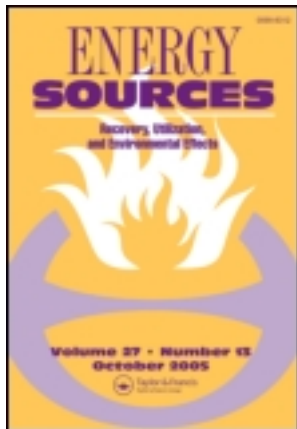


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The Catalytic Dehydrogenation of Methylcyclohexane over Monometallic Catalysts for On-board Hydrogen Storage, Production, and Utilization

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Abstract *A methylcyclohexane-toluene-hydrogen system employs methylcyclohexane as a recyclable organic hydride for the on-vehicle production, storage, and utilization of hydrogen gas. The success of the methylcyclohexane-toluene-hydrogen system lies in the success of the dehydrogenation reaction of methylcyclohexane. A highly active, selective, and stable catalyst is required to carry out the dehydrogenation reaction. A range of commercial and in-house development catalysts are studied for the dehydrogenation of methylcyclohexane. The catalytic data is compared with the study in the literature. Alumina-supported Ni metal catalyst and Pt/ β -zeolite show poor activity and selectivity towards toluene. Pt/ Al_2O_3 in-house development catalysts show reliable results of activity, selectivity, and stability.*

Keywords dehydrogenation, methylcyclohexane, MTH system, Pt catalysts, recyclable organic hydride

1. Introduction

In the current scenario of the energy demands, nations require alternative energy supplies that are not only sustainable and economical, but benign to the environment. One such solution is to use hydrogen as fuel in an internal combustion engine or a fuel cell. Hydrogen is a very clean fuel producing nothing other than water. However, hydrogen is not available naturally and must be produced by refining some hydrogen source. Also gaseous in nature and with extremely a low critical temperature (-253°C), it has problems with transportation and storage, especially for on-board hydrogen utilization (Tarasov et al., 2007). Thus, a successful transportation system based on the hydrogen economy is dependent entirely upon the practical, safe, and economical production, storage, and transportation of hydrogen and its appropriate utilization to produce the required power. Organic hydrides, such as methylcyclohexane (MCH), are promising as recyclable hydrogen precursors. MCH is stable, relatively involatile, contains high hydrogen mass (6.2 wt%), and its product when dehydrogenated, toluene, is capable of undergoing easy hydrogenation to return back to MCH. The methylcyclohexane-toluene-hydrogen system is frequently known as MTH system (Sultan and Shaw, 1975; Taube et al., 1983; Touzani et al., 1984; Cresswell et al., 1984; Manser Sonderer, 1992; Chaouki and Klvana, 1994; Maria et al., 1996; Schildhauer et al., 2001; Bustamante et al., 2005; Cresswell

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and Metcalfe, 2006; Clot et al., 2007; Tsakiris, 2007; Alhumaidan, 2008; Yolcular and Olgun, 2008a, 2008b). The production, storage, and utilization of hydrogen for on-board purposes can be successfully viewed in the MTH system. Vehicles are filled with MCH fuel instead of conventional fuel, such as gasoline. The dehydrogenation reactor installed within the vehicle itself produces hydrogen and toluene when charged with the reactant MCH. The hydrogen so produced can be used in an internal combustion engine or in a stack of fuel cells to generate enough power that can be effectively utilized to move the vehicle around. The by-product toluene is sent to a storage tank within the vehicle. On the filling station, toluene is pumped out while MCH is pumped in to recharge the vehicle for further travel. From the filling station, the tanker that brings MCH to the filling station takes toluene away to the hydrogenation plant where it is hydrogenated back to MCH. Hydrogen required for the hydrogenation is produced by splitting water molecules using any available, economical, and sustainable source like the sun. It is important to note that the existing motor fuel infrastructure for transportation and dispensation of liquid fuel (MCH) can effectively be utilized. The heart of the MTH system is the on-board catalytic dehydrogenation of MCH that requires an efficient dehydrogenation catalyst. The acceptable conversion, high selectivity, and long life are the challenges to the most suitable catalyst required for the MTH system. In this study, an effort is made to find a suitable catalyst and a number of commercial and in-house monometallic catalysts are analyzed for their activity, selectivity, and stability. Table 1 shows the list of the catalysts, with their relevant physical properties, that are used in the present study.

