deactivation, clearly indicates that acidity significantly influences selectivity and deactivation. Apparently there seems to be an optimum pair of acidic characteristics, i.e. acid strength, acid site density, which should be optimized for the production of MTBE with good selectivity and limited catalyst deactivation.

These factors, along with shape selectivity, need to be taken into account, in order to design a good MTBE synthesis catalyst. At high temperatures, the presence of high acid strength sites is unimportant, since it would mainly enhance byproduct formation and also catalyst deactivation. At low temperatures, where formation of MTBE is preferred to isobutene dimer and there is no significant deactivation, enhanced acidity is preferable.

2.   ETHER SYNTHESIS DURING FT REACTION

2.1   INTRODUCTION

A possible way of direct synthesis of MTBE from syngas is the incorporation of isobutylene during methanol synthesis from syngas. This incorporation could be envisioned to take place in one of two possible ways: (i) by interception of methanol reaction intermediates by isobutylene at methanol synthesis sites or (ii) by secondary reaction of the methanol produced from syngas and isobutylene on acid sites. Acid sites can be incorporated with a CO hydrogenation catalysts in a variety of ways, such as by physically mixing a CO hydrogenation metal catalyst capable of synthesizing methanol with an acid catalyst or by placing a bed of an acid catalyst downstream of the first bed consisting of the CO hydrogenation catalyst.

The work reported in this section examined two possible routes for the synthesis of MTBE during gas phase CO hydrogenation reactions:

1)   addition of isobutylene during CO hydrogenation over a supported metal catalyst active for methanol synthesis.

2)   addition of isobutylene during CO hydrogenation over composite catalysts comprised of physical mixtures or dual bed of a methanol synthesis catalyst and a zeolite.

Synthesis of MTBE from methanol and isobutylene is equilibrium limited at temperatures much above 100°C. However, CO hydrogenation generally requires reaction temperatures >200°C. Therefore any CO hydrogenation catalyst chosen must

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have high activity for methanol synthesis even at temperature $\leq 200°C$. Since most of the catalysts active for CO hydrogenation are also good olefin hydrogenation catalysts (22,23), the hydrogenation of the added isobutylene over the metal catalysts must be limited in order that it will be available for the reaction with methanol to produce MTBE.

Pd/SiO_2 which is known to produce methanol with high selectivity (24-28), was chosen as the CO hydrogenation catalyst for this portion of the study. Alkali promotion of group VIII metals has been shown to reduce their hydrogenation activity (29,30). Lithium, which has been reported earlier as a promoter for methanol synthesis during CO hydrogenation over Pd/SiO_2 (27,28), was selected as a promoter for reducing the hydrogenation activity of the metal catalyst. Amberlyst-15, a typical commercial MTBE synthesis catalyst, could not be used in this study as an acid catalyst because of its instability above 100°C, where it gradually loses its activity by losing acid groups from the resin copolymer network in the form of sulfonic or sulfuric acid (31,32). Two types of zeolites, Mobil's ZSM-5 and Linde's LZ-210-12 HY zeolite which can tolerate high temperatures, were selected to provide acid sites for the reaction of isobutylene with methanol to produce MTBE. These two zeolites were shown in the previous studies to have a high resistance to deactivation and a good selectivity for MTBE.

2.2   EXPERIMENTAL

2.2.1 Catalyst Preparation

Pd/SiO_2

A series of SiO_2-supported Pd catalysts was prepared having various levels of Li promotion. The SiO_2 used was Davison grade 59, having a surface area 300 m^2/g, a pore volume of 1 cm^3/g, and a pore diameter of 140 Å (1Å = 10^{-8} cm).

In order to minimize the effect of different metal particle sizes for different promotion levels, a large batch of Pd/SiO_2 base catalyst was prepared by incipient wetness using an aqueous solution of PdCl$_2$ (Aldrich, 99.999%). The impregnated catalyst was dried in an oven for 5 hours at 90°C and then calcined at 400°C for four hours. The calcined catalyst was then reduced in flowing hydrogen (80 cc/min) at 400°C for 5 hrs.

Two separate base-catalyst preparations were performed and they are referred by the nomenclature S1 and S2, respectively.

The treated base catalyst was further promoted with $LiNO_3$ (Aldrich, 99.99%) using solutions appropriately diluted with distilled water to the desired Li concentrations such that, following incipient wetness, catalysts would have nominal Li/Pd ratios of 1, 2, 4, and 6.

Composite catalysts

Composite catalysts were prepared by physically mixing a supported metal catalysts in a 10:1 weight ratio with LZ210-12 HY (Linde) or ZSM-5 (Mobil) zeolite. Prior to reaction, the catalyst was treated in-situ by heating at 1°C/min to 400°C in 50 cc/min of hydrogen and holding at that temperature for 5 hours.

Dual Beds

Dual beds of catalysts were prepared by placing the supported metal catalysts at the top and the zeolite at the bottom in a down flow reactor configuration. The amounts of catalysts and pretreatment procedure was the same as used for composite catalysts.

2.2.2 Catalyst Characterization

X-Ray Diffraction (XRD)

X-ray measurements were taken using a Phillips X'Pert instrument with monochromatic Cu K_α radiation and Ni filter. The X-ray diffractometer was operated at 40 kv and 30 mA. The catalyst was supported as a powder on a glass slide and scanned at the rate of 0.2 deg/min (2θ).

Elemental Analysis

The SiO_2 support and all the SiO_2-supported Pd catalysts studied were analyzed for traces of metal impurities and Pd, respectively, using inductively coupled plasma (ICP) spectroscopy.

CO Chemisorption

CO chemisorption was carried out at ambient temperature in a conventional volumetric apparatus. An ultimate pressure below 10^{-6} Torr could be reached in the system. Airco UHP grade H_2, CO, and He were used. H_2 and He were purified by passing through a liquid N_2 trap, whereas for CO a dry ice trap was used. Typically

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about one gram of the prereduced catalyst was evacuated and gradually heated to 400°C. The catalyst was held under vacuum at that temperature for two hours. H_2 was then introduced for 5 hours at the same temperature in order to re-reduce the catalyst. The sample was evacuated at 400°C for 2 hours and cooled to room temperature. The total uptake of CO was determined from 50 to 400 Torr and the linear isotherm was extrapolated to zero pressure. For the first point of the isotherm, the system was allowed to equilibrate during 24 hours; for subsequent points, equilibrium was reached in about 2 hours. A second isotherm was performed in the same manner after evacuating the catalyst for a short period of time (ca. 10 min). The difference between the two isotherms, extrapolated to zero pressure, was used to calculate the number of surface metal atoms, the percent metal dispersion, and the average metal particle size (33).

2.2.3 Reaction Studies

Reaction studies were carried out in a fixed bed, 0.3 inch ID stainless steel U-tube microreactor capable of working up to 10 bar. A schematic of the experimental system is shown in Figure 2.1. Flow rates of the feed gases, CO and H_2 and a premixed mixture of 10% isobutylene (IB) in helium, were controlled using mass flow controllers. Pressure in the system was controlled using a backpressure regulator. To prevent the possibility of condensation of the products in the backpressure regulator which could later affect product analysis, most the product gases were vented after the backpressure regulator and only a small fraction were leaked to the sampling system using a high temperature needle valve. All the lines in the reaction system downstream of the isobutylene injection point were kept heated to 175°C to avoid any product and/or isobutylene condensation.

Prior to reaction, the catalysts were re-reduced in a H_2 flow of 50 cc/min at 400°C for 5 hours. CO hydrogenation was studied using differential conversions (below 5%). The total flow rate of the CO/H_2 mixture (CO:H_2 = 1) was 30 cc/min and 1.0 g of catalyst was used. Reactions were carried out at 7 atm pressure.

