[Review Paper]

Process Intensification of Dehydrogenation Reactions by Pressure Swing Reactor

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Integration of catalytic reaction and separation operations is important for process intensification (PI). Experimental studies on promotion of the dehydrogenation reaction using hydrogen adsorbent during catalytic dehydrogenation reaction were reviewed. The promotion effect was lost after saturation of the adsorbent, so that regeneration under reduced pressure was essential to start the reaction again. The developed reactor was the so-called pressure swing reactor (PSR) or pressure swing adsorption type reactor (PSA reactor) after the cyclic operations of pressurization and evacuation. Dehydrogenation of cyclohexane, and dehydroaromatization of *n*-hexane, propane and methane were investigated. Pt/Al₂O₃-CaNi₅, Zn/H-ZSM-5-Mg₅₁Zn₂₀, Zn/H-ZSM-5-Ti fine powder, and Mo/H-ZSM-5-Ti fine powder catalysts showed high promotion effects. Because of the differences in reaction temperature, the recommended combination of catalyst and adsorbent varies depending on the reaction. Swing of partial pressure of hydrogen by inert purge gas regenerated the promotion effect showing the potential of the PSR for PI.

Keywords

Pressure swing reactor, Process intensification, Catalytic dehydrogenation, Multifunctional reactor, Hydrogen adsorbent, Dehydroaromatization

1. Introduction**1.1. Multifunctional Reactor and Process Intensification**

Establishment of a sustainable society in the future will require a paradigm shift in chemical processes. Process intensification (PI) is one such strategy for the next generation of chemical processes. PI is intended to increase process efficiency dramatically through reduction in plant size and/or fewer process steps¹⁾.

Recently, many new processes have been proposed which integrate several unit operations. Integration of reaction and separation is a representative “multifunctional operation” which reduces the number of unit processes within the overall process and provides various advantages, such as isolation of reaction intermediates in the consecutive process, removal of catalyst poisons, and selective feeding of specific reactants. These advantages are essential to the development of process intensification for green chemical processes^{1),2)}. Integration of separation with catalysis processes is particularly important^{2)~5)}, because high conversions above apparent equilibrium limitations can be obtained if a specific product is removed from a reversible reaction system.

Our various studies on integration of catalytic reactions with separation operations have proposed promotion of dehydrogenation reactions by using hydrogen adsorbents such as hydrogen adsorbing metals and alloys under catalytic dehydrogenation conditions^{2)~4)}. This review summarizes experimental studies on the integration of catalyst with hydrogen adsorbent and applications to actual reaction systems.

1.2. Pressure Swing Reactor in Integrated Reaction and Separation Processes

The integrated reaction and separation process is very important among the various PI processes. Reactive distillation and reactive precipitation are well-known representative industrial processes. Recently, membrane reactors using molecular selective membranes such as palladium membrane or solid electrolyte membrane have been studied in detail under catalytic reaction conditions. However, the use of membranes under reaction conditions has caused various problems such as limitation of diffusion caused by the geometrical distance between catalyst to membrane, limitation of permeation by inferior operating conditions (partial pressure or temperature limited by the reaction conditions), and poisoning of membrane by the reactants and/or products.

Use of molecular selective adsorbents has been proposed to solve these problems. The use of adsorbent

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can increase the potential to use separation reactors. However, saturation of the adsorbent results in loss of the promotion effect. Therefore, periodic operation by cycling the reaction-separation conditions to optimize the reaction (adsorption) and regeneration (desorption) steps becomes essential. Typical switching parameters are pressure and temperature, and such reactors are usually called the Pressure Swing Reactor (PSR) and Temperature Swing Reactor (TSR), respectively. The PSR is also called the PSA reactor because of the similarity with the Pressure Swing Adsorption (PSA) operation in the gas purification process. The details of

these swing reactors were reviewed previously⁶⁾.

Figure 1 shows representative PSA type reaction operation models. The models range from the simple “pressurized-evacuation scheme” (**Fig. 1 (a)**)⁷⁾ to multiple step schemes such as pressurized-(reaction)-evacuation-regeneration-partially pressurized (**Fig. 1 (b)**)⁸⁾. Many studies have been reported with the single column system, but complex systems using multiple columns have been applied to industrial processes⁹⁾. Numerical modeling of these reactors has been well summarized⁶⁾.

