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Ni/Al_2O_3 catalysts and their activity in dehydrogenation of methylcyclohexane for hydrogen production

Sevim Yolcular [*], Özden Olgun

Ege University, Engineering Faculty, Chemical Engineering Department, 35100 Bornova, İzmir, Turkey

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ABSTRACT

Previous results on different catalysts revealed that methylcyclohexane underwent selective dehydrogenation to form toluene and hydrogen. This reaction system is a useful prototype model for similar systems in the chemical process and petroleum refining industries, such as hydrotreating for aromatics reduction, desulfurization, denitrogenation, reforming for aromatics reduction, dehydrocyclization, and fuel processing of liquid hydrocarbons in the generation of hydrogen feed for fuel cells. Dehydrogenation of methylcyclohexane to toluene is a method for hydrogen storage in the form of liquid organic hydrides. The efficiency of the dehydrogenation reactions and the quantity of products depend on the catalyst used. In the case of the dehydrogenation of methylcyclohexane to toluene, a metallic function, usually platinum is required as the catalyst. Although, there were some different catalysts used by former researchers, there was almost no investigation about the use of the nickel catalysts for this reaction. From the economical point of view, more efficient catalysts and reaction engineering methods should be developed for these reactions.

In this work dehydrogenation of methylcyclohexane was performed in a fixed-bed catalytic reactor in the temperature range of 653–713 K on prepared Ni/Al_2O_3 catalysts having 5, 10, 15 and 20 wt.% Ni content. The inlet flowrates of methylcyclohexane and hydrogen to the reactor were changed by keeping one of them constant in order to investigate their effects on this reaction.

1. Introduction

Hydrogen as an energy carrier is environmentally friendly, versatile, and has many potential energy uses, including powering non-polluting vehicles, heating homes and offices, and fueling aircrafts. Various methods have been investigated for hydrogen storage, e.g., natural gas reforming, electrolysis, biomass gasification, photobiology, metal hydrides and inorganic chemical hydrides [1,2].

The dehydrogenation of cyclic hydrocarbons (e.g., methylcyclohexane (MCH)) is another alternative method to store and transport hydrogen. The cyclic hydrocarbons have relatively high hydrogen contents (6–8 wt.%). MCH has 6.2 wt.% hydrogen content and it can be dehydrogenated to produce gaseous hydrogen and a liquid aromatic product toluene (TOL) (Table 1) [3]. Standard formation enthalpies in dehydrogenation of cyclic hydrocarbons are given in Table 2 [3]. For environmental reasons, TOL is a preferable product of a dehydrogenation reaction compared to benzene. Recently, from an environmental point of view, more attention has been focused on MCH as one of the hydrogen storage materials for fuel-cell vehicles. Since MCH is in the liquid state under room temperature and pressure, it can be used to store and to supply hydrogen in a stable form as a hydrogen carrier. Moreover, MCH has higher storage performance than the other candidates, e.g., compressed hydrogen, liquid hydrogen, hydrogen storing metal alloys and carbon materials [4–7].

The dehydrogenation of MCH is a reaction which is reversible, highly endothermic and strongly limited by thermodynamic equilibrium [3]:

$$C_7H_{14} \Leftrightarrow C_7H_8 + 3H_2, \quad \Delta H_{673} = 215.3\,\mathrm{kJ/mol} \tag{1}$$

Because the dehydrogenation of cyclic hydrocarbons is an endothermic reaction and the chemical equilibrium is favorable for dehydrogenation at high temperature, the reactions are performed at high temperature under steady-state operation in gas phase.

It has been found that MCH is adsorbed on metal surfaces in a chair-like configuration which is the stable configuration (D3*d* symmetry) in the gas phase [8].

The choice of nickel is mainly due to its availability and reasonable cost, in comparison with noble metals, e.g., platinum. It

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[*] Corresponding author. Tel.: +90 232 388 4000/2260; fax: +90 232 388 77 76.
E-mail address: sevim.yolcular@ege.edu.tr (S. Yolcular).