The addition of isobutylene during CO hydrogenation was studied over both supported metal and composite catalysts. For these studies, the flow of IB:He:CO:H_2 was maintained at 0.4:3.6:15:15cc/min. Since it took about ten to twenty hours for most of the catalysts to reach steady-state activity, all reaction studies were started with syngas
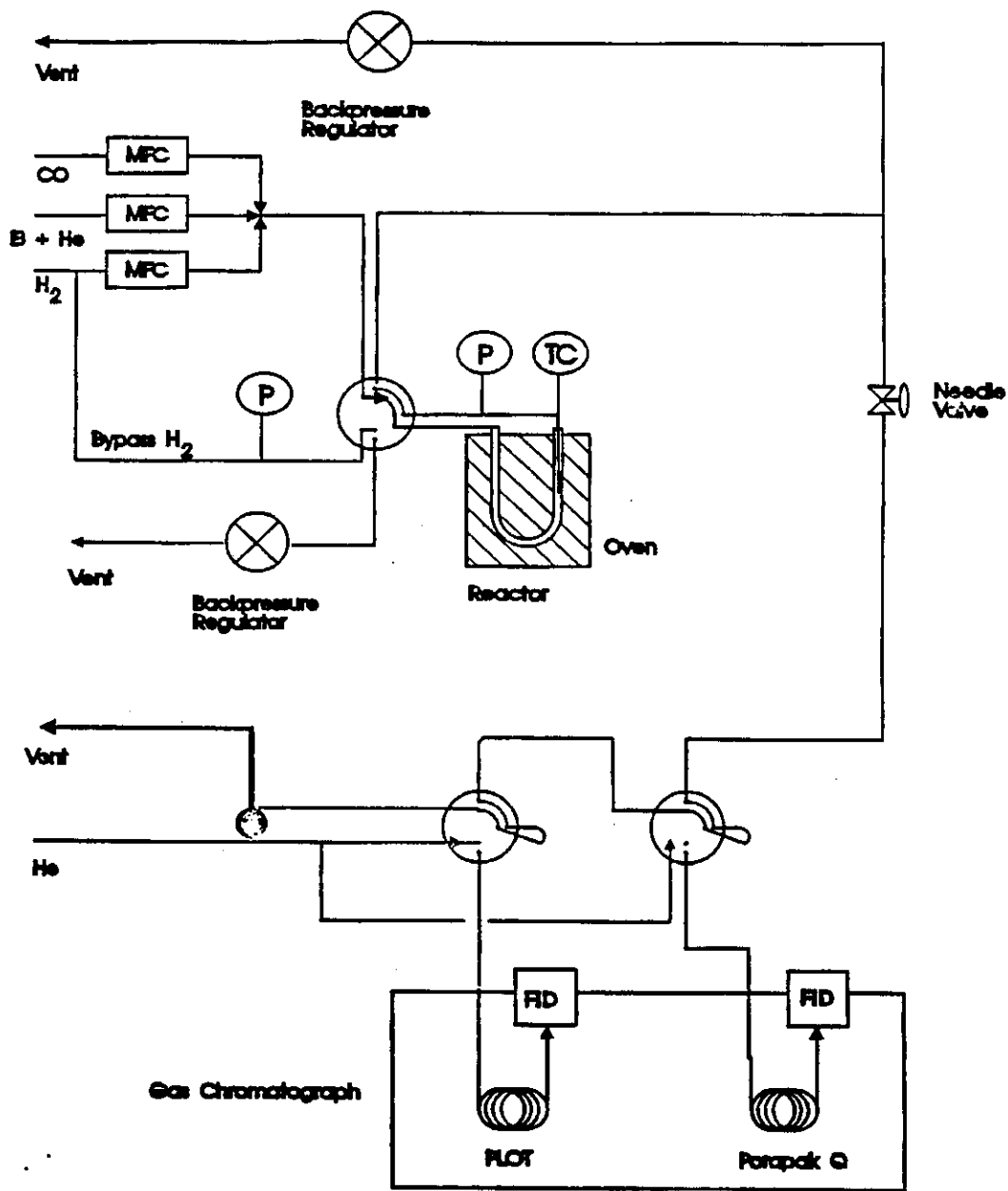
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Figure 2.1   Schematic of reaction system used in syngas studies

only. Addition of isobutylene during CO hydrogenation was only done after the rate of methanol formation had reached steady-state. Two sets of experiments were carried out with each catalyst: one for observing the time-on-stream performance of the catalyst and the other for studying the activity of the catalyst at different temperatures.

All products were analyzed on-line using a Varian 3700 gas chromatograph equipped with a Megabore capillary GS alumina PLOT (porous layer open tubular) column, a Porapak-Q filled packed column, and flame ionization detectors. The first column (PLOT) was used for the analysis of light hydrocarbons and the second column (Porapak-Q) was used for oxygenate analysis. A Spectra-Physics integrator was used to determine peak areas and compositions. All sampling was done using automated sampling valves controlled by the integrator which enabled sample acquisition and data analysis at similar time intervals for the long time-on-stream experiments.

2.3   RESULTS

2.3.1 Elemental Analysis

Table 2.1 shows the major impurities present in the silica support. None of these impurities were in sufficient concentration to adversely affect the reaction results. Table 2.2 shows the weight percent of various components along with the nomenclature used for referring to these catalysts. The last column shows the analyzed Li/Pd atomic ratio.

2.3.2 X-ray Diffraction

X-ray diffraction line broadening was used to determine the average Pd particle sizes on the support. All of the catalysts exhibited the Pd(111) X-ray line at $2\theta =$ 40.15°. For calculation of Pd particle size by XRD method, the refraction line of the Pd(111) face and the Scherrer equation was used. The results are summarized in Table 2.3. No X-ray lines for Li species were seen, probably because of its low loadings.

2.3.3 CO Chemisorption

The results of CO chemisorption at room temperature on the various Li-promoted Pd/SiO$_2$ are shown in Table 2.3. Irreversible CO chemisorption was used to determine the amount of exposed Pd in the base, unpromoted catalysts. This was then used to

Table 2.1   Impurity Concentration in SiO_2 Support

Metal	Conc[a] (ppm)
Na	580
Ca	580
Mg	190
Al	280
Fe	130
S	35

a)   As measured by inductively coupled plasma.

Table 2.2   Metal and Promoter Loadings from Elemental Analysis

Catalyst[a]	Description	Pd (wt%)	Li (wt%)	Li/Pd Atomic
Pd/S1	Pd/SiO$_2$	4.36	-	-
Li4/Pd/S1	Li-Pd/SiO$_2$	"	1.17	4.1
Li6/Pd/S1	Li-Pd/SiO$_2$	"	1.66	5.9
Pd/S2	Pd/SiO$_2$	5.01	-	-
Li1/Pd/S2	Li-Pd/SiO$_2$	"	0.26	0.8
Li2/Pd/S2	Li-Pd/SiO$_2$	"	0.65[b]	2.0[b]
Li4/Pd/S2	Li-Pd/SiO$_2$	"	1.14	3.6

a)   S1 and S2 denotes two separate preparations of base Pd/SiO$_2$ catalysts.
b)   Based on nominal loading.

Table 2.3   Properties of Li Promoted Pd/SiO₂

Catalyst	CO_{irrev} (μmol/g)	Dispersion[a] (%)	Pd average particle size (Å)	
			CO Chem[a]	XRD
Pd/S1	81.5	19.3	49	127
Li4/Pd/S1	86.1	"	"	107
Li6/Pd/S1	84.2	"	"	104
Pd/S2	105.4	22.4	42	154
Li1/Pd/S2	139.5	"	"	108
Li2/Pd/S2	122.5	"	"	138
Li4/Pd/S2	125.6	"	"	131

a)   Based on CO_{irrev} chemisorption on the base, unpromoted catalysts.