2. Experimental

Experiments were performed in a conventional fixed bed tubular reactor. Methylcyclohexane was obtained from Sigma-Aldrich and had a purity of 99 wt%. The dehydrogenation experiments were performed under integral conditions at varying operating conditions of space time, reactor wall temperature, and feed compositions. The reaction products were analyzed by gas chromatography (GC) technique. The Varian 3400 gas chromatograph fitted with a flame ionization detector was employed for this purpose. Two columns were used for the analyses of the products: in one case, a non-polar capillary column (BP-5: 5% phenyl and 95% dimethylpolysiloxane) and in other case, fused silica column (CP-Sil PONA CB: 100% dimethylpolysiloxane). A typical GC method employed is as follows. Each time 2.0 μL volume of the sample was injected. The injection temperature was 250°C. Initial column temperature was 40°C and was maintained for 7 min. A 3°C/min ramp was applied till the temperature reached 120°C. A slight hold time was given here and then a final ramp of 15–20°C/min was provided to reach 220°C. A hold time of 20–30 min, if necessary, was applied at this temperature for heaviers. All in-house development catalysts, except 20.0 wt% Ni/Al₂O₃ and 1.0 wt% Pt/ β -zeolite (Si/Al molar ratio = 164.3), were prepared a using wet impregnation technique. The procedure for the wet impregnation may be found in Usman (2010). Ni/Al₂O₃ catalyst was prepared by dry impregnation taking twice as much water as the total mass of the support taken. Pt/ β -zeolite, however, was prepared by an ion exchange method. Hexachloroplatinic acid was used with alumina support, while tetraamine platinum chloride was used with β -zeolite.

3. Results and Discussion

3.1. Activity

Figure 1 and Table 2 show the activities of the catalysts used in the present study and

Table 1
Catalysts used in the study

Catalyst	Assay	Supplier	Dispersion type	Method of preparation	BET, m ² /g	Pore volume, cm ³ /g	Median pore diameter, Å	Reference
CAT-A	0.3 wt% Pt/Al ₂ O ₃	Commercial	Egg-shell	—	—	—	—	This study
CAT-B	x wt% Pt/θ-Al ₂ O ₃	Commercial	Egg-shell	—	—	—	—	This study
CAT-C	1.0 wt% Pt/γ-Al ₂ O ₃	Development	Uniform	Wet impregnation	208	0.58	69	This study
CAT-D	1.0 wt% Pt/θ-Al ₂ O ₃	Development	Uniform	Wet impregnation	99.1	0.84	291.3 ^a	Alhumaidan (2008)
CAT-E	20.0 wt% Ni/γ-Al ₂ O ₃	Development	Uniform	Dry impregnation	208	0.58	69	This study
CAT-F	1.0 wt% Pt/β-zeolite	Development	Uniform	Ion exchange	509.8	0.38	33.3 ^a	This study
CAT-G	1.0 wt% Pt/γ-Al ₂ O ₃	Commercial	Uniform	—	302.3	0.51	67.2 ^a	Tsakiris (2007)
CAT-H	0.5 wt% Pt/γ-Al ₂ O ₃	Commercial	Egg-shell	—	124.6	0.35	110.3 ^a	Alhumaidan (2008)
CAT-I	0.3 wt% Pt/γ-Al ₂ O ₃	Development	Uniform	Wet impregnation	220	0.62	70 ^a	Tsakiris (2007)
CAT-J	0.3 wt% Pd/γ-Al ₂ O ₃	Development	Uniform	Wet impregnation	220	0.62	70 ^a	Alhumaidan (2008)
CAT-K	0.1 wt% Pt/γ-Al ₂ O ₃	Commercial	—	—	172.7	0.58	131.4 ^a	Alhumaidan (2008)
CAT-L	0.3 wt% Pt/α-Al ₂ O ₃	Development	Uniform	Wet impregnation	14.2	0.05	133	Tsakiris (2007)
CAT-M	1.0 wt% Pt/α-Al ₂ O ₃	Development	Uniform	Wet impregnation	14.3	0.05	127.7	Tsakiris (2007)

^aAverage pore diameter.

x: No data available.

