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CO-free hydrogen production via dehydrogenation of a Jet A hydrocarbon mixture

Bo Wang [a], Gilbert F. Froment [a], D. Wayne Goodman [b,*]

[a] *Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, USA*
[b] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*

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Abstract

The dehydrogenation of a Jet A hydrocarbon mixture was investigated for the production of hydrogen for fuel cell applications. This process differs from steam/partial oxidation reforming of hydrocarbons in that the hydrogen produced is free of CO, and therefore can be used in low temperature fuel cells without further purification. Because of their relative importance with respect to the spectrum of hydrocarbons in the mixture, cyclohexane and decalin were investigated independently. A hybrid catalyst, Pt/γ-Al_2O_3-ZrO_2/SO_4^{2-}, was designed to enhance the hydrogen production yields.

Keywords: Hydrogen; Dehydrogenation; Fuel cell; Cyclohexane; Decalin; Jet A

1. Introduction

Onboard hydrogen storage imposes a serious challenge to the implementation of fuel cells in transportation [1,2]. For this purpose chemical hydrides have been explored for in situ generation of hydrogen. Hydrolysis, reforming and dehydrogenation are the most widely used reactions to produce hydrogen from hydrocarbon sources. Hydrolysis reactions utilizes the oxidation of chemical hydrides with water to produce hydrogen [3,4]. Obviously water is needed onboard the vehicle and thus increases the weight and decreases the useful vehicle volume. Hydrolysis for hydrogen production has directed considerable efforts toward sodium borohydride as the hydrogen storage medium. Steam reforming of natural gas is mainly used for large scale hydrogen production in industry [5–7]. The reaction is highly endothermic and hence requires a substantial energy input. Another drawback is that steam reforming generates CO which poisons the typical catalysts used in low temperature fuel cells. Dehydrogenation of hydrocarbons is an attractive method for hydrogen production since only hydrogen and dehydrogenated hydrocarbons are formed in this reaction [8–12]. The absence of carbon oxides eliminates the need for further purification of the hydrogen product. Another advantage of using liquid hydrocarbons as a H_2 storage medium is that the current distribution infrastructure can be used for the transportation, storage, and dispersal of the liquid hydrocarbon. Since the dehydrogenation of cycloalkanes is a reversible process, the dehydrogenated products (benzene, toluene, naphthalene, etc.) can be easily hydrogenated back to the parent cycloalkane at local nodes in a hydrogen distribution system.

Since jet fuels are widely used in large quantities for military applications, this fuel is an attractive source of hydrogen for fuel cells in this environment. Steam/autothermal reforming of these hydrocarbons to produce hydrogen involves the co-production of large amounts of CO [13]. Typically used low temperature fuel cells, e.g. proton exchange membrane (PEM) fuel cells, are highly sensitive to poisoning by CO (tolerance is at ppm levels). Several post-reforming procedures are required for remediation of CO. These additional procedures are detrimental to the process economics. More importantly, the CO removal treatments increase the complexity and bulkiness of the PEM system and effectively minimize the main advantage (compactness and weight) offered by PEMs. Accordingly fuel reforming to produce CO-free hydrogen is currently the most important problem associated with PEM fuel cells. It is there-

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[*] Corresponding author.
E-mail address: goodman@mail.chem.tamu.edu (D.W. Goodman).

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fore desirable to explore other avenues for hydrogen production with specific applications for the current PEM fuel cells. Hydrogen production via dehydrogenation of a Jet A hydrocarbon mixture is an attractive route for the production of CO-free hydrogen and is investigated in this study for the first time. As an added bonus, for fuel cells used in conjunction with internal combustion or turbine driven vehicles, the dehydrogenation reaction can be carried out at or near the accessible exhaust temperatures, i.e., the waste heat from the exhaust can be used to drive the reaction. Preliminary data show that limited dehydrogenation of Jet fuel does not significantly compromise its fuel properties, thus allowing the fuel with its current composition to serve as a hydrogen storage medium.