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calculate the average metal particle size as well as the percent dispersion of the Pd on the support for both promoted and unpromoted catalysts. The differences observed between the particle sizes as determined by XRD and CO chemisorption are not unusual and are likely due to a combination of the ability of XRD to selectively detect larger particles and to multiple CO molecules adsorbing on an individual metal site.

2.3.4 CO Hydrogenation over Supported Metal and Composite Catalysts

2.3.4.1 Pd/SiO$_2$ and Li-Pd/SiO$_2$

Results on CO hydrogenation for all the Pd/SiO$_2$ based catalysts studied are summarized in Table 2.4. In all the cases the main product observed was methanol. Methane and trace amounts of other hydrocarbons were also observed. For all the catalysts the selectivity for methanol was above 90%. By comparing the steady-state rates of CO conversion over the second series of catalysts, it is evident that Li promotion of Pd/SiO$_2$ significantly enhanced the activity of CO hydrogenation for the lowest level of promotion (Li/Pd = 1). The rate of CO conversion on Li1/Pd/S2 was almost twice as much on Pd/S2. However, the highest level of Li promotion (Li/Pd = 4) gave considerably reduced activity. Figure 2.2 shows the effect of reaction time on the rate of methanol formation over various catalysts studied. It can be seen that catalytic activity changes considerably with time-on-stream and reached steady-state after ten to twenty hours of reaction. A high Li level (Li/Pd = 4) resulted in very low initial activity which increased to a significant rate at steady-state.

2.3.4.2 {Li-Pd/SiO$_2$ + Zeolite} Composite Catalysts

Since Li promotion was shown to enhance activity as well as reduce the hydrogenation activity of the Pd/SiO$_2$, only Li-promoted Pd/SiO$_2$ catalysts with various levels of promotion were used as the methanol synthesis component for the composite catalysts.

Table 2.4   Product Distribution during CO Hydrogenation over Li Promoted Pd/SiO$_2$ Catalysts[a,b]

Catalyst	Pd/S1[c]	Li4/Pd/S1	Li6/Pd/S1	Pd/S2	Li1/Pd/S2	Li4/Pd/S2
Temp(°C)	175	175	175	200	200	200
CO conv (%)	0.03	0.20	0.15	0.71	1.79	0.13
Rate(μmol/g hr)	32	69	54	290	573	53
Selectivities (mol%)						
MeOH	96.5	90.2	98	96.3	96.8	94.2
C$_1$	1.7	7.3	1.7	2.8	1.2	4.4
C$_2$	1.8	2.3	0.3	0.6	1.0	1.2
C$_3$	-	0.2	-	0.3	0.6	0.2
C$_4$	-	-	-	-	0.4	-

a) P = 7 atm, H$_2$/CO = 1.
b) After 12 hours of reaction.
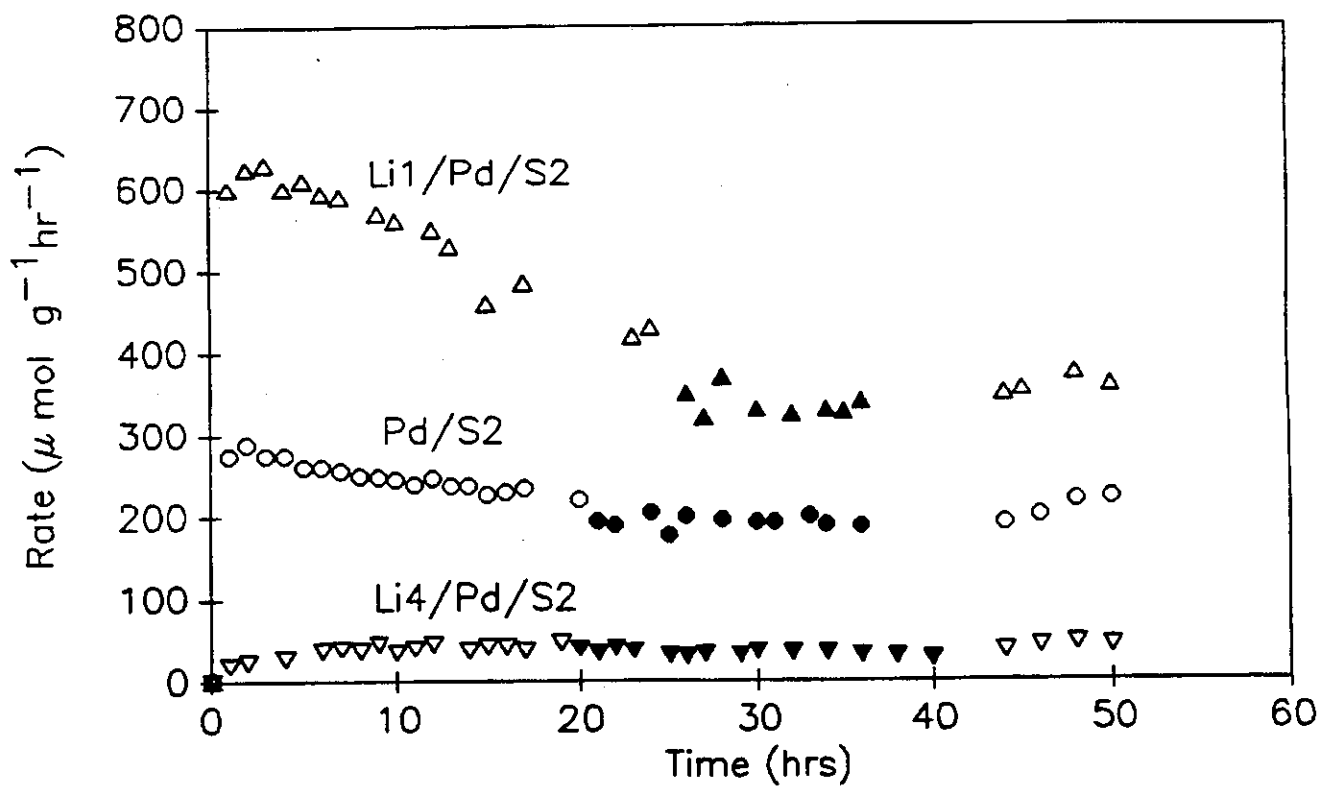c) Initial reaction data.

Figure 2.2   Rate of methanol formation over Pd and Li-Pd catalysts. Open and closed symbols represent rates in the absence and presence of isobutylene, respectively.

Table 2.5 Rate of Methanol Elution and MTBE Formation during CO Hydrogenation[a] with Isobutylene Addition over a Composite Catalysts: Li6/Pd/S1 + Zeolite (10:1 wt. ratio)

Configuration	Zeolite	Rate$_{MeOH}$[b] (μmol/g/hr)	Rate$_{MTBE}$[c] (μmol/g hr)
single catalyst[d]	-	60	0
dual bed[e]	LZ210-12	6.5	T[f]
physical mixture	LZ210-12	3.5	0.22
dual bed[e]	ZSM-5	5.5	0.44
physical mixture	ZSM-5	8.3	1.8

a) T = 175°C, P = 7 atm., H_2/CO = 1.

b) Average rate of MeOH elution per gram of Li6/Pd/S1, 4-5 hrs before IB addition.

c) Average rate of MTBE formation per gram of Li6/Pd/S1, 4-7 hrs after IB addition.

d) Same weight of Li6/Pd/S1 used as for dual bed and physical mixture.

e) Top catalyst bed was Li6/Pd/S1 and bottom bed zeolite.

f) Trace amount.