Table 1 summarizes experimental studies on the PSR^{9)~23)}. Many studies investigated the promotion of reversible reactions beyond apparent equilibrium, such as removing carbon dioxide or hydrogen with molecular specific adsorbent during the reforming reaction or dehydrogenation reaction, respectively. Adsorbents which are effective under reaction conditions and catalysts which can make use of adsorbent during reaction are important to develop. **Table 1** (lower) summarizes our studies on the promotion of dehydrogenation reaction with hydrogen adsorbents^{17)~23)}.

2. Experimental Apparatus

Figure 2 shows the typical experimental apparatus used in our catalytic dehydrogenation studies^{17)~24)}. A quartz tubular reactor with 10-mm inner diameter and 300-mm length was used under atmospheric pressure. Pressure swing cycles between reaction gas and purge gas (argon) were conducted with a 6-way valve equipped prior to the reactor tube. Pressure swings between reaction gas and vacuum were achieved by changing the argon line to the evacuation line. A mixture of catalyst particles and hydrogen adsorbent powder was packed into the reactor tube. Liquid reactant was saturated into the carrier gas at the required temperature^{20)~22)}.

Operation of a pilot plant using a single column reactor with 25.4-mm inner diameter and 6.1-m length for methane steam reforming achieved a promotion effect by adsorptive removal of CO₂ under 445 kPa¹²⁾. A two

(a) 2-stage model, (b) multi-stage model.

Fig. 1 Operation of PSR (pressure swing reactor)

Table 1 Experimental Studies of the Pressure Swing Reactor

Reaction	Catalyst	Adsorbent	Reference
$2\text{CH}_2=\text{CHCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{CH}=\text{CHCH}_3$	$\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$	13X-zeolite	10
$\text{CH}_2=\text{CHCH}_2\text{CH}_3 \rightarrow \text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{H}_2$	$\text{CrO}_2/\text{Al}_2\text{O}_3$	K,Y-zeolite	11
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Reforming catalyst	Hydrotalcite	12, 13
$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$	Ni-catalyst	Hydrotalcite	14
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	WG-shift catalyst	Na, X-zeolite	15
$\text{C}_6\text{H}_{11}-\text{CH}_3 \rightarrow \text{C}_6\text{H}_5-\text{CH}_3 + 3\text{H}_2$	$\text{Pt}/\text{Al}_2\text{O}_3$	Clay adsorbent	9
$\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$	Pt catalyst	MS-5A	16
$\text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_6 + 3\text{H}_2$	$\text{Pt}/\text{Al}_2\text{O}_3$	CaNi_5	17, 18, 19, 20
$n\text{-C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_6 + 4\text{H}_2$	$\text{Zn}/\text{H-ZSM-5}$	Mg alloy	21
$2\text{C}_3\text{H}_8 \rightarrow \text{C}_6\text{H}_6 + 5\text{H}_2$	$\text{Zn}/\text{H-ZSM-5}$	Ti powder	22
$6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 5\text{H}_2$	$\text{Mo}/\text{H-ZSM-5}$	Ti powder	23

Fig. 2 Reaction Apparatus

parallel tube system with stainless tubes with 17.5-mm diameter and 175-mm length was also described¹⁰. We have investigated dehydrogenation of cyclohexane, dehydroaromatization of *n*-hexane, dehydroaromatization of propane, and dehydroaromatization of methane.

To design an efficient PSR system for dehydrogenation, selection of dehydrogenation catalyst which is active enough at low temperature to produce a high hydrogen partial pressure so that the hydrogen adsorbent can adsorb hydrogen is essential, as well as the selection of hydrogen adsorbent which is efficient enough to adsorb hydrogen at a high temperature allowing the catalyst to produce a minimum hydrogen partial pressure. In the following sections, selection of suitable catalysts and hydrogen adsorbents will be summarized.

3. Results and Discussion

3.1. Selection of Catalyst

Catalysts should be sufficiently active and stable to achieve equilibrium, so that removal of hydrogen will result in high promotion effect. Figures 3-6 show the results of the screening tests.

