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ORIGINAL ARTICLE

Synthesis of Pd Composite Tubes by Electroless Plating for Isobutane Dehydrogenation

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ABSTRACT

Isobutene is used as a raw material in the production of ethers for increasing the octane rating and reducing exhaust emissions in gasoline. Dehydrogenation of isobutane is an endothermic equilibrium-limited reaction. Recent studies have focused on overcoming equilibrium limitations by removing the product hydrogen through a membrane. In this study, alumina-modified porous glass supports were plated with Pd using electroless plating (ELP). Plating studies were carried out at 35°C and pH 10-11 in a hydrazine-based plating bath. The thickness of the Pd layer was approximately 100-130 εm. The synthesized composite tube was tested in an isobutane dehydrogenation process over a pure Cr2O3 catalyst in a fluidized bed reactor. The reaction tests were performed at 450oC at slightly greater than atmospheric pressure. The fractional conversion of i-C4H10 to i-C4H8 was approximately 40% at the beginning of the first reaction trial. This value decreased to 5% after 60 minutes. High conversion values were observed in the first trial despite loss of isobutane through the Pd membrane. It was thought that this was due to Pd catalysis of an isobutane hydrogenation reaction using ambient hydrogen, and that this side reaction helped shift the reaction equilibrium to the product side. The conversion decreased as the catalytic activity was reduced by carbon deposits from rapid cracking of methane at the high temperatures resulting from the hydrogenation reaction.

Key Words: *Pd composite tube, electroless plating, isobutane dehydrogenation.*

1. INTRODUCTION

Motor vehicle exhaust is an important source of air pollution. Addition of MTBE (methyl tert-butyl ether) or ETBE (ethyl tert-butyl ether) to gasoline reduces CO and unburned hydrocarbon emissions as well as increasing the octane number. For this reason the demand for isobutene as a raw material for MTBE and ETBE production has increased. Because isobutene production at oil refineries is rather inefficient, it is also produced through dehydrogenation of isobutane. This process is a highly endothermic equilibrium-limited reaction. It is possible to achieve high conversion values at low pressure and high temperature.

Studies of isobutane dehydrogenation have generally focused on catalyst development and overcoming

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[♠] Corresponding author, e-mail: meltem@gazi.edu.tr equilibrium limitations. In a study by Cortright et al. (2000), catalysts were prepared by loading Pt and Sn on L-zeolite and SiO_2 supports. The L-zeolite-supported catalysts had a higher resistance to deactivation. The addition of K to the catalysts increased isobutene selectivity and prevented coke formation reactions.[1] Castillo et al. (2003) studied isobutane dehydrogenation over H-mordenite and β-zeolite.[2] Silvestre-Albero et al. (2005) reported that Zn added to Pt/activated carbon catalysts increased isobutene selectivity.[3] n-butane dehydrogenation over VO_x/SiO_2 catalysts was investigated by Xu et al. (2009). The highest conversion was obtained over 12%(wt) VO_x catalyst.[4] In a review by Shiju et al. (2009), the effects of dehydrogenation catalyst structure and composition on the reaction were evaluated.[5] The first study aimed at overcoming equilibrium limitations by removing hydrogen from the reaction medium using a Pd membrane was conducted by Matsuda et al. (1993). [6]Casanave et al. (1999) studied isobutane dehydrogenation over Pt-In catalyst in a packed-bed zeolite membrane reactor operated under both co-current and counter-current conditions.[7] The separation factor was higher in counter-current operation, but the isobutene yield was the same in both cases, four times higher than obtained in the conventional reactor. [8-10] Sznejer and Sheintuch (2004) investigated isobutane dehydrogenation over a Cr_2O_3/alumina catalyst in a carbon membrane reactor. Reduced pressure was the driving force and 40% isobutane conversion was obtained at 500°C.[11] Guo et. al. (2003) prepared a composite tube by coating Pd-Ag alloy (8.6εm) on an Ŭ-alumina support. Isobutane conversion over Cr_2O_3/alumina catalyst in the membrane reactor was approximately 51% compared to approximately 16% in a fixed-bed reactor.[12] A reactor system for isobutane dehydrogenation using a Pd-Ag/stainless steel composite tube was constructed by Liang and Hughes (2005). Their experiments were carried out at 485°C over Pt/Al_2O_3 catalysts. The isobutene yield was 29% at a sweep gas flow rate of 1000 mL/min. In a similar conventional reactor the isobutene yield was 20%.[13]