The dehydrogenation of hydrocarbons to produce hydrogen has been reported on a number of supported metal catalysts in different types of reactors. Ni and Pt are among the most used metal catalysts. While Ni is much cheaper than Pt, the selectivity for the dehydrogenation reaction is much lower than that on Pt, and, in particular, cracking reactions are pronounced on Ni at high temperatures. Ichikawa et al. investigated the dehydrogenation of cyclohexane, methylcyclohexane and decalin over activated carbon supported Ni, Pt, and Ni–Pt catalysts using a spray pulse mode reactor operating at 287–375 °C [8,9]. It was assumed that pulse spray operation could increase the reaction rate by suppressing the reverse reaction. The conversions were 25–35% with the selectivity for dehydrogenation reactions above 98.8%. Okada et al. reported results for alumina supported Pt catalysts for methylcyclohexane dehydrogenation in a fixed bed reactor [10]. This catalyst could generate hydrogen from methylcyclohexane with a conversion of 95% and toluene selectivity above 99.9% at 320 °C. Recently, Huffman used stacked-cone carbon nanotubes (SC-CNT) as a support medium to prepare Pt and Pd catalysts for the dehydrogenation of cyclohexane and methylcyclohexane [11]. The catalysts exhibited 100% selectivity for dehydrogenation reactions. It was reported that a 0.25 wt% Pt/SC-CNT catalyst had approximately the same activity as a commercial 1 wt% Pt/Al_2O_3 catalyst. The regeneration of the deactivated, carbon-supported catalyst is a problem, and thus limits its potential.

In the present study the dehydrogenation of Jet A to produce hydrogen was investigated over $Pt/\gamma\text{-}Al_2O_3$ and $Pt\text{-}Sn/\gamma\text{-}Al_2O_3$ catalysts and the operating conditions optimized for this range of reaction conditions. Because of their overall relevance to the reaction chemistry, the dehydrogenation of cyclohexane and decalin was also investigated. To generate additional hydrogen from paraffins, the major components of Jet A, catalytic reforming of paraffins to aromatics on a bifunctional catalyst is desirable. Accordingly, a $Pt/\gamma\text{-}Al_2O_3\text{-}ZrO_2/SO_4^{2-}$ hybrid catalyst was synthesized to increase the acidity of the catalyst and thus increase the hydrogen production at low temperature.

2. Experimental

2.1. Catalyst preparation

The catalysts used in the dehydrogenation of cyclohxane and decalin were supported Pt catalysts, prepared by an evaporative impregnation method [14]. Three different kinds of high surface area supports, γ-alumina, silica and activated carbon, were investigated for preparation of the catalysts.

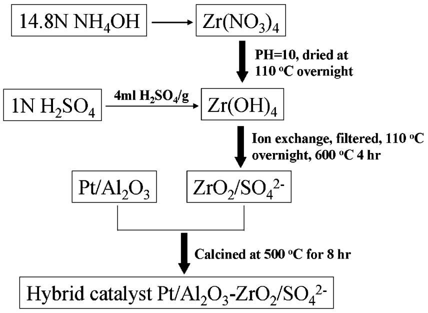

Fig. 1. Preparation of a $Pt/\gamma\text{-}Al_2O_3\text{-}ZrO_2/SO_4^{2-}$ hybrid catalyst.

The Pt/alumina-ZrO_2/SO_4^{2-}hybrid catalyst was prepared from two components, 0.9 wt% Pt/alumina and sulfated zirconia. The sulfated zirconia was prepared according to a published protocol (Fig. 1) [15]. Zirconium nitrate was precipitated with 14 N ammonium nitrate at pH 10. The precipitate was filtered, washed, and then dried overnight at 110 °C. Zirconium hydroxide was then ion exchanged with 1 N sulfuric acid and filtered. The solid was dried overnight at 110 °C and calcined at 600 °C in air for 3 h. The hybrid catalyst was made by physically mixing 0.9 wt% Pt/alumina and sulfated zirconia with a mass ratio of 6 to 4, then pelletized to particle sizes ranging from 0.15–0.5 mm. The catalyst was loaded into the reactor, and activated by calcination in air at 500 °C for 8 h with a subsequent reduction in hydrogen at 300 °C.

2.2. Fixed-bed reactor setup

The dehydrogenation of cyclohexane, decalin and Jet A were carried out over supported Pt catalysts at atmospheric pressure in a fixed bed reactor described elsewhere [14]. A HP-PLOT/alumina capillary column with a FI-detector was used to analyze the hydrocarbon components for the dehydrogenation of cyclohexane. A HP-5 capillary column was used to analyze the hydrocarbons for the dehydrogenation of decalin and Jet A.