Pt/Al₂O₃ catalyst was selected for the dehydrogenation of cyclohexane, which has been used in the same reaction with the hydrogen permeable membrane reactor. In our experiments, apparent equilibrium was observed above $W/F = 3000$ (kg·s)/mol in the temperature range 423-463 K²⁰. Pt/Al₂O₃, Pt/FKL, and Zn/H-ZSM-5 were evaluated for dehydroaromatization of *n*-hexane. Pt/Al₂O₃ and Pt/FLK lost all activity after initial deactivation for about 2 h. Zn/H-ZSM-5 showed steady state activity and constant activity was observed above $W/F = 400$ (kg·s)/mol at 673 K. Pt/FKL, and Zn/

Fig. 3 Screening of Catalysts for *n*-Hexane Dehydroaromatization Fig. 4 Effect of $W/F_{A,0}$ on *n*-Hexane Dehydroaromatization

H-ZSM-5 were examined for dehydroaromatization of propoane. As for *n*-hexane, Zn/H-ZSM-5 showed higher activity and constant conversion was observed above $W/F_{A,0} = 160$ (kg·s)/mol at 773 K²². 4 wt% Mo/H-ZSM-5 and H-ZSM-5 catalyst were evaluated for the dehydroaromatization of methane. H-ZSM-5 showed no activity at 923 K. 4 wt% Mo/H-ZSM-5 achieved constant conversion above $W/F_{A,0} = 60$ (kg·s)/mol²³.

3.2. Selection of Hydrogen Adsorbents for Promotion of Dehydrogenation

To promote dehydrogenation by removing hydrogen during the catalytic reaction, use of membrane reactors made of palladium and its alloys is well known. However, the operating conditions and the geometrical structure are limited, which limit the possible applications. Various hydrogen adsorbent alloys have been developed which can be used under various condi-

Yield represents yield of aromatic compounds.

Fig. 5 Screening of Catalysts for Propane Dehydroaromatization

C6 select. represents selectivity for benzene.

Fig. 6 Effect of $W/F_{A,0}$ on Methane Dehydroaromatization

tions^{21),24)}. However, the trend to develop hydrogen adsorbent alloys was aimed at lowering the operating temperature range as far as possible, which made high temperatures difficult to apply preventing the chemical reactions from reaching equilibrium. Therefore, it is important to select hydrogen adsorbents which can remove hydrogen under very low partial pressure at the reaction temperature under the flow of various reactant gases.

Figure 7 shows the results of the screening test on the promotion effect during dehydrogenation of cyclohexane on Pt/Al₂O₃ catalyst. Nickel-containing alloys showed promotion effects, but this effect decreased after 10 min^{17)~20)}.

Magnesium-containing alloys were evaluated for the dehydroaromatization of *n*-hexane, because the reaction temperature was so high that nickel-containing alloys could not adsorb hydrogen. The results are shown in

○: 5 min, ●: 10 min.

Fig. 7 Promotion Effect of Hydrogen Adsorbent on the Dehydrogenation of Cyclohexane

Fig. 8 Promotion Effect of Hydrogen Adsorbing Alloys on *n*-Hexane Dehydroaromatization at 543 K over Zn/H-ZSM-5

Fig. 8. Mg₂Cu, Mg₂Ni, and Mg₅₁Zn₂₀ catalysts showed high promotion effects. However, Mg_{2.2}La_{0.8}Ni showed negative effect. Scanning electron microscope-energy dispersive X-ray fluorescence spectrometer (SEM-EDX) observation showed that part of the Mg migrated onto the catalyst surface in the case of Mg_{2.2}La_{0.8}Ni alloy, which might have caused the catalyst deactivation²¹⁾.

Higher temperature is needed for the dehydroaromatization of propane. Therefore, ultrafine powders (325 mesh under) of Ti and Ta were tested²²⁾. As shown

in **Fig. 9**, Ti powder showed greater promotion effects than Ta powder. Larger particles above 60 mesh did not show any promotion effect. Ti ultrafine powder also showed promotion effects on the dehydroaromatization of methane over /H-ZSM-5 at 923 K²³).

Table 2 summarizes the screening tests of the combinations of catalyst and hydrogen adsorbents. Effective adsorbents were classified according to the operating temperatures. Nickel-containing alloys, magnesium-containing alloys, and titanium were effective at low (423 K), medium (573 K), and high temperatures (773 K, 923 K), respectively. These findings suggest the importance of coordination between hydrogen adsorbing temperature and reaction temperature. Studies on hydrogen adsorption showed that the promotion effect depended on the initial rate of hydrogen adsorption rather than the total amount of adsorbed hydrogen¹⁹. An example is shown in **Fig. 10** in the case of *n*-hexane dehydroaromatization¹⁹.

