Lower Temperature Dehydrogenation of Methylcyclohexane by Membrane-assisted Equilibrium Shift

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Selective removal of hydrogen by the palladium membrane of novel configuration shifts the equilibrium in the dehydrogenation of methylcyclohexane allowing a continuous operation at below the critical temperature of palladium α–β phase transition.

Toluene (TOL) can store hydrogen in the form of methylcyclohexane (MCH) with a specific volume of 46 kg H_2 m^{-3}. Since TOL and MCH are liquid at ambient pressure and temperature, the system by use of the reversible reaction given in (1) is one of the feasible options for storage and transportation of hydrogen.[1–3]

$$C_7H_{14} = C_7H_8 + 3H_2 \quad H_R{}^{298} = 204\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

This reversible reaction is highly endothermic and strongly restricted by the thermodynamic equilibrium. When hydrogen is contentiously removed from the system, the reaction can be shifted toward the product side. In other words, higher conversion can be attained at lower temperature and moreover pure hydrogen can be recovered at the same time.

Palladium membranes, which allow exclusive permeation of hydrogen, have been applied by combination with catalytic dehydrogenation in order to fulfill the industrial demands.[4–6] However, conventional thin palladium membrane tends to be suffered from hydrogen embrittlement due to α–β transition of palladium hydride at below the critical temperature (573 K). This accompanied by a lattice expansion and the resulting internal stress generates the defect in the membrane. To assure the membrane stability, the reaction temperature should be kept above 573 K. However in such condition formation of coke tends to occur leading to decrease the catalyst activity.[7,8]

Recently, we have developed the novel membrane in which palladium nanoparticles are packed in the pores of support layer.[9] The "pore-filled type" configuration of palladium membrane realized remarkable durability despite operated at below the critical temperature of α–β phase transition. In this work, we have examined the catalytic dehydrogenation of MCH in the temperature range of 423–598 K by combination with the pore-filled type membrane to attain an improved efficiency in the lower temperature operation.

A 0.5 g of catalyst loaded with 1 wt % of platinum on alumina powder (Aldrich Co.) was mixed with 4 g of quartz sand and then packed into the tubular membrane (ϕ 10 mm). Catalyst bed (6 cm) was fixed in the palladium membrane with quartz wool along the permeation zone (8 cm) (Figure 1).[5] The thickness of the palladium layer was estimated to be 5 µm. The hydrogen-permeation rate and selectivity against nitrogen are more than $1 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$ and well over 1000, respectively, at 573 K under a 400 kPa pressure difference. Membrane preparation, characterization and the permeation properties were described previously.[9] The membrane was placed inside of the stainless steel tube as depicted in Figure 1. For use in blank test, the porous alumina tube (ϕ 10 mm) was completely coated with glass enamel in order to stop the gas permeation.

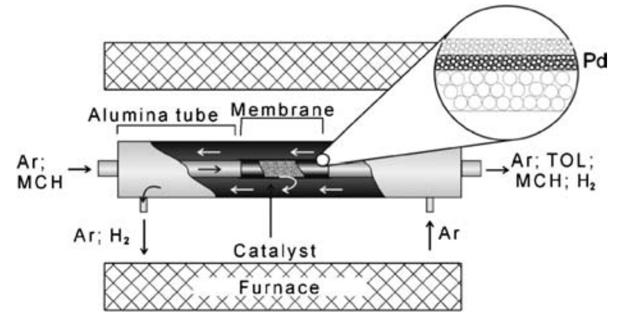

Figure 1. Schematic overview of the membrane reactor. Ar flow rates: inside the membrane tube: 0.024–0.106 mol h^{-1}; outside of the membrane tube: 0.012–0.212 mol h^{-1}, feeding rate of MCH: 1–6 mmol h^{-1}.

The dehydrogenation of MCH was tested in the temperature range between 423 and 598 K under the total pressure of about 100 kPa. The furnace was controlled by thermocouples located at its inner wall and inside the catalytic bed as well. The reactor was set to the reaction temperature and the liquid MCH was continuously injected into carrier gas flow at 398 K. Argon was used as a carrier gas and a sweeping gas. Reactant and products at tube side and shell side were analyzed by gas chromatography either with FID or TCD method.

The Pt/Al_2O_3 catalyst showed appreciable stability and selectivity at the temperature range of operation, and no deactivation was observed for about 600 h of repeated runs. Only hydrogen and toluene were detected as the reaction products, indicating that other side reactions were practically negligible. Reaction at higher temperature leads to stronger adsorption of aromatic compounds and is followed by decomposition and graphitic carbon formation in long term operation. By the use of low-temperature window we successfully avoided the decline of the catalyst activity due to coke formation.