3. Results and discussion

3.1. Definition of conversion, selectivity, and hydrogen production yield

The definitions for the subsequently quoted conversions, selectivities, and hydrogen production yields are as follows:

Conversions:

$$X_i = \frac{\text{moles of } i \text{ in} - \text{moles of } i \text{ out}}{\text{moles of reactant in}} \times 100.$$

Selectivity:

$$\text{selectivity} = \frac{\text{moles of product } i \text{ formed}}{\text{moles of reactant converted}} \times 100.$$

Hydrogen production yield in Jet A dehydrogenation:

$$\text{yield (\%)} = \frac{H_2 \text{ production rate in mol } \times 2}{\text{Jet A molar feed rate } \times 21} \times 100.$$

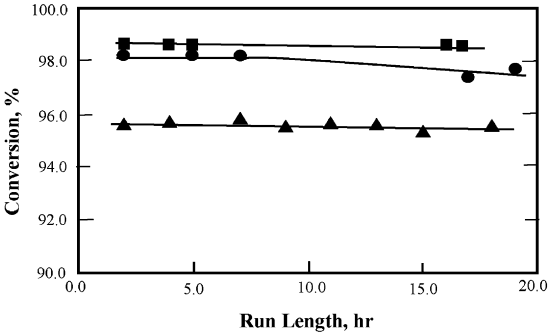

Fig. 2. Cyclohexane dehydrogenation over various supported Pt catalysts. Temperature = 340 °C, space time = 20 kg cat h/kmol, and H_2/cyclohexane = 1/2.

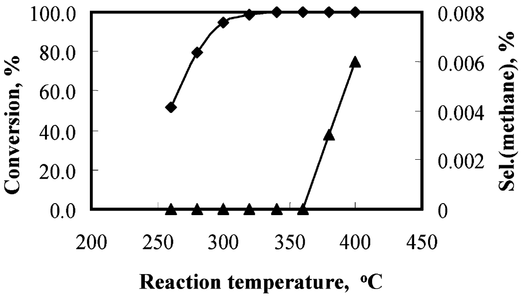

Fig. 3. Effect of temperature on cyclohexane dehydrogenation over 0.8 wt% Pt/γ-alumina. Reaction conditions: space time = 30 kg cat h/kmol and H_2/cyclohexane = 3.

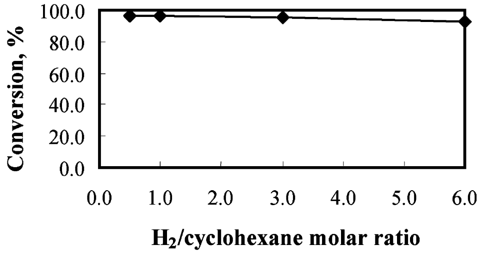

Fig. 4. Effect of H_2/cyclohexane molar ratio on cyclohexane dehydrogenation over 0.8 wt% Pt/γ-alumina. Reaction conditions: 320 °C and space time = 25 kg cat h/kmol.

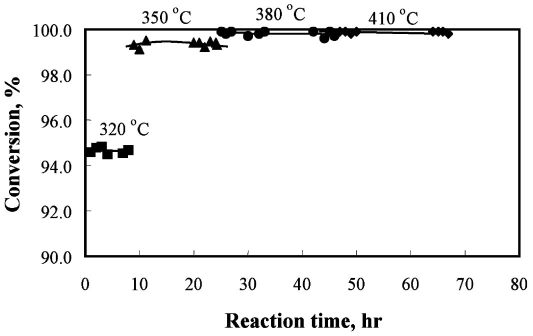

Fig. 5. Catalyst stability in cyclohexane dehydrogenation to produce H_2 over 0.8 wt% Pt/γ-alumina. Reaction conditions: space time = 20 kg cat h/kmol and H_2/cyclohexane = 1/2.

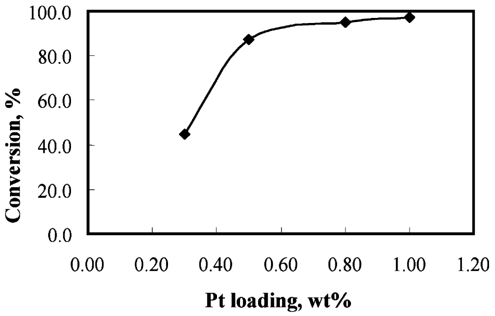

Fig. 6. Effect of Pt loadings on cyclohexane dehydrogenation. Reaction conditions: 320 °C, space time = 20 kg cat h/kmol, and H_2/cyclohexane = 3.