Therefore, the selection of hydrogen adsorbents should consider the following factors: Hydrogen can be adsorbed at the reaction temperature; initial rate of hydrogen adsorption should be high; and hydrogen adsorbents should not cause poisoning in direct contact

Fig. 9 Promotion effect of ○: Ti Powder (325 mesh under) and □: Ta Powder (325 mesh under) on Propane Dehydroaromatization over Zn/H-ZSM-5 (●) Catalyst at 773 K

with the catalyst.

3.3. Integration of Catalyst and Hydrogen Adsorbent

Arrangement and structure are quite important to integrate the catalyst and adsorbent. **Figure 11** shows the schematic concept of the packing arrangement of catalyst and adsorbent. Three or five layers of catalyst particles (32-60 mesh) and adsorbent particles (32-60 mesh) are packed alternately in layers. The catalyst and adsorbent particles were mixed in the test tube and then packed into the reactor tube in the case of physical mixing. Wet mixing of the particles with a ball mill was conducted in the case of mechanical alloying. **Figure 12** shows the changes in the arrangement of Pt/Al₂O₃ catalyst and CaNi₅ particles in the case of cyclohexane dehydrogenation at 443 K. Equilibrium conversion was observed without adsorbent. Mixing of CaNi₅ alloy caused remarkable increase in conversion exceeding the apparent equilibrium²⁰.

The promotion effect increased in the order of: 5 layer packing < physical mixture < mechanical alloying.

Fig. 10 Effect of Initial Rate of Hydrogen Adsorption ($P_{H_2,0} = 0.1$ MPa) on the Promotion Effect of *n*-Hexane Dehydroaromatization

Table 2 Screening of Hydrogen Adsorbing Materials for the Pressure Swing Reactor

Temp. [K]	Reactant	Catalyst	Adsorbent	
			Effective	Not effective
423	Cyclohexane	Pt/Al ₂ O ₃	CaNi ₅ LaNiAl Mg ₂ Cu	FeTi FeMnTi Mg ₂ Ni
573	<i>n</i> -Hexane	Zn/H-ZSM-5	Mg ₂ Cu Mg ₂ Ni Mg ₅₁ Zn ₂₀ CeMg ₁₂	MgLaNi CaMgNi
773	Propane	Zn/H-ZSM-5	Ti powder Ta powder	Ti particle
923	Methane	Mo/H-ZSM-5	Ti powder

Fig. 11 Arrangement of Catalyst (○) and Adsorbent (●)

Fig. 12 Changes in Conversion with the Arrangement of Pt/Al₂O₃ Catalyst and CaNi₅ Particles in the Case of Cyclohexane Dehydrogenation at 443 K

These findings suggest that close contact between the catalyst and adsorbent was essential. In the case of layer packing, reaction-adsorption to form the metal hydride of the adsorbent would proceed following the gas phase path;

Increase in the number of contact points between catalyst particles and adsorbent particles by physical mixing or mechanical alloying allows hydrogen transfer through spillover without recombination to gas phase hydrogen molecules;

If the rates of desorption from the catalyst, gas phase mass transfer, and dissociative adsorption onto the adsorbent are slow, the rate of metal hydride formation could be enhanced by mixing treatment resulting in opening of surface transfer routes. If the rate of hydrogen transfer is faster than the rate of dehydrogenation, hydrogen will be removed from the active site and the rate of reverse reaction could be ignored. This effect might be the cause of the promotion effect of the integration of dehydrogenation catalyst and hydrogen adsorbent.

Similar results were obtained in the case of Zn/H-ZSM-5 catalyst. As shown in Fig. 13, physical

Fig. 13 Changes in Conversion with the Arrangement of Zn/H-ZSM-5 Catalyst and Mg₅₁Zn₂₀ Particles in the Case of *n*-Hexane Dehydroaromatization at 573 K

Fig. 14 Changes in Conversion with the Arrangement of Zn/H-ZSM-5 Catalyst and Ti Particles in the Case of Propane Dehydroaromatization at 773 K

mixture with Mg₅₁Zn₂₀ alloy showed enhanced dehydroaromatization of *n*-hexane for about 80 min at 573 K, but layer packing resulted in no apparent enhancement effect. For example, in Fig. 12, the area above X_{Aeq} (apparent equilibrium) is related with the promotion effect with adsorption of hydrogen. The amount of adsorbed hydrogen was measured by integrating this area. The amount of adsorbed hydrogen was found to be about 1/1000 that of the adsorbent metal. Therefore, only surface layers of adsorbent contributed to the promotion of the reaction, and the inside bulk had no effect because of the slow rate of hydrogen mass transfer. This finding also suggests that degradation of adsorbent into fine powders could be avoided because the bulk could maintain the material shape.

