

Use of Pd/Activated Carbon Fiber Catalyst to Dehydrogenate Cyclohexane

Serkan Baş and Yuda Yürüm

Sabancı University, Faculty of Engineering and Natural Sciences, Tuzla, Istanbul, Turkey

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Abstract

In this work, activated carbon fibers (ACFs) were prepared from polyacrylonitrile fibers, Pd catalyst was loaded onto the ACFs. The BET surface areas noted before activation were in the range of 120-140 m²/g. Activation of the fibers with carbon dioxide increased the surface areas of the fibers to about 150-190 m²/g. Diameters of metallic Pd particles loaded along the fibers ranged from 50 nm to 100 nm. The shape of the Pd particles was generally spherical albeit some non-spherical Pd particles were also noted. The catalytic activity of the Pd/ACF system in dehydrogenating cyclohexane at 350°C under liquid-phase conditions was investigated. Utilizing the Pd/ACF system in the micro-autoclave of a differential scanning calorimetric system was described for the liquid-phase catalytic dehydrogenation of cyclohexane. The DSC thermogram of the non-catalytic system yielded fewer endothermic events compared to the catalytic dehydrogenation of cyclohexane in the presence of Pd/ACF. The dehydrogenation of cyclohexane at 350°C was a first-order reaction with a rate constant, $k = 3.5 \times 10^{-4} \text{ s}^{-1}$. GC-MS analyses of the products of catalytic dehydrogenation revealed a wide distribution of saturated and unsaturated hydrocarbons that were not present in the corresponding non-catalytic experiment. The presence of high molecular weight products could be explained by the recombination of carbon radicals during reaction.

INTRODUCTION

Porous carbon materials have attracted growing attention among the different types of supports used in heterogeneous catalysis because of certain favorable characteristics, which are essentially their resistance to acidic/basic media, significant pore and surface tailorability, and ease of recovery of catalytic metals via combustion of the support material. Carbon fibers typically feature a relatively

low surface area of 50–350 m²/g when compared to activated carbons and activated carbon fibers [1]. Activated carbon fibers (ACFs) depict a comparatively contemporary variety of porous carbon material with a number of important advantages such as a high apparent specific surface area, generally in the range of 1500–3000 m²/g, and a high adsorption capacity, as well as very rapid adsorption kinetics from the gas and liquid-phases [2]. ACFs have attracted considerable interest because of their wide applicability for separation purposes and as catalyst supports.

ACFs have been shown as suitable catalytic

* Correspondence to: Yuda Yürüm

Sabancı University, Faculty of Engineering and Natural Sciences, Tuzla, 34956 Istanbul, Turkey

Tel: +90216 483 9512 Fax: +90 216 483 9550

E-mail: yyurum@sabanciuniv.edu

supports for noble metals [3-7]. The chemistry and synthesis of supported palladium catalysts, relevant support properties and case studies for carbon-supported catalysts has been reviewed by Toebes et al. [8] and Tien et al. [9-11] investigated the catalytic hydrogen evolution from tetrahydronaphthalene under normal liquid phase conditions using palladium catalysts supported on activated carbon fibers. It was found that ACFs that possessed high specific surface areas were adequate as the supports. It was also noticed that Pd-catalysts supported on activated carbon fibers, which were prepared by an impregnation method, showed higher activity compared to commercial catalysts.

In the fine chemical industry, catalysts based on precious metals on activated carbon supports are often utilized, because such systems show interesting characteristics with regard to their application. Activated carbons are stable in both acidic and basic media, which is not valid for alumina or silica. Precious metal on carbon catalysts are mostly used in liquid phase hydrogenation, dehydrogenation or oxidation reactions in the fine chemicals area. With respect to the fine chemicals business, powder precious metal catalysts are the most commonly used catalysts. About 30% of the catalysts in this area are supported palladium catalysts, most of them being used for hydrogenation and dehydrogenation reactions [12]. The dehydrogenation of saturated hydrocarbons to yield useful alkene intermediates in the production of new fuels and fuel additives has acquired increasing visibility in the chemical industry in the past several decades. The demand for olefins and olefinic products continues to increase and commercially has resulted in a number of catalytic dehydrogenation processes. Cyclohexene is one intermediate chemical of considerable industrial importance for producing cyclohexanol, cyclohexanone, epoxy cyclohexane, adipic acid, the

precursors for nylon-6,6 and nylon-6 [13-15]. However, producing cyclohexene selectively from cyclohexane is difficult owing to the ease of continued dehydrogenation to yield benzene, which is a thermodynamically much more favorable end-product. Pd⁰ catalysis is very selective in achieving mild dehydrogenation conditions and it is generally devoted to promoting dehydrogenations under heterogeneous conditions.