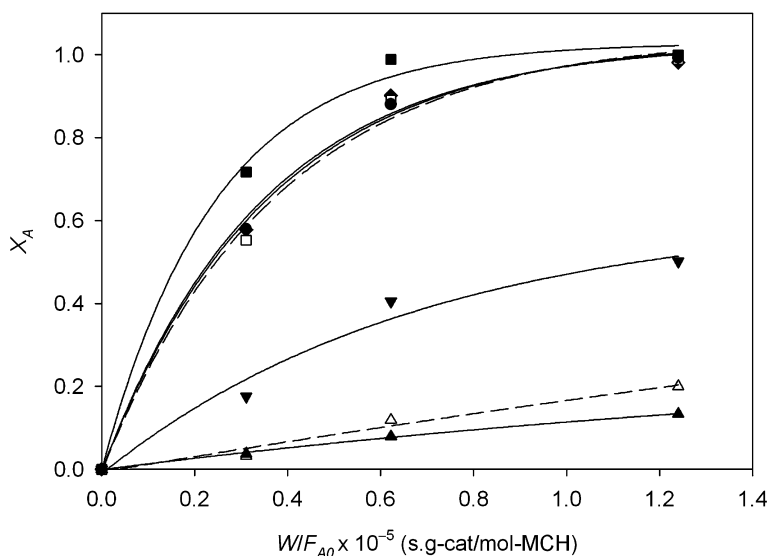


Figure 1. Comparative study of the effect of space time on the conversion of MCH for the range of in-house development and commercial catalysts. $T_w = 380^\circ\text{C}$, $p = 1.013$ bar, H_2 to MCH ratio = 8.4 (CAT-A: Δ ; CAT-B: \blacktriangle ; CAT-J: \blacktriangledown ; CAT-I: \blacksquare ; CAT-H: \blacklozenge ; CAT-G: \square ; CAT-C: \bullet).

compare with the previous study in the field carried out by Alhumaidan (2008). Figure 2, on the other hand, presents hydrogen production rates as a function of space time. Here, the activity of the catalyst means the conversion of methylcyclohexane, which is defined as the change in moles of MCH per mole of MCH fed in the reactor. Commercial catalysts CAT-A and CAT-B and in-house development catalyst $\text{Ni}/\text{Al}_2\text{O}_3$ (CAT-E) showed poor activities. In-house development catalysts, 1.0 wt% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (CAT-C) and 1.0 wt% $\text{Pt}/\theta\text{-Al}_2\text{O}_3$ (CAT-D) showed the highest and comparable activities and corresponding highest hydrogen production rates, while 1.0 wt% $\text{Pt}/\beta\text{-zeolite}$ (CAT-F) showed moderate activities. Comparing the results to the study performed by Alhumaidan (2008), it is shown that the Pt metal is a much better catalyst for the dehydrogenation of MCH than the Pd and Ni metals. Increasing the loading of Pt on the support from 0.3 wt% to 1.0 wt% had a slight but negative effect on the activity of the catalyst. This may, however,

Table 2

Comparative activity and selectivity for in-house development catalysts
 $W/F_{A0} = 0.62 \times 10^5 \text{ s} \cdot \text{g-cat/mol MCH}$, $T_w = 360^\circ\text{C}$, $p = 1.013$ bar,
 H_2 to MCH molar ratio = 1.0

