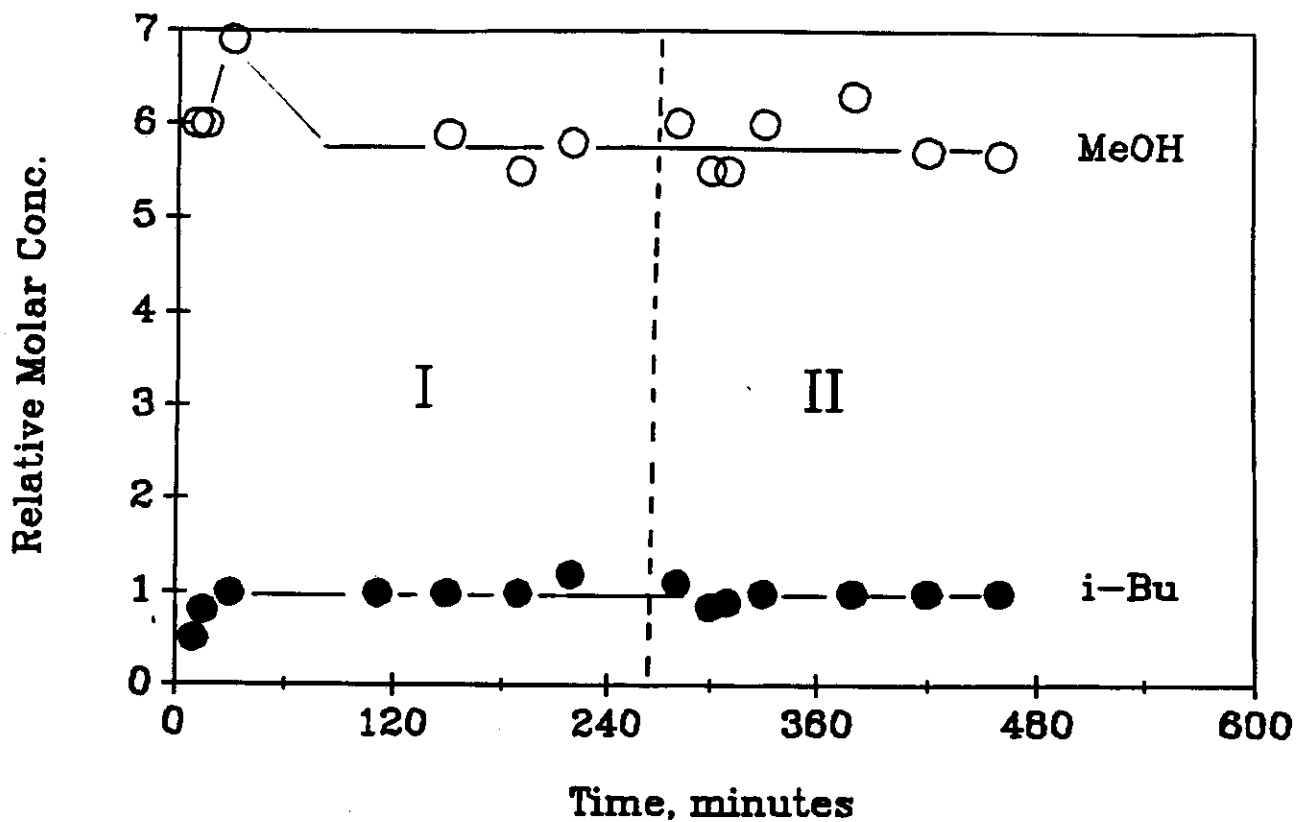


Figure 3.5 Relative molar concentrations of methanol and i-butylene feeds in SBCR. Experimental conditions and meaning of regions I and II are explained in text. Catalyst used was H-ZSM-5.

represents analyses after introduction of the catalyst. Figure 3.5 shows the relative molar concentration of the reactants. It remained at approximately 6 throughout the entire run.