The present work describes the catalytic activity of a Pd/ACF system in dehydrogenating cyclohexane at 350°C under liquid-phase conditions. The preparation of ACFs from PAN fibers and the method to load Pd on ACFs is also presented. The structure of the ACFs was explored by surface analysis and scanning electron microscopy (SEM) methods.

EXPERIMENTAL

Preparation of ACFs

Commercial 1.1 decitex PAN fibers (weight of 10,000 m of single fiber in gram is 1 decitex) obtained from AKSA Acrylic Chemical Industries, Yalova, Turkey, were stabilized in air at 300°C for 1 hour while they were stretched in a vacuum oven. The stabilized fibers were carbonized at 600, 700, 800 and 1000°C heated with a rate of 10°C/min and held at the final temperature for 3 hours under a nitrogen atmosphere. Carbon fibers were activated under a carbon dioxide atmosphere in tube furnace at 800°C for 1 hour.

Loading of ACFs with Pd

0.5 g ACF and 0.0417 g PdCl₂ (Aldrich, 99.999 %) were stirred with 20 ml of water in a beaker at room temperature. Stoichiometric amount of NaBH₄ (Merck, 96%) was added to this solution as reducing agent for Pd²⁺. Metallic Pd appeared on the surface of ACFs after several hours of reaction time. The

metal loaded ACFs were then washed with distilled water to clean the ACFs from the residual matter and organics, and dried in an oven at 70°C under a nitrogen atmosphere. Washing of the fibers with fresh distilled water leached negligible amounts of metallic Pd particles.

Surface analysis

Surface areas of ACFs were measured by Quantachrome NOVA 2200e series Surface Analyzer. The determination is based on the measurements of the adsorption isotherms of nitrogen at 77 K. Surface area of the samples were determined by using BET equation in the relative pressure range of between 0.05 to 0.3, seven adsorption points and BJH (Barrett-Joyner-Halenda) method was utilized for the measurement of pore size distributions. Before all of the measurements, moisture and gases such as nitrogen and oxygen adsorbed on the surface or held in the open pores, were removed under reduced pressure at 100°C for 5 h.

SEM Analysis

The ACFs were examined with a Leo G34-Supra 35VP scanning electron microscope. All samples were coated with gold before taking any image because of insufficient conducting of the ACF samples.

Liquid-phase dehydrogenation of cyclohexane

Cyclohexane (Merck, 99%) was heated in a Mettler micro-autoclave placed into a Netzsch DSC 204 Phoenix Differential Scanning Calorimetry (DSC) system at 350°C. Experiments were performed with and without Pd-loaded ACFs. In the experiments with Pd/ ACF system, 0.0060 gram Pd/ ACF system and 100 µL cyclohexane put into the micro-autoclave of 270 ml volume, under a nitrogen atmosphere and the cap was tightly closed. This micro-autoclave was placed to the sample side of the measuring cell while an empty identical micro-

autoclave was placed into the reference side of the measuring cell of the DSC. Micro-autoclaves were heated to 350°C with a rate of 20K/min at nitrogen atmosphere and held at this temperature for 15, 30 and 60 minutes. The experiment was repeated at least three times and all of the results reported were at average of these experiments.

Products obtained after the experiments were analyzed using a Shimadzu QP5050A gas chromatography-mass spectrometry (GC-MS) system. Pure helium was used as the carrier gas in the GC-MS system. The flow rate of the carrier gas was 3 mL/min. A capillary DB-5 ms column (length 30 m, diameter 0.25 mm, and thickness 0.25 µm) was used in the analyses. Both the temperatures of the injection port and column oven were constant at 135°C. Pure cyclohexane and products of cyclohexane heated with 20 K/min up to 350°C in the micro-autoclave without Pd/ACF system were also analyzed in the GC-MS system using the same analytical conditions for comparison purposes.

Kinetic analysis of the empirical data

Calculation of the conversion values of non-catalytic, C_{nc} , and catalytic, C_c , dehydrogenation reactions based on the determination of the amount of unconverted cyclohexane remained in the micro-autoclave using quantitative gas chromatographic methods. C_c values, were used to determine the order of reactions according to standard tests [16].