There is increasing interest in using Pd and Pd-based membranes in dehydrogenation applications. [14,15] In order to minimize the material cost and achieve a high hydrogen permeability, applying a thin Pd film to an appropriate support is preferred to using free standing thick foils.[16,17] Porous ceramics, metal oxides, and metallic materials have been employed as membrane supports. Among the methods for depositing thin metallic membranes, the electroless plating technique provides advantages over other alternatives in terms of operational flexibility, complexity of equipment, cost performance, and applicability to non-conductive materials with complicated shapes. Electroless plating refers to the autocatalytic or chemical reduction of aqueous metal ions and subsequent plating onto a substrate.

In this study, a Pd layer was plated over an alumina-modified porous glass tube using the electroless plating technique (ELP). The thickness, composition, and surface morphology of the plated layer were analyzed using SEM/EDS. The composite tubes were tested in an isobutane dehydrogenation reaction over a fluidized pure Cr_2O_3 catalyst.

2. EXPERIMENTAL

2.1. Pd Composite Tube Synthesis and Characterization

Kilicarslan et al. (2008) observed that a denser metallic film was obtained when the electroless plating (ELP) technique was applied after modification of the porous support with alumina.[17] In this study, porous glass supports (ID:1 cm, OD:1.4 cm, H:10 cm) supplied by the Robu GlasFilter company were modified with alumina according to the procedure in the previous reference. Alumina layer was deposited onto the outside of porous glass tube. Aluminum hydroxide ($Al(OH)_3$) was obtained by the reaction between aluminum nitrate and urea. The support was then dipped into $Al(OH)_3$ gel and the gel was forced to the surface of the tube by applying a vacuum. Support was heated at 550°C and $Al(OH)_3$ transformed to γ-Al_2O_3. Contact between the inner surface of the support and the activating solutions was prevented and the outer surface of the support was activated by sequentially dipping the support into acidic $SnCl_2$ and $PdCl_2$ solutions. The plating studies were performed by dipping the activated support into the plating bath (3.7 g/L $PdCl_2$, 7.8 g/L Na_2EDTA, 650 mL/L NH_4OH-15M, 15 mL/L N_2H_4-1M). The bath temperature was maintained at 35°C and pH 10-11. The bath solution was renewed for each plating step. After four repeated plating steps, two additional steps were performed in which the plating bath solution was forced into the tube surface by applying a vacuum to the tube. The plating steps were carried out for periods of two hours at a loading value of $0.2 mL/mm^2$. After each step, the plated support was dried at 120°C and weighed. Figure 1 contains SEM photographs of the original support and a composite tube.