Physical Mixtures and Dual Beds of {Li6/Pd/S1 + ZSM-5} and {Li6/Pd/S1 + LZ210-12}

The initial set of experiments was conducted at 175°C. Steady-state rates of methanol elution over each catalysts studied are summarized in Table 2.5 (from here onward the term "elution" as opposed to "formation" will be used for the composite catalysts since methanol formed on a metal site can undergo secondary reaction before exiting the reactor and the concentration observed at the reactor outlet may not be a true representation of the actual rate of methanol formation). For all cases there was a significant decrease in the rate of methanol elution over a composite as compared to the rate of its formation over the Li6/Pd/S1 only. There appeared to be also a minor increase in the rate of C_1^+ hydrocarbons formation, but due to very low overall CO conversion this change was within the range of experimental error and therefore no conclusion can be drawn on the basis of this observation. Effluent analysis during CO hydrogenation over these catalysts is summarized in Tables 2.6 and 2.7. It should be noted that dimethyl ether in measurable amounts was formed only with LZ210-12, both in the dual bed and physical mixture configurations, whereas only traces of it were present when ZSM-5 was used as the acid catalyst.

Physical Mixtures of {Li1/Pd/S2 + ZSM-5}, {Li4/Pd/S2 + ZSM-5}, and {Li4/Pd/S2 + LZ210-12}

In order to increase the CO conversion, reaction temperature for these experiments was increased to 200°C while keeping all other conditions the same as before. Time-on-stream rate of methanol formation over these catalysts is schematically presented in Figures 2.3, 2.4, and 2.5. For all cases there was a decrease in the rate of methanol elution as compared to the rate of methanol formation observed in the absence of a zeolite over the respective Li/Pd/SiO$_2$ catalysts. The rate of elution of individual hydrocarbons over the composite catalysts is compared with the rate of their formation over the metal catalysts in Table 2.8 and effluent analyses are shown in Table 2.9. As can be seen, there was a general increase in the rate of ethane and some heavy hydrocarbons formation. This effect was more pronounced with a physical mixture of

Table 2.6 Effluent Analysis During CO Hydrogenation[a] in Absence and Presence of Isobutylene over the Physical Mixture and the Dual Bed[b] of Li6/Pd/S1 and ZSM-5 (10:1 wt. ratio)

| Reaction Parameters	Dual Bed		Physical Mixture	
	@ 21 hrs w/o IB	@ 28.5 hrs with IB	@ 21.6 hrs w/o IB	@ 28 hrs with IB
CO Conv[c] (%)	0.05	-	0.03	-
Rate[d] (μ mol/g/hr)	18.2	-	12.65	-
Relative Molar Conc (%)				
C_1	32.3	1.5	12.0	0.2
C_2	9.6	0.7	4.1	0.1
C_3	4.7	1.9	1.4	0.4
$n-C_4$	1.8	3.4	-	1.2
I-butane	-	37.5	-	61.4
C_5	3.0	2.6	-	3.5
C_6	4.3	1.5	-	0.9
C_7	-	0.7	-	1.4
C_8	-	49.1	-	28.5
MeOH	44.3	0.7	82.5	2.2
DME	-	-	-	-
MTBE	-	0.4	-	0.2

(a) T = 175°C, P = 7 atm, H_2/CO = 1.
(b) Top bed and bottom bed consisted of Li6/Pd/S1 and ZSM-5, respectively.
(c) CO conversion based on effluent analysis.
(d) Rate of CO conversion per gram of Li6/Pd/S1.

Table 2.7 Effluent Analysis During CO Hydrogenation[a] in Absence and Presence of Isobutylene over the Physical Mixture and Dual Bed[b] of Li6/Pd/S1 and LZ210-12 (10:1 wt ratio)

Reaction Parameters	Dual Bed		Physical Mixture	
	@ 25 hrs w/o IB	@ 29 hrs with IB	@ 22 hrs w/o IB	@ 24.8 hrs with IB
CO Conv[c] (%)	0.06	-	0.02	-
Rate[d] (μ mol/g/hr)	28.4	-	9.15	-
Relative Molar Conc (%)				
C_1	32.0	1.4	22.1	1.7
C_2	5.0	0.5	4.0	0.8
C_3	2.1	0.5	-	0.8
$n\text{-}C_4$	-	0.5	-	1.7
I-butane	-	83.1	-	53.4
C_5	-	0.9	-	1.7
C_6	-	0.7	-	0.8
C_7	-	8.6	-	-
C_8	-	2.6	-	32.1
MeOH	41.1	0.5	55.7	6.8
DME	19.9	0.2	18.2	-
MTBE	-	0.02	-	0.2