RESULTS AND DISCUSSION

Structural characteristics of the ACFs

The SEM micrograph of carbon fibers stabilized at 300°C and carbonized at 800°C is presented in Figure 1a. Subsequent activation at 800°C for 1 hour under carbon dioxide is presented in Figure 1b. The shape of the fibers was cylindrical as they were before the carbonization experiments. Fibers of

cylindrical shape but with rougher surface structure were produced after stabilization and carbonization experiments. It seemed that some of the fibers had bonded to one another during the thermal treatment due to softening of the fibers, Figure 1a. The fiber surface featured some mesoscale roughness, presumably due to activation reactions which volatilized some of the carbon material present along the exterior of the fibers, Figure 1b. Activation of the fibers with carbon dioxide also destroyed the regular cylindrical shapes of the fibers by creating irregular channels on the surface.

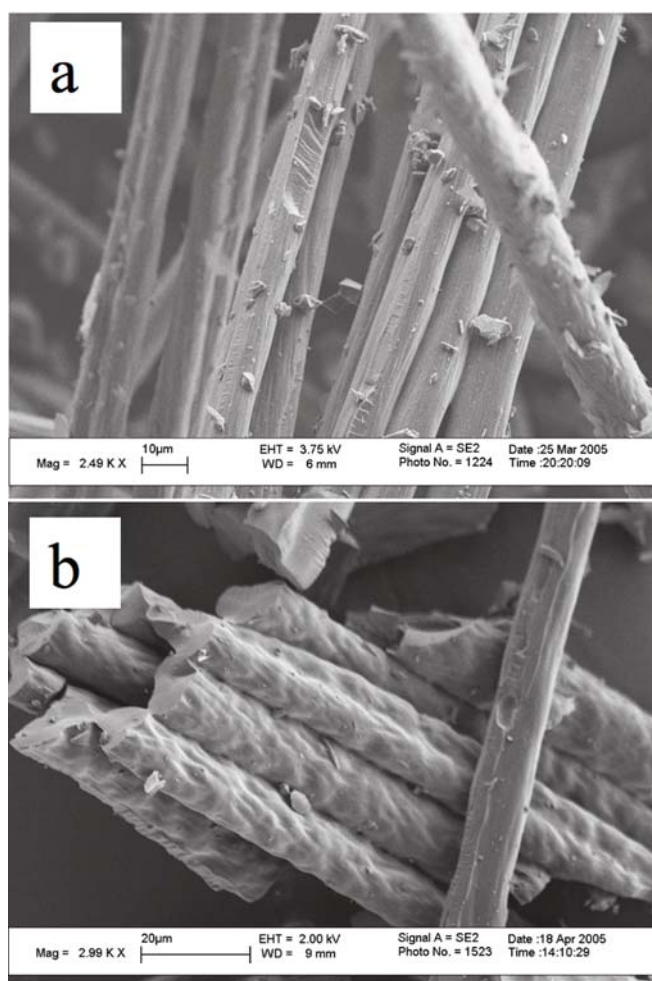


Figure 1. SEM micrographs of carbon fibers a) stabilized at 300°C and carbonized at 800°C and b) same sample after activation with carbon dioxide at 800°C.

Activation experiments performed within 700-900°C produced ACFs with higher surface areas compared to the respective starting materials whereas attempts to activate above 900°C caused sample volatilization in most cases. The optimal temperature and duration of activation for carbon fibers were defined as 800°C and 1 hour. BET surface areas before activation ranged between 130-140 m²/g, Table 1. Fibers activated at 700°C and 800°C with carbon dioxide displayed increased fiber surface areas of 150 m²/g and 190 m²/g, respectively, the latter treatment yielding an apparent 39% increase of surface area. The ACFs displayed a mesoscale pore structure as characterized by pore diameters in the typical range of 2-5 nm [17].

Fiber samples bearing the highest surface areas were used to load the Pd catalyst. Typical fiber diameters measured between 0.4-1.1 mm. Metallic Pd particles loaded along the fibers ranged from approximately 80-90 nm in diameter. The Pd particles generally appeared spherical although some non-spherical Pd particles were also noted on the fibers. After successive washings, gravimetric analysis indicated an approximate 5wt% loading of Pd along the ACFs.