The observed conversion of isobutylene is depicted in Figure 3.6. As in the case of the LZ210-12 catalyst, deactivation of the catalyst occurred very rapidly. In fact, no measurable activity was evident after 90 minutes of reaction. The principal products observed were heavy hydrocarbons, presumably oligomers of the isobutylene. Only traces of MTBE were seen and only during the early stages of the reaction.

It is likely that the cause of the deactivation is coke or heavy oligomer formation on the catalyst surface. The catalyst was quite dark and gummy when removed.

3.3.2.3 Effect of Isobutylene and Methanol Solubilities on the Reaction

The large amounts of heavy products and the low selectivity to MTBE were surprising in view of our previous experiments in the gas phase and the high methanol-to-i-butylene ratio used in these runs. In the gas-phase and with methanol/i-butylene=0.5, over 95% selectivity to MTBE was observed with these catalysts at this temperature. The higher level of methanol used here would be expected to further improve the MTBE selectivity.

It is suspected that one major reason for the poor MTBE selectivity relates to the relative solubilities of the reactants in the Synfluid changing the effective methanol/i-butylene ratio. This theory was tested by conducting an experiment in which the methanol/isobutylene was fed through the Synfluid, at operating temperature, in the absence of a catalysts. After reaching a constant effluent composition one of the reactants was shut-off and the concentration of that component in the effluent gas was followed with time. Figure 3.7 shows the relative molar concentration of i-butylene and methanol with time. Whereas the methanol concentration in the effluent quickly dropped, analyses showed that i-butylene continued to elute from the reactor for nearly 2 hours. This thus indicates that the i-butylene is highly soluble in the Synfluid. This is perhaps not surprising since they are both non-polar hydrocarbons. This results in the methanol/i-butylene ratio in the liquid medium being very low, favoring the oligomerization of i-butylene and severely limiting the yield of MTBE that can be obtained. Indeed, the only time that MTBE selectivity was high was after the i-butylene

