

Dehydrogenation Catalyst for Production of MtBE

by

Josephine M. Hill, Randy D. Cortright,
Dale F. Rudd, and James A. Dumesic
University of Wisconsin, Madison
Madison, WI 53706

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Project Officer

Paul Randall
Sustainable Technology Division
National Risk Management Research Laboratory
Cincinnati, OH 45268

NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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Foreword

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E. Timothy Oppelt, Director
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Abstract

The objectives of this project were to better understand the effect of different catalyst preparation parameters, the effect of different catalyst treatment parameters, and the mechanism of deactivation. Accordingly, catalysts were made using various preparation methods and with a range of platinum (Pt) and tin (Sn) contents. Catalysts were also tested under a variety of reaction conditions. Catalysts were characterized using kinetic studies, chemisorption, transmission electron microscopy and temperature programmed oxidation. The results indicate that **Pt/L-zeolite** catalysts are not selective without Sn. Sn reduces the size of the Pt ensembles thus inhibiting the hydrogenolysis, isomerization and coking reactions. At high Sn loadings, or after long periods at high temperature (-873 K) the surface Pt ensembles become enriched with Sn and metal sintering occurs; thus, the number of exposed Pt atoms and subsequently the activity, are decreased. It is difficult to reverse the results of these processes. Reacting isobutane at a lower temperature (-798 K) in the absence of feed hydrogen reduces the Sn enrichment and the metal sintering. At these conditions the main mechanism of deactivation is coking, a process which is relatively easy to reverse with flowing oxygen at a moderate temperature.

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Acronyms and Abbreviations

LaB₆	Lanthanum Boride
MtBE	Methyl tert-butyl ether
QA	Quality assurance
SCCM	Standard cubic centimeters per minute
TEM	Transmission electron microscopy
TOF	Turnover frequency
TPO	Temperature programmed oxidation
WHSV	Weight hourly space velocity

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Chapter 1 Introduction

Industrial catalytic reaction pathways for the production of methyl *tert*-butyl ether (**MtBE**), an important motor fuel oxygenate, typically involve 1) the production of synthesis gas from hydrocarbon feedstocks, 2) the conversion of synthesis gas into methanol, 3) the production of isobutene by the cracking, alkylation, isomerization and dehydrogenation of light hydrocarbons, and 4) the conversion of methanol and isobutene into **MtBE** (see Figure 1-1). The weak link in this sequence of steps is the production of the isobutene, a presently inefficient reaction that requires a chromium-based catalyst that must be regenerated frequently (approximately every half hour). Chromium is a heavy metal that is known to be toxic. Substantial advances in pollution prevention could be achieved by the discovery of a clean and efficient catalytic technology for the production of isobutene. The annual productions of **MtBE** and isobutene were 17.62 and 3.23 billion lbs in 1995[1].

Our research group has recently invented a new class of dehydrogenation catalysts that is capable of achieving these pollution prevention goals in our laboratory. This new catalyst, the UW Dehydrogenation Catalyst, is highly selective and extremely active for the dehydrogenation of isobutane to isobutene, with the formation of virtually no pollutant by-products, such as methane, ethane, propane, n-butane and carbon on the catalyst. Specifically, the catalyst achieved a greater than 99% selectivity to isobutene at an average conversion of 55% over a 10 day period. This is better than that achieved by the commercial catalyst used in UOP's Oleflex process - 92% selectivity and 50% conversion[2]. Furthermore, this non-chromium catalyst requires only infrequent regeneration. A patent will be issued for this new catalytic technology through the Wisconsin Alumni Research Foundation in the spring of 1998.

The favorable catalytic properties of the UW Dehydrogenation Catalyst are a result of a unique combination of metals, modifier, and support. Each of the four components of the **Pt/Sn/K-L**-zeolite dehydrogenation catalyst is important in allowing this system to be highly selective and stable for isobutane dehydrogenation. Platinum (Pt) catalyzes the removal of hydrogen from isobutane to produce isobutene. The addition of tin (Sn) reduces the size of the surface platinum ensembles and suppresses isomerization and hydrogenolysis reactions. The presence of potassium (K) neutralizes the support, which inhibits the acid-catalyzed isomerization and coking reactions; moreover, potassium suppresses the competing isomerization and hydrogenolysis reactions, and enhances the dehydrogenation rate. The L-zeolite micropore structure supports small **Pt/Sn** particles and perhaps also stabilizes adsorbed isobutyl species.

While it is known that each of the four components of the UW Dehydrogenation Catalyst are necessary, it is not known how the various catalyst preparation and treatment parameters influence the reactivity of the **Pt/Sn/K** ensembles in the L-zeolite. For example, it is known that the addition of both tin and potassium are necessary to produce a selective and active dehydrogenation catalyst, but the optimum amounts of these components have not yet been established. In addition, different process conditions may require different catalyst formulations. While the UW Dehydrogenation Catalyst exhibits good stability under reaction conditions, it still deactivates. It is necessary, therefore, to also investigate the mechanism for deactivation.

The objectives of this project were to better understand the effect of different catalyst preparation parameters, the effect of different catalyst treatment parameters, and the mechanism of deactivation. Accordingly, catalysts were made using various preparation methods and with a range of Pt and Sn contents. Catalysts were also tested with a variety of reaction conditions. The parameters by which the performance of the catalyst was measured were isobutane activity, dehydrogenation selectivity and stability. Chemisorption measurements and transmission electron microscopy (**TEM**) analysis,

as well as *kinetic* studies, were used to characterize the catalysts. Temperature programmed oxidation (TPO) was used to determine the extent of carbon deposition on the catalysts after reaction.

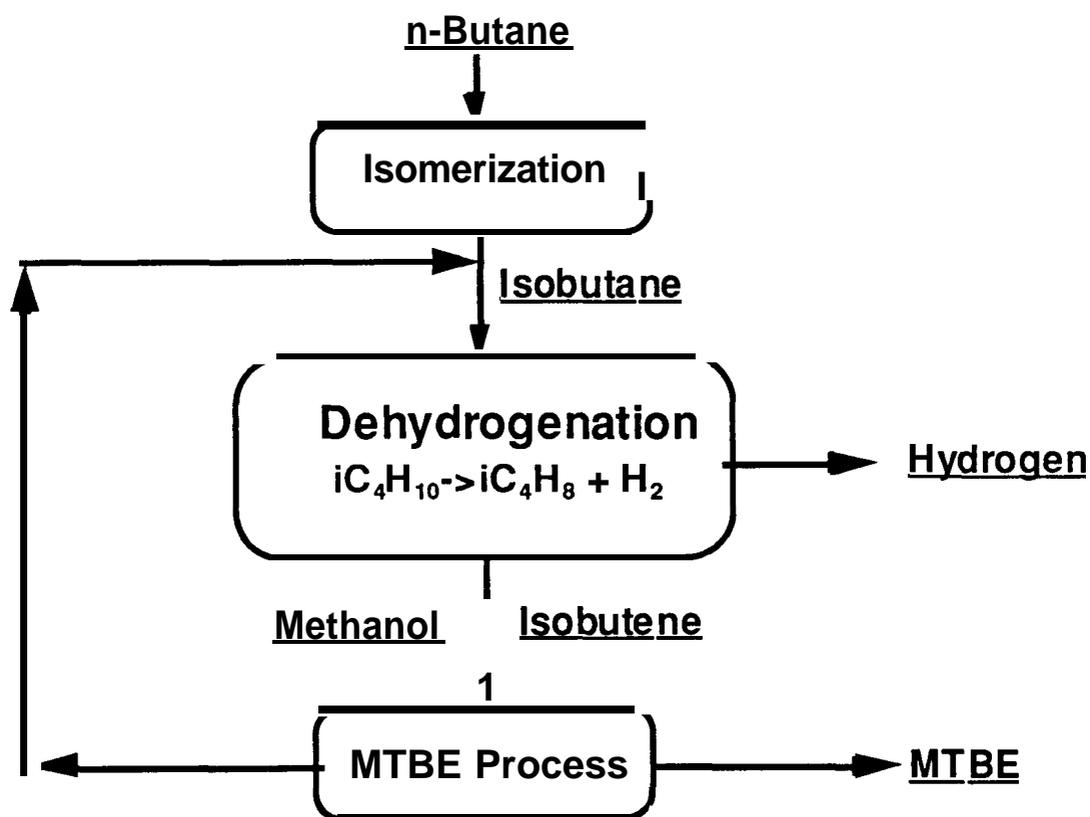


Figure 1-1. The production of MtBE from methanol and isobutene.

Chapter 2 Conclusions

The metal particles of the **Pt/Sn/K-L** UW Dehydrogenation Catalyst are contained within the pores of the L-zeolite. This catalyst is very selective for isobutane dehydrogenation because the Sn reduces the size of the Pt ensembles, thus hindering hydrogenolysis, isomerization and coking reactions. Potassium also reduces the size of the Pt ensembles and neutralizes the support, inhibiting the acid catalyzed isomerization and coking reactions.

In preparation of the catalyst, Sn must be introduced prior to Pt and no acidity should be introduced by the metal precursors. A **Pt/Sn** ratio of 1:2.5 and a Pt content of 0.5 wt% were found to be optimal in terms of activity, selectivity and stability. **Pt/Sn** ratios lower than 1:2.5 (i.e. the addition of more Sn) had better stability but did not significantly improve the selectivity and did decrease the activity. With less Sn the catalyst is not very selective.

In the pretreatment of the catalyst, a slow heating rate of less than 2 **K/min** should be used to obtain higher activities. Calcination of the catalyst during pretreatment results in significant particle sintering.

A feed of isobutane only (i.e. in the absence of hydrogen) can be used for the reaction at 798 K but the stability of the catalyst is related to its selectivity. For example, the unmodified **Pt/L** catalyst is not very selective and its activity decreases to essentially zero within minutes on stream in isobutane only. Conversely, the highly selective 1:2.5 **Pt/Sn/L** catalyst maintains its activity in isobutane for at least 20 h on stream.

At 873 K and in the presence of hydrogen, the **Pt/Sn/K-L** catalysts deactivate by coking, enrichment of the surface with tin, and/or sintering of the metal particles. At 798 K and in the absence of hydrogen, the major mode of deactivation for the **Pt/Sn/K-L** catalyst is coking. The addition of Sn and K to supported Pt catalysts improves the resistance of these catalysts to coking. Both additives decrease the size of the Pt surface ensembles, thereby suppressing the hydrogenolysis, isomerization and coking reactions. The presence of Sn may also help to transport coke precursors from the active sites to the support.

Chapter 3 Recommendations

Based on the deactivation studies, the UW catalyst is most suited for use at temperatures of 798 K and below. Low temperature applications for this catalyst may include the dehydrogenation of higher **paraffins**. This application would be limited by the size and shape of paraffins that can fit into the pores of the **Pt/Sn/K-L-zeolite** catalyst. Another application, in which Sn would play an active role in the chemistry as opposed to having only a geometric effect (i.e. reducing the size of the Pt ensembles), is the hydrogenation of saturated aldehydes to saturated alcohols.

The role of potassium should be further investigated. It may be possible to take advantage of potassium to reduce the carbon deposition on a working catalyst. With less carbon deposition the catalyst will have to be regenerated less frequently.

Chapter 4 Experimental Procedures

Catalyst Preparation

The standard procedure for preparing a **Pt/Sn/K-L-zeolite** catalyst is as follows. The K-L-zeolite (**Tosoh**) was calcined in dry air at 873 K for 20 h, dried in flowing He at 673 K for 2 h, and transferred to a dry nitrogen atmosphere. Tin was then added to the L-zeolite using incipient wetting impregnation with a solution of **tributyltin acetate** (Aldrich) in methanol. The catalyst was then dried in air at 390 K for 2 h and treated at 573 K in a flowing mixture of 25 mol-% oxygen in helium for 1 h. The **Sn/L-zeolite** was then transferred to a dry nitrogen atmosphere and the platinum added using an aqueous solution of tetraammineplatinum nitrate (Aldrich). After treatment at 533 K in a flowing mixture of 25 mol-% oxygen in helium for 1 h, the **Pt/Sn/L** catalyst was reduced in hydrogen at 873 K for 6 h (temperature ramp of 2 K/min), transferred to a glass vial in a dry nitrogen atmosphere and stored for further use. The concentrations of the Sn and Pt solutions were adjusted to obtain the desired weight percents of each metal. The absolute amount of Pt was varied between 0.1 and 0.5 wt%, while the **Pt/Sn** ratio was varied between 1:0 and 1:14.

Variations in this procedure have been used to determine the effect of certain preparation variables. Each of the following variations was done independently: 1. the Sn precursor was changed from **tributyltin acetate** in methanol to an aqueous solution of stannic chloride, and 2. the order of impregnation of the metals was reversed (i.e. **Pt** before **Sn**).

To determine the effect of the support on the deactivation of the catalyst, silica-supported platinum catalysts were prepared by ion-exchange, using the method of Benesi *et al.*[3]. After ion-exchange, the **Pt/silica** catalysts were filtered, washed with deionized water and dried overnight in air at 390 K. A portion of the catalyst was treated in flowing oxygen at 573 K for 2 h, followed by reduction in flowing hydrogen at 673 K for 2 h. Tin was added to the remaining uncalcined **Pt/silica** catalyst by evaporative impregnation of a **tributyltinacetate/pentane** solution, after which the catalyst was dried overnight in air at 390 K. Potassium was added to some of the **Pt/Sn/silica** catalyst by incipient wetness impregnation with an aqueous solution of KOH, and the catalyst was then dried in air at 390 K. The **Pt/Sn/silica** and **Pt/Sn/K/silica** catalysts were calcined with flowing oxygen at 673 K for 2 h **and** subsequently reduced in flowing hydrogen at 773 K for 7 h.

Kinetics/TPO apparatus

The kinetics and **TPO** apparatus is constructed of stainless-steel, with an attached Gas Chromatograph (GC) and Residual Gas Analyzer (RGA). Figure 4-1 is a schematic of the kinetic apparatus. The gas out can be flowed to the RGA or directly vented if the mass spectrometer is not used. The inlet gases are flowed through mass flow controllers (Hastings). Isobutane (Liquid Carbonic, 99.5%) is passed over a bed of reduced nickel on alumina at 333 K to remove sulfur impurities. Hydrogen (Liquid Carbonic) is flowed through a Deoxo unit (Engelhard) and a bed of molecular sieves (13X) at 77 K. Helium (Liquid Carbonic) is flowed through Cu turnings at 423 K and a bed of molecular sieves (13X) at 77 K. The reactor inlet and outlet gases are analyzed by an HP-5890 GC with a TCD detector and a 30 ft, 23% AT Chromosorb PAW column at 333 K. The RGA is a Quad 250B Residual Gas Analyzer with an electron multiplier detector. The RGA is usually operated at pressures of 10^3 Pa with an electron energy of 70 volts, and an emission current of 150 μ amps. Calibration of the Mass 44 signal is done using a gas mixture of 5% CO, in He (AGA).