Catalyst	Assay	MCH conversion, X_A	By-product selectivity, %
CAT-C	1.0 wt% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$	0.92	0.63
CAT-D	1.0 wt% $\text{Pt}/\theta\text{-Al}_2\text{O}_3$	0.91	0.10
CAT-E	20.0 wt% $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$	0.31	7.87
CAT-F	1.0 wt% $\text{Pt}/\beta\text{-zeolite}$	0.73	22.48

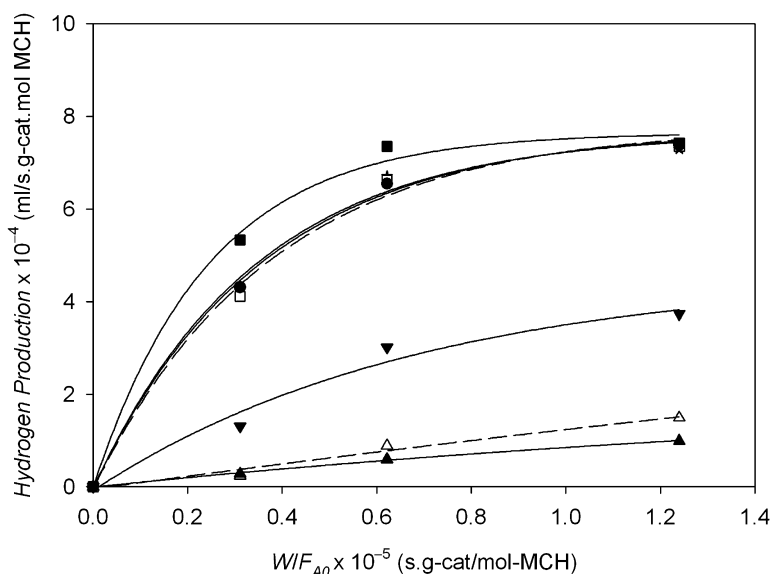


Figure 2. Hydrogen production rate for various catalysts as a function of space time. $T_w = 380^\circ\text{C}$, $p = 1.013$ bar, H_2 to MCH ratio = 8.4 (CAT-A: Δ ; CAT-B: \blacktriangle ; CAT-J: \blacktriangledown ; CAT-I: \blacksquare ; CAT-H: \blacklozenge ; CAT-G: \square ; CAT-C: \bullet).

be explained when considering metal dispersion and the orientation of the metal atoms exposed to the surface. Comparing 1.0 wt% Pt/ γ - Al_2O_3 (CAT-C) and 1.0 wt% Pt/ β -zeolite (CAT-F), alumina support was observed to be a much better support for the dehydrogenation of MCH.

3.2. Selectivity

The success of the MTH system lies in a high selectivity of methylcyclohexane towards toluene. Any parallel reaction, such as isomerization, will lead to a potential leakage in the recyclable organic hydride and will require makeup toluene. The dehydrogenation reaction under all the conditions and with all the catalytic samples, except Ni/ Al_2O_3 (CAT-E) and Pt/ β -zeolite (CAT-F), was found to be very clean and toluene was observed to be the only major product. Upon analyzing the samples, a number of byproducts were identified. The somewhat important byproducts detected were benzene, cyclohexane, n-heptane, dimethylcyclopentanes, ethylcyclopentane, 4-methylcyclohexene, naphthalenes, fluorenes, and biphenyls. Figure 3 and Table 2 show the selectivity of total byproducts formed during the course of MCH dehydrogenation. Figure 3 is the graphical relationship between the total selectivity of the byproducts and the space time, W/F_{A0} . Total byproduct selectivity is defined as the difference between the moles of MCH consumed per mole of MCH fed and moles of the major product, toluene, formed per mole of MCH fed. So, the smaller the number the more selective is the catalyst. Ni/ Al_2O_3 and Pt/ β -zeolite were found to be least selective with total byproducts selectivity surpassing 7.0%. Benzene is found to be the major byproduct with Ni catalyst, while ring-closed products (ethylcyclopentane and dimethylcyclopentanes) were found to be major byproducts over zeolite catalyst. The remaining catalysts had somehow comparable selectivities. The presence of a large amount of benzene with supported nickel catalyst shows that the toluene hydrodealkylation reaction may be the dominant side reaction. Grenoble (1979),