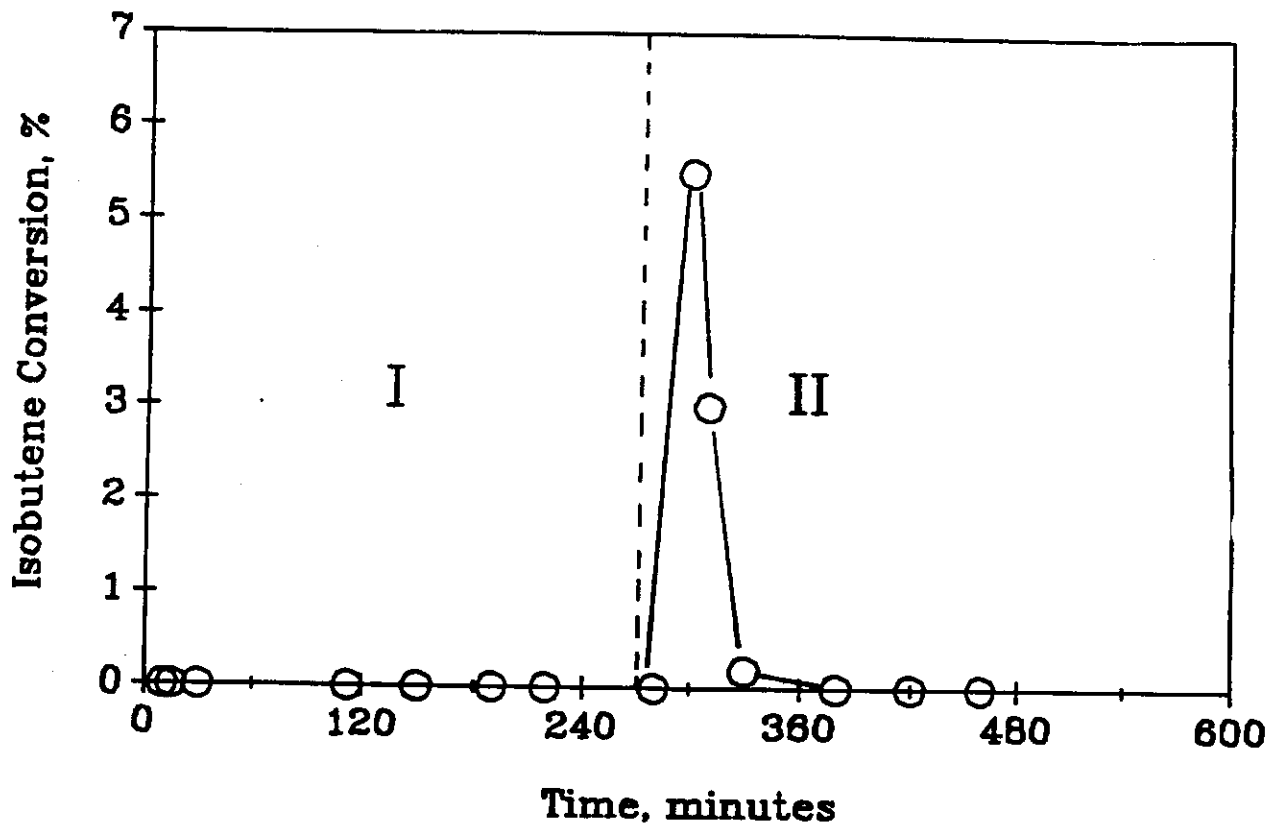


Figure 3.6. Iso-butylene conversion during reaction of methanol and i-butylene in SBCR. Experimental conditions and meaning of regions I and II are explained in text. Catalyst used was H-ZSM-5.