Figure 4-2 is a schematic of the reactors used. Both reactors are made from quartz. The U-tube has a lower surface area and thus, minimizes gas phase reactions. The fritted reactor has a larger catalyst capacity.

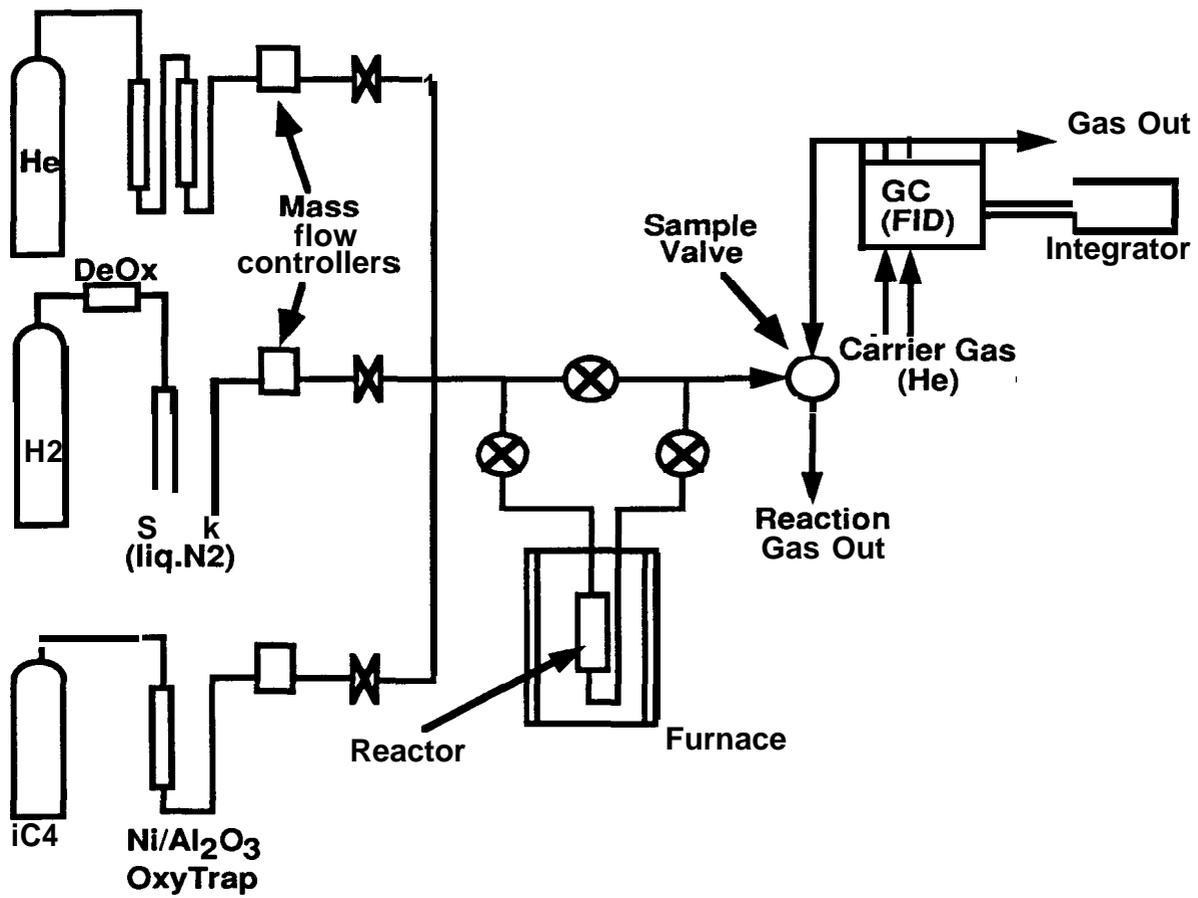


Figure 4-1. Schematic of kinetics apparatus.

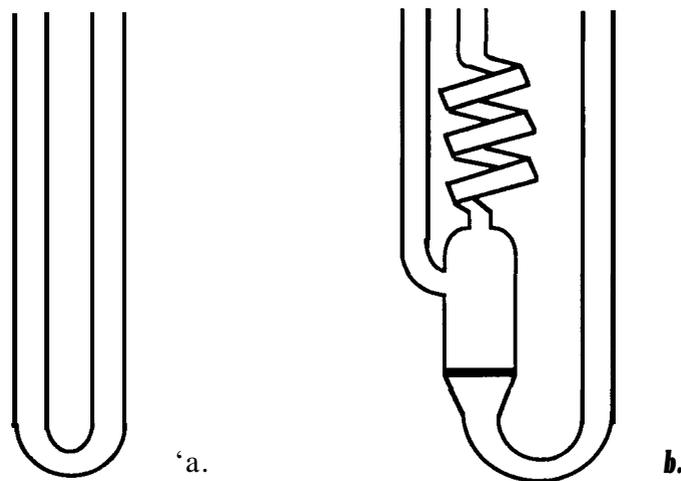


Figure 4-2. Schematic of reactors: a. U-tube, b. fritted reactor.

Chemisorption apparatus

The vacuum apparatus used for chemisorption measurements is constructed from glass, with a stainless steel dosing section and a Baratron capacitance manometer. Carbon monoxide (Liquid Carbonic) is purified by passage through a heated quartz wool trap at 573 K to remove metal carbonyl compounds, and then dried by passage through molecular sieves at 77 K. Isobutane (Liquid Carbonic) is purified with three freeze/pump/thaw cycles immediately before starting adsorption measurements. The gas uptake amounts ($\mu\text{mol/g}$) are calculated by extrapolating the plateau of the isotherm to zero pressure.

Transmission Electron Microscopy

Transmission electron microscopic studies were conducted using a high resolution microscope (Phillips CM 200 equipped with a LaB₆ filament) at a point resolution of 0.2 nm and a magnification range of 25x to 1,600,000x. A spot size of 120 nm was used to minimize damage to the specimens. Samples were prepared by grinding the catalyst in a mortar and pestle with filtered water (18 Mohm deionised water). A drop of the solution was then placed on specially prepared copper grids (1000 mesh, Ted Pella Inc.). Before adding the drop of solution, the grids were dipped in an adhesive solution made by dissolving the adhesive from double sided tape in naphtha. The sticky grid with the drop of catalyst solution was then placed over a hot plate to evaporate the water. The resulting grid contains many particles which overhang the edge of the grid bars and are transparent to the electron beam.

Description of Measurement Parameters

The following list is a definition of the terms used to describe the experimental conditions and results.

$$\text{Pt:Sn ratio: } \frac{w_{\text{Pt}}}{195.08} * \frac{118.69}{w_{\text{Sn}}}$$

$$\text{Weight hourly space velocity (WHSV): } \frac{F^i * x_{iC_4H_{10}}}{w * \rho_{iC_4H_{10}}}$$

$$\text{Isobutane conversion: } \left(1 - \frac{F^o * x_{iC_4H_{10}}}{F^i * x_{iC_4H_{10}}} \right) * 100\%$$

$$\text{Turnover frequency (TOF Total Pt basis): } \frac{K + kGC_{iC_4H_{10}}}{1} * \frac{F^o}{22.4 * 10^3} * \frac{1}{60} * \frac{1}{M} * \frac{195.08}{w_{\text{Pt}}}$$

$$\text{Turnover frequency (TOF per site basis): } \frac{K + kGC_{iC_4H_{10}}}{1} * \frac{F^o}{22.4 * 10^3} * \frac{1}{60} * \frac{1}{M} * \frac{1}{m_{\text{sites}}}$$

$$\text{Isobutene selectivity: } \left(\frac{x_{iC_4H_6}}{\frac{1}{4} \sum_i x_i n_i} \right) * 100\%$$

where:

F^i	inlet flow rate (sccm)
F^o	outlet flow rate (sccm)
$GC_{C_4H_{10}}$	GC area of isobutane peak
k, K	conversion factor for the GC
M	mass of catalyst (g)
m_{sites}	moles of sites per gram of catalyst (mol/g) (as defined by CO adsorption)
n_i	number of carbon atoms in the product compound
w_{Pt}	mass of Pt per gram of catalyst (g/g)
w_{Sn}	mass of Sn per gram of catalyst (g/g)
x_i	mole fraction of products (methane, ethane, propane, propene, isobutene, butenes)
$x_{iC_4H_8}$	mole fraction of isobutene
$x_{iC_4H_{10}}$	mole fraction of isobutane

Quality Assurance

Quality assurance (QA) objectives have been outlined for this project in order to ensure that comparisons can be made between kinetic runs. These quality assurance objectives have been met and thus, there exists a high degree of confidence in the conclusions drawn from this study.

Calibrations of the equipment (e.g. mass flow controllers, GC and Mettler balance) have been done on a regular basis. Figures 4-3 and 4-4 show representative GC calibrations for the C1-C4 hydrocarbons.

As an additional verification of the performance of the equipment, carbon balances are calculated and checked for each kinetic run. In all cases, the carbon balance was $100 \pm 2.5\%$. The carbon balance is given by

$$\text{Carbon balance} = \frac{\text{Moles of Carbon to Reactor}}{\text{Moles of Carbon out of Reactor}} * 100\%$$

Duplicate kinetic runs have been done. Figure 4-5 is representative of the results from duplicate kinetic runs.

This has been an exploratory project designed to investigate the effects of a number of process and catalyst preparation variables on the performance of the UW Dehydrogenation Catalyst system. As such, there should be no legal or regulatory ramifications if the QA objectives were not met.

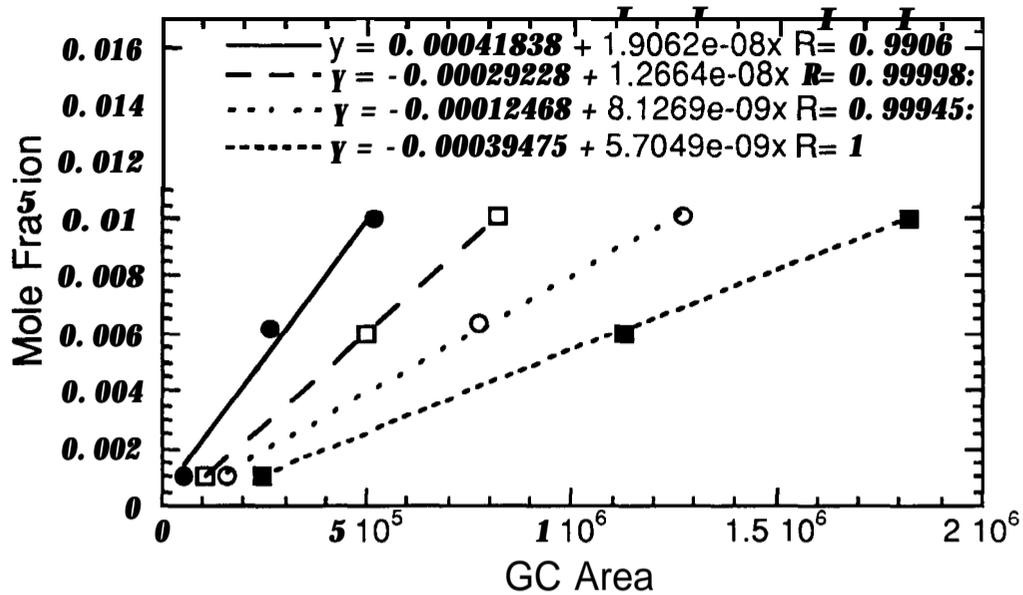


Figure 4 - 3. GC calibration curves for ●, methane, ◻, ethane, ○, propane and ■, n-butane.

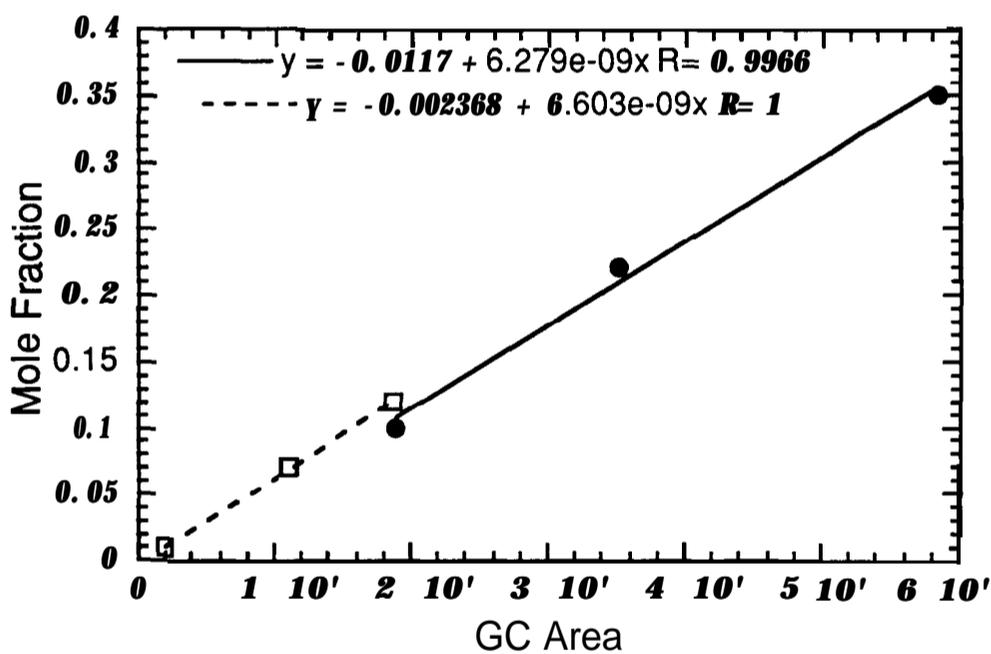


Figure 4 - 4. GC calibration curves for ●, isobutane and ◻, isobutene.