3.2. The dehydrogenation of cyclohexane in a fixed-bed reactor

3.2.1. Effect of various supports

Three different kinds of high surface area supports, e.g., γ-alumina, silica, and activated carbon, were used for the preparation of the catalysts. Fig. 2 shows that the catalytic activity decreases in the order γ-alumina > silica > activated carbon. The catalyst prepared with a γ-alumina support also shows good stability, with no decrease of cyclohexane conversion at 98.7% after 20 h. Therefore, γ-alumina was chosen as the support for the Pt catalysts used in the study of the dehydrogenation of cylohexane and decalin.

3.2.2. Effect of temperature and H_2/cyclohexane molar ratio

The dehydrogenation of cyclohexane was carried out at 260, 280, 300, 320, 340, 360, 380, and 400 °C, respectively. It is shown in Fig. 3 that at space time of 30 kg cat h/kmol the conversions increase from 51.7% at 260 °C to 100% for temperatures above 360 °C. Furthermore, trace amounts of cracking products such as methane and ethane were detected at 380 and 400 °C.

Fig. 4 shows the conversion of cyclohexane as a function of the H_2/cyclohexane molar ratio at 320 °C. The dehydrogenation of cyclohexane is not thermodynamically limited at 320 °C, therefore the effect of hydrogen is not significant. The conversion of cyclohexane decreases only slightly with an increase in the H_2/cyclohexane molar ratio. The addition of hydrogen is known to minimize coking during dehydrogenation processes [16,17]. Accordingly, the stability of a Pt/γ-alumina catalyst was tested in a reactant stream with a hydrogen to cyclohexane molar ratio of 1:2.

3.2.3. Stability of the Pt/γ-alumina catalyst

The dehydrogenation was carried out over 0.8 wt% Pt/γ-alumina catalyst at a cyclohexane space time of 20 kg cat h/kmol, a hydrogen to cyclohexane molar ratio of 1 to 2, and reaction temperatures in the range 320–410 °C. As shown in Fig. 5, the conversions of cyclohexane at 320 (10 h), 350 (16 h), 380 (23 h), and 410 °C (22 h) were 94.4, 99.5, 99.8, and 99.9%, respectively, with no apparent catalyst deactivation.

3.2.4. Effect of Pt loading and of the addition of Sn

Fig. 6 indicates that the conversions of cyclohexane on four Pt/alumina catalysts with 0.3, 0.5, 0.8, and 1.0 wt% of Pt loadings are 41.0, 87.2, 94.6, and 97.2%, respectively. Fig. 7 shows that the addition of Sn to a Pt/alumina catalyst decreases the

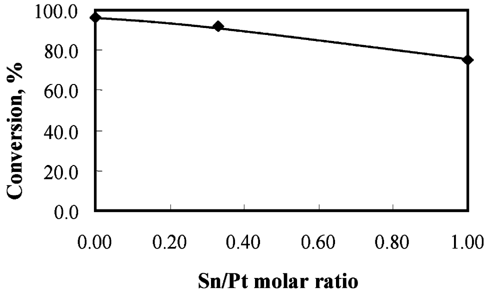

Fig. 7. Effect of Sn/Pt molar ratio on cyclohexane dehydrogenation. Reaction conditions: 320 °C, space time = 20 kg cat h/kmol, and H_2/cyclohexane = 3.

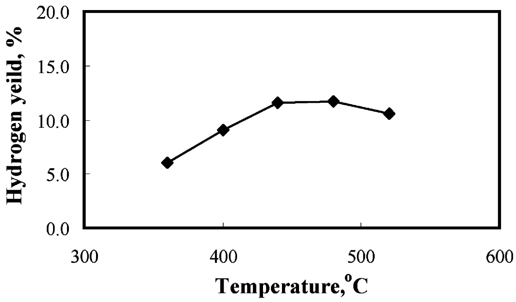

Fig. 8. Hydrogen production yield as a function of reaction temperature in the dehydrogenation of Jet A surrogate over a Pt/γ-alumina catalyst. Feed of Jet A surrogate = 10 ml/min, H_2 = 10 ml/min, and N_2 = 40 ml/min.