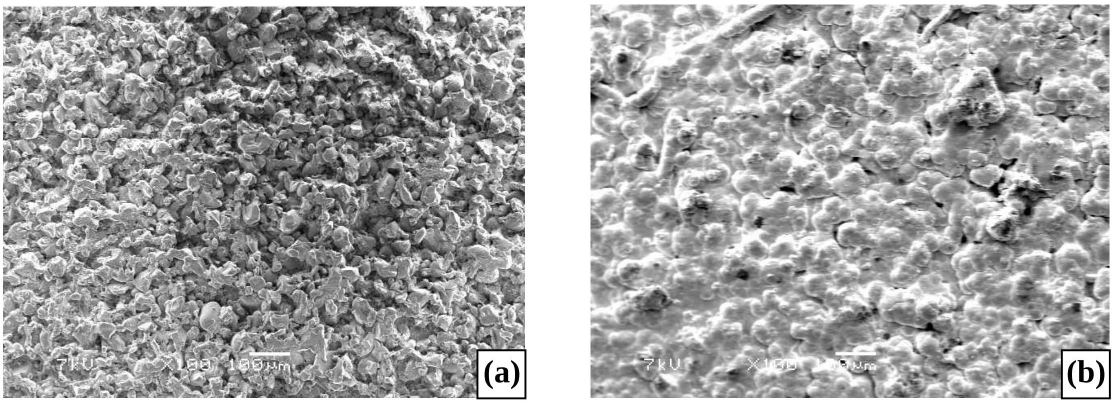


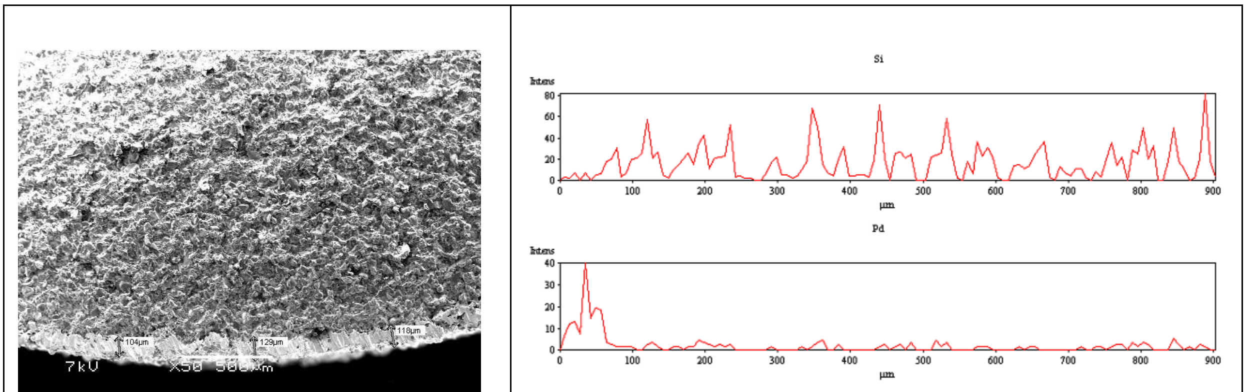
Figure 1. SEM photographs of the surfaces**:** original support (a), composite tube (b).

The surface compositions of the composite tubes were determined using EDS analyses and are described in Table 1.

Table 1. Surface compositions of the composite tube (%wt, EDS analysis).

Pd	Zr	Na	Si	Ca	Fe	Mg	Al	O
89.21	6.65	1.88	1.22	0.42	0.23	0.22	0.17	0.00

Figure 2 contains a cross-sectional SEM photograph of a composite tube and the distribution of Pd and Si over the cross-section.



(a) **(b)**

Figure 2. Cross-sectional SEM phtograph of the composite tube (a) distribution of Pd and Si over the cross-section (b).

The plating thickness was approximately 130 μm (Figure 2a). Figure 2b reveals that the Pd coating was dense to a depth of 100 εm from the surface, which was confirmed in the SEM photograph. The total mass gain after activation of the synthesized composite was 48 mg/cm^2.

2.2. Determination of Hydrodynamic Parameters of the Fluidized Bed Reactor

Pure chrome oxide (Cr_2O_3) catalyst obtained from Alfa Aesar (Johnson Matthey Company) was used in the reactor tests. The physical properties of the catalyst are provided in Table 2.

Table 2. Physical properties of the catalyst used in reaction tests.

Solid density	Average pore diameter	BET surface area	Particle size
5 g/cm^3	1000 nm	1.63 m^2/g	84 εm

Prior to the dehydrogenation tests experiments were carried out to determine the hydrodynamic parameters of fluidized-bed reactors equipped with Pd composite tubes. Fluidization occurs when the gravitational force acting on the catalyst granules balances the upward forces due to the gas stream. The minimum fluidization velocity (u_{mf}) is the most important hydrodynamic parameter in fluidized beds. A glass tube having the same dimensions as the composite tube was used in determining the minimum fluidization velocity. Pressure drops caused by the presence of the catalyst were measured at 17°C at several carrier gas velocities. The maximum pressure drop was observed at a velocity of approximately 1.5 cm/s, and this was assumed to be the minimum fluidization velocity. A minimum velocity of 1.6 cm/s was predicted using the correlation suggested by Wen and Yu (1966).[18] After sight of harmony between theoretical and experimental u_{mf} values, u_{mf} at 450^{o}C was calculated as 0.8 cm/s. Kunii and Levenspiel (1991) demonstrated that system pressure did not affect the minimum fluidization velocity for Ar<1000.[19] Because Ar (Archimedes number) was less than 1000 for our experimental conditions, the minimum fluidization velocity was measured at atmospheric pressure.