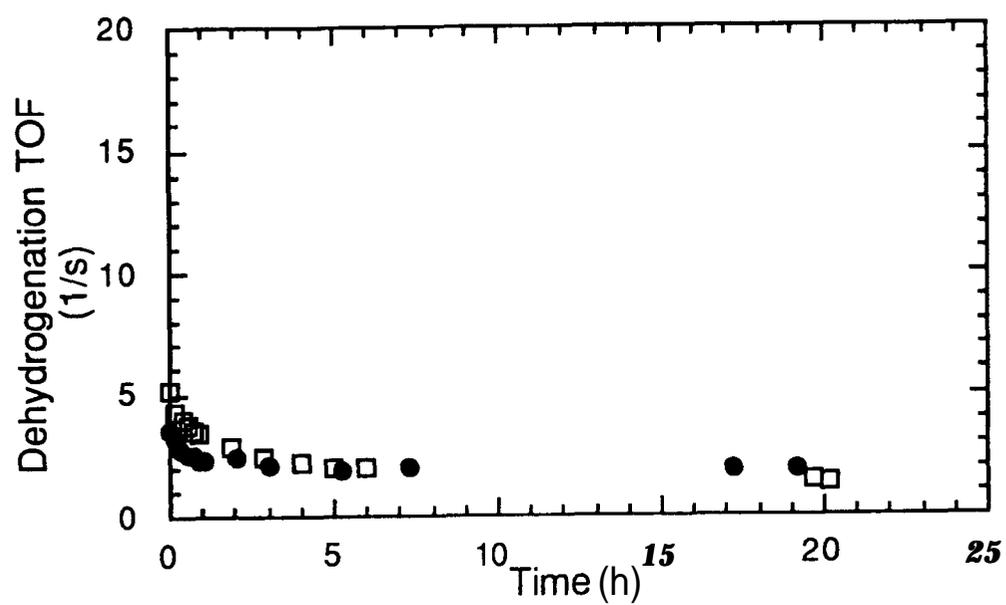


Figure 4 - 5. Duplicate kinetic runs for isobutane dehydrogenation at 873 K, 1 atm, and $H_2/i-C_4H_{10}$ ratio of 2 over 1:7 Pt/Sn/L-zeolite catalyst (0.1 wt% Pt, 0.42 wt% Sn).

Chapter 5 Results and Discussion

Catalyst Preparation

It has been suggested that the favorable properties of Pt/Sn/L catalysts stem partially from the interaction between the metals and the pores of the zeolite[4, 5]. Thus, one of the first tasks on this project was to determine if indeed the metals were within the pores of the zeolite. The TEM was used to examine a 1:2.5 Pt/Sn/L catalyst. Very few particles were visible on the external surface of the catalyst. It is then assumed that because the catalyst is active but particles are not visible, that the metals must be within the pores. Subsequently, each catalyst was examined in the TEM following preparation as a quality control check. If significant numbers of particles were visible then the catalyst would be rejected and a fresh sample prepared.

The activity profiles (turnover frequencies (TOF) versus time plots) are obtained using approximately 5 mg of catalyst in a U-tube reactor with an isobutane conversion of less than 15% of the equilibrium value for the dehydrogenation reaction. The TOF is on a total Pt basis unless otherwise stated. Conversion and selectivity profiles are obtained using between 0.2 and 1 g of catalyst in a U-tube or fritted reactor with an initial isobutane conversion close to or at the equilibrium value for the dehydrogenation reaction.

The effect of tin precursor and impregnation sequence is shown in Figures 5- 1 and 5-2. The WHSV was 13.2 h^{-1} for these experiments and the catalysts contained 0.5 wt% Pt. When the catalyst was prepared using a stannic chloride precursor rather than tributyltinacetate, both the conversion and selectivity decrease (see Figures 5-1 and 5-2). The chlorine from the SnCl_4 solution introduces acidity to the catalyst, which promotes the isomerization and hydrogenolysis reactions, thus lowering the selectivity of the catalyst. One of the features of K-L-zeolite is that it is a neutral support.

The effect of impregnation sequence is also shown in Figures 5-1 and 5-2. When Sn is impregnated **first**, the activity of the catalyst is significantly higher than when Pt is impregnated first. The latter catalyst has better selectivity for the first 5 hours on stream, after which time the selectivities are similar. It is likely that when Sn is impregnated second, it blocks a large fraction of the Pt sites and the Pt that is exposed is in very small ensembles. Small Pt ensembles are desirable because the dehydrogenation reaction is structure insensitive while the undesired side reactions, isomerization and hydrogenolysis, are structure sensitive. Hydrogenolysis, isomerization and coking reactions require several adjacent Pt surface sites[6, 7]. Thus, the dehydrogenation reaction will be favored on small Pt ensembles.

The effects of Pt and Sn content on activity were studied by varying both the absolute amount of Pt and the Pt:Sn ratio. The results are shown in Figures 5-3 to 5-6. At low Pt:Sn ratios the activity decreases significantly. The catalyst activity is stable, although low, with a sufficient amount of Sn. A Pt content of 0.5 wt% appears to be optimal for the catalyst in terms of activity.

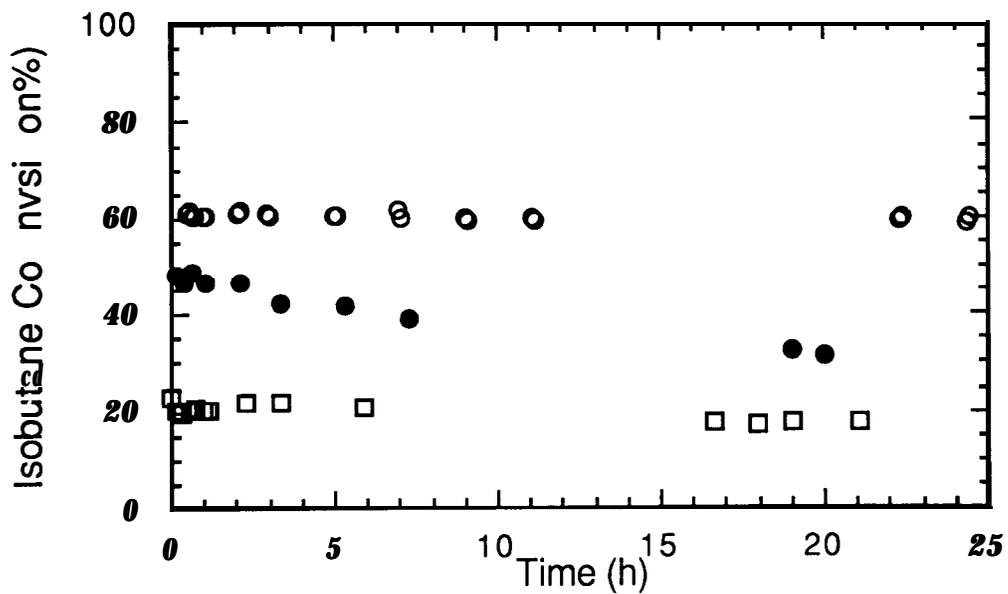


Figure 5 - 1. Effects of preparation methods of 1:2 Pt/Sn/L zeolite on isobutane conversion at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2; sequential impregnation of: ○, Sn then Pt; ●, SnCl₄ then Pt; and □, Pt then Sn.

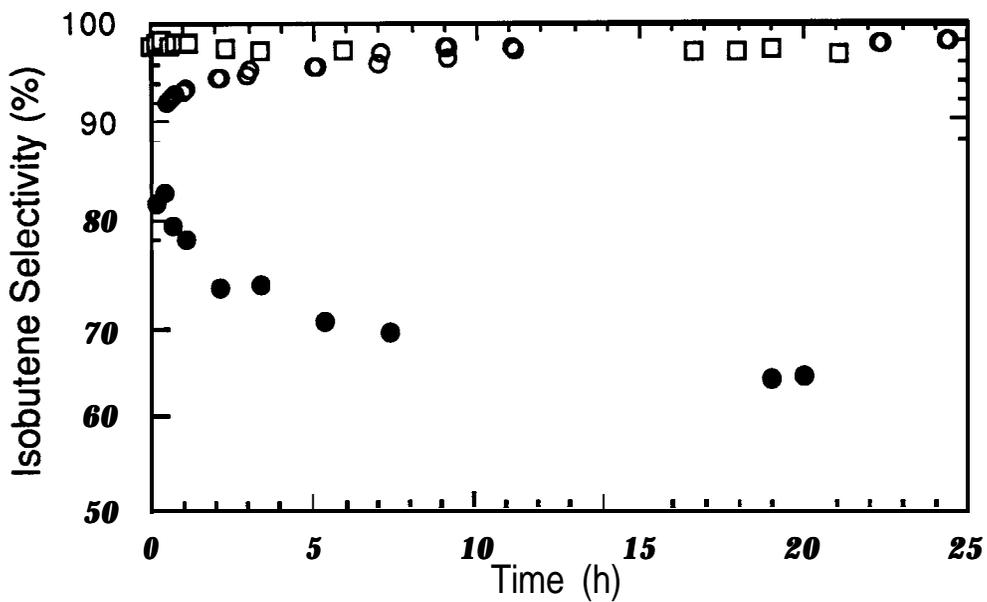


Figure 5 - 2. Effects of preparation methods of 1:2 Pt/Sn/L-zeolite on isobutane dehydrogenation selectivity at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2; sequential impregnation of: ○, Sn then Pt; ●, SnCl₄ then Pt; and □, Pt then Sn.

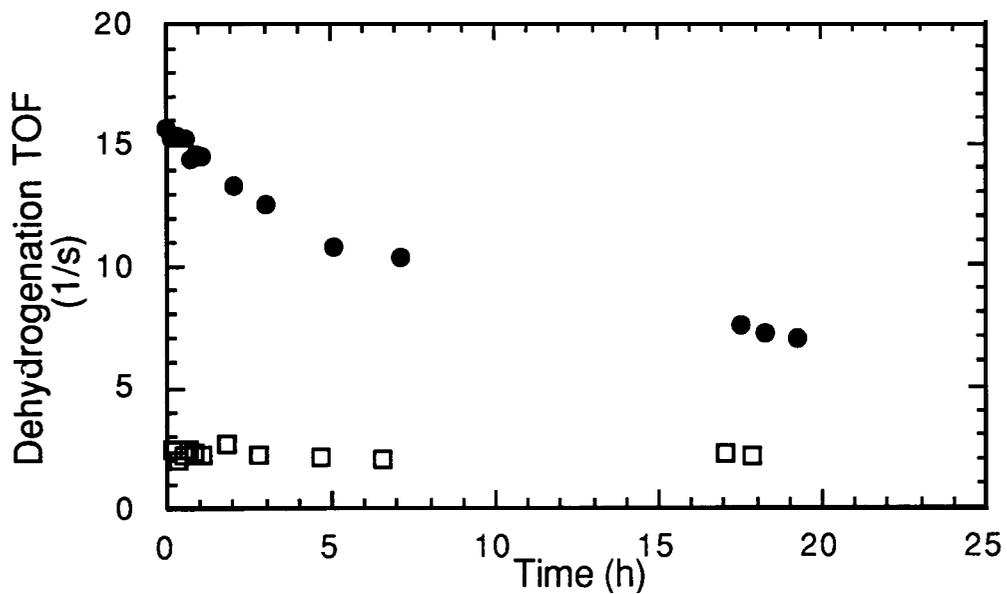


Figure 5 - 3. Effects of platinum content on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over Pt/Sn/L-zeolite (0.83 wt% Sn); ● ,0.5 wt% Pt (1:2.7 Pt/Sn); and □, 0.1 wt% Pt (1:14 Pt/Sn).

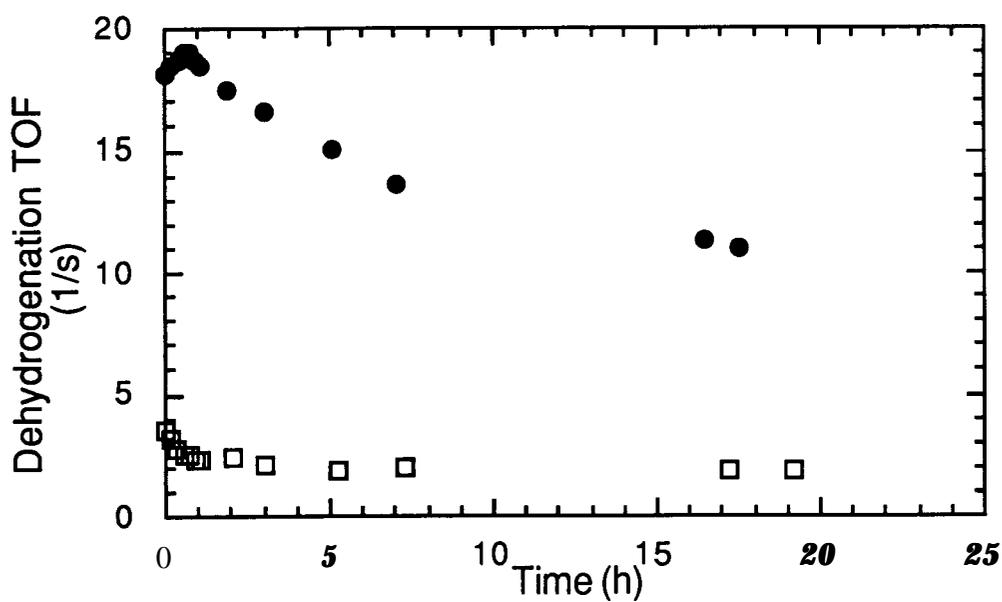


Figure 5 - 4. Effects of platinum content on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over Pt/Sn/L-zeolite (0.42 wt% Sn); ● ,0.5 wt% Pt (1: 1.4 Pt/Sn); and □, 0.1 wt% Pt (1:7 Pt/Sn).