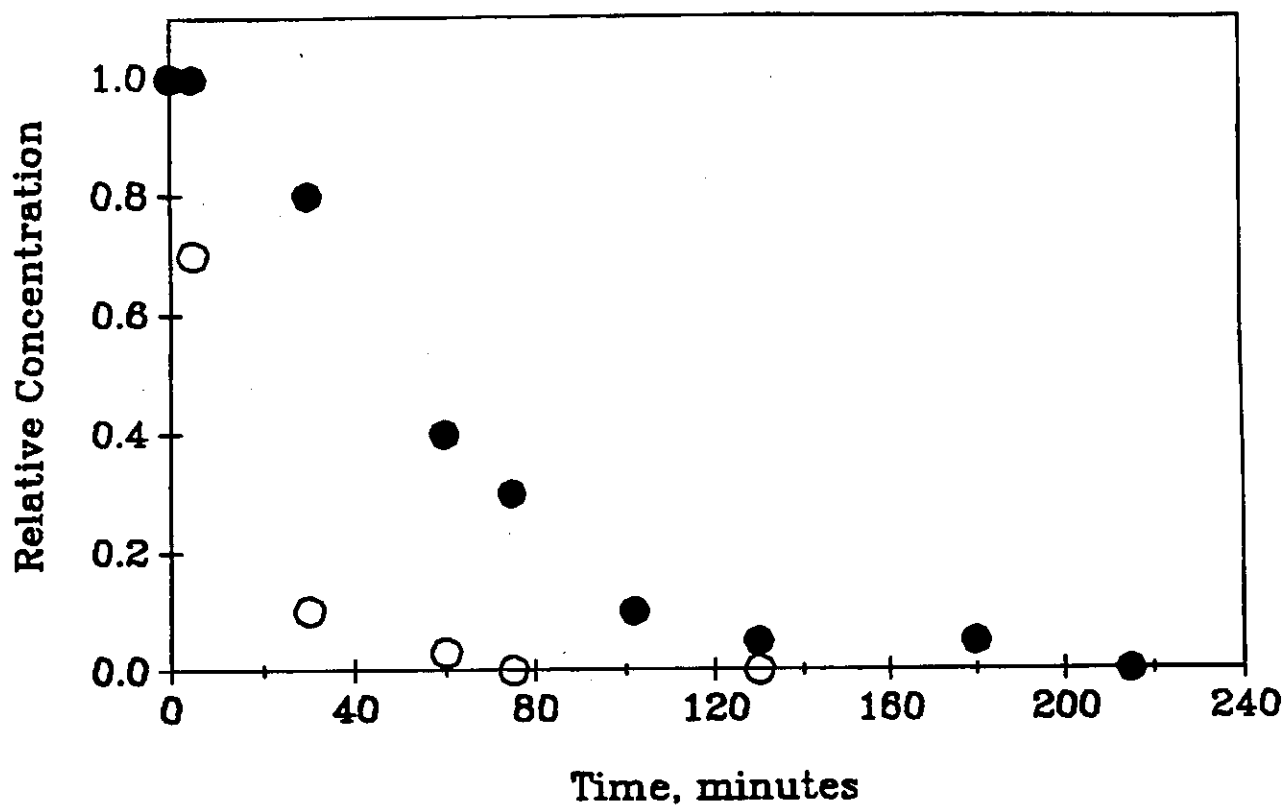


Figure 3.7. Relative concentrations of i-butylene (●) and methanol (○) in SBCR effluent after feed shut-off in the absence of reaction. SBCR was maintained at 100°C.

supply was shut-off during the experiments with LZ210-12. A similar experiment with H-ZSM-5 was not possible due to the fast deactivation.

3.3.3 MTBE Synthesis from Syngas and Isobutylene

The typical product distribution obtained after 1 and 2 hours on-stream with catalyst Li-Pd-HY is shown in Table 3.1. Conversions under these conditions were very low, less than 1% CO conversion, and only methane and methanol were detected as products. Because of the low conversion, the analyses are only approximate. Addition of the isobutylene resulted in an immediate and complete loss of catalyst activity. As in previous cases, the recovered catalyst was very dark in color and gummy.

Attempts to use the Li-Pd/SiO₂ catalyst in the SBCR were unsuccessful. No catalytic activity was observed. It is believed that the catalyst was not successfully dispersed in the bubble column.

4. CONCLUSIONS

Several important conclusions have resulted from this work regarding the feasibility of making ethers, specifically MTBE, directly from a feed containing syngas. One important conclusion relates to the possibility of making MTBE directly on methanol-synthesis catalysts by addition of isobutylene during reaction. The experiments performed using supported metals indicate that this is not possible. In fact, methanol-synthesis catalysts tend to perform strictly as hydrogenation catalysts, catalyzing the conversion of isobutylene to isobutane.

Incorporating an acid functionality into a methanol-synthesis catalyst, however, results in the catalyst making measurable quantities of MTBE from a syngas/isobutylene feed. The way in which this acid functionality is incorporated does not appear to matter, as evidenced by the comparable results obtained, in the gas phase, using different zeolites or the different bed arrangements. The major difficulty with this approach is that the zeolite tends to deactivate fairly rapidly, depending on the zeolite used. ZSM-5 zeolite was found to retain its activity longer, probably due to its ability to resist the formation of coke within its pores.

The processes did not perform as well in a slurry medium, primarily due to the very rapid deactivation of the catalysts. This deactivation is suspected to be due to the

TABLE 3.1 Summary of Reaction of Syngas/Isobutylene over Pd-Li-HY Catalyst in a Slurry Medium.

	1 Hour	2 Hours
CO Conversion, %	1.	<0.5
<u>Product Selectivity</u>		
Methane	39	40
Methanol	25	20
Other	36	40

coke or oligomers coating the catalytic sites. It is suggested that the relative solubilities of the MTBE-forming components, i.e., methanol and isobutylene, are widely different in the Synfluid medium used, and that Synfluid favors the solubility of the non-polar isobutylene. This, in turn, leads to a high isobutylene/methanol ratio which favors the formation of oligomers rather than MTBE. Such a scenario is consistent with all our observations.

5. RECOMMENDATIONS

This work clearly showed the difficulty of making ethers by intercepting a methanol molecule or a methanol intermediate during CO hydrogenation to alcohols. The formation of ethers via this route does not appear possible using simply a metal catalysts and is severely limited by thermodynamic considerations at the temperatures commonly used to synthesize alcohols. Although it is an interesting and potentially useful route, any further work in etherification during FT or alcohol synthesis should probably be limited to processes operating at low temperature, i.e., below 150°C. It is recognized that no low temperature alcohol synthesis process has been commercially proven and perhaps some research effort should also be directed to that area.

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