(a) T = 175°C, P = 7 atm., H_2/CO = 1.   (b) Top and bottom bed consisted of Li6/Pd/S1 and LZ210-12, respectively.
(c) CO conversion based on effluent analysis.   (d) Rate of CO conversion per gram of Li6/Pd/S1.
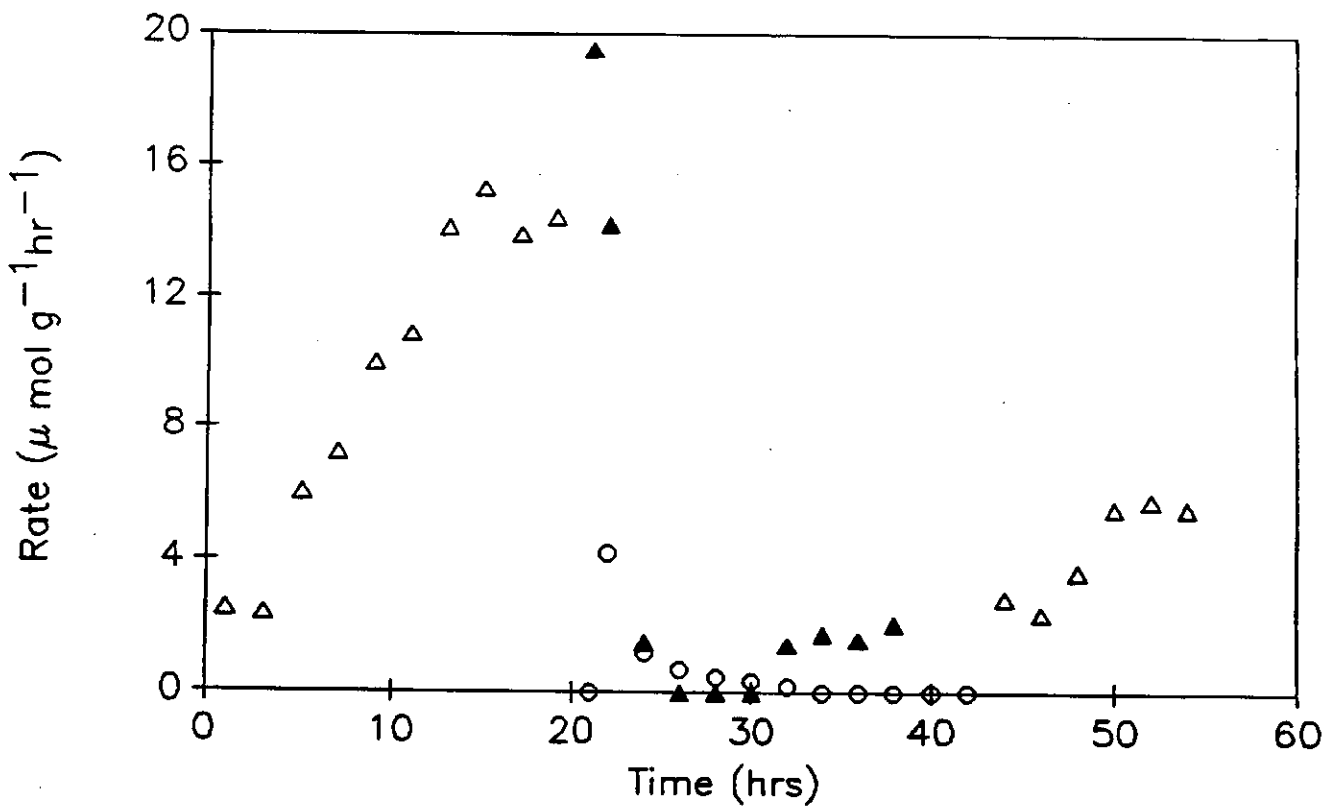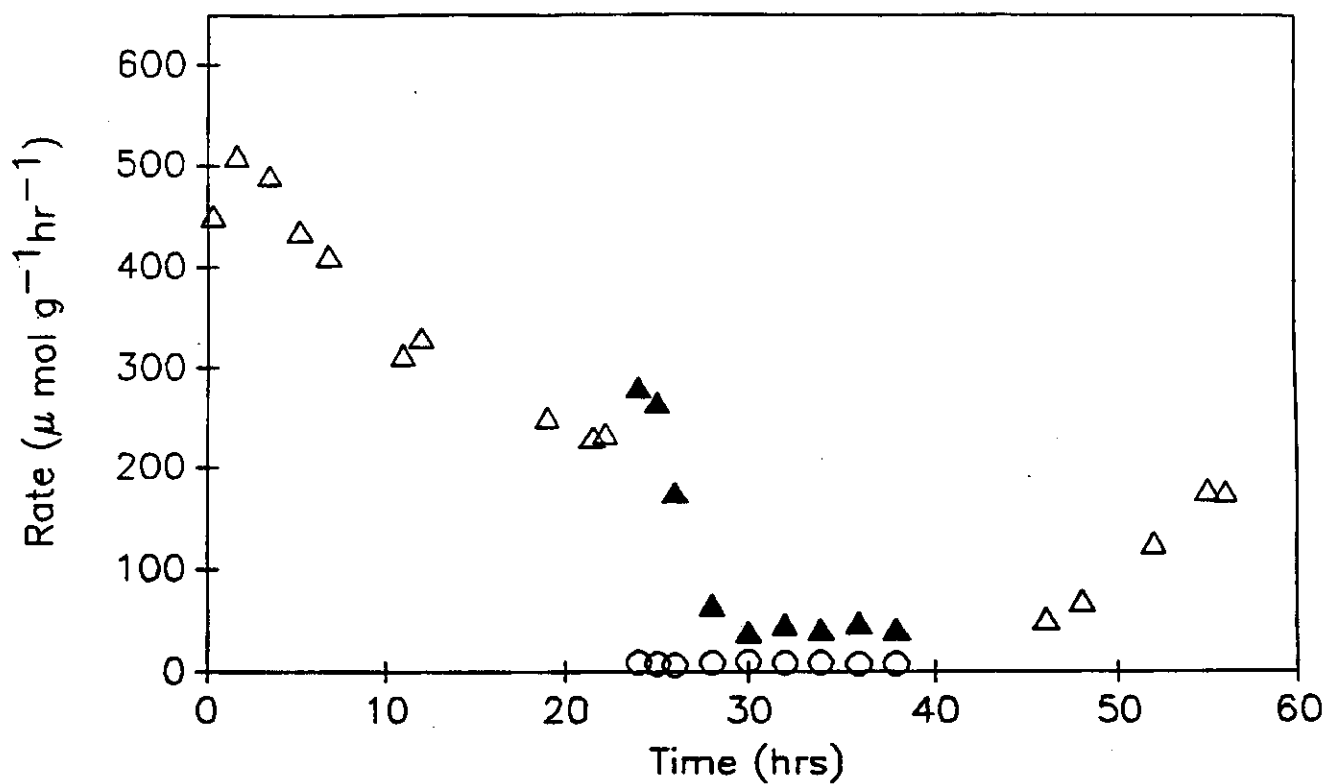
Figure 2.3   Rate of methanol and MTBE formation over Li4/Pd/S2 + ZSM-5. Open and closed triangles represent methanol rates in the absence and presence of isobutylene, respectively. Open circles represent rate of MTBE formation.
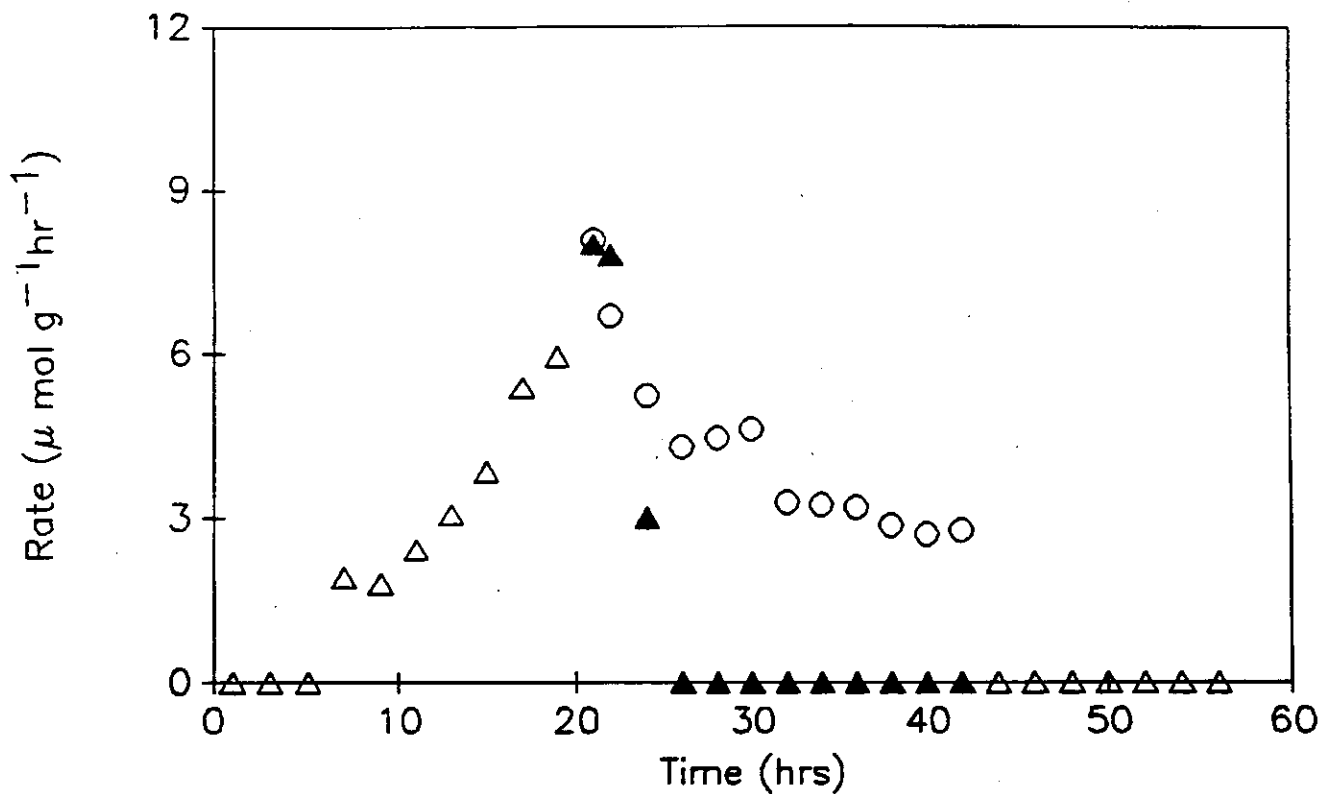
Figure 2.4   Rate of methanol and MTBE formation over Li4/Pd/S2 + LZ210-12. Open and closed triangles represent methanol rates in the absence and presence of isobutylene, respectively. Open circles represent rate of MTBE formation.