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Table 1
Capacity for hydrogen storage

Hydrogen medium	Hydrogen content		bp/mp (°C)
	wt.%	10^{28} (mol m^{-3})	
Liquid H_2	100.0	4.2	−252.9/−259.1
Cyclohexane[a]	7.2	3.3	80.7/6.5
Methylcyclohexane[b]	6.2	2.8	100.9/−126.6
Tetralin[c]	3.0	1.8	207.6/−35.8
cis-Decalin[d]	7.3	3.8	194.6/−43.0
trans-Decalin[d]	7.3	3.8	185.5/−30.4
$LiH + H_2O$[e]	7.8	4.1	−/680
$LiBH_4 + 4H_2O$[f]	8.6	2.4	−/268
$LaNi_5H_6$	1.4	6.2	–
Mm[g]$Ni_{4.5}Al_{0.25}Co_{0.25}H_{3.4}$	1.2	4.8	–

[a] Calculation based on $C_6H_{12} \rightarrow C_6H_6 + 3H_2$.
[b] Calculation based on $C_7H_{14} \rightarrow C_7H_8 + 3H_2$.
[c] Calculation based on $C_{10}H_{12} \rightarrow C_{10}H_8 + 2H_2$.
[d] Calculation based on $C_{10}H_{18} \rightarrow C_{10}H_8 + 5H_2$.
[e] Calculation based on $LiH + H_2O \rightarrow LiOH + H_2$.
[f] Calculation based on $LiBH_4 + 4H_2O \rightarrow LiB(OH)_4 + 4H_2$.
[g] "Misch metal", a mixture of rare-earth elements.

is also well known that nickel is ferromagnetic. Previous studies show that the magnetic moments can be enhanced at a nickel surface relative to its bulk, and that molecular adsorbates are able to reduce the magnetic ordering of nickel, particularly in the bonding region between adsorbate and substrate [9,10].

Therefore, in this work, to improve the selectivity of MCH to TOL, catalyst screening and optimization were undertaken with the goal of increasing the dehydrogenation activity. As part of this catalyst development, different Ni wt.% ratios were taken as parameters to be considered most relevant for this study. It is well known that the activity and selectivity of catalysts depend on the method of preparation. Dehydrogenation activity of the catalyst depend to a great extent on the metal loading (Ni wt.% content).

In this work Ni/Al_2O_3 catalysts with 5, 10, 15 and 20 wt.% Ni were used in the dehydrogenation of MCH reaction. The reactions were carried out in a fixed-bed catalytic reactor between 653 and 713 K temperatures. The effects of the change in the flowrates of MCH and hydrogen on this reaction were investigated by keeping one of these flowrates constant. The activation of the catalysts were performed at 723 and 823 K with air or H_2 flow.

2. Experimental

In this work, Ni/Al_2O_3 catalysts with 5, 10, 15 and 20 wt.% Ni content were prepared. Ni^{2+} solutions with different concentrations were prepared by dissolving $Ni(NO)_3 \cdot 6H_2O$ in deionized water. The adjusted amounts (g) of Al_2O_3 supports were immersed in these Ni^{2+} solutions (adjusted amounts of solutions (ml)) and NH_4OH, baker (basic) or HNO_3, baker (acidic) solutions were used to control pH at 5. Approximately 1 h contact time was enough to reach the equilibrium adsorption. These impregnated precursors were then vacuum-filtered and oven dried at 423 K for 2.5 h and at 698 K for 8 h under dry air flow. Particle size of Ni catalyst particles needed to be reduced to improve their catalytic activity. They were ground in a ball mill to obtain small particles. 5, 10, 15, 20 wt.% Ni catalysts were pelleted and activated for 10 h at 723 and 823 K with air and H_2 flow in the reactor.

Table 2
Standard formation enthalpy in dehydrogenation of cyclic hydrocarbons (101.3 kPa)

Reactant (bp/mp, °C)	Product (bp/mp, °C)	ΔH° (kJ mol^{-1})
Cyclohexane (80.8/6.5)	Benzene (80.1/5.5)	+205.9
Methylcyclohexane (10 0.9/−12 6.6)	Toluene (110.6/−95.0)	+204.8
Tetralin (207.6/−35.8)	Naphthalene (218.0/80.3)	+126.2
cis-Decalin (194.6/−43.0)	Naphthalene (218.0/80.3)	+319.5
trans-Decalin (185.5/30.4)	Naphthalene (218.0/80.3)	+332.5

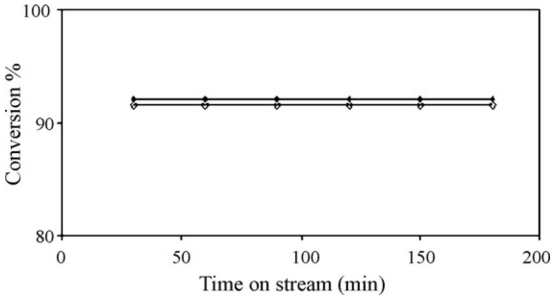

Fig. 1. Conversion (%) vs. time on stream (min) diagram of 20/A catalyst activated at 723 K with H_2 flow. Reaction temperature (713 K); fresh catalyst (◆) and regenerated catlyst (◇).