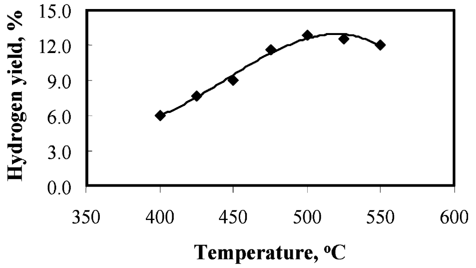

Fig. 9. Hydrogen production yield as a function of temperature in the dehydrogenation of Jet A on Pt/γ-alumina catalyst. Jet A = 10 ml/min, H_2 = 10 ml/min, and N_2 = 40 ml/min.

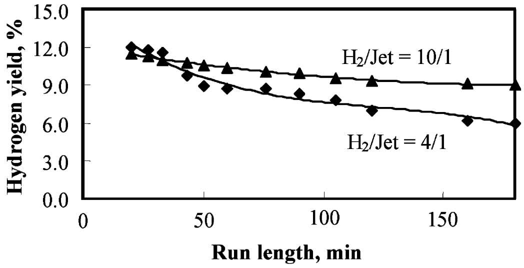

Fig. 10. Effect of H_2/Jet A molar ratio on the dehydrogenation of Jet A at 500 °C. Feeds were as follows: Jet A = 10 ml/min, H_2 = 10 ml/min, and N_2 = 40 ml/min.

catalyst activity, presumably by coverage of the active Pt sites. However, it has been reported in catalytic reforming work that the addition of Sn prevents the sintering of Pt clusters and improves catalyst stability toward deactivation by coking [18].

3.3. Dehydrogenation of decalin

The conversion of a decalin mixture, consisting of 24% cis- and 76% trans-isomers, was also investigated on a Pt/alumina catalyst. Isomerization between the two decalin isomers occurs on the acid γ-Al_2O_3 sites, whereas both isomers are dehydrogenated on the Pt sites into an intermediate, tetralin, which, in turn, is dehydrogenated to naphthalene thereby generating more H_2. With appropriate space times and temperatures very high selectivities for naphthalene and low selectivities for tetralin can be achieved. These results along with the kinetic modeling are detailed in another paper [14].

3.4. Dehydrogenation of Jet A

3.4.1. Dehydrogenation of Jet A surrogate on Pt/γ-Al_2O_3 catalyst

The Jet A surrogate blend used in this experiment has a molar average formula of $C_{10}H_{19}$ and consists of six components with the following weight percentages: 30% decane, 35% dodecane, 14% methylcyclohexane, 6% decalin, 10% *t*-butyl benzene, and 5% 1-methyl naphthalene. Fig. 8 shows the hydrogen yield from a Jet A surrogate via dehydrogenation as a function of temperature. The hydrogen yield, defined as the hydrogen produced per total hydrogen content in the fuel, increases with temperature up to 480 °C, then falls. The maximum yield obtained at 480 °C is 11.6%, lower than the yield obtained in the dehydrogenation of pure cyclohexane and decalin, 47.5 and 52.0%, respectively. Gas chromatographic analysis of the reactant and product streams showed that the conversions of paraffins were low. If the Jet A paraffin components, which account for 60 molar% in the Jet fuel composition, could be reformed to aromatics as in industrial naphtha reforming, the H_2 yield could obviously be substantially increased.

3.4.2. Dehydrogenation of Jet A on various catalysts

3.4.2.1. Pt/γ-alumina catalyst The Jet A used in this experiment consists of 18% aromatics, 20% naphthenes, 60% paraffins, and 2% olefins. Fig. 9 shows the hydrogen production yield on a 0.8 wt% Pt–0.3 wt% Sn/alumina catalyst as a function of temperature. The maximum yield obtained at 500 °C is 12.8%. The low yield indicates that paraffins in Jet A are not reformed to aromatics, probably because the acidity of γ-alumina is not sufficiently high to promote this reaction. Also, the catalyst is prone to deactivation in Jet A dehydrogenation. The hydrogen yield, defined as hydrogen produced per total hydrogen content in Jet A, decreases from 12.0 to 7.2% after 180 min (Fig. 10). Due to the deactivation of the catalyst, the H_2/Jet A molar ratio was increased to 10. The yield of hydrogen decreased from 11.2 to 9.2% after 180 min. Subsequently, a USY zeolite with acidity substantially higher than alumina was used as a support for Pt.