The novel configuration of membrane allowed us to use it below the critical temperature for α–β phase transition of palladium hydride. Only hydrogen was found in the perm side of the membrane, indicating that no defect was present in the membrane. Figure 2 shows the MHC conversion as the function

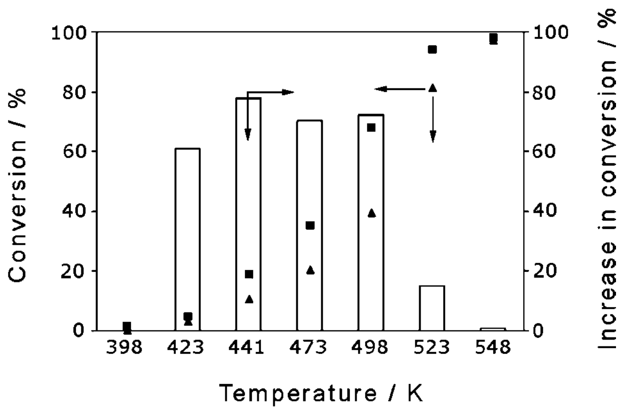

Figure 2. Temperature dependence of reaction conversion: (■) membrane reactor, (▲) blind tube, bar graph indicates the increase of conversion. Feeding rate of MCH: 4 mmol h^{-1}, Ar flow rate: 0.053 mol h^{-1}.

of temperature. Data were obtained with membrane and with blind tube as the blank. The conversion in terms of MCH to TOL was stable (±1) and reproducible in every tested temperature. According to these data, the dehydrogenation reaction starts to proceed at temperature above 398 K. The blind tube results were well correlated with values theoretically calculated for equilibrium conditions. By continuous removal of H_2 with the membrane, an obvious improvement of conversion was attained as given with bar graph in Figure 2. For example, 70% conversion was attained at 498 K, whereas about 518 K is required to attain the same conversion when membrane was not employed. Since the reaction is enhanced by removal of hydrogen increase of sweep gas rate or apply vacuum at perm side can induce the increase of the conversion. Optimization of the reaction condition is under investigation.

The membrane was examined continuously for over 600 h at several temperature ranges and different feeding rate of MCH and Ar gases. We did not observe decrease of membrane performance after 600 h of use in the present temperature range (398–598 K). For example, as given in Figure 3, the conversion and hydrogen found at perm side at 473 K after 500 h operation were almost equal to that observed at early stage (after 100 h).

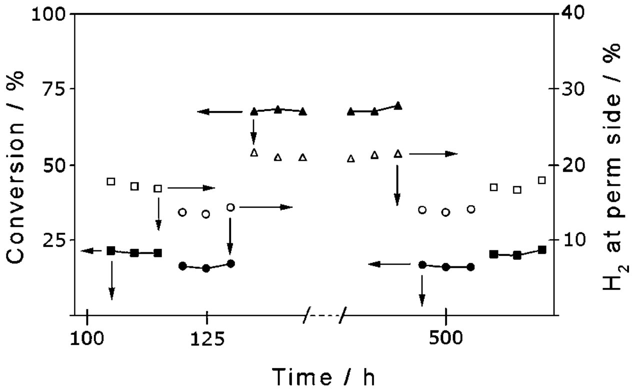

Figure 3. Time dependence in the performance of the membrane reactor. Solid marks indicate the conversion of MCH and blank marks the % hydrogen at perm side. Conversion: (●) at 448 K, (■) at 473 K, (▲) at 498 K; hydrogen found at perm side (○) at 448 K, (□) at 473 K, (△) at 498 K.

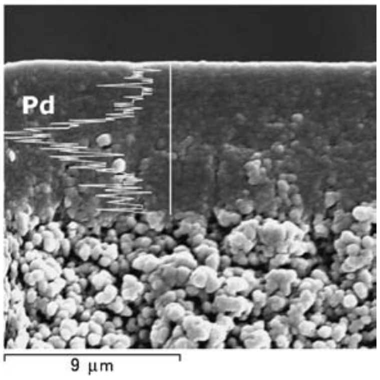

Figure 4. The cross sectional SEM image of the membrane and EDX line profile of palladium after use.

We did not observe any leak of organic compound into perm side indicating that no appreciable defect was generated during the operations. Both the performance of catalyst and membrane were stable leading to constant and repetitive conversion throughout experiment.

Figure 4 shows the cross sectional SEM image of the membrane after 600 h repeated use. The pore-filled palladium phase indicated by EDX analysis appeared similar to that observed of freshly prepared species.[9] The improved durability of the pore-filled type membrane can be attributed to small size of palladium grains, which can suppressed the stress associated with crystal phase transition.[10]

In conclusion continuous removal of hydrogen through the pore-filled type membrane enhanced MCH conversion around 70% in the temperature range of 423–498 K. Membrane and catalyst showed high durability in wide temperature range and can be used without decline of the performance below 598 K for more than 600 h.

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