The prepared Ni/Al_2O_3 catalysts were placed in the fixed-bed catalytic reactor 1 g (fresh) for each experimental run for MCH dehydrogenation reaction and TOL and hydrogen were obtained as products. The catalyst was activated by passing air or hydrogen at 723 and 823 K for 10 h. The experiments were performed in the temperature range of 653–713 K with activated catalysts. Feed rate of MCH was between 8.6×10^{-5} and 15.3×10^{-5} mol s^{-1} and feed rate of H_2 was between 4.47×10^{-7} and 8.18×10^{-7} mol s^{-1} in the performed experiments.

MCH was fed into the reactor through a saturator using nitrogen as the carrier gas and inert diluent. Hydrogen was also used during the reaction especially to keep catalyst activity. Having only TOL and H_2 as the reaction products shows that the catalyst is selective. The experiments were conducted in a fixed-bed reactor under the condition of a differential reactor (less than 10% of conversion of MCH) at atmospheric pressure. The external and internal diffusional limitations were calculated and found negligible at the experimental conditions. Some experiments were carried out to prove that these catalysts can reach higher conversions without significant deactivation. These catalysts reached to a maximum conversion of 92% (20/A catalyst gave 92% conversion). In Fig. 1 the conversion vs. time on stream diagram shows that the activity of (20/A catalyst activated at 723 K with H_2 flow) fresh and regenerated catalysts are very close to each other, but fresh catalysts have a small increase in their activities than the regenerated catalysts at 713 K. Thus, the stability of the catalyst activity at steady state was quite high and this can also be seen in the IR analysis of fresh and used catalysts with IR – 470 Schimadzu. But, fresh catalyst was used in each experiment.

A comparison was made between the conversions obtained with the catalysts used in MCH dehydrogenation experiments of this study and the previous studies of the authors which were made with R-50 (UOP) (UK) catalyst. R-50 commercial catalyst is 0.25% Pt, 0.25% Re, 0.9–1.0% Cl, sulphided catalyst, which had particle shape as extrusions, with 0.16/0.32/0.45 cm nominal diameter, 832.82 kg/m^3 shock loaded density, 171 m^2/g surface area. Fig. 2 shows conversion vs. temperature results of the catalysts Ni/Al_2O_3 and Pt. As can be seen from the figure the conversion of Ni/Al_2O_3 catalyst is very close to the conversion of commercial Pt catalyst.

The effluent from the reactor was cooled by an ice trap, and the liquid condensate was analyzed by a gas chromatography (Hewlett-Packard 5890 A).

The surface area of the prepared catalysts was measured by using Omnisorb 100CX Volumetric Adsorption equipment.

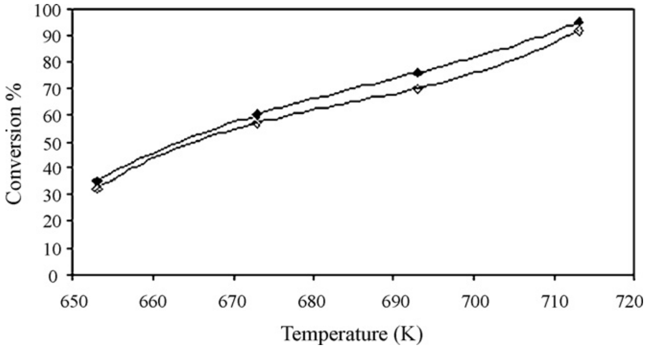

Fig. 2. Conversion vs. temperature results of the catalysts Ni/Al_2O_3 and Pt (R-50) (UOP). Pt (R-50) (UOP) catalyst (◆) and Ni/Al_2O_3 catalyst (◇).

XRD patterns of the catalysts were measured by a RIGAKU 2000 DMAX diffractometer (Cu Kα radiation).