A second important parameter in fluidized-bed reactors is the transport disengaging height (TDH). TDH is the distance from the surface of the moving bed to the region where the solid concentration is lowest. No solid transport is expected in reactors longer than the TDH.[19] The TDH was estimated at 6.6 cm using the method proposed by Fournal et al. (1973) for fluidized beds containing small particles.[20] Kunii and Levenspiel (1991)[19] proposed 1 as a safe value for the bed aspect ratio (H/D, static bed height/column diameter), and we therefore selected an H/D ratio of 1 for our experiments. The amount of catalyst providing this ratio was 0.8g.

2.3. Investigation of Isobutane Dehydrogenation in Fluidized Bed Reactor Employing Pd Composite Tube

The feed flow rate was maintained at 1.7 times the minimum fluidization velocity in reaction experiments. The reactor height was 3.6 times the TDH value and a glass extension was welded to the composite tube to reach this height. A cyclone suitable for retaining the catalyst particles was placed at the reactor outlet. Figure 3 is a schematic diagram of the reactor system.

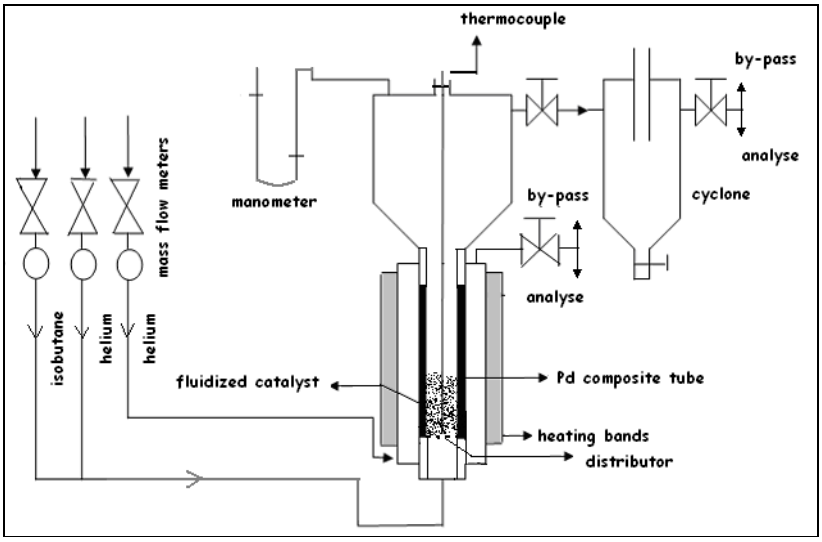


Figure 3. Schematic diagram of the reactor system.

The feed flow composed of 60% isobutane and 40% helium was introduced to the reactor at a rate of 32 mL/min. The catalyst was placed into the composite tube and fluidized. As seen in Figure 3, a glass apparatus surrounded the tube to collect the gas permeating through the tube. Helium (62 mL/min) was passed through this apparatus as a sweep gas. The reactor was operated at slightly above atmospheric pressure (P_{atm} + 0.005 atm). Reaction studies were performed at 450^{o}C. The temperature was controlled by heating bands wrapped around the reactor. The feed flow was continuously introduced to the reactor for 60 minutes. Gas samples from the inside and outside of the composite tube were analyzed using gas chromatography. In these analyses, gas samples (1ml) passed through the silica column were analyzed using TCD detector. Helium was used as carrier and reference flow.

3. RESULTS AND DISCUSSIONS

Isobutane dehydrogenation is an endothermic and equilibrium-limited reaction. We aimed to overcome the equilibrium limitation by removing hydrogen from the reaction medium using a tubular synthetic Pd membrane. The catalyst was placed in the tube and fluidized with the feed gas. Fractional conversions of isobutane to isobutene were observed for 60 minutes beginning with the admission of isobutane to the reactor. The conversion of isobutane to isobutene was determined by analyzing samples removed simultaneously from the inside and outside of the tube. Four sequential reaction trials were performed with the catalyst being renewed after each trial. The change in fractional conversion with time in the first and fourth trials is plotted in Figure 4. The fractional conversion of isobutane to isobutene in the first trial was approximately 40% between 5 and 15 minutes. The fractional conversion began to decrease after 15 minutes and reached 5% after 60 minutes. In repeat experiments with renewed catalyst but using the same composite tube, conversion values also began to decrease after 15 minutes. However, the highest conversion value in these experiments was approximately 20%. Under the experimental conditions employed, the equilibrium conversion was calculated to be 24%.[21] The conversion levels greater than the equilibrium value observed during the first trial may be explained by improved hydrogen removal.

