[Regular Paper]

Durability of Ru/CeO₂/γ-Al₂O₃ Catalyst for Steam Reforming of Dodecane

Tomoya MURAMOTO, Ken-taro NARIAI, Hiroaki OHARA, and Hiroyuki KAMATA*

IHI Corp., 1 Shin-nakahara-cho, Isogo-ku, Yokohama 235-8501, JAPAN

(Received August 18, 2008)

Durability of the Ru/CeO₂/γ-Al₂O₃ catalyst for steam reforming of dodecane was investigated using a packed bed type tubular reactor with multiple gas sampling ports along its length. The catalyst, before and after the durability test, was characterized by BET and measurement of carbon deposition. The Ru/CeO₂/γ-Al₂O₃ catalyst showed nearly complete conversion of dodecane to H₂ enriched gas and stable performance for as long as 5000 h of time-on-stream. The technique using multiple gas sampling port allowed evaluation of the decay of the catalyst performance. The catalyst started to deactivate from the inlet of the catalyst bed, where severe carbon deposition was observed. Assuming that the number of active catalyst sites was decreased by carbon deposition, kinetic analysis was performed to evaluate the decay of catalyst activity. Steam reforming of dodecane may proceed through the formation of active hydrocarbon species bound to the active catalyst sites. At lower temperatures, the activated hydrocarbons bound to the active sites become less reactive and tend to form deposited carbon. As temperature increases, the reaction between the active hydrocarbon species and steam proceeds predominantly over carbon formation.

Keywords

Hydrogen production, Dodecane, Steam reforming, Ruthenium catalyst, Catalyst durability test

1. Introduction

Hydrogen is a valuable raw material for the chemical and petroleum industries and is expected to become a cleaner energy source for use in H₂/O₂ fuel cells and internal combustion engines. Catalytic steam reforming of hydrocarbons is an important route for hydrogen production¹⁾. Kerosene is one of the most promising hydrogen sources for fuel cell applications because of its high energy density (about 43 MJ/kg). Relatively easy storage and well-developed distribution in Japan also make kerosene an attractive source for hydrogen.

Carbon deposition on the catalyst surface is one of the major problems with catalytic steam reforming of hydrocarbons. In particular, Ni based catalyst is well known to suffer from carbon deposition during steam reforming of hydrocarbons^{2),3)}. Kerosene is produced by fractional distillation of oil between about 423 and 523 K, so consists of heavy hydrocarbons and various aromatic compounds. Consequently, steam reforming of kerosene is associated with more severe carbon deposition than that for lighter hydrocarbons such as methane and liquefied petroleum gas (LPG). Many efforts have been made to develop modified catalysts, which can potentially inhibit coke deposition.

Ni-La based catalyst was reported to show relatively good stability in the steam reforming of kerosene, within a reaction period of 50 h at 873 K⁴⁾. Addition of ruthenium to Ni based catalyst considerably improved the resistance to carbon deposition⁵⁾. Compared to Ni based catalyst, Ru based catalyst generally has better and more stable performance^{6)~9)}. Ru/CeO₂/Al₂O₃ catalyst can sustain activity for 8000 h without deactivation in the steam reforming of kerosene desulfurized prior to the reaction⁷⁾. Addition of CeO₂ to Ru/Al₂O₃ catalyst improved the stability to trace amounts of sulfur and/or coke deposition. Similar beneficial effects of CeO₂ were also confirmed in the oxidative steam reforming of a mixture of C₅-C₈ hydrocarbons¹⁰⁾. Trace addition of cerium to Ni-Pd/γ-Al₂O₃ catalyst improved the stability of hydrogen production.

Durability of the steam reforming catalyst is generally evaluated up to several tens or hundreds hours in the laboratory. These evaluation periods are not adequate compared to the catalyst lifetime required for an industrial application such as fuel cells. Therefore, prediction of the catalyst lifetime is very important to develop highly active and stable catalysts.

