

## Producing Hydrogen Catalytically from Liquid Organic Hydride

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### Introduction

Hydrogen has been proposed as a clean energy carrier helping to alleviate environmental pollution caused by fossil fuels. The future of this energy source is primarily dependent on the development of suitable technology for safe and cost effective storage and transport. Over the past decades, hydrogen storage options explored have been included hydrogen compression, liquefaction, adsorption in metal hydrides, cryogenic storage with hydrogen adsorbing materials.

Here we explore liquid organic hydrides (i.e. methylcyclohexane) for hydrogen storage as a promising alternative providing the simple, safe and feasible handling of hydrogen. This energy storage system is based on a highly selective reversible hydrogenation-dehydrogenation reaction. Firstly, the hydrogen is chemically stored into an organic carrier through a catalytic hydrogenation reaction. When the demand of energy exists, the hydrogen is extracted by a highly selective dehydrogenation reaction and fed into fuel cells to generate electricity. Environmentally, this system maintains a closed carbon cycle drastically reducing chemical and thermal pollution. Economically, the system does not require heavy capital investment as the existing energy infrastructure is compatible with it. Socially, dealing with liquid organic hydride is not that different from gasoline we use today. Technically, we have linked previously this system to a SOFC for potential application on a vehicle and are currently underway developing a PEMFC stack to allow exploitation in stationary production of energy.

This paper will deal with the development of a catalyst that has high dehydrogenation activity, high product selectivity toward aromatics, rapid elimination of hydrogen from reaction surface to shift chemical equilibrium toward product formation, fast desorption of aromatic product to free the active sites for reactant molecules, and low deactivation rate. A detailed study of the dehydrogenation kinetics of methylcyclohexane (MCH), of which there is much discussion in literature, is also reported.

### Materials and Methods

Methylcyclohexane (MCH) is dehydrogenated to toluene using mono and bi-metallic Pt catalysts. The reaction is carried out using a fixed bed micro-reactor hydrogenation-dehydrogenation unit, which has the ability to operate at relatively elevated temperature and pressure and the flexibility of operating at various liquid hourly space velocities (Table 1). Samples collected are analyzed by a GC and a GC-MS to determine the activity and selectivity.

Various Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalysts have been prepared to optimize the catalytic parameters, different synthesis aspects have been investigated such as metal (active-phase) composition, metal loadings, metal distribution profile, support type, preparation technique, and pretreatment procedures.

Table 1: Range of operating conditions

Operating Variable	Unit	Value Range
Temperature	°C	340 - 450
Pressure	Bar	1 - 9
MCH flow rate	ml/hr	7.5 - 30
H <sub>2</sub> flow rate	Nl/min	0 - 800

### Results

The debate around MCH dehydrogenation kinetics is concerned with the reaction mechanism, the rate controlling step, and the rate expression. Work has been carried out on MCH dehydrogenation using various catalysts and operating conditions in an attempt to shed more light on these issues. Initial efforts, using a generalized power law model has been helpful and some results are illustrated in Figure 1. Some of the information obtained from that model are extremely valuable and provide clues as to the form of function needed in developing more mechanistic model. We are currently developing mechanistic models for MCH dehydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub>. These mechanistic models should be more practical and useful as they provide two major advantages: (1) the rate equation can be extrapolated more accurately beyond the range of experimental data (2) it provides insight into the reaction mechanism.

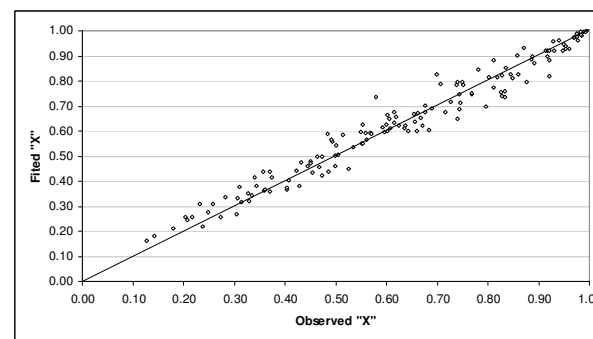


Figure 1: Graphical comparison between the fitted and observed conversions for the general power law model (Pt<sub>1.0</sub>/γ-Al<sub>2</sub>O<sub>3</sub>)

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