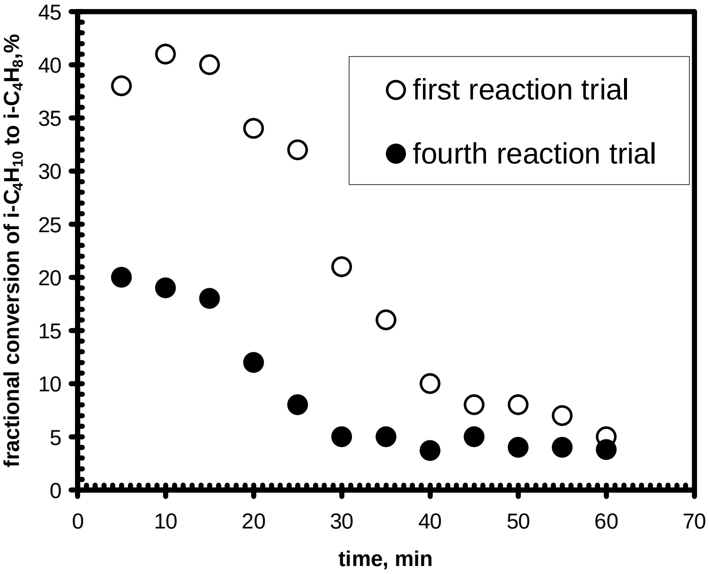


Figure 4. Fractional conversion of i-C_4H_{10} to i-C_4H_8 vs. time in the reactor (T=450°C, P=atmospheric, Feed flow=32mL/min).

The failure to obtain the initial high conversion values in subsequent trials with renewed catalyst was thought to be due to changes in the composite structure. SEM/EDS studies were conducted on the composite surface and cross-sections after the reaction experiments. Figure 5 contains SEM photographs of the composite surface before the first trial and after the fourth trial. New formations on the aggregated grains were observed in the micrograph obtained after the fourth trial. The initial bright metallic appearance of the tube also disappeared. A composition analysis of the composite surface was carried out using EDS in order to define the observed differences. The results are presented in Table 3 together with composition data obtained before the reaction. A significant amount of deposited C was found on the surface after reaction. EDS mapping of Pd and C concentrations was carried out on the surface and cross-section to determine the distribution of C in the composite structure (Figure 6). Dense C deposits occurred particularly in regions containing Pd both on the surface and in the cross-section.

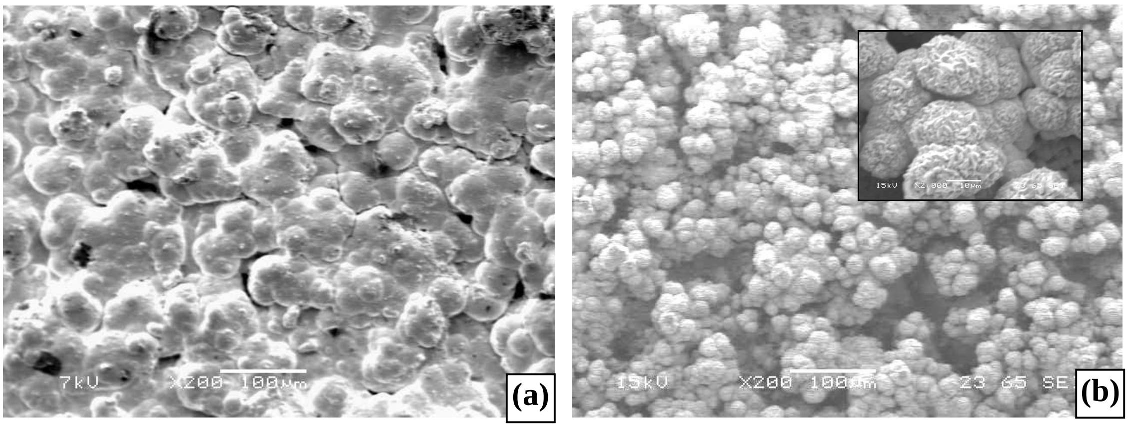


Figure 5. SEM photographs of the composite surface: before reaction trials (a), after fourth reaction trial (b).