Figure 2.5   Rate of methanol and MTBE formation over Li1/Pd/S1 + ZSM-5. Open and closed triangles represent methanol rates in the absence and presence of isobutylene, respectively. Open circles represent rate of MTBE formation x 10.

Table 2.8 Rate (μ mol/g/hr) of Formation/Elution of Individual Hydrocarbons During CO Hydrogenation[a,b] over Li-Pd/SiO$_2$ and Composite Catalysts[c]

Product	Li1/Pd/S2	Li1/Pd/S2 + ZSM-5	Li4/Pd/S2	Li4/Pd/S2 + ZSM-5	Li4/Pd/S2 + LZ210-12
MeOH	550	330	49	2.8	11.5
DME	–	T[d]	–	–	–
C$_1$	7.2	6.0	2.3	2.5	3.5
C$_2$	3.1	30.4	0.6	3.1	2.7
C$_3$	1.4	12.5	0.1	0.2	0.2
C$_4$	0.6	7.6	–	–	–
C$_5$	–	4.0	0	–	–
C$_6$	–	4.3	–	–	–
Aromatics	–	13.6	–	–	–

a) T = 200°C, P = 7 atm, H$_2$/CO = 1.
b) After 12 hours of reaction.
c) Physical mixture of Li-Pd/SiO$_2$ and ZSM-5 in 10:1 wt. ratio.
d) Trace amount.

Table 2.9 Effluent Analysis During CO Hydrogenation[a] in Absence and Presence of Isobutylene over the Physical Mixture of Li-Pd/SiO$_2$ and ZSM-5 (10:1 wt. ratio)

Reaction Parameters	Li1/Pd/S2 @ 12 hrs w/o IB	+ ZSM-5 @ 22 hrs with IB[b]	Li4/Pd/S2 @ 12 hrs w/o IB	+ ZSM-5 @ 22 hrs with IB[b]	Li4/Pd/S2 @ 12 hrs w/o IB	+ LZ210-12 @ 22 hrs with IB[b]
CO conv (%)	1.4	-	0.02	-	0.06	-
Relative Molar Conc						
C$_1$	1.5	3.3	38.7	0.2	19.6	0.6
C$_2$	7.4	1.1	14.2	0.2	15.1	0.5
C$_3$	3.1	3.9	4.0	3.3	1.1	0.5
n-C$_4$	1.9	59.2	-	49.7	-	89.1
i-butane	-		-		-	
C$_5$	1.0	5.5	-	10.5	-	1.5
C$_6$	1.1	3.2	-	6.6	-	1.0
C$_7$	T[c]	2.5	-	6.2	-	0.8
C$_8$	-	8.4	-	21.3	-	4.3
MeOH	80.6	11.6	43.1	1.1	64.1	1.3
MTBE	-	0.1	-	1.0	-	0.4
Aromatics	4.2	1.1	-	-	-	-

(a) T = 200°C, P = 7 atm., H$_2$/CO = 1. (b) After two hours of isobutylene addition.
(c) trace amounts.

{Li1/Pd/S2 + ZSM-5} where, in addition to other hydrocarbons, significant amounts of aromatics were also produced.

2.3.5 Addition of Isobutylene during CO Hydrogenation

2.3.5.1   Pd/SiO₂ and Li-Pd/SiO₂

All experiments were started with syngas only. Addition of isobutylene was done only after the rate of methanol formation approached steady-state, which was typically achieved after 10-20 hours on stream.

(a) Formation of Methanol

Table 2.10 and Figure 2.2 summarize the steady-state CO hydrogenation in the presence of isobutylene over the Pd/S2, Li1/Pd/S2, and Li4/Pd/S2 catalysts. Upon addition of isobutylene, a sudden decrease in the activity for methanol formation was noted leading to a new steady-state. Later, when isobutylene addition was stopped, there was gradual increase in the activity of the catalysts.

(b) Conversion of Isobutylene

Table 2.11 summarizes the results for the conversion of isobutylene to various products during CO hydrogenation over Pd/S2, Li1/Pd/S2, and Li4/Pd/S2 catalysts. The only significant product observed during the addition of isobutylene to the syngas feed over these Pd catalysts was the hydrogenated product isobutane. Since with Pd/S2 and Li1/Pd/S2 conversion of isobutylene to isobutane was 100%, the effect of Li promotion on the hydrogenation activity was not evident. However for Li4/Pd/S2, a significant decrease in the rate of isobutylene hydrogenation was observed compared to Pd/S2 and Li1/Pd/S2. To elucidate the effect of Li promotion on isobutylene hydrogenation activity of Pd/SiO₂ under actual CO hydrogenation conditions, rates of isobutylene hydrogenation were also measured at 175°C and are presented in Table 2.12. Over Pd/S2, even at 175°C, isobutylene was completely hydrogenated to isobutane. On the other hand, the two Li-promoted catalysts clearly showed the effect of Li promotion on their hydrogenation activity of the Pd/SiO₂ catalysts. No dimer of isobutylene was formed over Pd/S2 and Li1/Pd/S2 whereas a small fraction of isobutylene was converted to its dimer on Li4/Pd/S2. Dimer formation gradually decreased and reached a steady-state rate after 10 hours of isobutylene addition.

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Table 2.10 Rate of Methanol Formation[a] over Li-Promoted Pd/SiO_2 in the Absence and Presence of Isobutylene

Catalyst	Rate of MeOH (μ mol/g/h)			
	@ 12 hrs. w/o IB	@ 22 hrs with IB for 2 hrs	@ 30 hrs with IB for 10 hrs	@ 50 hrs 10 hrs after stopping IB
Pd/S2	275	200	195	218
Li1/Pd/S2	550	330[b]	325[c]	395
Li4/Pd/S2	49	41	32	45

(a) T = 200°C, P = 7 atm, H_2/CO = 1.
(b) 2 hrs after the addition of IB started. Total reaction time 28 hrs.
(c) 10 hrs after addition of IB started. Total reaction time 36 hrs.

Table 2.11 Selectivity and Conversion of Isobutylene Added During CO Hydrogenation[a,b] over Li-Pd/SiO$_2$ and Composite Catalysts. After 2 and 22 hours of Starting IB Addition.

Catalyst	IB-ene Conv%		IB-ane Select%		C$_3$-C$_7$ Select%		C$_8$ Select%	
	2 hrs	22 hrs	2 hrs	22 hrs	2 hrs	22 hrs	2 hrs	22 hrs
Pd/S2	100	100	100	100	0	0	0	0
Li1/Pd/S2	100	100	100	100	0	0	0	0
Li4/Pd/S2	7.7	7.6	93.2	97.8	0	0	6.7	2.0
Li1/Pd/S2 + ZSM-5[c]	100	100[d]	34.5	75.7[d]	57.5	9.3[d]	7.9	14.9[d]
Li4/Pd/S2 +ZSM-5[c]	75.6	56.1	4.8	6.3	60.2	34.4	34.2	58.9
Li4/Pd/S2+ LZ210-12[c]	51.5	12.0	17.7	44.4	68.4	0	13.3	55.6

(a) T = 200°C, P = 7 atm., H$_2$/CO = 1.
(b) 20 hours total reaction time before IB addition started.
(c) Physical mixture of metal catalysts and zeolite in 10:1 ratio.
(d) 16 hours after the addition of IB started. 36 hours total reaction time.