3. Results and discussion

Highly efficient production of hydrogen without CO_2 emission is achieved in the dehydrogenation of cyclic hydrocarbons over different catalysts. MCH was efficiently dehydrogenated by Pt catalysts. There may be some other alternative catalysts cheaper and more available than Pt to dehydrogenate MCH. Ni catalysts can also be used for this reaction efficiently. In this work, catalysts with 5, 10, 15 and 20 wt.% Ni content with Al_2O_3 support were prepared in the laboratory.

The axial-H atom of the MCH is extracted toward the Ni by initial adsorption of MCH on Ni, and is then followed by the dehydrogenation steps. Since the catalytic reactivity of the prepared Ni catalyst is quite high, it can be considered to be an appropriate catalyst for MCH dehydrogenation. Table 3 shows the textural properties of the prepared catalysts, e.g., 5/A shows that 5 wt.% Ni on Al_2O_3.

The XR-diffractograms show similar results for all the prepared catalysts (5/A, 10/A, 15/A, and 20/A). Thus, as an example to explain these results X-ray diffraction patterns of the 20/A catalyst activated by air and by hydrogen are given in Figs. 3 and 4, respectively. From these figures, it can be seen that catalysts activated by air for 10 h at 723 K produce crystalline NiO-phase with an amorphous Al_2O_3. The increase of activation temperature up to 823 K leads to solid–solid interaction between Al_2O_3 and NiO forming a spinal $NiAl_2O_4$ crystalline phase. The excess NiO appears as crystalline NiO phase.

The catalysts activated by hydrogen at 723 K shows crystalline Ni-metal phase on the XR-diffractogram. The increase of the activation temperature up to 823 K increases the degree of crystallinity of the produced Ni-metal phase. This may be attributed to the reduced atmosphere caused by hydrogen which prevents the formation of NiO and consequently no aluminate can be formed.

Table 3
Textural properties of the 5, 10, 15, 20 wt.% Ni calcined impregnated catalysts

Catalyst	SA[a] ($m^2\,g^{-1}$)	PV[b] ($cm^3\,g^{-1}$)	d_p[c] (Å)
Al_2O_3	150	0.45	120
5/A	145	0.43	120
10/A	135	0.42	120
15/A	130	0.41	100
20/A	125	0.40	100

[a] Surface area.
[b] Pore volume.
[c] Pore diameter.

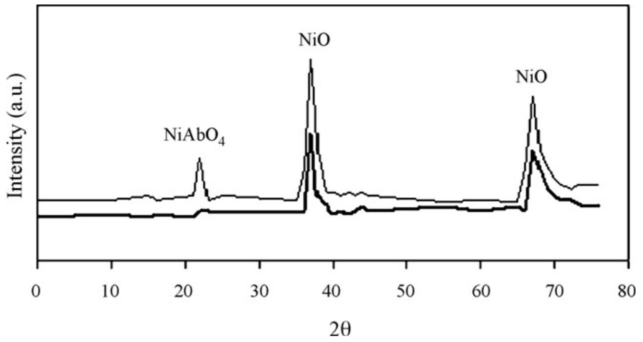

Fig. 3. XRD patterns of 20/A catalysts activated by air at 723 K (–) and at 823 K (–).

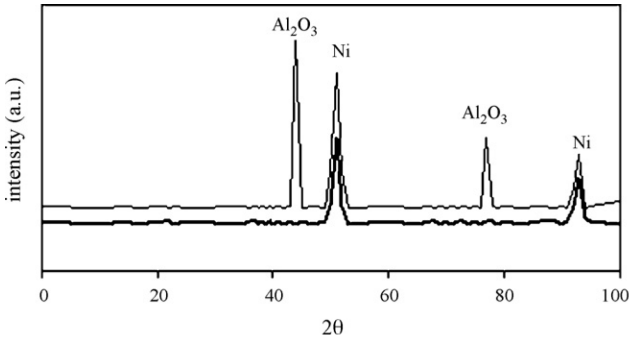

Fig. 4. XRD patterns of 20/A catalysts activated by hydrogen at 723 K (–) and at 823 K (–).

Gas chromatograph results of the reaction product showed that there were no other aromatics produced, there was only MCH and TOL peaks. This shows that, the dehydrogenation of MCH reaction is favored on the metal sites of the catalyst.

In this work, as the amount of Ni content in the catalyst was increased, there was an increase in the conversion. 20/A Ni catalyst gave the best results when compared to the other Ni catalysts of this work.