Table 3. Compositions of composite surface obtained before and after reactions (wt%, EDS analysis).

	Pd	**C**	**Zr**	**Na**	**Si**	**Ca**	**Fe**	**Mg**	**Al**	**O**
Before reactions	89.21	-	6.65	1.88	1.22	0.42	0.23	0.22	0.17	0.00
After fourth reaction trial	71.82	23.33	0.19	0.54	0.25	0.00	0.13	0.16	0.07	3.51

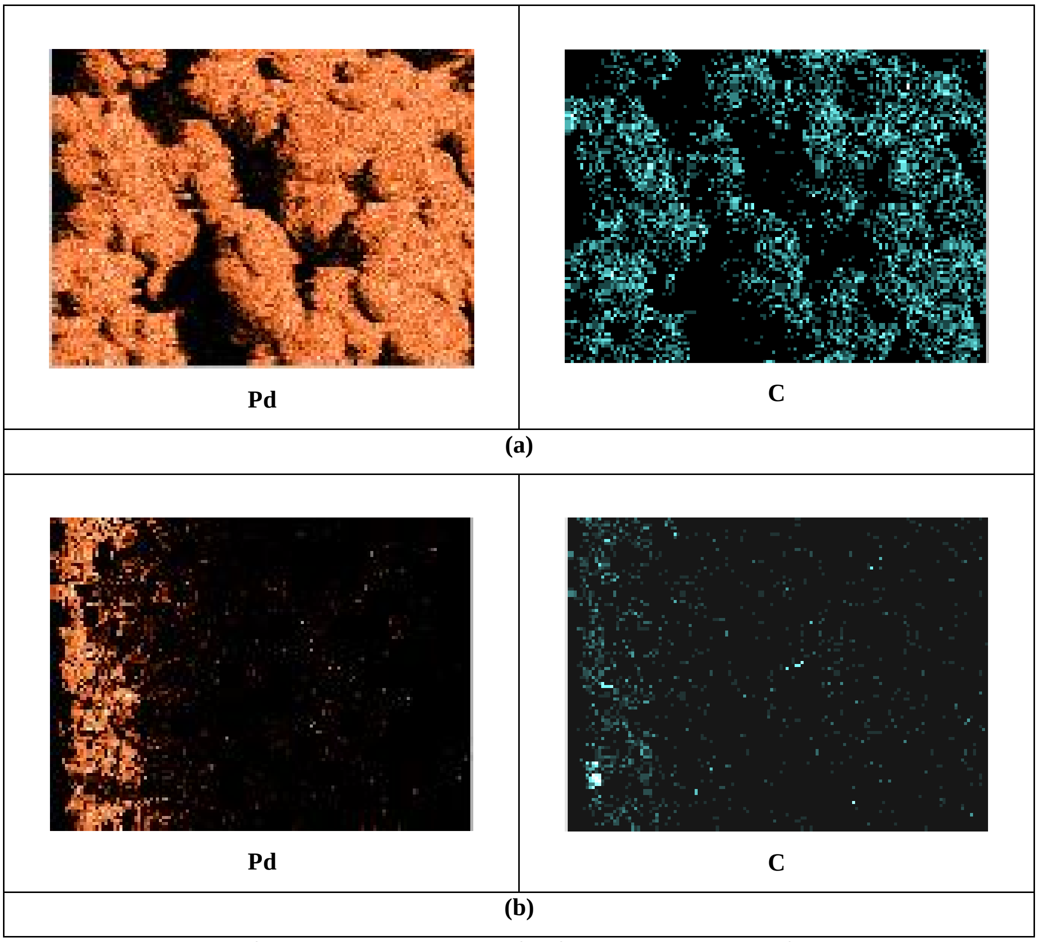


Figure 6. EDS mapping of Pd and C concentrations after fourth reaction trial: surface (a), cross-section (b).