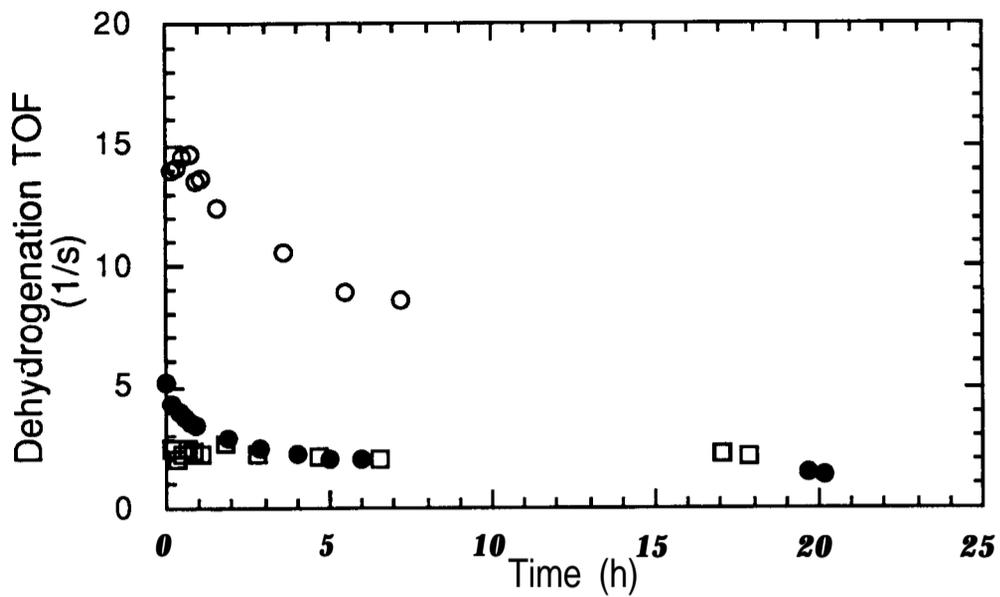


Figure 5 - 5. Effects of tin content on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over Pt/Sn/L-zeolite (0.1 wt% Pt); ○, 0.15 wt% Sn (1:2.5 Pt/Sn); ●, 0.42 wt% Sn (1:7 Pt/Sn); and □, 0.83 wt% Sn (1:14 Pt/Sn).

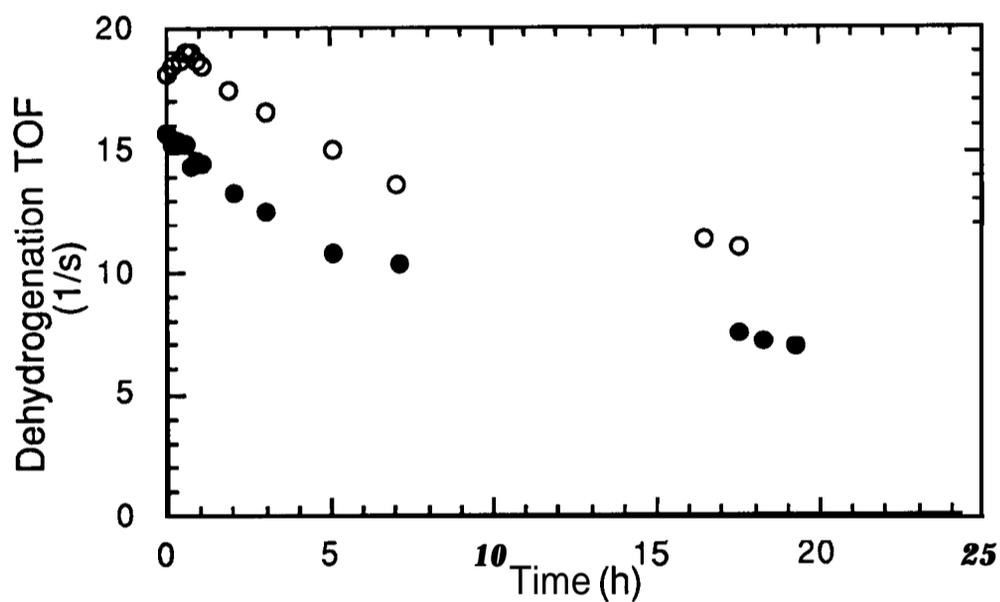


Figure 5 - 6. Effects of tin content on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over Pt/Sn/L-zeolite (0.5 wt% Pt); ○, 0.42 wt% Sn (1:1.4 Pt/Sn) and ●, 0.83 wt% Sn (1:2.7 Pt/Sn).

Based on the results of the previous studies with various Pt and Sn contents, three catalysts were prepared and studied in more detail (see also the results in the Catalyst Deactivation section). The catalysts all contain 0.5 wt% Pt and Pt/Sn ratios of 1:0 (Pt/L), 1:1.4 (1:1.4 Pt/Sn/L) and 1:2.4 (1:2.4 Pt/Sn/L). The activities of these catalysts are shown in Figure 5-7. Note that the TOF is on a per site basis, where the number of sites was determined by CO chemisorption. Without Sn the Pt/L catalyst is much less active for the production of isobutene.

The selectivities of these catalysts are compared in Figure 5-8 and the corresponding conversions in Figure 5-9. Although the isobutane conversions are similar over all three catalysts, the selectivities are different. Note that the reactor configuration used for these experiments was designed for the TPO experiments and significant gas phase reactions may have occurred. Therefore, the absolute selectivities are lower than if the experiments had been designed to minimize gas phase reactions (as in Figure 5-2). It is evident that a certain amount of Sn is required to achieve a reasonable selectivity as the unpromoted Pt catalyst is very unselective to isobutene formation and instead, methane, ethane, propane and coke are formed.

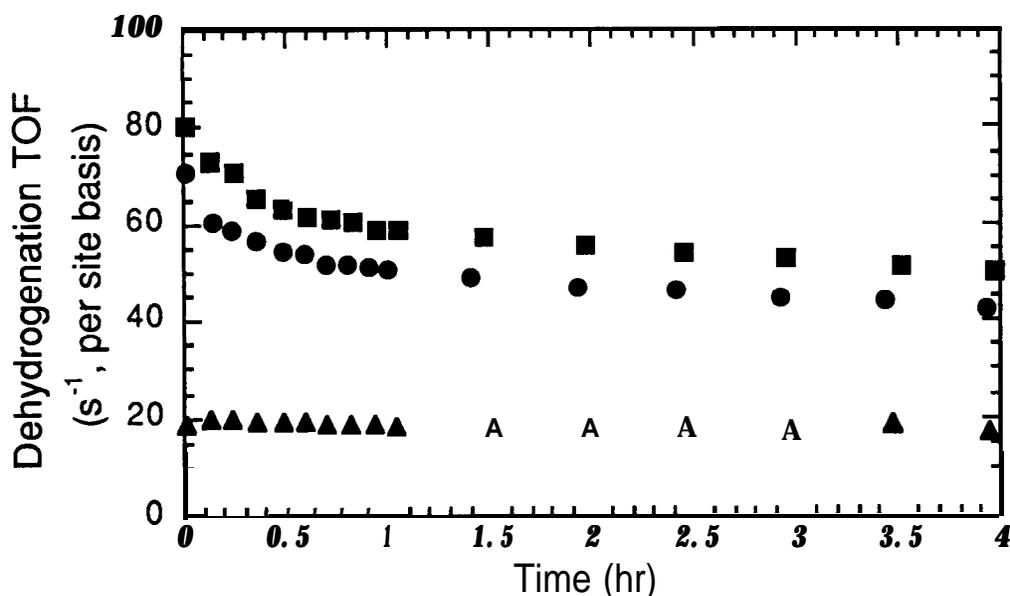


Figure 5 - 7. Comparison of the isobutane dehydrogenation rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over A, Pt/L-zeolite, ●, 1: 1.4 Pt/Sn/L-zeolite and ■, 1:2.4 Pt/Sn/L-zeolite.

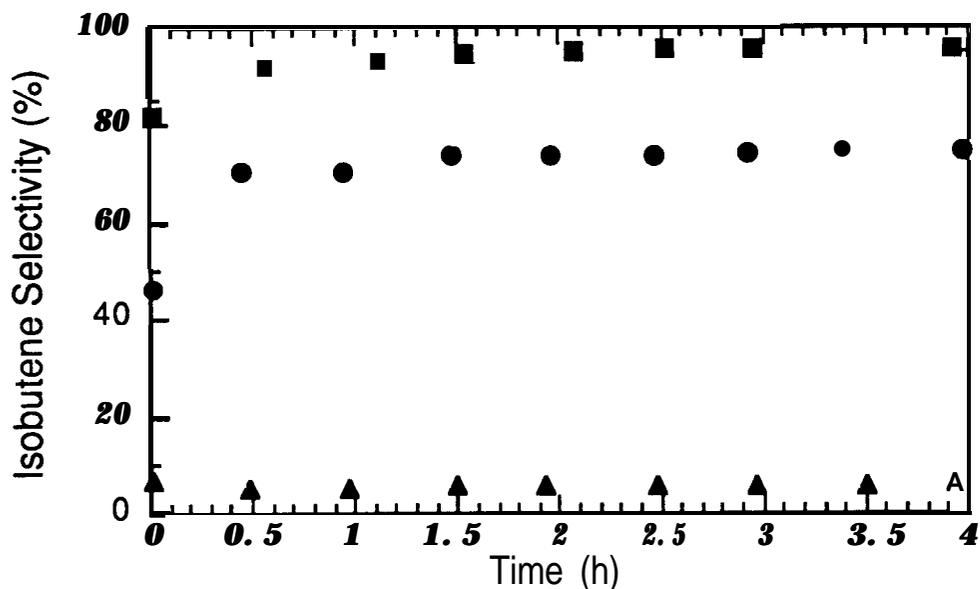


Figure 5 - 8. Comparison of the isobutene selectivity at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over A, Pt/L-zeolite, ●, 1:1.4Pt/Sn/L-zeolite and ■, 1:2.4Pt/Sn/L-zeolite.

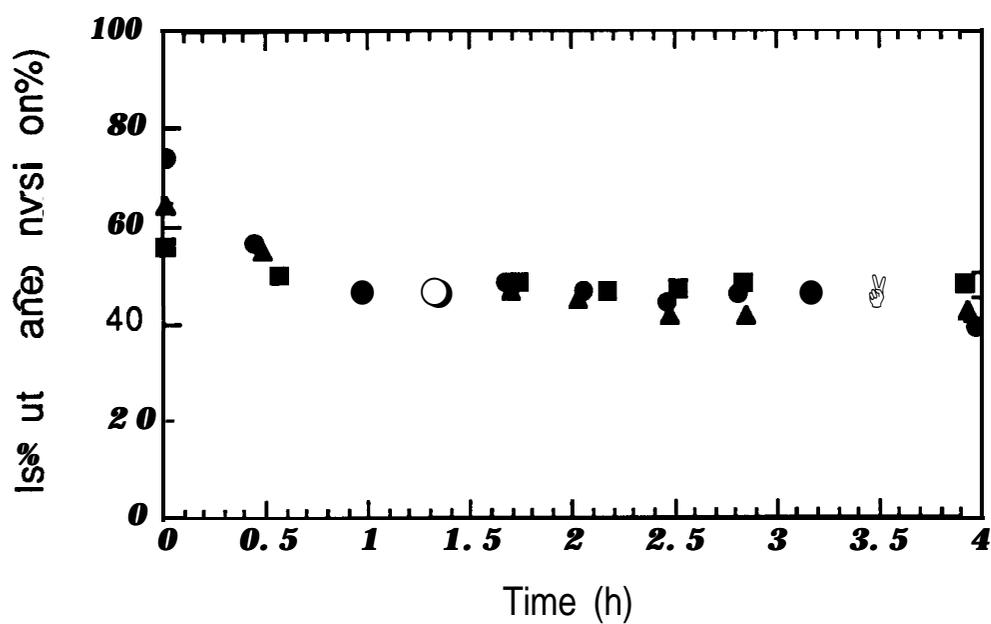


Figure 5 - 9. Comparison of the isobutane conversion at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over A, Pt/L-zeolite, ●, 1:1.4 Pt/Sn/L-zeolite and ■, 1:2.4 Pt/Sn/L-zeolite.

Catalyst Treatment

The properties of the catalyst are affected by both the pretreatment (*i.e.* the reactivation during which the catalyst is taken from being exposed to air at room temperature to being fully reduced at the temperature of reaction) and the reaction conditions. It has been established that supported metal catalysts must be heated slowly to avoid sintering the metals and to avoid damage to the support by the evaporating absorbed water (from exposure to the air) [8-10]. A study was thus undertaken to determine how best to pretreat or reactivate the Pt/Sn/L catalysts.

The following pretreatments were used with a 1:2.5 Pt/Sn/L catalyst (0.5 wt% Pt):

1. The catalyst was heated in a 10% H₂ in He flow from room temperature (RT) to 400 K over 30 min, held for 1 h at 400 K, heated to 873 K over 2 h and then held at 873 K for 1 h in H₂ (4 h 30 min pretreatment).
2. The catalyst was heated in a 10% H₂ in He flow from room temperature (RT) to 873 K at 2 K/min and then held at 873 K for 1 h in H₂ (6 h pretreatment).
3. The catalyst was heated in He to 400 K over 1 h, held at 400 K for 2 h, heated to 533 K over 1 h 10 min, held at 533 K for 1 h, cooled to RT, and then reduced by heating from RT to 873 K over 16 h in a 10% H₂ in He flow, held at 873 K for 1 h in H₂ (22 h pretreatment).
4. The catalyst was heated in 25% O₂ in He to 533 K over 2 h, held for 1 h at 533 K, cooled in He to RT, and then reduced by heating from RT to 873 K over 16 h in a 10% H₂ in He flow and held at 873 K for 1 h in H₂ (20 h pretreatment).

The kinetic measurements were performed with approximately 5 mg of catalyst in a quartz U-tube reactor. After each pretreatment, the samples were exposed to a 2:1 ratio of H₂ to isobutane at 873 K and the activity measured. For TEM analysis, approximately 0.04 g of catalyst was placed in a fritted reactor. Instead of being exposed to reaction conditions after the pretreatment, the samples for the TEM were cooled to RT in He and passivated with a flowing stream of 0.2% O₂ in He for 30 min.

The 1:2.5 Pt/Sn/L catalyst is essentially free of particles after preparation. After the pretreatments, however, particles are visible on the catalyst. The number and size of particles depends on the pretreatment. The pretreatment involving calcination before reduction, treatment #4, resulted in the greatest amount of particle migration and agglomeration with 80% of the catalyst having evidence of particles, while the drying at 533 K followed by a 16 h reduction (treatment #3) resulted in the least. In the latter case, metal particles were only visible on approximately 10-20% of the catalyst. A few more particles were visible on the 6 h pretreated (treatment #2) sample and considerably more particles were visible on the 4 h 30 min pretreated (treatment #1) sample, with 50% of the catalyst having evidence of particles.

The activities of the catalyst after the pretreatments are compared in Figure 5-10. Included in this comparison, is the activity of the catalyst immediately after preparation (*i.e.* after the 6 h reduction at 873 K, the reaction was started without cooling to RT and without exposing the catalyst to air). The catalysts that have been passivated and reactivated are significantly less active than the catalyst that had not been exposed to air. It has also been observed that if the Pt/Sn catalysts are exposed to air for extended periods after the Sn or Pt impregnation during preparation, significant particle agglomeration occurs. This agglomeration does not happen on a Pt catalyst without Sn, which suggests the oxidized Sn species may be the cause for the metal agglomeration.