Figs. 5 and 6 show kinetic results of 20/A catalysts which were activated by air and H_2 flow at 723 and 823 K, respectively, giving the conversion of MCH converted (X_{MCH}) as a function of varying W/F_{MCH} ratios where W is the mass of the catalyst and F_{MCH} the MCH feed flowrate in mol min^{-1} under differential conditions of conversion. Table 4 shows the MCH conversion% results of 5/A, 10/A and 15/A catalysts.

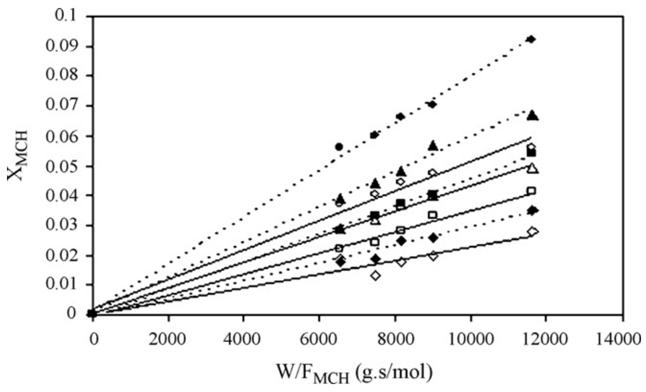

Fig. 5. X_{MCH} vs. W/F_{MCH} results with 20/A catalyst activated at 723 and 823 K with air flow. (—) 723 K and (–) 823 K. Reaction temperatures: (◆), (◇) 653 K; (■), (□) 673 K; (▲), (△) 693 K and (●), (○) 713 K.

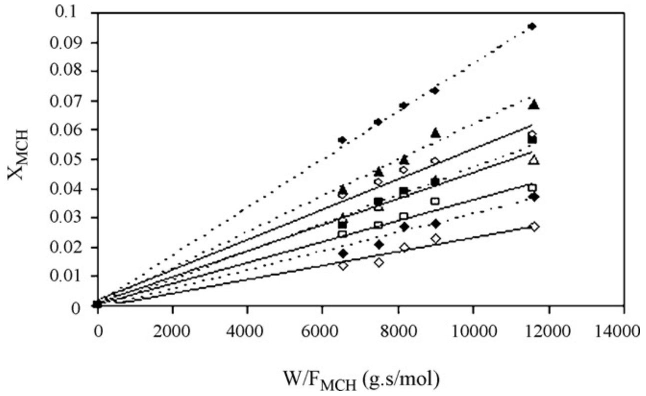

Fig. 6. X_{MCH} vs. W/F_{MCH} results with 20/A catalyst activated at 723 K and 823 K with H_2 flow. (—) 723 K and (‐) 823 K. Reaction temperatures: (◆), (◇) 653 K; (■), (□) 673 K; (▲), (△) 693 K and (●), (○) 713 K.

It can be seen from these figures and Table 4 that the conversion of MCH to TOL increased with increasing reaction temperature as expected. The catalytic conversion of MCH on catalysts activated by hydrogen at 823 and 723 K showed that their activity was very similar to the catalysts which were activated by air, as can be seen from Figs. 5 and 6 and Table 4. There is very little activity difference between the catalysts activated with air and the catalysts activated with H_2. These figures (Figs. 5 and 6) and Table 4 show that the catalysts activated at 723 K have higher activities than the catalysts activated at 823 K. The increase in the calcination temperature cause a noticable decrease in the activity of the catalyst towards the dehydrogenation. This decrease can be a result of transformation of nickel oxide into less active nickel aluminate compound. In the MCH dehydrogenation reaction some amount of MCH can be consumed for the reduction of NiO with the catalysts which were activated by air and also the deposition of a certain types of condensation products on the catalyst surface may be considered as an additional evidence for lowering the activity in comparison with catalysts activated by hydrogen. Although all of the catalysts have very similar catalytic activity and there is small differences between the MCH conversion percentage results according to the air or H_2 flow (Figs. 5 and 6, Table 4), 20/A catalyst activated with H_2 flow at 723 K gives comparatively better conversion results than the other catalysts in this work.