Liquid-phase dehydrogenation of cyclohexane with Pd/ ACF system

DSC thermograms obtained by heating cyclohexane in the micro-autoclave are presented in Figures 2a and 2b, respectively. The DSC thermogram of cyclohexane without the Pd/ACF catalyst highlights only one endothermic event with an onset at about 120°C, an end at 200°C and a peak at about 140°C.

Table 1. Change of BET surface area of carbon fibers after carbonization and activation

Carbonization Temperature (°C)	BET Surface Area of CFs after carbonization (m ² /g)	BET Surface Area of ACFs after activation (m ² /g)	Increase in Surface Area (%)
700	129	150	16
800	136	190	39

This peak was likely related to various bond rupture events developing in cyclohexane over this temperature range. The DSC thermogram depicting the contribution of Pd/ACF, i.e., Figure 2b, was rather different and complicated to interpret when compared to the negative control system with no catalyst. Endothermic events appeared to begin at 50°C, peaking at 140°C and again ending at about 200°C. The area under this peak was much greater than the endotherm of the initial cyclohexane experiment, Figure 2a. The difference likely reflected the greater number of bond cleavage reactions taking place in the presence of catalyst. The DSC thermogram of the cyclohexane-Pd/ACF system also contained two smaller endotherms peaking at 260°C and 290°C, showing the existence of other endothermic reactions at these temperatures. The lack of endothermic peaks beyond 350°C suggested there were no major cleavage reactions taking place at these temperatures. When the reaction was performed in the presence of Pd/ACF catalyst,

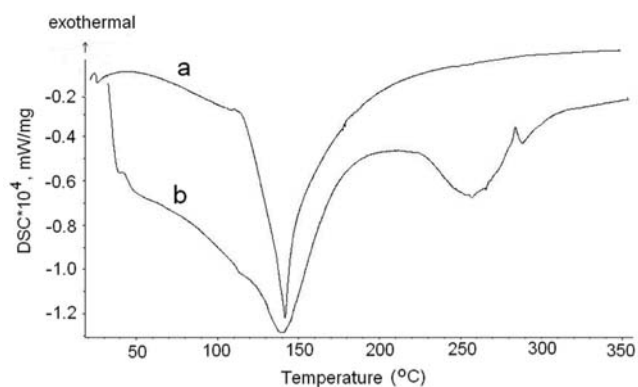


Figure 2. DSC thermograms of cyclohexane dehydrogenation experiment done in micro-autoclaves, a) cyclohexane and b) cyclohexane and Pd/ACF system.

alternative lower-activation-energy pathways predominated, increasing the variety of the reactions occurring at relatively lower temperatures and also enabling cyclohexane to pyrolyze at modest temperatures such as 260°C and 290°C to produce a variety of new products that were not observed in the non-catalytic experiment.

Non-catalytic conversion of cyclohexane at the end of first 30 minutes was calculated as 2.5%. Catalytic conversion of cyclohexane using the Pd/ACF system increased the conversion to 5.7%, Table 2. Conversion values of catalytic dehydrogenation of cyclohexane increased with time in that conversion values calculated at 12, 15, 30 and 60 minutes were 3.9%, 4.3%, 5.7% and 10.9%, respectively. In plotting $\ln C_c$ versus time, a straight line with a maximum R^2 value of 0.998 indicated a first-order reaction [16] with a forward rate constant, $k = 3.5 \times 10^{-4} \text{ s}^{-1}$.

The total ion chromatogram of cyclohexane is presented in Figure 3a. A major elution peak appeared at the 2nd minute interval, indicative of cyclohexane. Smaller peaks to appear with greater retention times probably reflected impurities present in the sample.

The total ion chromatogram of cyclohexane heated in the micro-autoclave for 30 minutes at 350°C is presented in Figure 3b. Heating cyclohexane without Pd/ACF at 350°C for 30 minutes produced fewer products than those observed in the

Table 2. Non-catalytic and catalytic conversion of cyclohexane at 350°C as a function of time and post-reaction R^2 calculations to elucidate reaction order.