The activity of the catalyst pretreated for 4 h 30 min (treatment #1) is lower than that of the other pretreatments. In this pretreatment, the catalyst is heated at **4K/min** from 400 K to 873 K. A decrease to **2K/min** in the 6 h pretreatment appears to improve the activity of the catalyst. Decreasing the heating rate to **0.6K/min** and preceding the reduction by drying at 533 K (22 h pretreatment) does not seem to significantly improve the activity, even though fewer particles were visible on the catalyst. Also, the activity of the calcined sample (20 h pretreatment) is higher than that of the catalyst pretreated for 4 h 30 min, even though significantly more agglomeration occurred on the former catalyst. The **TEM** analysis may be somewhat misleading because the particles that were seen were probably only a small fraction of the total number of particles in the catalysts.

The other pretreatment variable that has been studied is the time for which the catalyst is reduced immediately before reaction. A **1:2.7 Pt/Sn/L** and a **1:1.4 Pt/Sn/L** catalyst were reduced for 1 or 16 h and their dehydrogenation activities compared (see Figures 5-11 and 5-12). A significant loss in activity occurs when either catalyst is reduced for 16 h compared with 1 h. This loss of activity could be due to sintering of the metal particles or enrichment of the Pt particles with Sn. A **1:2.5 Pt/Sn/L** catalyst was held at 873 K for 24 h in He and then reacted with 651 Torr He and 109 Torr isobutane (see Figure 5-13). In He, the reduction of the Sn should be significantly reduced. Again, a decrease in activity occurs after the high temperature soak. This suggests that the temperature is causing some sintering of the metals. **TEM** examination of a **Pt/Sn/L** catalyst after a 16 h soak at 873 K in H₂, confirms that particle agglomeration does occur.

Finally, the reaction conditions have been varied. Figure 5-14 is a comparison of the activity of a **1:2.5 Pt/Sn/L** catalyst at 798 K in a pure isobutane feed, a 2:1 **hydrogen/isobutane** feed and a 2:1 helium/ isobutane feed. The activity is lower in the presence of hydrogen because the reaction is negative order in hydrogen (*i.e.* the hydrogen inhibits the production of isobutene). The catalyst, however, is more stable in the presence of hydrogen. In fact, a Pt catalyst without Sn has essentially no activity when used in the absence of hydrogen (see Figure 5-15). A **1:1.4 Pt/Sn/L** catalyst is active for isobutane conversion for a few hours on stream only, compared to a **1:2.5 Pt/Sn/L** catalyst which maintains reasonable conversion for 20 h on stream (see Fig 5-16). Thus, the catalyst must be highly selective to be used with an isobutane feed stream that does not contain hydrogen.

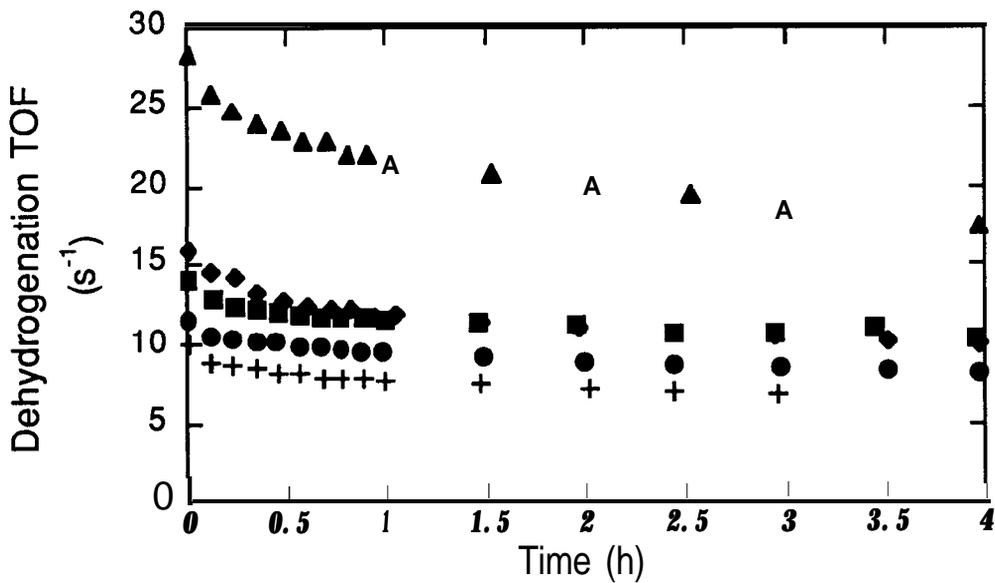


Figure 5 - 10. Comparison of the isobutane dehydrogenation rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over 1:2.5 Pt/Sn/L-zeolite. Pretreatment: A, none, ●, 22 h, ■, 6 h, ●, 20 h, and +, 4 h 30 min.

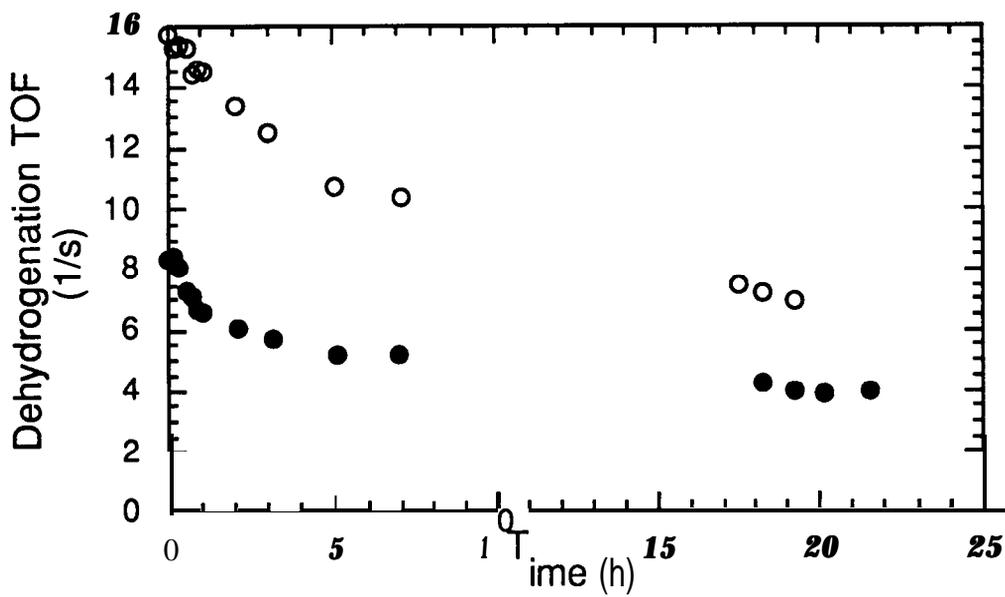


Figure 5 - 11. Effects of reduction time on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over 1:2.7 Pt/Sn/L-zeolite (0.5 wt% Pt, 0.83 wt% Sn); ○, 1 h reduction and ●, 16 h reduction.

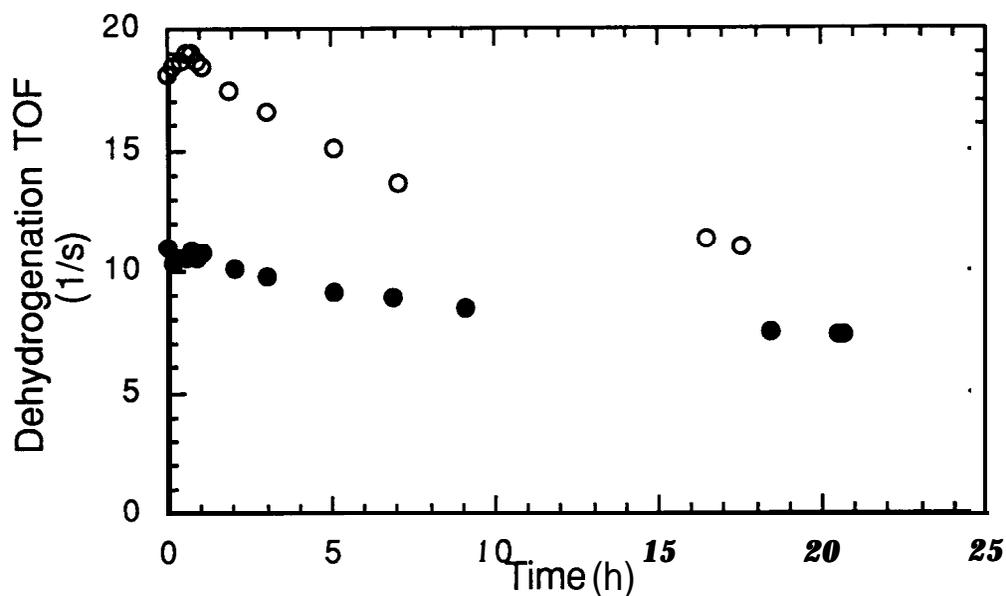


Figure 5 - 12. Effects of reduction time on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over 1: 1.4 Pt/Sn/L-zeolite (0.5 wt% Pt, 0.42 wt% Sn); ○, 0, 1 h reduction and ●, 16 h reduction.

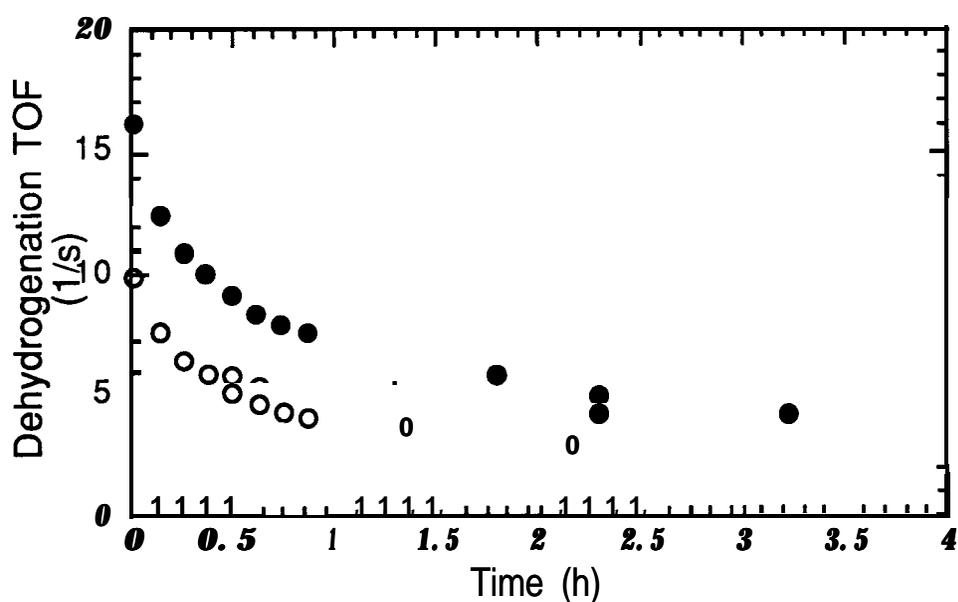


Figure 5 - 13. Effect of He soak on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a 651 Torr He and 109 Torr $i-C_4H_{10}$ over 1:2.5 Pt/Sn/L-zeolite (0.5 wt% Pt, 0.83 wt% Sn); ●, 1 h reduction, and ○, 24 h He soak.

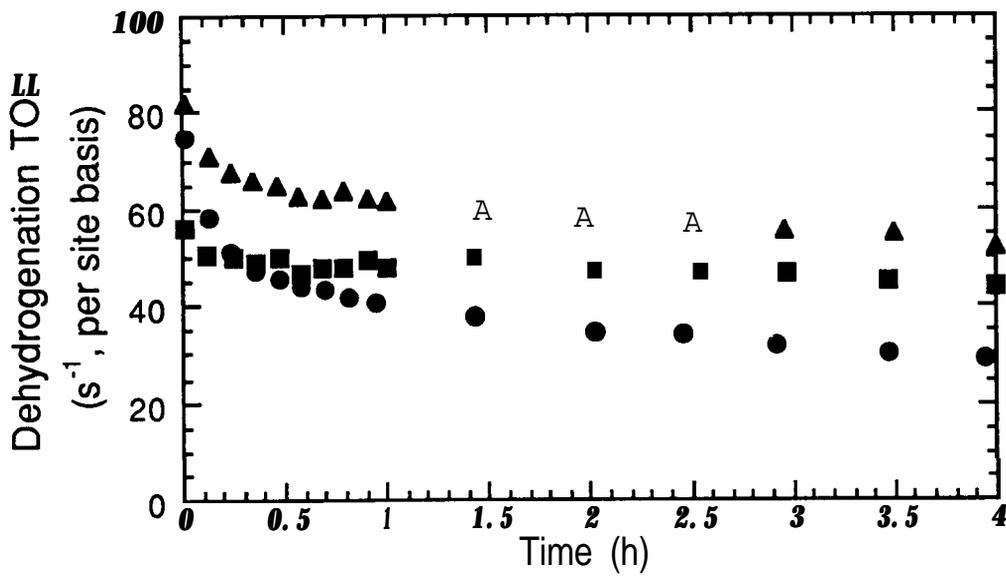


Figure 5 - 14. Comparison of the isobutane dehydrogenation rates at 798 K over 1:2.5 Pt/Sn/L-zeolite with different feed streams. A i-C₄H₁₀ only, ■, 2: 1 H₂/i-C₄H₁₀, and ●, 2: 1 He /i-C₄H₁₀.