3.4.2.2. Pt/USY catalyst Fig. 11 compares the dehydrogenation of Jet A over various catalysts. In industry, bifunctional catalysts with both metal and acid sites are employed in catalytic reforming to convert paraffins into aromatic compounds, producing H_2 as a by product. In this process the metal sites are responsible for the dehydrogenation of paraffins. The acid

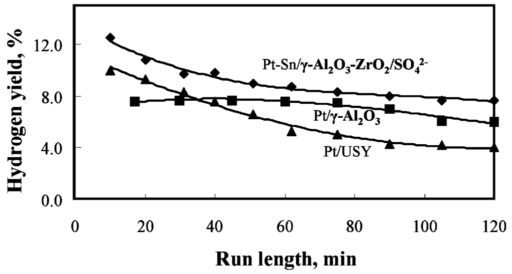

Fig. 11. Dehydrogenation of Jet A over various catalysts at 425 °C. Feeds were as follows: Jet A = 10 ml/min, H_2 = 10 ml/min, and N_2 = 40 ml/min.

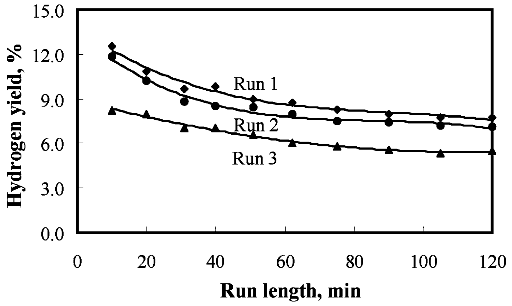

Fig. 12. Regeneration of Pt-Sn/γ-Al_2O_3-ZrO_2/SO_4^{2-} hybrid catalysts used in the dehydrogenation of Jet A by oxidation in air at various temperatures. Run 1—fresh catalyst; Run 2—oxidation at 500 °C in air, then reduction at 300 °C in H_2; and Run 3—oxidation at 500 °C in air, then reduction at 300 °C in H_2.

sites are essential to transform these dehydrogenated long chain hydrocarbon intermediates into cycloalkanes. Acid sites may also crack the paraffins to generate H_2. The acidity of USY is higher than that of γ-Al_2O_3 and consequently H_2 production over Pt/USY at 425 °C is 2% higher than that on Pt/γ-Al_2O_3 catalyst. However, due to the relatively small channel openings of USY, deactivation is much more rapid.

3.4.2.3. Pt-Sn/γ-Al_2O_3-ZrO_2/SO_4^{2-} hybrid catalysts Sulfated zirconia is a well known superacid catalyst and can be incorporated into a Pt/γ-alumina catalyst to increase its acidity. Pt-Sn/γ-alumina-ZrO_2/SO_4^{2-} hybrid catalysts were prepared by calcining a physical mixture of Pt-Sn/γ-Al_2O_3 to ZrO_2/SO_4^{2-} consisting of a mass ratio of 6 to 4 at 550 °C for 12 h. For identical operating conditions the hydrogen production yield over this hybrid catalyst is 5% higher than achieved with Pt/γ-alumina. This is clearly not an optimized catalyst, therefore there is great potential for further optimization.

3.4.2.4. Catalyst regeneration The catalysts used in this study are prone to deactivation. The hybrid catalyst was regenerated by two ways as shown in Fig. 12: (1) regeneration by oxidation in air at 500 °C, then reduction in H_2 at 300 °C; and (2) regeneration by oxidation in air at 300 °C, then reduction in H_2 at 300 °C. Fig. 12 shows that oxidation at 500 °C is essential for complete remove of the deposited coke and full recovery of the catalyst activity.

4. Conclusions

The dehydrogenation of a Jet A hydrocarbon mixture was investigated over Pt/γ-Al_2O_3 and Pt/γ-Al_2O_3-ZrO_2/SO_4^{2-} for the production of hydrogen for low temperature fuel cell applications. The distinct advantage of this process is that the hydrogen so produced is free of CO and can be used in typical low temperature fuel cells without further purification. For dehydrogenation of Jet A on Pt/γ-Al_2O_3, the conversions of paraffins, the major component in Jet A, are low, most likely because the acidity of γ-alumina is not sufficiently high. Bifunctional catalysts with both metal and acid sites are essential to increase the hydrogen yield for this application. The acidity can be increased by the addition of a strong acid component, sulfated zirconia, or by using a strong acid support. The strong acid sites promote the cracking ability of Pt-Sn/γ-Al_2O_3 as well as the transformation of paraffins to aromatics, leading to an increase in the hydrogen production. The strong acidity may also promote coke formation and thus to rapid deactivation of the catalyst. Nevertheless, the deactivated catalyst can be regenerated by oxidation at 500 °C.

Acknowledgments

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