Table 4
X_{MCH} vs. W/F_{MCH} results with 5/A, 10/A and 15/A catalyst activated at 723 and 823 K with air flow and hydrogen flow

W/F_{MCH} (g s mol^{-1})	X_{MCH}			
	380[a]	400[a]	420[a]	440[a]
5/A				
Activated at 823 K with air flow				
6545.5	0.006	0.015	0.021	0.028
7500	0.007	0.018	0.026	0.033
8181.8	0.01	0.022	0.031	0.038
9000	0.013	0.027	0.033	0.041
11612.9	0.017	0.031	0.041	0.05
Activated at 823 K with H_2 flow				
6545.5	0.007	0.019	0.025	0.032
7500	0.009	0.02	0.029	0.034
8181. 8	0.016	0.0245	0.031	0.029
9000	0.017	0.027	0.038	0.044
11612.9	0.02	0.031	0.042	0.051
Activated at 723 K with air flow				
6545.5	0.01	0.017	0.03	0.042
7500	0.012	0.026	0.037	0.055
8181. 8	0.019	0.032	0.041	0.061
9000	0.021	0.034	0.052	0.063
11612.9	0.026	0.047	0.06	0.072
Activated at 723 K with H_2 flow				
6545.5	0.011	0.022	0.034	0.05
7500	0.014	0.027	0.04	0.057
8181. 8	0.022	0.034	0.044	0.062
9000	0.022	0.038	0.053	0.065
11612.9	0.03	0.047	0.061	0.076
10/A				
Activated at 823 K with air flow				
6545.5	0.008	0.02	0.027	0.033
7500	0.01	0.02	0.031	0.038
8181.8	0.0146	0.026	0.033	0.04
9000	0.016	0.029	0.039	0.043
11612.9	0.02	0.034	0.044	0.052
Activated at 823 K with H_2 flow				
6545.5	0.01	0.022	0.026	0.033
7500	0.013	0.023	0.03	0.038
8181.8	0.016	0.026	0.035	0.045
9000	0.019	0.034	0.039	0.047
11612.9	0.023	0.036	0.046	0.054
Activated at 723 K with air flow				
6545.5	0.012	0.03	0.035	0.051
7500	0.017	0.029	0.04	0.053
8181.8	0.021	0.035	0.044	0.062
9000	0.022	0.036	0.055	0.066
11612.9	0.031	0.05	0.063	0.08
Activated at 723 K with H_2 flow				
6545.5	0.015	0.023	0.036	0.051
7500	0.017	0.031	0.042	0.058
8181.8	0.023	0.035	0.046	0.064
9000	0.026	0.036	0.055	0.069
11612.9	0.033	0.052	0.065	0.084
15/A				
Activated at 823 K with air flow				
6545.5	0.015	0.027	0.025	0.033
7500	0.016	0.022	0.03	0.038
8181.8	0.018	0.026	0.035	0.042
9000	0.02	0.031	0.038	0.045
11612.9	0.023	0.038	0.047	0.055
Activated at 823 K with H_2 flow				
6545.5	0.019	0.022	0.029	0.037
7500	0.013	0.024	0.032	0.04
8181.8	0.018	0.028	0.037	0.044
9000	0.02	0.033	0.04	0.047
11612.9	0.028	0.041	0.049	0.056
Activated at 723 K with air flow				
6545.5	0.017	0.025	0.035	0.054
7500	0.018	0.031	0.042	0.056
8181.8	0.023	0.035	0.046	0.066
9000	0.024	0.038	0.055	0.072
11612.9	0.034	0.055	0.065	0.085
Activated at 723 K with H_2 flow				
6545.5	0.018	0.028	0.039	0.056
7500	0.019	0.033	0.044	0.06
8181.8	0.025	0.037	0.048	0.066
9000	0.026	0.04	0.057	0.07
11612.9	0.035	0.054	0.067	0.092

[a] Reaction temperature (K).

4. Conclusions

The reversible dehydrogenation of cycloalkanes such as MCH is one of the potential systems to store and transport hydrogen. The appropriate experimental conditions and catalysts can give very successful results for these systems.

There are not any other products than TOL and hydrogen in this work, because dehydrogenation takes place on the metal centers of the catalyst. The activation temperature and the use of hydrogen or air in the activation process comparatively affected the activity of the catalyst. In this work, catalyst activity was not affected too much by the use of air or hydrogen, but was affected by the activation temperature. Thus, the prepared 20/A catalyst activated at 723 K by hydrogen flow dehydrogenates MCH to TOL and hydrogen better than the other catalysts used in this study.

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