Table 2.12 Rate of Isobutylene Hydrogenation[a,b] during CO
Hydrogenation over Li-promoted Pd/SiO$_2$

Catalyst	IB Conversion (%)	Rate (μmol/g.hr)
Pd/S2	100	> 1070
Li1/Pd/S2	85	908
Li4/Pd/S2	4.6	49

(a)   T = 175°C, P = 7 atm.
        H$_2$/CO/He/IB flow = 15/15/3.6/0.4 cc/min
(b)   2 hours after addition of isobutylene started.

(c) Formation of MTBE

In spite of lowered hydrogenation activity over Li-promoted Pd/SiO$_2$ catalysts, no interception of methanol intermediate by the isobutylene, resulting in MTBE formation, was observed.

2.3.5.2   Li-Pd/SiO$_2$ + Zeolite Composite Catalysts

Physical Mixtures and Dual Beds of {Li6/Pd/S1 + ZSM-5} and {Li6/Pd/S1 + LZ210-12}

The steady-state kinetic results for MTBE synthesis during CO hydrogenation at 175°C, over each catalyst studied are presented in Tables 2.6 and 2.7 and Figures 2.6, 2.7, and 2.8. With the addition of isobutylene, MTBE was formed over all the catalyst systems. However, as a result of catalyst deactivation there was a significant decrease with time in its rate of formation. With the dual bed of {Li6/Pd/S1 and LZ210-12}, MTBE in measurable amounts was formed only after 1.5 hours of isobutylene addition after which only traces of it were seen due to catalyst deactivation for MTBE synthesis. ZSM-5 showed relatively higher resistance to deactivation than LZ210-12 HY zeolite.

Physical mixtures of {Li1/Pd/S2 + ZSM-5}, {Li4/Pd/S2 + ZSM-5} and {Li4/Pd/S2 + LZ210-12}

(a) Formation of methanol

Table 2.13 and Figures 2.3, 2.4, and 2.5 show the rates of MeOH elution and MTBE formation as a function of time over the three catalyst systems studied. For all the catalysts, there was a slight increase in the rate of methanol formation over its steady-state value upon addition of isobutylene. This was observed only for the initial few hours of addition of isobutylene. After this, the rate of methanol started to decrease rapidly. When isobutylene addition was stopped, the rate of methanol formation gradually started to increase, but never attained its pre-isobutylene addition steady-state value.

