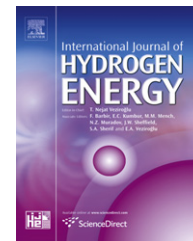


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Dehydrogenation of methylcyclohexane over Pt/V₂O₅ and Pt/Y₂O₃ for hydrogen delivery applications

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ABSTRACT

Dehydrogenation of methylcyclohexane (MCH) for hydrogen transportation and delivery application was carried out over 3 wt% Pt/V₂O₅ and 3 wt% Pt/Y₂O₃ catalyst. The catalytic activity was tested using a spray-pulse mode of reactor. Effective dehydrogenation of MCH under spray-pulse mode of reactant injection was observed. In terms of hydrogen evolution rate at 60 min from start of reaction the activity of 958 mmol/g/min was obtained at temperature of 350 °C. Nearly 100% selectivity toward hydrogen was obtained. A relatively high conversion of 98% was observed with 3 wt% Pt/Y₂O₃ at 60 min using an advanced spray-pulse reactor system. The catalysts were characterized using x-ray diffraction pattern (XRD), CO-chemisorption metal analysis, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analysis.

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1. Introduction

Use of cycloalkanes such as cyclohexane, methylcyclohexane (MCH), decalin, etc. has been reported for efficient hydrogen storage and transportation [1]. A reaction pair of hydrogenation of aromatics at hydrogen production facility to produce cycloalkanes and subsequent dehydrogenation of cycloalkanes at fueling station would help in delivering hydrogen to fuel cell vehicles [2]. Having relatively higher hydrogen storage capacity of 6–8 % wt and 60–63 kg/m³ in terms of weight and volume basis is an advantage with cycloalkanes. Besides a high storage capacity, the reaction of dehydrogenation is very selective toward hydrogen and aromatics (condensable) over Pt containing catalysts. The hydrogen delivered using this method therefore is free from any contaminants including CO or CO₂ [2]. Among the cycloalkanes MCH was considered as a potential candidate in this study due to two

major reasons. The first was that the dehydrogenated product of MCH is toluene which is safer in health impact point of view as compared to benzene a product of cyclohexane dehydrogenation. The second reason was MCH has relatively higher capacity of hydrogen storage.

While using Pt as a catalyst for dehydrogenation reactions a few important aspects need to be considered for the catalyst's design [3,4]. These include oxidation state of Pt, its interaction with support and with second metal in case of bimetallic catalyst [2]. The interaction with support or other metal is due to hydrogen spillover, reverse spillover or surface migration [2]. Literature reports metal oxides and perovskites can be good option for several catalytic reactions [5]. Exploring the role of support we have earlier reported the dehydrogenation of MCH over Pt supported on various metal-oxides namely, La₂O₃, Al₂O₃, CeO₂, MnO₂, TiO₂, Fe₂O₃ and ZrO₂ [3]. Use of metal oxides as support promotes the activity and

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selectivity through strong metal support interaction. It has been reported that hydrogen spillover phenomenon has been observed in materials such as MoO_3 and WO_3 [6]. The observed hydrogen spillover in metal oxides is attributed to the favorable thermodynamics and the small energy barriers of H-migration from catalyst to the substrate and the subsequent proton diffusion in bulk lattice derived from the massive H-bonding network intrinsic to these materials. A mechanism that invokes high proton mobility cannot account for spillover in carbon based materials because a similar H-bonding environment does not exist [6].

The unsteady-state conditions for maintaining a high temperature of the catalyst's surface would favor the endothermic reaction of dehydrogenation [7]. Accordingly use of super-heated film [8] and spray-pulsed reactors [2] have been reported for creating unsteady-state reaction conditions on the surface of the catalysts. In this heterogeneous system wherein a liquid reactant such as MCH is used and the catalyst is solid the contact between reactant and catalysts is rather difficult. If the MCH is fed to the reactor in liquid phase in a packed bed reactor, the catalyst surface temperature is limited to the boiling point of the reactant under liquid pool conditions. If the evaporation of reactant occurs and reaches to the catalyst's bed in vapor phase, the contact of the reactant molecule with catalyst surface is limited by the diffusion through a boundary-layer between the catalysts and gas phase [7]. Creating alternate wet and dry conditions on the