The compositions of gas samples collected after 15 minutes from inside and outside the tube are listed in Table 4. The streams contained isobutane, isobutene, propane, and hydrogen in addition to the carrier helium.

Table 4. Compositions of gas samples after 15 minutes (T=450^{o}C).

	first reaction trial		fourth reaction trial	
component	from tube inside	from tube outside	from tube inside	from tube outside
i-C_4H_{10}	4.00	26.00	24.40	31.85
Ķ-C_4H_8	8.78	10.62	2.48	4.37
C_3H_8	14.26	28.02	2.12	1.65
H_2	48.28	8.01	14.63	3.60
He	24.68	27.35	56.37	58.53

It has been suggested that the following side reactions (equations 2 and 3) can occur during isobutane dehydrogenation: [13]

$$i-C_4H_{10} \Leftrightarrow i-C_4H_8 + H_2 \qquad \Delta H = 117.08\ kJ/mol \qquad (1)$$

$$i-C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4 \qquad \Delta H = -45.02\ kJ/mol \qquad (2)$$

$$i-C_4H_{10} \rightarrow C_3H_6 + CH_4 \qquad \Delta H = 79.37\ kJ/mol \qquad (3)$$

Under the current reaction conditions, the equilibrium constant for Eq. 2 was 256 and for Eq. 3 was 4029, while the equilibrium constant for the main reaction was 0.03, indicating that neither side reaction was equilibrium limited. The presence of propane in the product stream demonstrated the occurrence of isobutane hydrogenation, the first side reaction (Eq. 2). However, this reaction also produces methane, which was not detected in the gas streams. This suggests that the methane is quickly decomposed, producing C deposits.

In the first trial, the fractional conversion of isobutane to isobutene was greater than the equilibrium conversion level. Overcoming the equilibrium limitation for Equation 1 is possible by removal of one or both of the products from the reaction medium. An examination of Table 4 reveals that isobutane passed through the composite tube even during the first trial. High conversions were obtained between 5 and 15 minutes despite the isobutane permeation. The inside of the tube was maintained at a pressure slightly greater than atmospheric pressure while the outside of the tube was at atmospheric pressure. This pressure gradient forced hydrogen and other gaseous components to pass through the tube, in conjunction with the concentration gradient between the inside and outside of the tube. The helium sweep gas outside the tube was used to keep this driving force strong. Since low conversion values were expected when isobutane permeated the composite tube, the observed 40% conversion was thought to be due to a side reaction that consumed the hydrogen in reaction medium. The outer gas stream contained approximately 8% hydrogen. In addition to this low hydrogen content, high ratios of propane were detected in the stream passing through the tube. The external surface of the support tube was plated with Pd, and the catalyst was placed inside the tube. An evaluation of the characterization studies and the results of gas analyses suggest that isobutane hydrogenation (Equation 2) occurs around Pd grains not yet coated with C, with high conversion values obtainable using ambient hydrogen. Dittmeyer et al. (2001) reported that Pd could be catalytically active in hydrogenation reactions.[22]

The composite tube prepared in this study was subjected to heat treatment twice at the intended reactor temperature (450°C) before being used in reactions. SEM analyses conducted after heat treatment and nitrogen permeability measurements indicated that the composite structure was preserved. In SEM photographs of the surface, the metal grains forming the Pd layer became smaller and clustered after the reaction. This was expected to occur at higher temperatures. In the experimental studies, the catalyst bed was assumed to be at the reactor temperature. As mentioned above, an exothermic hydrogenation reaction occurred in a region close to the outer surface of the tube, and it is possible that the temperature in these regions was higher than the overall reaction temperature. The composite layer exposed to high temperatures was deformed, and coke formation caused by methane decomposition was initiated at temperatures over 450°C. [23, 24] The absence of methane in the gas streams could be explained by rapid coke formation in the localized high-temperature regions.