Time, min	Non-catalytic Conversion, C_{nc} (%)	Catalytic Conversion, C_c (%)	$\ln C_c$	$1/C_c$
12	-	3.88	1.36	0.26
15	-	4.33	1.46	0.23
30	2.5	5.67	1.74	0.18
60	-	10.90	2.39	0.09
	R^2 value	0.984	0.998	0.983

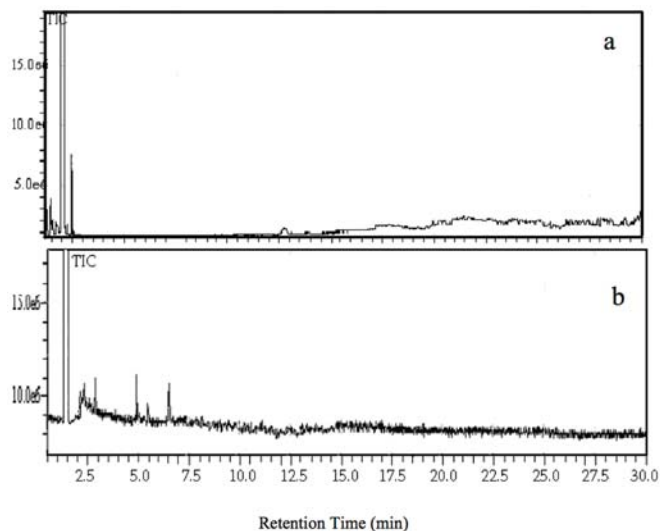


Figure 3. Total ion chromatograms of a) cyclohexane, b) cyclohexane heated in the micro-autoclave at 350°C for 30 min

chromatograms of cyclohexane heated in the presence of Pd/ACF. In particular, groups of compounds were observed at retention times of 1-3 min, 4-6 min, and 6.5 min (Table 3). Compounds identified amongst the products of the non-catalytic experiment were more or less the same as those identified in the catalytic experiments up to the 6th minute. This finding implied that heating cyclohexane at 350°C in both catalytic and non-catalytic environments produced similar, relatively low-boiling and low-molecular weight compounds. Other compounds with longer retention times were not observed in the non-catalytic system, in direct contrast to cyclohexane subjected to catalytic dehydrogenation.

Total ion chromatograms of the products after catalytic dehydrogenation of cyclohexane are presented in Figure 4. The chromatograms presented in Figure 4 are quite different than those of in Figure 3. In particular, the chromatograms of Figure 4 contained many new peaks, which were absent in the chromatogram of pure cyclohexane (Figure 3a) and cyclohexane subjected to non-catalytic dehydrogenation. Retention times of these new groups of peaks in the chromatograms of the catalytic experiments were around 13 min, 13.5-15.5

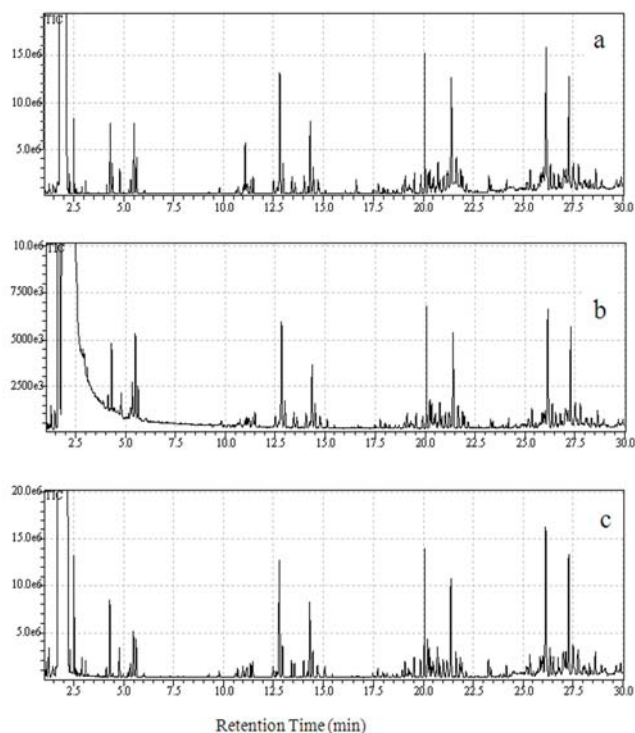


Figure 4. Total ion chromatogram of products of cyclohexane dehydrogenation experiments performed in the micro-autoclave with Pd/ACF system at 350°C for a) 15 min, b) 30 min and c) 60 min.

min, 17.5-22.5 and 23-30 min. The intensity of these peaks did not change greatly over the duration of the experiments.