Figure 14 also shows the case of Zn/H-ZSM-5 catalyst with Ti powder for dehydroaromatization of pro-

Fig. 15 Changes in Conversion with the Particle Size of Ti in the Case of Methane Dehydroaromatization at 923 K

pane at 773 K. The physical mixture showed high enhancement effect, but addition of quartz diluents reduced the effect. Five layer packing showed no apparent enhancement effect but 19 layer packing showed slight enhancement.

Figure 15 shows the effect of particle size of Ti powder in the case of propane dehydroaromatization at 773 K²²⁾. Conversion enhancement decreased with particle size; 325 mesh > 100-60 mesh > 20-10 mesh. Large particles (20-10 mesh) had no apparent effect. The enhancement effect increased with additional Ti powder until 13 g-Ti/g-catalyst. Further addition of Ti powder showed no increase in conversion.

Figure 16 shows the case of methane dehydroaromatization at 923 K²³⁾. The promotion effects were observed with various arrangements, but no apparent differences were observed between physical mixture, 5 layer packing and 3 layer packing as shown in **Figs. 14-16**, but close contact between the catalyst particles and adsorbent particles was generally important regardless of the reactants. At high temperature (923 K), no differences between the packing methods was apparent, suggesting that transfer of hydrogen through the gas phase as molecular hydrogen became comparable to the spillover path at high temperature.

However, no apparent promotion effect was observed by the mechanical alloying method in the case of zeolite catalysts, despite the apparent importance of close contact between catalyst and adsorbent. We assume that the dehydroaromatization reaction took place inside the cavity of the zeolite, and molecular hydrogen was formed in the cavity. Therefore, hydrogen adsorption occurred mainly through mass transfer in the gas phase.

Fig. 16 Changes in Conversion with the Arrangement of Mo/H-ZSM-5 Catalyst and Ti Particles in the Case of Methane Dehydroaromatization at 923 K

Table 3 Regeneration of Hydrogen Adsorbing Alloy with the Pressure Swing Reactor (cyclohexane to benzene, Pt/Al₂O₃ + CaNi₅, 423 K)

Operation	Initial $X_{A,max}$	After 20 min $X_{A,max}$	After 60 min $X_{A,max}$
Evacuation ^{a)}	75.8 %	39.1 %	54.0 %
Sweep gas ^{b)}	75.8 %	42.9 %	58.2 %

a) Reactor outlet was connected to vacuum line.

b) Helium purge under atmospheric pressure, 1.67×10^{-6} m³/s.

3. 4. Regeneration of Adsorbent and Pressure Swing Operation

During the reaction step, hydrogen was adsorbed in the adsorbent but saturation caused loss of the enhancement effect. Therefore, the adsorbent should be regenerated in the pressure swing step for use in further steps. Regeneration methods are compared in **Table 3**. Partial pressure swing with inert sweep gas could regenerate CaNi₅ alloy to almost the same extent as pressure swing by evacuation. Therefore, we used the partial pressure swing method with sweep gas as the standard method²⁰⁾. **Figure 17** shows the effect of regeneration time in the case of CaNi₅. Sweep for 20 min was not enough for complete regeneration, and 40 min was found to be the minimum required sweep time for regeneration²⁰⁾.

Examples of pressure swing operation on zeolite catalysts are shown in **Figs. 18-20** for dehydroaromatization of *n*-hexane, propane and methane, respectively. The reaction conditions are summarized in **Table 4**. In the case of *n*-hexane, the reaction rate was not so high because of the low reaction temperature which resulted in low conversion. The promotion effect was also not so high but was reproducible with repeated pressure swing operation²¹⁾. In the case of propane, the conversion was higher than that of *n*-hexane.

$$C_{A,0} = 1.96 \text{ mol/m}^3, F_{A,0} = 2.56 \times 10^{-6} \text{ mol/s.}$$

Fig. 17 Effect of Regeneration Time on Partial Pressure Swing with Helium at 443 K in the Case of Cyclohexane Dehydrogenation over Pt/Al₂O₃-CaNi₅ System

Fig. 18 Periodic Pressure Swing Operation in the Reaction of *n*-Hexane

The promotion effect was also high, but gradually decreased with reaction time and reached an apparent equilibrium after about 5 h. The promotion effect as well as the breakthrough effect were repeated with pressure swing operation²²⁾. In the case of methane, the initial promotion effect of titanium powder was not so high. However, regeneration of Ti powder with purge gas overnight increased the promotion effect. This high promotion effect was repeatedly observed with pressure swing operation²³⁾.