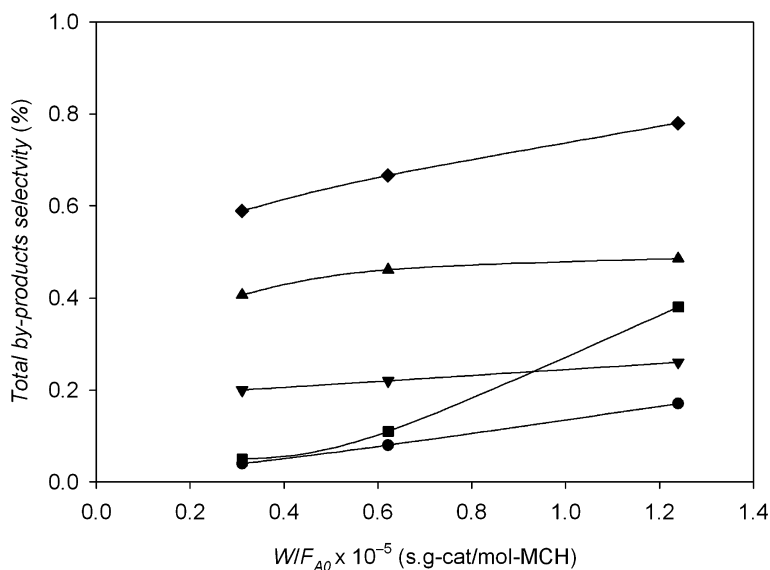


Figure 3. Effect of space time on the total selectivity of the by-products. Total selectivity of the by-products is defined as the conversion of MCH less the total toluene formed per mole of MCH fed. $T_w = 380^\circ\text{C}$, $p = 1.013$ bar, H_2 to MCH ratio = 8.4 (CAT-B: ▲; CAT-J: ▼; CAT-I: ■; CAT-H: ●; CAT-C: ◆).

while comparing various metals loaded on $\gamma\text{-Al}_2\text{O}_3$, has found that the Ni metal is a much better catalyst than Pt metal for hydrodealkylation of toluene to benzene. Although the Si/Al ratio of β -zeolite is quite high and it has low acidity, the presence of ring-closed products explains the active acidic function of the zeolite support. Pt supported over alumina is, therefore, found as the selective catalyst for the MTH technology. Corma et al. (1979) have observed the formation of dimethylcyclopentanes over 0.5 wt% Pt-NaY zeolite while Al-Sabawi and de Lasa (2009) have observed an appreciable selectivity of ring-closed products while working on fluid catalytic cracking commercial catalysts (USY, Ultrastable Y-zeolites).

3.3. Stability

A highly active and highly selective catalyst with active and/or selective life of only a few hours or days is of no use for the MTH system, where the motorists expect the catalyst to work for months without any regeneration. In the long-term deactivation tests, catalysts were subjected to pure methylcyclohexane at atmospheric pressure and 380°C reactor wall temperature with W/F_{A0} equal to $6.22 \times 10^5 \text{ s} \cdot \text{g-cat/mol MCH}$ (severe conditions of experimentations as no hydrogen in the feed and the highest conversion was expected). The long-term deactivation was performed for a maximum of 240 h. The results of deactivation for the selected catalysts are plotted in Figure 4. While 1.0 wt% Pt/ θ - Al_2O_3 showed exceptional stability, Pt/ β -zeolite, on the other hand, showed poor resistance to deactivation and conversion of MCH dropped from 84% to 20% within 45 h. Including the literature study performed by Alhumaidan (2008) and Tsakiris (2007), poor stability was acquired by most of the catalysts at the end of the 240-h period. Commercial 1.0 wt% Pt/ Al_2O_3 catalyst showed a rapid decline in activity in the initial