surface of the catalyst using spray-pulsed injection of the reactant is reported as a solution for the same [9]. When the reactant is fed in the form of a pulse of atomized spray over heated catalysts for a short period generally in the range of 1–10 ms then the reactant gets in contact with surface of the catalysts and evaporates on the surface. The evaporation of the reactant on the catalyst's surface produces a dense vapor phase in the vicinity to catalyst. A next pulse of reactant is injected after a definite interval by controlling the injection frequency in the range of 0.3–1 Hz. This interval before the arrival of next pulse provide time for complete reaction and removal of reactant/product from the surface of the catalysts. The phenomena can be considered as creating alternate wet-dry conditions on the surface of the catalysts. The wet condition referred herein is with respect to dense vapor phase formed near to catalysts surface.

It is well reported that vanadium(v) in V_2O_5 on exposing to hydrogen at 400°C reduces to lower oxidation state [10]. V_2O_5 is an acidic oxide wherein vanadium ions are present in distorted octahedrons. They become oxygen deficient on reduction with hydrogen and carbon monoxide. Thus, this phenomenon enhances the removal of oxygen and increases the hydrogen evolution [10]. Y_2O_3 is an active catalyst for dehydrogenation reactions. Considering these aspects, V_2O_5 and Y_2O_3 were chosen as supports for Pt catalysts in this study. We report herewith enhanced hydrogen evolution rates during dehydrogenation of MCH over $\text{Pt}/\text{Y}_2\text{O}_3$ and $\text{Pt}/\text{V}_2\text{O}_5$. The

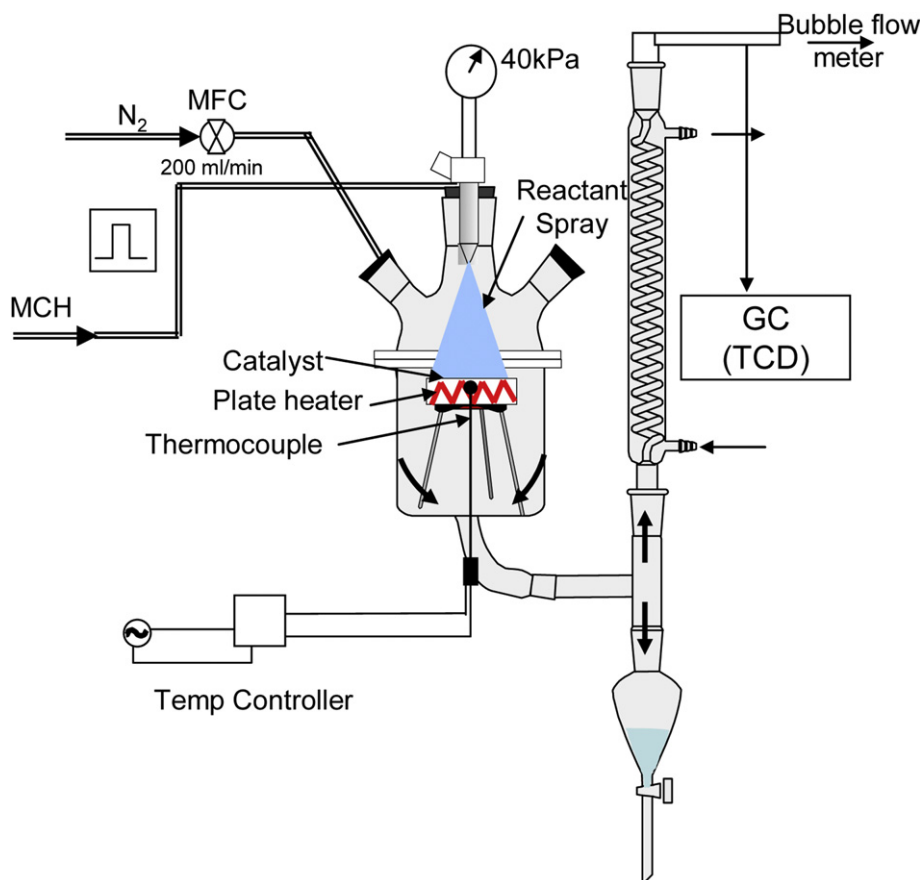


Fig. 1 – Details of experimental setup including a spray-pulsed reactor equipped with injection nozzle, plate type heater, frequency controller and product separation by condenser.

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