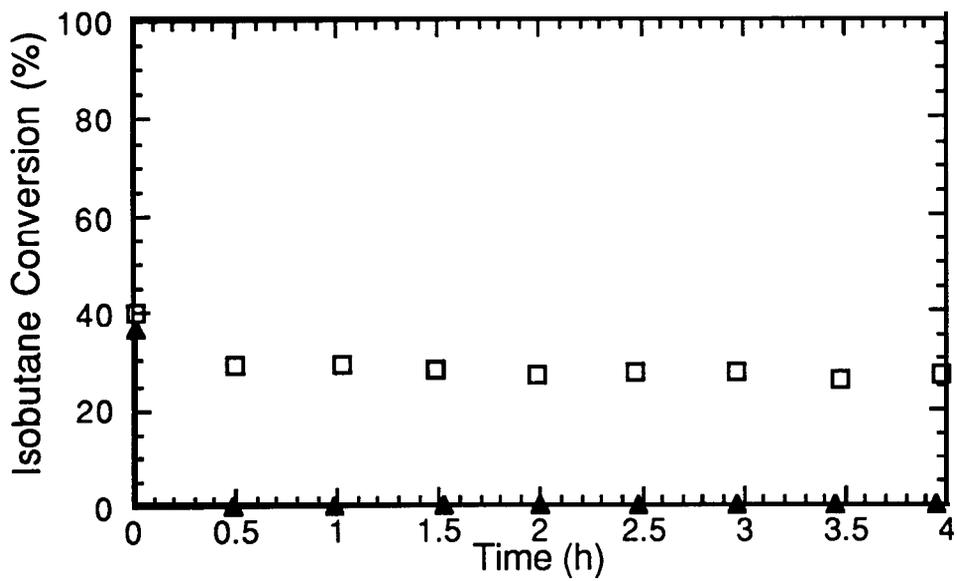


Figure 5 - 15. Comparison of the isobutane conversion at **798** K and in i-C₄H₁₀ only over A, Pt/L-zeolite, and □, 1:2.5 Pt/Sn/L-zeolite.

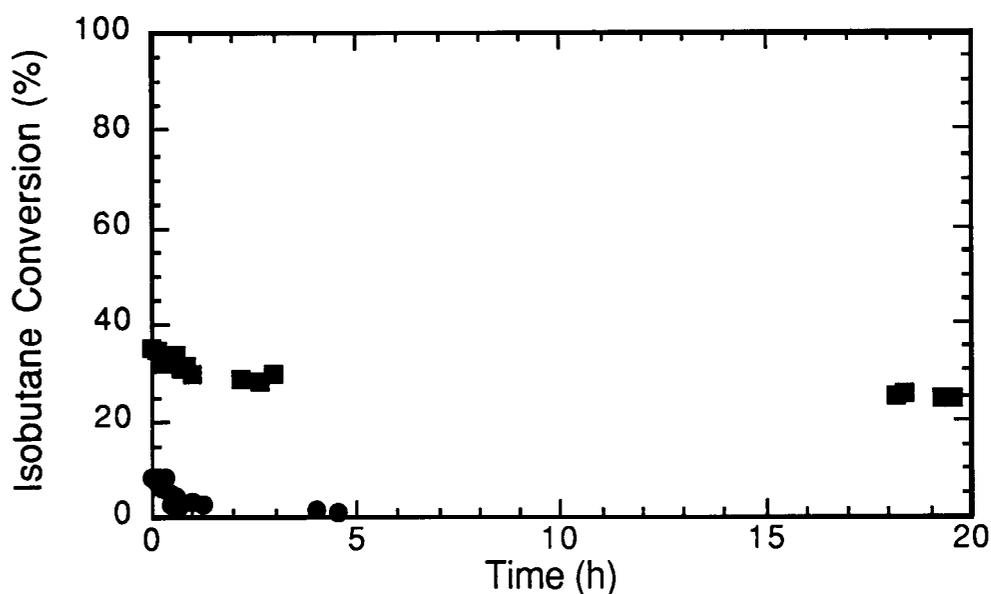


Figure 5 - 16. Comparison of the isobutane conversion at 798 K and in $i\text{-C}_4\text{H}_{10}$ only over ●, 1:1.4 Pt/Sn/L-zeolite and ■, 1:2.5 Pt/Sn/L-zeolite.

Catalyst Deactivation

It is evident that deactivation is occurring in the activity profiles of the Pt/Sn/L-zeolite catalysts (for example, see Figures 5- 10 and 5- 11). As previously mentioned, coking, metal sintering and Sn enrichment of the Pt particles can all contribute to the deactivation of the catalyst. Accordingly, the catalysts were analyzed with TPO and TEM after 4 h of reaction at two conditions - 873 K in a 2: 1 hydrogen to isobutane feed stream and 798 K in a pure isobutane feed stream. The former condition is similar to commercial conditions, and the latter condition maximizes coking while minimizing sintering.

For the experiments at **873** K, approximately 0.75 g of catalyst was loaded into a quartz sample cell which could be transferred between the kinetics/TPO apparatus and the chemisorption apparatus without exposing the catalyst to air. The catalyst was first reduced in H_2 by heating overnight in a 10% H_2 in He flow to 873 K, held at 873 K for 1 h in H_2 , and evacuated for 30 min at 673 K. The CO uptake was then measured at 298 K, after which the catalyst was heated to 873 K over 2 h in H_2 and treated for 4 h under reaction conditions (H_2 to $i\text{C}_4\text{H}_{10}$ ratio of 2 at 873 K). After purging the catalyst with He at 673 K for 1 h to remove adsorbed H_2 , the catalyst was evacuated at 298 K for 2 h and the CO uptake was measured. Finally, the catalyst was heated to 873 K at 10 K/min in a 2% O_2 in He flow to obtain the TPO spectrum. Any carbon that has accumulated on the catalyst during reaction will be removed as CO, when the catalyst is heated in the presence of oxygen. During the collection of the TPO spectrum, the exit gas stream from the catalyst was analyzed using a mass spectrometer which monitored the mass 44 signal (mass 44 corresponds to the signal for CO_2). Calibration of the mass 44 signal was achieved using a gas mixture of 5% CO_2 in He (AGA).

At the low space velocity of these experiments, the isobutane conversions were initially equal to 75%, 65% and 55% for the 1:1.4 Pt/Sn/K-L, Pt/K-L, and 1:2.4 Pt/Sn/K-L, respectively, and these values decreased to ~40% after 4 h on stream. The CO uptakes before and after reaction are given in Table 5-1. An increase in the amount of Sn in the catalyst causes a decrease in the number of sites on the fresh catalyst, as seen in other studies[11-13]. The CO uptake is low on the Pt/L catalyst, in comparison with previous studies of this catalyst system[14]. Therefore, CO uptakes were measured on a Pt/L catalyst that was reduced at 673, 798 and 873 K for 1 h (temperature ramp of 2K/min). The corresponding CO uptakes are listed in Table 5-2. Higher temperatures of reduction lead to a decrease in the CO uptake, which accounts for the low uptake on the fresh Pt/L catalyst. Similar results have been observed by Vaarkamp and co-workers[10]. After reaction, the CO uptake decreases on all catalysts; however, the relative decrease in the number of sites is smaller as the percentage of Sn in the catalyst increases.

Table 5-1: CO uptake on fresh catalysts and after reaction at 873 K in 2: 1 H₂:iC₄H₁₀.

Catalyst	CO Uptake (μmol/g)*	
	Fresh	After Reaction
1:2.4 Pt/Sn/L	5.0	3.4
1:1.4 Pt/Sn/L	7.5	4.1
Pt/L (II)	7.8	1.2

*error is ±0.5 μmol/g

Table 5-2: CO uptake versus reduction temperature for Pt/L.

Reduction Temperature	CO Uptake (μmol/g)
673 K	21
798 K	15
873 K	10

The TPO spectra of the Pt/L, 1:1.4 Pt/Sn/L and 1:2.5 Pt/Sn/L catalysts after 4 h of reaction in isobutane and hydrogen at 873 K are shown in Figure 5- 17. Peaks occur at approximately 680 and 780 K for the Pt/L and 1: 1.4 Pt/Sn/L catalysts. The TPO spectrum of the 1:2.5 Pt/Sn/L catalyst has a broad peak between 600 and 760 K. The amount of carbon on each catalyst is given in Table 5-3. Increasing the amount of Sn in the catalyst decreases the amount of carbon deposited under these reaction conditions.

Analyses of the catalysts by TEM indicate that sintering of the metal particles occurs after reaction at 873 K. Before the reaction, the L-zeolite-supported samples have few particles visible on the external surface of the zeolite, and these visible particles are 1-2 nm in size. The 1:1.4 Pt/Sn/L catalyst looks similar to the 1:2.5 Pt/Sn/L catalyst before and after reaction. After reaction some particles, up to 5 nm in size, are visible. However, even though more particles are visible after reaction, the majority of the zeolite specimen (~70%) does not show visible particles. The Pt/L catalyst is similar to the Pt/Sn/L catalysts before reaction (i.e. few particles are visible), but after reaction particles are visible on a significant fraction of the zeolite (~50%). The average size of the particles appears to be smaller (e.g., 1 nm) on the Pt/L catalyst after reaction compared to the Pt/Sn/L sample.

Table 5-3: CO uptakes and extents of carbon deposition on catalysts.

Catalyst	CO Uptake* ($\mu\text{mol/g}$)	Carbon Deposition+ ($\mu\text{mol C/g}$)	Carbon Deposition+ ($\mu\text{mol C}/\mu\text{mol site}$)
<i>Reaction at 873 K in $i\text{C}_4\text{H}_{10}/\text{H}_2$</i>			
1:1.4 Pt/Sn/L	5.0	90	18
Pt/L	7.5	170	22
Pt/L(II)	7.8	500	64
<i>Reaction at 798 K in $i\text{C}_4\text{H}_{10}$</i>			
1:2.5 Pt/Sn/L	6.1	260	43
Pt/L(I)	15	560	38
1:1 Pt/Sn/silica	16	770	45
1:1:3 Pt/Sn/K/silica	10	210	21
Pt/silica	18	2400	132

*error is $\pm 0.5 \mu\text{mol/g}$

†error is $\pm 20\%$

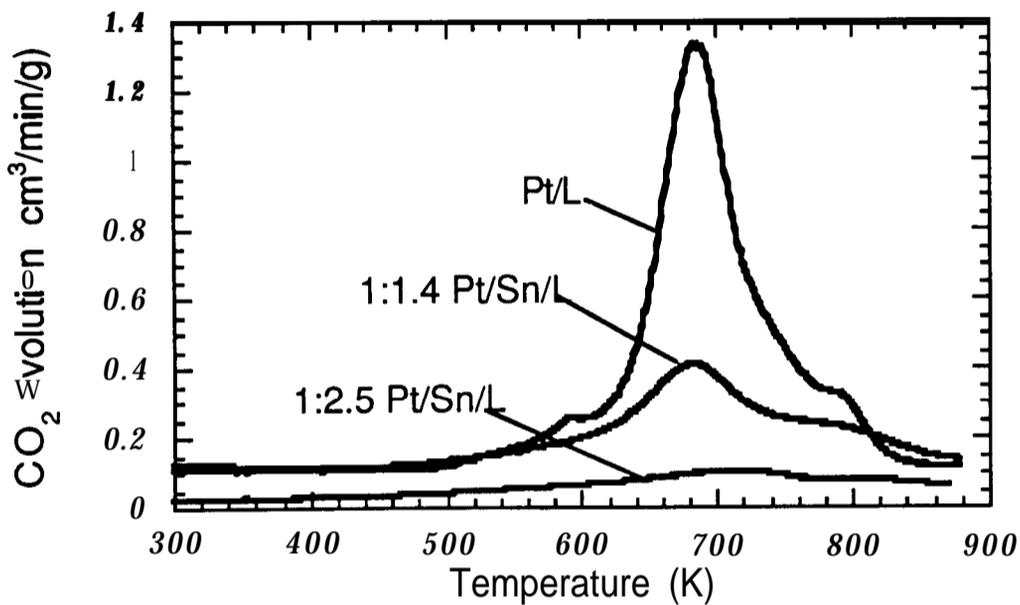


Figure 5 - 17. Comparison of the TPO spectra after 4 h reaction at 873 K, 1 atm, and a $\text{H}_2/i\text{-C}_4\text{H}_{10}$ ratio of 2 for Pt/L-zeolite, 1:1.4 Pt/Sn/L-zeolite and 1:2.5 Pt/Sn/L-zeolite.

The uptake of isobutane was measured on the 1:2.5 Pt/Sn/L catalyst before and after reaction. The adsorption of isobutane occurs primarily on the L-zeolite (the Pt/Sn/L sample contains a relatively small number of surface Pt sites), and this uptake is thus a measure of the accessible interior surface area of the catalyst. The change in uptake is negligible within the error of the experiment (see Table 5-4). This results is consistent with the observation that only a small amount of carbon is deposited on the catalyst during 4 hours of reaction.

Table 5-4. Isobutane uptake on catalysts.

Catalyst	Isobutane Uptake ($\mu\text{mol/g}$)*	
	Fresh	After Reaction
L-zeolite	713	
<i>Reaction at 798 K in $i\text{C}_4\text{H}_{10}$</i>		
Pt/L (I)	603	528
<i>Reaction at 873 K in $i\text{C}_4\text{H}_{10}/\text{H}_2$</i>		
1:2.4 Pt/Sn/L	568	545

*error is $\pm 15 \mu\text{mol/g}$

Measurable catalytic activity for isobutane conversion in the absence of H_2 is maintained by all catalysts for reaction times of 4 h, except for the Pt/L-zeolite catalyst (see Figure 5-18). The isobutane conversion of the 1:2.5 Pt/Sn/L catalyst is lower than that of the Pt/Sn/silica and Pt/Sn/K/silica catalysts because the reactor contained only 3 μmol of sites compared to 8 and 5 μmol s of sites, respectively, for the silica-supported catalysts. The activity of the Pt/L catalyst decreases to essentially zero within 30 minutes on stream. For all catalysts except Pt/Sn/K/silica, the selectivity increases significantly between 1 and 30 minutes on stream, as shown in Figure 5-18. This increase in selectivity may be caused by the formation of coke which decreases the size of the Pt ensembles, thus suppressing the isomerization and hydrogenolysis reactions compared to the dehydrogenation reaction.

Figure 5-19 shows TPO spectra for catalysts after 4 h reaction at 798 K in isobutane. The TPO spectrum of the Pt/silica catalyst has peaks at 710 and 790 K, while the 1:1 Pt/Sn/silica catalyst displays broad peaks at 690, 760 and 820 K. The spectra of Pt/L and 1:2.5 Pt/Sn/L have peaks near 680 and 780 K, while the 1:1:3 Pt/Sn/K/silica has a peak around 680 K. The peak at 360 K in the spectrum of the 1:2.5 Pt/Sn/L catalyst is from weakly bound carbon on the surface, that can be removed by purging the catalyst with He at 673 K for 1 h. Comparing Pt/silica with Pt/Sn/silica, and comparing Pt/L with Pt/Sn/L, it appears that Sn suppresses the extent of coke formation and it appears to alter the relative areas of the high and low temperature peaks, (*i.e.*, decrease the ratio of the 680 peak to the 780 K peak). The addition of K to the Pt/Sn/silica catalyst significantly decreases the amount of carbon deposited on the catalyst.