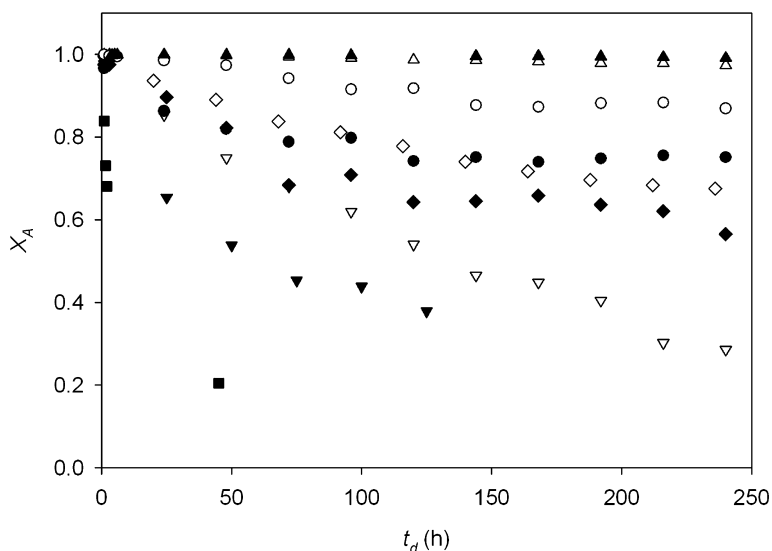


Figure 4. Effect of time on-stream on the deactivation behavior of the catalysts. $W/F_{A0} = 1.24 \times 10^5 \text{ s} \cdot \text{g-cat/mol MCH}$, $T_w = 380^\circ\text{C}$, $p = 1.013 \text{ bar}$, and pure MCH feed (CAT-M: ∇ ; CAT-L: \blacktriangledown ; CAT-H: \bullet ; CAT-G: \diamond ; CAT-K: \blacklozenge ; CAT-C: \triangle ; CAT-I: \circ ; CAT-D: \blacktriangle ; CAT-F: \blacksquare).

200 h and then showed a rather stable character. Only the in-house monometallic Pt metal catalysts showed acceptable endurance. Although 0.3 wt% Pt/ Al_2O_3 might have better dispersion of platinum metal clusters, due to less loading, it might have fewer active sites remaining after initial deactivation. In-house 1.0 wt% Pt/ Al_2O_3 catalysts showed extraordinary stability and the drop in conversion after 240 h was virtually negligible.

4. Conclusion

Alumina-supported Ni metal catalyst and Pt/ β -zeolite showed poor activity and selectivity towards toluene. Benzene was found to be the major byproduct over Ni/ Al_2O_3 catalyst in the dehydrogenation of MCH, which shows Ni/ Al_2O_3 to be a better catalyst for the hydrodealkylation. Pt/ β -zeolite showed a marked drop in selectivity with effective parallel isomerization of MCH to ethylcyclopentane and dimethylcyclopentanes. Pt containing catalysts with alumina support showed reliable results of activity, selectivity, and stability. Therefore, 1.0 wt% Pt/ Al_2O_3 catalysts being more stable than 0.3 wt% Pt/ Al_2O_3 , although more costly due to increased Pt contents, are recommended for the MTH technology.

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References

Alhumaidan, F. S. 2008. *Hydrogen storage in liquid organic hydrides: Producing hydrogen catalytically from methylcyclohexane*. Ph.D. Thesis. The University of Manchester, Manchester, UK.