In addition to the reactor equipped with a Pd composite tube, reactions were also carried out in a fluidized-bed reactor system prepared using a non-porous glass tube similar in size to the composite tube. The reaction conditions, catalyst, and amount were the same as those of the composite tube reactor. Methane and propane were not detected in product stream and this case showed that isobutene hydrogenation did not occurred. Fractional conversions of isobutane to isobutene obtained in the glass tube reactor are presented together with the values for the fourth reaction trial in Figure 7. The fractional conversion remained at approximately 20% from 5-25 minutes in the glass tube reactor, then began to decrease. The conversion values fell below 20% earlier in the reactor containing the Pd composite tube. After repeated reactions, the Pd in the composite structure became covered with C. As a result of this covering, the composite structure lost its selectivity to hydrogen and was unable to remove hydrogen from the reaction medium through a hydrogenation mechanism. As a result of the disadvantages created by C deposition and escape of isobutane from the reaction medium, the conversion values were lower than in the reactor employing a non-porous tube.

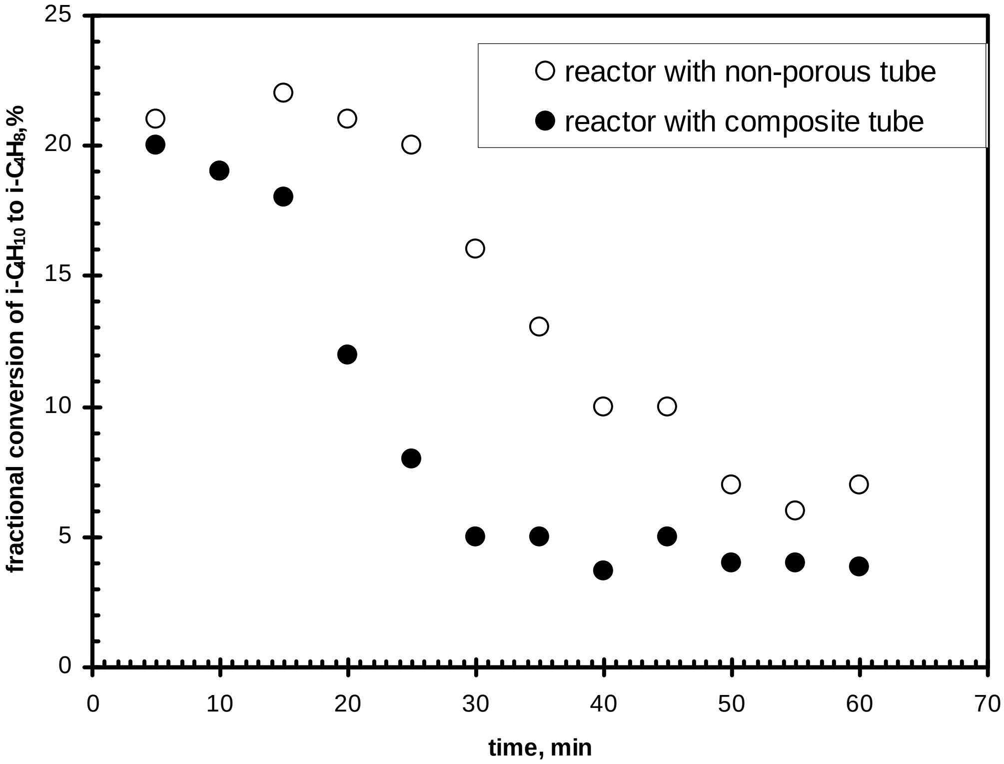


Figure 7. Fractional conversion of i-C_4H_{10} to i-C_4H_8 vs. time in the reactors with non-porous tube and composite tube (T=450°C, P=atmospheric Feed flow=32mL/min).

CONCLUSIONS

Alumina-modified porous glass tube was plated with Pd by electroless plating technique. This composite tube was tested for use in isobutane dehydrogenation over pure Cr_2O_3 catalyst in a fluidized bed reactor system. In addition to hydrogen, isobutane, propane, and isobutene also permeated the composite tube during the reaction. The presence of propane in the product stream showed that the occurrence of isobutene hydrogenation (side reaction). The conversion levels greater than the equilibrium value observed in the initial reaction trials were explained by this side reaction consumed the hydrogen in reaction medium. Methane (another product of the hydrogenation reaction) was not detected in gas analyses because it was rapidly decomposed to carbon at the high temperatures created by the exothermic hydrogenation reaction. In experiments with non-porous tube, products of hydrogenation reaction were not detected. This case confirmed that Pd layer was active in isobutene hydrogenation.

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