Figure 21 shows the case of optimized cyclohexane dehydrogenation over Pt/Al₂O₃ with CaNi₅ at 463 K. The promotion effect was high with complete conversion for 20 min. Partial pressure swing with sweep gas was started before breakthrough of the complete conversion. Purge for 40 min regenerated the promotion effect repeatedly²⁰⁾. **Figure 22** shows the schematic diagram of the multicolumn pressure swing reactor system. Alternate pressure swing operation could produce continuous product flow with complete conversion as well as hydrogen-rich purge gas.

Fig. 19 Periodic Pressure Swing Operation in the Reaction of Propane

$$T_{\text{rea}} = 923 \text{ K}, F_{A,0} = 2.3 \times 10^{-6} \text{ mol/s}, W_{\text{cat}} = 0.3 \text{ g}, W_{\text{Ti}} = 0.5 \text{ g.}$$

Fig. 20 Periodic Pressure Swing Operation in the Reaction of Methane

Table 4 Representative Operating Conditions

Reaction	<i>n</i> -Hexane	Propane	Methane
Catalyst	Zn/H-ZSM-5 0.2 g	Zn/H-ZSM-5 0.2 g	Mo/H-ZSM-5 0.3 g
Adsorbent	Mg ₅₁ Zn ₂₀ 2.6 g	Ti 1.3 g	Ti 0.5 g
Temp. [K]	573	793	923
$F_{A,0}$ [mol/s]	2.5×10^{-7}	2.53×10^{-5}	2.3×10^{-6}

This system could eliminate the separation and purification steps of the effluent gas, as well as the recycle process of unreacted reactant limited by the equilibrium from the entire process. These findings demonstrate the potential for process intensification of dehydrogenation reactions using the pressure swing reactor (PSR).

4. Conclusion

Our studies of process intensification, the pressure swing reactor, and experimental findings are reviewed. Integration of reaction and separation operations is one of the possible improvements of catalytic systems to ex-

Fig. 21 Periodic Pressure Swing Operation in the Reaction of Cyclohexane

Fig. 22 Schematic Diagram of Multicolumn Pressure Swing Operation

ceed the limitations of apparent equilibrium. Adequate combination of catalyst and hydrogen adsorbents enables such efficient reaction systems. Modeling studies are necessary to optimize operation procedures for multicolumn systems. Screening tests were conducted with commercially available catalysts and hydrogen adsorbents such as hydrogen adsorbing alloys and metallic titanium to achieve promotion effects. The effects could be repeated with pressure swing operation, indicating the potential of the PSR for process intensification of dehydrogenation reactions. For further efficiency, the ideal catalyst-hydrogen adsorbent system should be designed based on material design. Collaboration between catalysis, materials science, and reaction engineering should be promoted.

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要 旨

圧力スイング反応器による脱水素反応のプロセス強化

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プロセス強化 (PI) の一環として反応と分離を統合化させる試みが注目されている。触媒反応中に水素吸蔵材料を併用することで脱水素反応を促進する実験的検討について紹介した。吸蔵材料の飽和とともに促進効果が消滅するため、減圧にして吸蔵材を再生し、再び反応を行う必要がある。圧力の上下を周期的に操作するため、圧力スイング反応器 (PSR) あるいは圧力スイング吸着型反応器 (PSA Reactor) と称される。シクロヘ

キサンの脱水素, *n*-ヘキサン, プロパン, メタンの脱水素芳香族化反応について検討した。反応に最適な温度域が異なるため、触媒-吸蔵材の組合せも反応に依存し, Pt/Al₂O₃-CaNi₅, Zn/H-ZSM-5-Mg₅₁Zn₂₀, Zn/H-ZSM-5-Ti 微粒子, Mo/H-ZSM-5-Ti 微粒子がそれぞれ高い促進効果を示した。不活性ガスでパージする分圧スイング操作によって効果は繰り返し再生され, PSR の可能性が実証された。

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