(b) Conversion of isobutylene

The overall conversion and the selectivity of the added isobutylene to various products over each catalyst are summarized in Table 2.11. Time-on-stream behavior over Li4/Pd/S2 + ZSM-5 and Li4/Pd/S2 + LZ210-12 in terms of rate of formation of various products before and after isobutylene addition is schematically presented in Figure 2.9
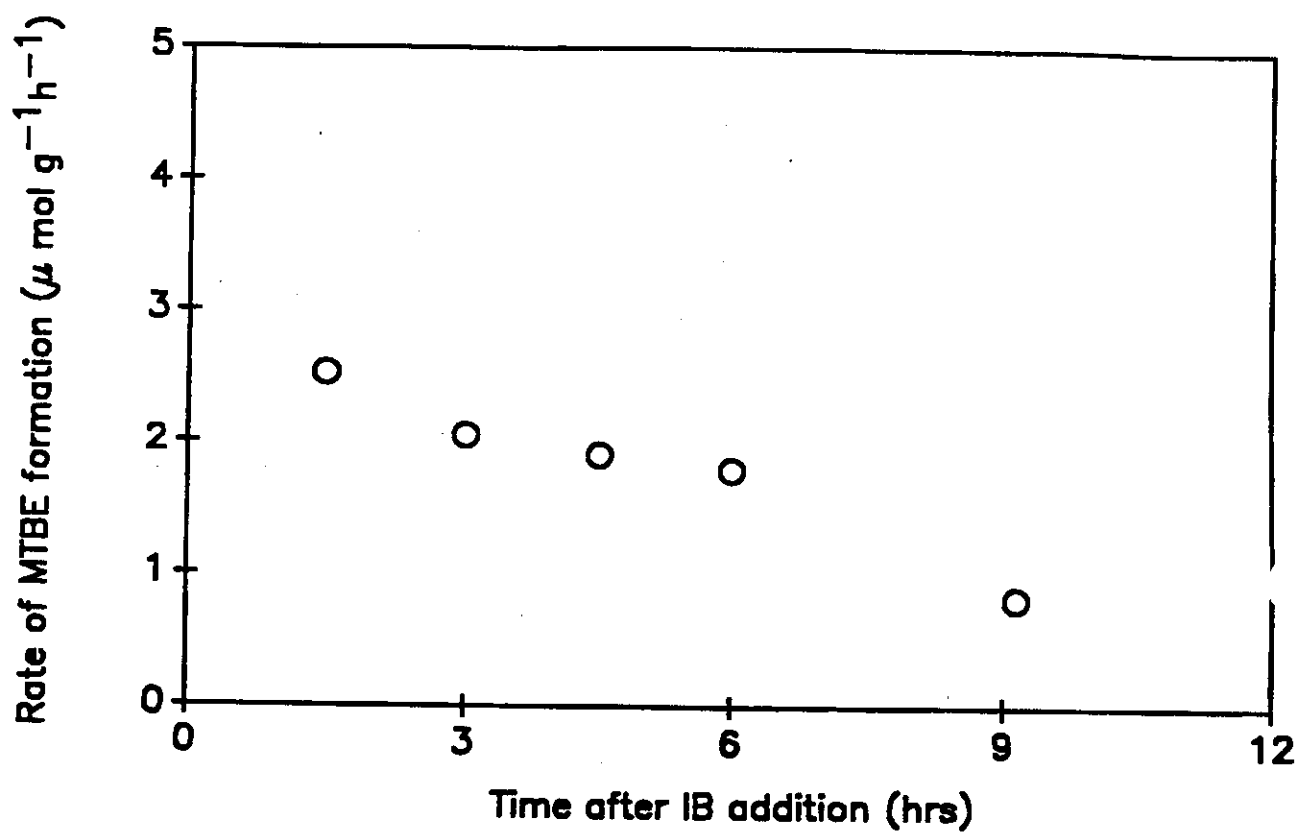
Figure 2.6   Rate of MTBE formation over Li6/Pd/S1 + ZSM-5 (physical mixture) using a syngas + isobutylene feed.
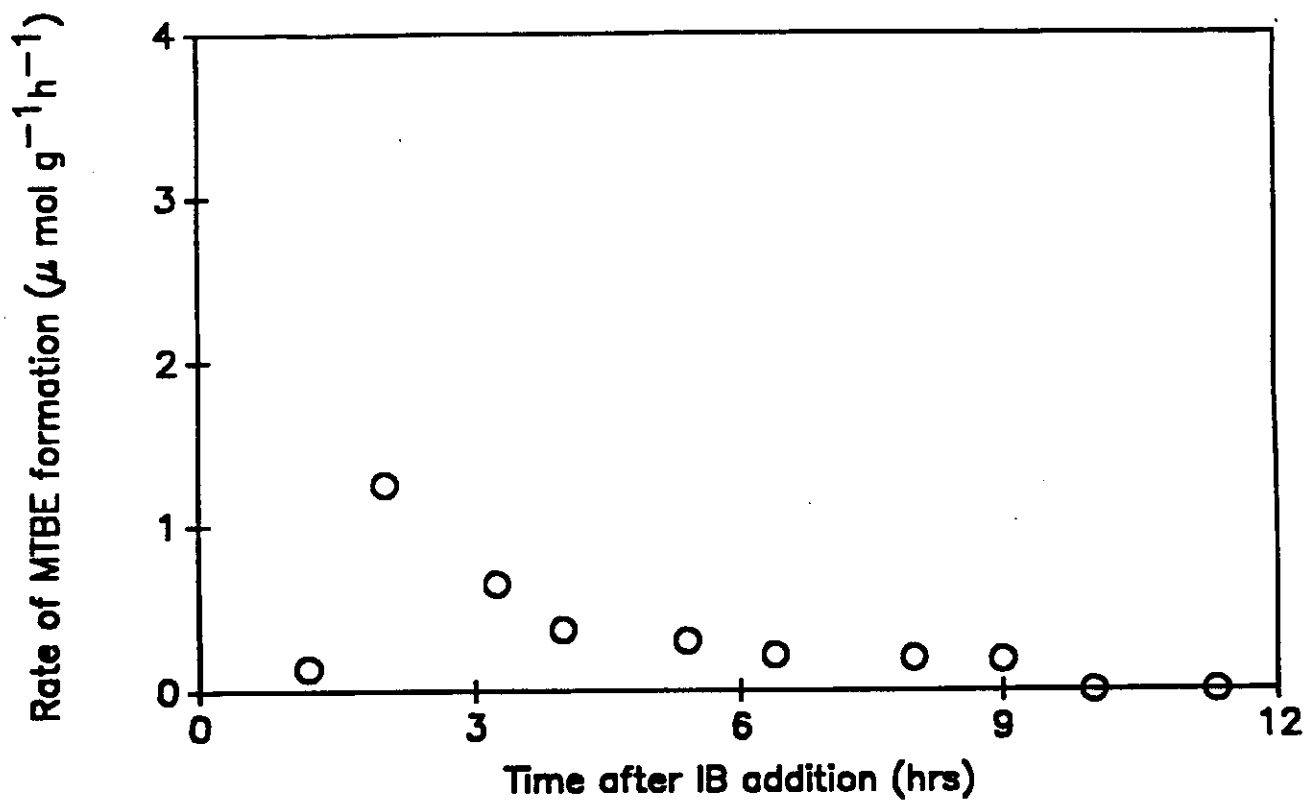
Figure 2.7   Rate of MTBE formation over Li6/Pd/S1   + LZ210-12 (physical
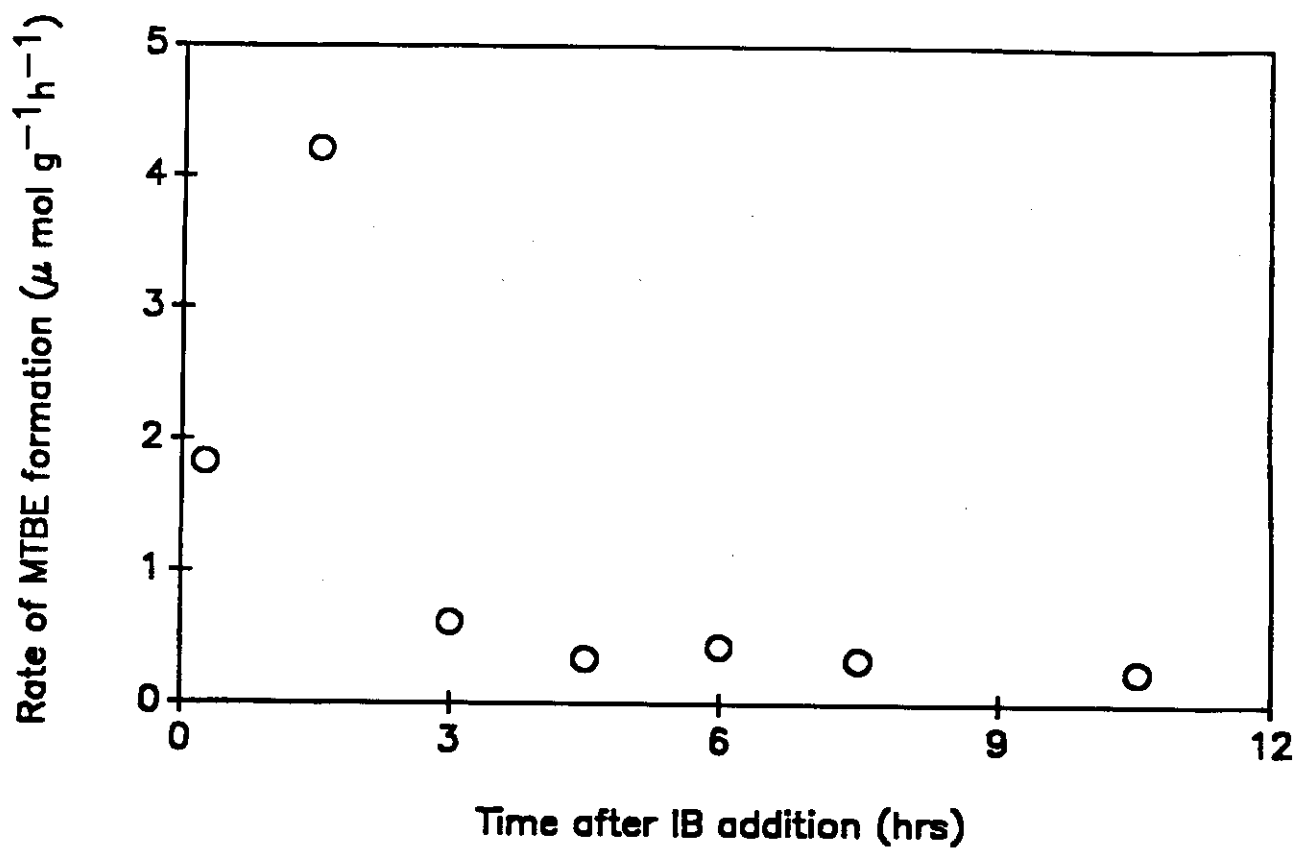mixture)   using a syngas + isobutylene   feed.

Figure 2.8   Rate of MTBE formation over Li6/Pd/S1 + ZSM-5 (dual bed) using a syngas + isobutylene feed.

Table 2.13 Rate of Methanol Elution and MTBE Formation During CO Hydrogenation[a] with the Addition of Isobutylene over the Physical Mixture of Li-Pd/SiO$_2$ and a Zeolite

Catalyst	Rate of MeOH (μ mol/g/h)					Rate of MTBE (μ mol/g/h)		
	@ 12 hrs w/o IB	@ 22 hrs with IB for 2 hrs	@ 30 hrs with IB for 10 hrs	@ 42 hrs with IB for 22 hrs	@ 50 hrs 10 hrs after stopping IB	@ 22 hrs with IB for 2 hrs	@ 30 hrs with IB for 10 hrs	@ 42 hrs with IB for 22 hrs
Li1/Pd/S2 + ZSM-5	330	104[b]	48[c]	*	175	0.9[b]	1.0[c]	*
Li4/Pd/S2 + ZSM-5	2.8	7.0	T[d]	T[d]	T[d]	6.7	4.6	2.8
Li4/Pd/S2 + LZ210-12	11.5	12.3	T[d]	2.1	5.6	4.2	0.4	0

(a) T = 200°C, P = 7 atm., H$_2$/CO = 1.
(b) Reaction time 28 hrs.
(c) Reaction time 36 hrs.
(d) Trace amounts.
* Data not available.