- Al-Sabawi, M., and de Lasa, H. 2009. Kinetic modeling of catalytic conversion of methylcyclohexane over USY zeolites: Adsorption and reaction phenomena. *AIChE J.* 55:1538–1558.
- Bustamante, G. V. S. C., Swesi, Y., Pitault, L., Meille, V., and Heurtaux, F. 2005. A hydrogen storage and transportation mean. *International Hydrogen Energy Congress and Exhibition*, IHEC, Istanbul, Turkey, July 13–15.
- Chaouki, J., and Klvana, D. 1994. Influence of the deactivation of an industrial Pt-Sn/Al₂O₃ catalyst on the performance of the dehydrogenation reactor. *Chem. Eng. Sci.* 49:4639–4646.
- Clot, E., Eisenstein, O., and Crabtree, H. 2007. Computational structure-activity relationships in H₂ storage: How placement of N atoms affects release temperatures in organic liquid storage materials. *Chem. Commun.* 2231–2233.
- Corma, A., Cid, R., and Agudo, L. 1979. Catalyst decay in the kinetics of methylcyclohexane dehydrogenation over Pt-NaY zeolite. *Can. J. Chem. Eng.* 57:638–642.
- Cresswell, D. L., and Metcalfe, I. S. 2006. Energy integration strategies for solid oxide fuel cell systems. *Solid State Ionics* 177:1905–1910.
- Cresswell, D. L., Milisavljevic, B., Rippin, D. W. T., and Srivastava, D. 1984. The catalytic production of hydrogen for the use of road vehicles: A status report. *International Chemical Reactor Engineering Conference*, Pune, India, January 9–11.
- Grenoble, D. C. 1979. The chemistry and catalysis of the toluene hydrodealkylation reaction: I. The specific activities and selectivities of group VIIB and group VIII metals supported on alumina. *J. Catal.* 56:32–39.
- Manser Sonderer, R. H. 1992. *Methylcyclohexane dehydrogenation kinetics, reactor design and simulation for a hydrogen powered vehicle*. Ph.D. Thesis. ETH No. 9996. Zürich, Switzerland: Swiss Federal Institute of Technology.
- Maria, G., Marin, A., Wyss, C., Müller, S., and Newson, E. 1996. Modelling and scalup of the kinetics with deactivation of methylcyclohexane dehydrogenation for hydrogen energy storage. *Chem. Eng. Sci.* 51:2891–2896.
- Schildhauer, T. H., Newson, E., and Müller, S. 2001. The equilibrium constant for methylcyclohexane-toluene system. *J. Catal.* 198:355–358.
- Sultan, O., and Shaw, M. 1975. *Study of automotive storage of hydrogen using recyclable chemical carriers*. TEC-75/003. Ann Arbor, MI: ERDA.
- Tarasov, B. P., Lototskii, M. V., and Yartys, V. A. 2007. Problems of hydrogen storage and prospective uses of hydrides for hydrogen accumulation. *Rus. J. Gen. Chem.* 77:694–711.
- Taube, M., Rippin, D. W. T., Cresswell, D. L., and Knecht, W. 1983. A system of hydrogen-powered vehicles with liquid organic hydrides. *Intl. J. Hydrogen Energy* 8:213–225.
- Touzani, A., Klvana, D., and Bélanger, G. 1984. Dehydrogenation of methylcyclohexane on the industrial catalyst: Kinetic study. *Stud. Surf. Sci. Catal.* 19:357–364.
- Tsakiris, D. E. 2007. *Catalytic production of hydrogen from liquid organic hydride*. Ph.D. Thesis. The University of Manchester, Manchester, UK.
- Usman, M. R. 2010. *Kinetics of methylcyclohexane dehydrogenation and reactor simulation for "on-board" hydrogen storage*. Ph.D. Thesis, University of Manchester, Manchester, UK.
- Yolcular, S., and Olgun, Ö. 2008a. Hydrogen storage in the form of methylcyclohexane. *Energy Sources* 30:149–156.
- Yolcular, S., and Olgun, Ö. 2008b. Liquid organic hydrides for hydrogen hydrogen storage. *Energy Sources* 30:309–315.

Nomenclature

F_{A0}	initial molar flow rate of methylcyclohexane, mol/s
p	reaction pressure, Pa
t_d	deactivation time, s
T_W	reactor wall temperature, K
W	weight of a catalyst, kg
X_A	methylcyclohexane conversion