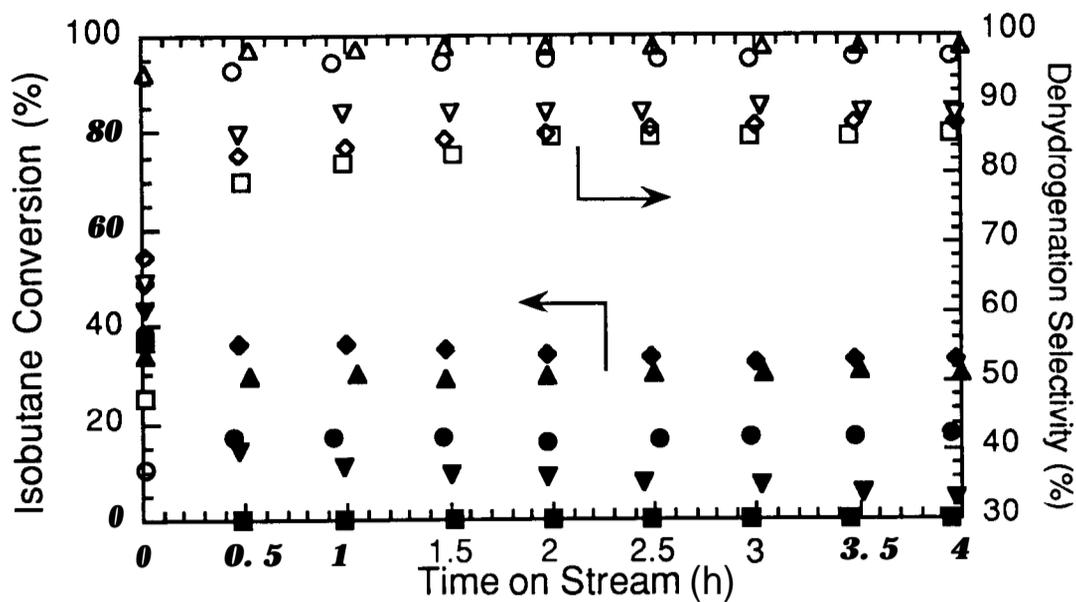


Figure 5 - 18. Isobutane conversions (filled symbols) and dehydrogenation selectivities (open symbols) over 1:2.5 Pt/Sn/K-L (circles), Pt/K-L (squares), 1:1 Pt/Sn/silica (diamonds), 1:1:3 Pt/Sn/K/silica (triangles), and Pt/silica (inverted triangles) at 798 K in isobutane.

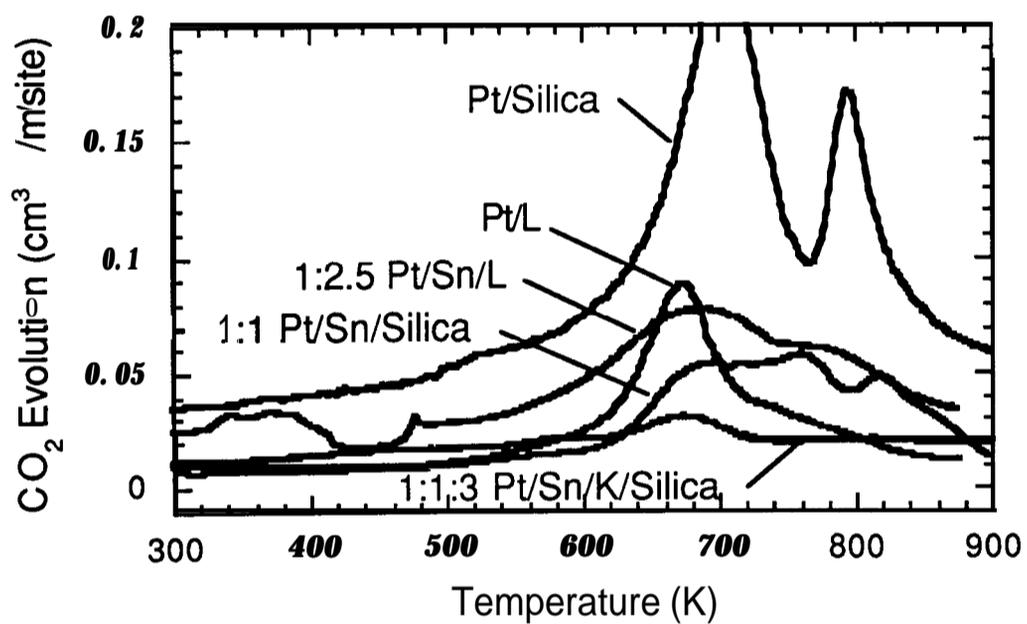


Figure 5 - 19. Comparison of the TPO spectra after 4 h reaction at 798 K, 1 atm, and in isobutane only for L-zeolite- and silica-supported catalysts.

The total carbon accumulated on the catalysts was determined from the area under the TPO spectra, where the baseline for integration was taken to be the CO₂ evolution at 300 K. Table 5-3 lists the amounts of carbon deposited on the basis of catalyst mass and also based on the number of sites determined by CO chemisorption on the fresh catalysts. The order of decreasing amount of carbon per site is **Pt/silica** >> **1:1 Pt/Sn/silica** > **1:2.5 Pt/Sn/L** > **Pt/L** > **1:1:3 Pt/Sn/K/silica**.

To obtain deactivation profiles corresponding to the above reaction conditions, approximately 0.005 g of catalyst was loaded into a quartz U-tube reactor with quartz wool. The deactivation profiles for the **1:2.5 Pt/Sn/L** and **Pt/L** catalysts are compared in Figure 5-20, at conditions for which the isobutane conversion was less than 10% of the equilibrium value. The **Pt/L** catalyst deactivates rapidly, whereas the **Pt/Sn/L** catalyst has a high initial activity, deactivates over the first 30 minutes on stream, and then continues to deactivate at a slower rate. The deactivation behavior of the **Pt/Sn/L** catalyst is typical for many catalysts [15-17].

Analyses of the catalysts by TEM before and after reaction in isobutane at 798 K indicate that little, if any, particle agglomeration occurs during the reaction. Essentially no particles are visible on the L-zeolite-supported catalysts after reaction at 798 K. The silica-supported catalysts have particles visible with diameters from 2-5 nm on the support before and after reaction. Isobutane uptake was measured on the **Pt/L** catalyst before and after reaction (see Table 5-4). After reaction, the uptake decreases by 75 $\mu\text{mol/g}$. This result indicates that carbon deposition had occurred within the pores of the zeolite, and this pore blocking may account for the rapid decline with time in catalyst activity.

Regeneration of the **Pt/Sn/L** catalyst has been attempted. Figure 5-21 shows the activity of a **1:2.5 Pt/Sn/L** catalyst at 873 K in 65 Torr He and 109 Torr isobutane. After 23 hours on stream, the catalyst was cooled to 573 K and held at this temperature for 2 hours in a flowing stream of 25% O₂ in He. The catalyst was then purged with He for 30 minutes, heated to 873 K at 8 K/min in 5% H₂ in He, held for 2h in H₂ at 873 K and exposed to reaction conditions. Only a fraction of the initial activity was recovered.

A different regeneration scheme was successful in reestablishing the performance of a **1:2.7 Pt/Sn/L** catalyst, provided that the catalyst was reduced for 16 h prior to the initial reaction and after each regeneration. Figure 5-22 shows isobutane dehydrogenation reaction rates over fresh **1:2.7 Pt/Sn/K-L-zeolite** (0.5 wt% Pt) at 873 K, 1 atmosphere, and a H₂/iC₄H₁₀ molecular ratio of 2.0. This catalyst was pretreated with H₂ at 873 K for 16 h before reaction and was allowed to deactivate over 80 h at reaction conditions. The catalyst was then regenerated with a 10% O₂ in He mixture for 2 h at 533 K, cooled to room temperature, reduced with a 10% H₂ in He mixture by increasing the temperature from room temperature to 873 K over 8 h, and then further reduced in pure H₂ at 873 K. After this regeneration, Figure 5-22 shows that the catalyst exhibited essentially the same dehydrogenation activity and stability. After running for 50 h, the catalyst was regenerated using the same procedure for a second time. After the second regeneration, the catalyst exhibited slightly lower dehydrogenation reaction rates compared to the fresh catalyst. The catalyst was allowed to deactivate for 24 h after this second regeneration and then was regenerated a third time. The third regeneration followed a procedure similar to the first two regenerations, but the catalyst was regenerated with 10% O₂ in He mixture for 2 h at 573 K instead of 533 K. The catalyst was then exposed to isobutane at 873 K in the absence of hydrogen. The catalyst was regenerated a fourth time using the same procedure as the third regeneration. After this fourth regeneration, the catalyst exhibited slightly lower dehydrogenation activity compared to the fresh catalyst. However, there was little change in the performance of the catalyst between the second and fourth regenerations.

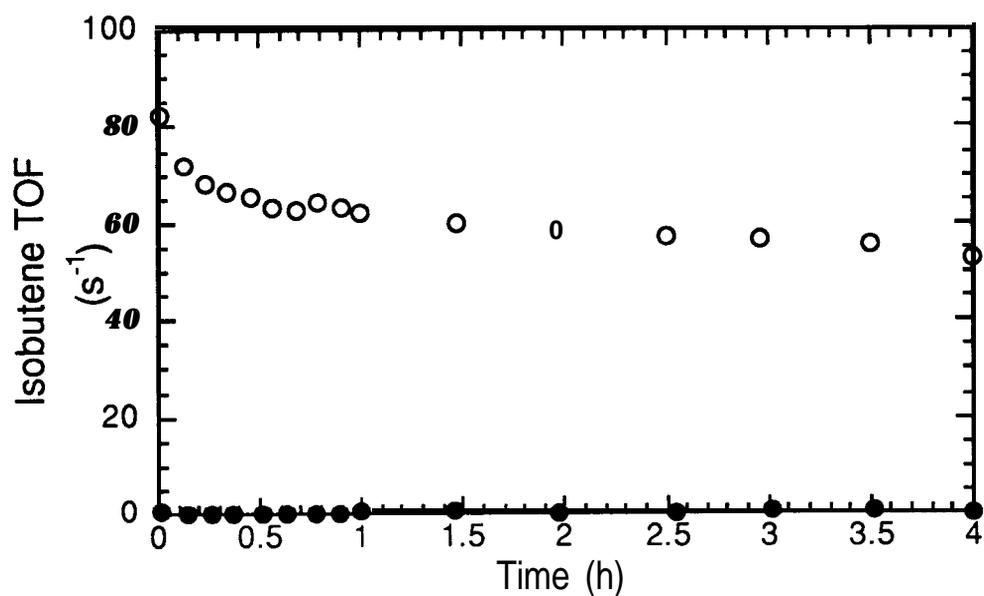


Figure 5 - 20. Isobutene turnover frequencies at 798 K in isobutane over ○, 1:2.5 Pt/Sn/K-L, and ●, Pt/K-L.

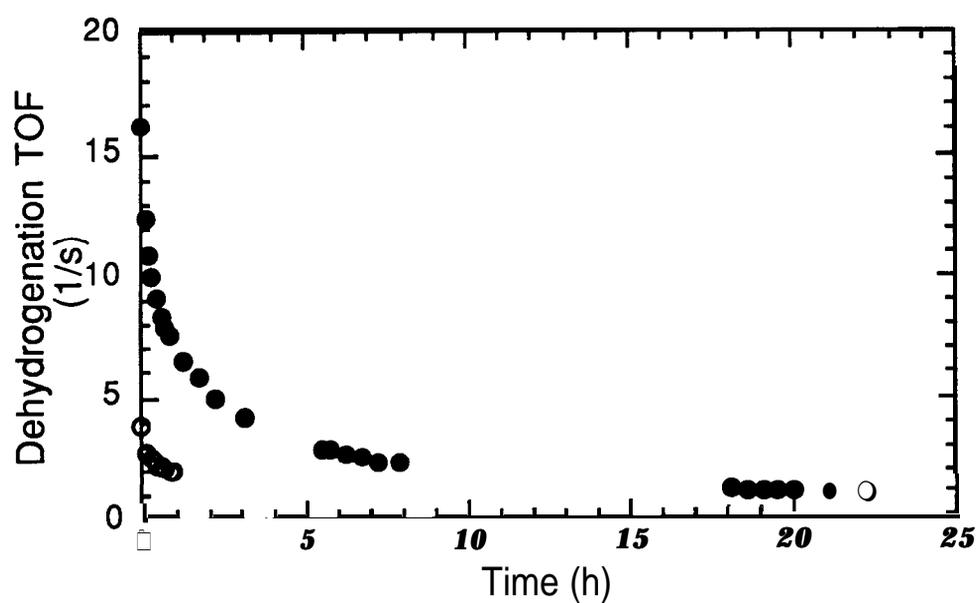


Figure 5 - 21. The activity of 1:2.5 Pt/Sn/L-zeolite at 873 K, 651 Torr He and 109 Torr iC_4H_{10} before and after regeneration in 25% O₂ in He at 573 K for 120 minutes; ●, fresh catalyst and ○, regenerated catalyst.