Compounds identified amongst the products of catalytic dehydrogenation experiments are presented in the Table 3. Many seemed to be unsaturated compounds, such as 1-methylcyclopentene, cyclohexene, 3-methylcyclopentene, 1,4-dihexene, 1-methylcyclopentene, 1-hexene and phenylacetylene. This product distribution could be attributed to the catalytic effect of Pd/ACF in dehydrogenating cyclohexane. There were also some oxygenated compounds present in the analyzed samples such as 2-methyl furan, 3-hexen-1-ol, 3-methylpentanol, 2,4-dimethyl-cyclopentanone, 3-hexanol, 1-hydroxy-2-butanone, 2-methyl-cyclopenten-2-one, 1-hexanol, 2,4,4-trimethyl-2-cyclohexen-1-one, 4,4-dimethyl-2-cyclopenten-1-one and benzylpropylether. These products were probably oxidative by-products arising from the interaction between residual oxygen

Table 3. Retention times and plausible compounds suggested from GC-MS data after cyclohexane was heated in the micro-autoclave, A) No catalyst, B) with Pd/ACF system at 350oC

A	B	Identified Compounds	Molecular Weight	Boiling Point,(°C)
Retention Time (min)	Retention Time (min)			
1-3	1-3	Isoprene	68.11	34.07
		2-methyl furan	82.10	63-79
		1-methyl-cyclopentene	82.12	167.88
		1-methylene cyclopentane	82.15	75.00
		cyclohexene	82.15	82.98
		2,3-dimethylbutene	84.16	55.67
		cyclohexane	84.16	80.74
4-6	4-6	3-methyl cyclopentene	82.15	65.00
		1,4 dihexene	82.15	65.00
		1-methyl cyclopentene	82.15	76.00
		1-hexene	84.16	63.35
		3-methyl-2,4-cyclohexadiene	94.08	107.00
6.5	-	methyl cyclopentane	84.16	71.80
		1,2 dimethyl cyclobutane	84.16	
-	13.0	3-hexen-1-ol	100.16	156.00
		3-methylpentanol	102.18	151.60
		2,4-dimethyl-cyclopentanone	112.09	
		3-hexanol	116.21	143.00
		1-ethyl-4-methylbenzene	120.20	161.30
-	13.5-15.5	styrene	104.16	145.20
		1,3,5-trimethylbenzene	120.20	169.35
-	17.5-22.5	1-hydroxy-2-butanone	88.12	73.00
		2-methyl-cyclopenten-2-one	96.13	158.00
		1-hexanol	102.18	158.00
		phenylacetylene	108.09	142.00
		2,4,4-trimethyl-2-cyclohexen-1-one	138.21	81.00
-	23-30	benzaldehyde	106.13	178.10
		4,4-dimethyl-2-cyclopenten-1-one	110.16	158.00
		benzyl propyl ether	136.09	
		decanal	156.27	208-9

in the autoclave and intermediates produced during dehydrogenation. Heating cyclohexane with Pd/ACF produced other compounds in addition to the ones produced under comparable but non-catalytic dehydrogenation conditions. GC-MS analyses of products arising from the catalytic experiment revealed the presence of higher-boiling and higher-molecular weight compounds. The presence of higher molecular weight products could be explained by the recombination high molecular-weight radicals during these reactions.

CONCLUSIONS

The BET surface areas noted before activation were in the range of 120-140 m²/g. Activation of the fibers with carbon dioxide increased the surface areas of the fibers to about 150-190 m²/g. The ACFs contained pores with diameters of 2-5 nm, thus qualifying as a mesoporous structure. SEM micrographs of Pd-loaded fibers indicated fiber diameters in the range of 0.5-1.0 mm. Diameters of metallic Pd particles loaded along the fibers ranged from 50 nm to 100 nm. The shape of the Pd particles was generally spherical albeit some non-spherical Pd particles were also noted.

The DSC thermogram of the non-catalytic system yielded fewer endothermic events compared to the catalytic dehydrogenation of cyclohexane in the presence of Pd/ACF. The dehydrogenation reaction of cyclohexane was a first-order reaction with a reaction rate constant, $k = 3.5 \times 10^{-4} \text{ s}^{-1}$.

GC-MS analyses of the products of catalytic dehydrogenation revealed a wide distribution of saturated and unsaturated hydrocarbons that were not present in the corresponding non-catalytic experiment. The presence of high molecular weight products could be explained by the recombination of carbon radicals during reaction.

NOTATIONS

- C_{nc} : percent conversion value of non-catalytic dehydrogenation of cyclohexane
- C_c : percent conversion value of catalytic dehydrogenation of cyclohexane
- R^2 : coefficient of linear regression

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