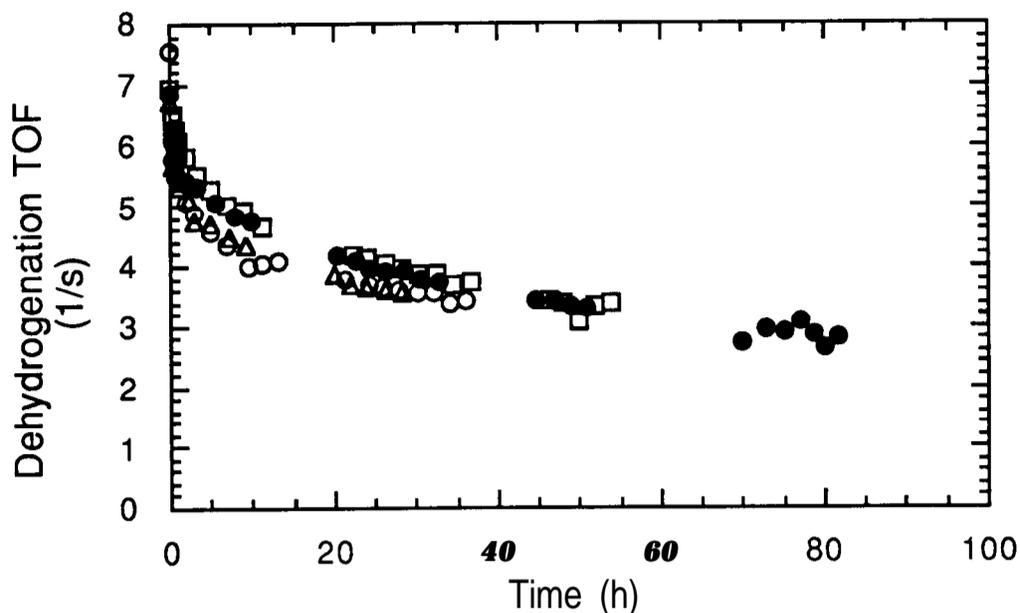


Figure 5 - 22. Effects of regeneration on isobutane dehydrogenation reaction rates at 873 K, 1 atm, and a $H_2/i-C_4H_{10}$ ratio of 2 over 1:2.7 Pt/Sn/L-zeolite (0.5 wt% Pt, 0.83 wt% Sn); ●, fresh catalyst; ○, regenerated catalyst (1st Regeneration); △, regenerated catalyst (2nd Regeneration); and □, regenerated catalyst (4th Regeneration).

Summary of Preferred Conditions

The following table lists the preferred preparation and pretreatment conditions for the dehydrogenation of isobutane using the UW Dehydrogenation Catalyst.

Table 5-5: Preferred preparation and treatment conditions for the catalyst.

Variable	Preferred Value
Pt:Sn Ratio	1:2.5
Pt Content	0.5 wt%
Sn Precursor	Tributyl tin acetate
Impregnation Order	Sn first, Pt second
Pretreatment	Heating rate $\leq 2K/min$ No calcination 1 h reduction in H_2 at rxn temp

Discussion

The goal of this project was to learn more about why the UW Dehydrogenation catalyst is such a good catalyst for isobutane dehydrogenation and how the preparation and pretreatment parameters could be chosen to achieve maximum performance from the catalyst. It is known that small Pt

ensembles are essential to achieve high activity, selectivity and **stability**[11]. Our results indicate some of the factors which affect whether the catalyst will have and/or maintain small Pt ensembles.

The first task in this project was to determine the location of the metal particles on the zeolite support. The TEM analysis indicated that the particles were within the pores of the zeolite after preparation. The TEM results support other work which showed that **Pt/Sn/L** catalysts were 50 times more active than **Pt/Sn/silica** catalysts[18]. One of the differences between silica and L-zeolite is their pore structure. The silica used in the study was non-porous. L-zeolite, however, has a unidimensional pore structure. It has been suggested that when the reaction occurs within the pores of the zeolite, favorable interactions between reaction intermediates and the pore walls can occur, thus promoting the rate of reaction.

As well as the location of the metals, the interaction between the metals is also important. Tin is necessary to make the catalyst selective (see Figure 5-8) but the exact role of tin is not fully **understood**[19]. It is likely that the interaction between the Pt and Sn changes during preparation, during pretreatment and over the course of the reaction as the environment to which the catalyst is exposed changes. Previous work on these catalysts has shown that platinum and tin form an alloy after high temperature **reduction**[5, 6]. In the preparation of the catalyst, the final step is a 6 hour reduction at 873 K, however, the catalyst is then exposed to air when it is transferred from the storage vial to the reactor. Work on model **Pt/Sn** systems on silica films has shown that oxidation will destroy a **Pt/Sn** alloy and cause Pt and Sn to **separate**[20]. The pretreatment is designed to reduce the metals and reform the alloy. It is shown from the pretreatment studies herein that the pretreatment method does affect the performance of the catalyst. In particular, the heating rate and atmosphere are important (see Figure 5-10). **Calcination** at 533 K before the reduction results in significant sintering of the catalyst particles. This result is in contrast to the preferred treatment for **Pt/L** catalysts in which a calcination before reduction is required to achieve high **dispersions**[21-23]. The higher activity observed with a slower rate of heating is consistent with the results of other **studies**[8, 9].

In a related **investigation**[11], it was shown that increasing the amount of tin relative to platinum on K-L-zeolite above a **1:2.5 Pt/Sn** ratio, marginally increases the dehydrogenation selectivity, but at the expense of decreased catalyst activity and stability. The results of this study **confirm** those results (see Figures 5-3 to 5-6). If the Sn content is too high, then the activity decreases significantly. In terms of selectivity, however, the Sn content cannot be too low or the catalyst is not highly selective (see Figure 5-8). The selectivity of the catalyst is also reduced if acidity is introduced (see Figure 5-2). If the catalyst is less selective, it will also be less stable. The TPO results show that the addition of Sn improves the resistance of the K-L-zeolite-supported Pt catalysts to the formation of coke during reaction at 873 K (Figure 5-17 and Table 5-3). In addition, Table 5-1 shows that the higher coke content blocks a higher percentage of sites for CO adsorption on the **Pt/K-L** catalyst than on the **Pt/Sn/K-L** catalysts. Tin improves the resistance of the catalysts to coking by reducing the Pt ensemble size, thus preventing the undesired reactions which lead to coke formation.

Although the amount of carbon deposited on the catalyst has an important effect on catalytic activity, it is also important to address the location of the carbon (e.g., whether carbon is on the active sites or on the support) [24]. It has been shown that the lower temperature peaks in TPO spectra generally correspond to carbon on Pt, while the higher temperature peaks correspond to carbon on the **support**[15, 17, 24-26]. Liwu *et al.* [17] studied carbon deposition on **Pt/Al₂O₃** and **Pt/Sn/Al₂O₃** after the dehydrogenation of n-butane. They observed that Sn decreased the ratio of the carbon deposited on the metal to the total carbon deposited. In agreement with this behavior, it has been observed in the studies herein, that the addition of Sn decreases the amount of carbon associated with Pt on both the silica- and L-zeolite-supported Pt catalysts. In addition, the CO

uptakes before and after reaction (see Table 5- 1) indicate that fewer sites are lost on the catalyst as the Sn content is increased.

It has been suggested that Sn transports coke from the active sites to the support on **Pt/Sn/alumina catalysts**[17, 27, 28]. Lieske *et al.* [27] proposed a drain-off mechanism to explain the stabilizing effect of Sn on **Pt/alumina** catalysts. The presence of Sn decreases the size of the surface Pt ensembles so that the hydrocarbon cannot readily form multiple carbon-metal bonds. Because the adsorbed species is attached less strongly to the metal surface, it is more mobile and can more easily migrate to the support. This effect is evident by the change in the ratio of the peak heights in the TPO spectra with the addition of Sn to the catalysts.

The ability of Sn to improve the resistance of the Pt catalyst to carbon accumulation becomes more evident when the reaction is run with an isobutane feed in the absence of feed hydrogen. In the absence of hydrogen, carbonaceous species can accumulate on the surface of the catalyst and block the active sites. In agreement with this behavior, the TPO results shown in Figure 5-19 and Table 5-3 indicate higher levels of coke after reaction in the absence of hydrogen at 798 K compared to reaction in the presence of hydrogen at 873 K. A **Pt/L** catalyst deactivates to near zero conversion in minutes (see Figure 5-20), a 1: 1.4 **Pt/Sn/L** catalyst deactivates to essentially zero conversion in 4-5 hours on stream, while the highly selective 1:2.5 **Pt/Sn/L** catalyst maintains over 20% conversion (equilibrium conversion for these conditions is 42%) for 20 hours on stream in isobutane at 798 K in the absence of feed hydrogen (see Figure 5-16). The TEM results showed that little, if any, particle agglomeration occurs during the reaction at 798 K in the absence of hydrogen and so coking is the main mechanism of deactivation. In the presence of hydrogen the stability of the catalyst is better but the activity will be lower because the reaction is negative order in hydrogen (see Figure 5-14). Hydrogen is produced by the dehydrogenation reaction and the reactor configuration can affect the product stream (see Figure 5- 15).

The deactivation studies on the silica catalysts indicate that K, as well as Sn, improve the resistance of the catalyst to carbon deposition (see Figure 5-19 and Table 5-3). As well as decreasing the size of the surface Pt ensembles, K may also hinder the dehydrogenation of adsorbed species. It has been shown that the addition of K to **Pt/Sn/silica** decreases the CO uptake but increases the **H₂ uptake**[29]. Barbier [30] has shown that the addition of K to alumina catalysts decreases the peak temperature in the TPO spectrum by 100 K, indicating that the carbon formed on the K-modified surface is more weakly bound. It is possible that the ion-exchanged potassium present within the L-zeolite may also help to suppress the formation of highly dehydrogenated carbonaceous species. This behavior may at least partially explain why the peaks in the TPO spectrum are at lower temperatures for the **Pt/K-L** sample compared to the **Pt/silica** catalyst.

It has been shown in previous studies that **Pt/L** catalysts are resistant to coking during reactions with hydrocarbons such as n-hexane[14, 3 1,321. In our experiments, the **Pt/K-L** catalyst accumulates much less carbon than the **Pt/silica** catalyst, but the isobutane conversion over **Pt/K-L** decreases to essentially zero within several minutes on stream. The L-zeolite support has unidimensional pores with diameters of 0.7 1 nm, and our isobutane adsorption studies (see Table 5-4) indicate that some of the pores become blocked during isobutane dehydrogenation over **Pt/K-L** in the absence of hydrogen. Thus, the coke that forms on the **Pt/K-L** catalyst may be present near the pore mouths, and thereby block Pt sites deeper within the pores of the L-zeolite from reaction with isobutane. In the aforementioned studies with n-hexane, the reaction was conducted in the presence of hydrogen, with hydrogen to hydrocarbon ratios between 5.5 and 8[14, 31, 32]. In agreement with these previous studies, the **Pt/K-L** catalyst maintains its activity for isobutane conversion in the presence of hydrogen, although this catalyst is not selective for isobutene production (see Figures 5-8 and 5-9). Hydrogen probably removes the highly dehydrogenated carbonaceous species from the surface as by-products (e.g., hydrogenolysis products), such that the

selectivity of **Pt/K-L** to isobutene is low. On the **Pt/Sn/K-L** catalysts, the deactivation profiles were similar with and without hydrogen. This behavior indicates that the presence of Sn is sufficient to prevent the formation of highly dehydrogenated surface species that lead to the formation of coke and other unwanted by-products.

The results of the 16 h reduction and the deactivation studies indicate that the extent of **Pt/Sn** interaction increases during the course of the reaction. After a long reduction in H_2 , the activity of the catalyst has decreased (see Figures 5-11 and 5-12). In fact, the catalysts exhibited a similar rate of isobutene production after treatment in hydrogen for 16 h as catalysts that were treated for 1 h in hydrogen and were subsequently exposed to hydrogen and isobutane for 16 h. Mössbauer spectroscopy has shown that Pt and Sn form alloy clusters in L-zeolite, but the majority of the Sn is present as Sn^{2+} [5]. Studies on **Pt/Sn/alumina** [19,331] and **Pt/Sn/NaY-zeolite**[13] have shown that the proportion of tin in metallic particles increased with metal particle size. Furthermore, Merlen *et al.* [19] have suggested that metallic tin cannot be stabilized in small particles. Thus, the Sn^{2+} in the **Pt/Sn/K-L-zeolite** catalyst may slowly become reduced in the presence of hydrogen during isobutane dehydrogenation at 873 K and migrate to the **Pt/Sn** alloy particles, resulting in surface enrichment with metallic Sn and the loss of accessible Pt sites. Thus, although the presence of Sn improves the resistance of the catalyst to coke formation, it may adversely affect the sintering of the catalyst, since larger particles were visible on the **Pt/Sn/K-L** catalysts compared to the **Pt/K-L** catalyst after reaction at 873 K. The 24 h He treatment at 873 K (see Figure 5-13) indicates that some activity is lost in a non-reducing atmosphere which suggests that particle sintering occurs at high temperatures. TEM analysis of catalysts held at 873 K for extended periods (over 16 h) in He or H_2 (no iC_4H_{10}) indicates that sintering of the metal particles does occur.

The regeneration scheme that was successful for the **Pt/Sn/L** catalyst required that the catalyst be reduced for 16 h prior to the initial exposure to isobutane and after each regeneration (see Figures 5-21 and 5-22). As discussed above, a longer reduction leads to increased Pt and Sn interaction but also some metal sintering. The regeneration in oxygen removes the carbon and also oxidizes the Sn, destroying the **Pt/Sn** alloy, which may have become highly surface enriched in Sn over the course of the reaction. A long reduction, therefore is needed to reform the **Pt/Sn** alloy. It is unknown whether this regeneration method redispersed the metals that had agglomerated on the external surface of the catalyst.

In summary, the **Pt/Sn/K-L-zeolite** UW Dehydrogenation Catalyst is a highly selective catalyst for isobutane dehydrogenation to isobutene. Through this project our research team has been able to understand the interactions between the components of the catalyst - namely, Pt, Sn, K and L-zeolite. Sn is necessary to make the catalyst selective by reducing the size of the Pt surface ensembles, thus hindering the competing reactions, such as isomerization, hydrogenolysis and coking, which require large Pt ensembles; K neutralizes the support; and L-zeolite provides a support in which the Pt can be highly dispersed by depositing the metals within the pores. Typical industrial conditions employ hydrogen in the feed stream to minimize the amount of coking. In the presence of hydrogen, however, the equilibrium dehydrogenation conversion is reduced and thus high temperatures are employed to maintain the conversion. At 873 K in a 2:1 hydrogen to isobutane feed stream, the catalyst deactivates by coking, metal agglomeration and surface enrichment of the Pt particles with Sn. It has been found, however, that **Pt/Sn/L** catalysts can be operated for isobutane dehydrogenation at 798 K in the absence of feed hydrogen and maintain a reasonable conversion, provided that the catalyst is highly selective. At these conditions, the temperature is low enough that metal agglomeration and Sn enrichment are significantly suppressed. Without hydrogen, the catalyst is more susceptible to coking but if the catalyst is highly selective, excessive coking does not occur. The coking that does occur is much easier to reverse than the metal sintering which occurs at higher temperatures. Thus, running the reaction in isobutane only at 798 K is very feasible for **Pt/Sn/L-zeolite** catalysts. Based on the results of this

study, this catalyst may also be applicable for the selective dehydrogenation of higher **paraffins** to olefins. Further study of this application is being undertaken in our laboratory.

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