Continuous monitoring of the fractional performance of the catalyst bed divided into given segments is an efficient way to examine the durability of the catalyst¹¹⁾. Such a technique allows observation of the deactivation of the catalyst from early in its lifetime. In this study,

* To whom correspondence should be addressed.

* E-mail: hiroyuki_kamata@ihi.co.jp

we employed dodecane as a model compound of kerosene and examined the decay mechanism of Ru based steam reforming catalyst using a reactor with multiple gas sampling ports along its length, which allowed us to observe the fractional performance of the catalyst continuously.

The present study evaluated the catalytic activity and durability of the Ru/CeO₂/γ-Al₂O₃ catalyst in dodecane steam reforming under practical conditions. The durability of the catalyst was examined up to 5000 h of time-on-stream. Characterization was performed before and after activity measurements. Kinetic analysis was attempted to evaluate the decay mechanism of the catalyst activity.

2. Experimental

2.1. Catalyst

Ru/CeO₂/γ-Al₂O₃ catalyst was prepared by sequential impregnation of sphere-shaped γ-Al₂O₃ pellets with 1.6 mm in diameter (Nikki-Universal Co., Ltd.) with aqueous solutions of Ce(NO₃)₃·6H₂O and RuCl₃·*n*H₂O. γ-Al₂O₃ was impregnated with aqueous Ce(NO₃)₃·6H₂O and aging at room temperature for 12 h, then dried at 393 K for another 12 h and calcined at 773 K for 4 h. Following the calcination, the CeO₂/γ-Al₂O₃ pellets were impregnated again with aqueous RuCl₃·*n*H₂O and aged at room temperature for 12 h and dried at 393 K for 12 h. To remove chlorine species in the catalyst, the catalyst was washed with 3 N aqueous NH₃ for 3 h and then washed again with de-ionized water. The catalyst had a composition of 1.6 wt% Ru and 1.7 wt% CeO₂ on γ-Al₂O₃. The composition of the catalyst was optimized by our preliminary tests to assure a good reforming performance prior to the catalyst durability test.

2.2. Activity Test

Dodecane steam reforming activity was measured under steady-state conditions in a continuous gas flow reactor with a catalyst volume of 7.9 cm³ (about 4.0 g) under atmospheric pressure. The reactant contained 2.2% dodecane, 80% H₂O, and 17% N₂ as an internal standard for analysis. Steam-to-carbon ratio was set at 3.0 and liquid hourly space velocity (LHSV) was 0.5 h⁻¹ as defined by dodecane volumetric flow rate to catalyst bulk volume.

Figure 1 shows the schematic reactor design of the experimental apparatus for the catalyst durability test. The catalyst bed was 19 cm in length and 0.73 cm in diameter, and was placed in the stainless steel reactor with multiple gas sampling ports along its length. To determine the fractional conversion of dodecane and product gas composition at given catalyst position, the product gas was sampled through five gas sampling ports in turn for analysis. Catalyst temperature was also measured at each gas sampling point. The reactor

Fig. 1 Schematic of the Tubular Catalyst Reactor

was heated in an electrical furnace to maintain an adequate temperature for the reaction in the catalyst bed. The temperature profile in the bed before the reaction is shown in **Fig. 2**. The catalyst bed temperature increased along its length from 773 K at the inlet to 1000 K at the outlet. The temperature was kept relatively low at the inlet to avoid excessive carbon deposition due to intense thermal decomposition of dodecane.

Before the durability test, the Ru/CeO₂/γ-Al₂O₃ catalyst was reduced under a flow of 30% H₂ and N₂ at 973 K for 2 h in the reactor. A mixture of dodecane, water, and N₂ was fed into a vaporizer and heated at 523 K before reaching the catalyst bed. The concentrations of H₂, N₂, CO, CO₂, CH₄, C₂H₄, and C₂H₆ in the effluent from the catalyst bed was determined by a gas chromatograph equipped with a thermal conductive detector (TCD) and a stainless metal column packed with active carbon, with Ar gas carrier. Since the gas analysis required 50 cm³/min of the effluent gas through the sampling port, the gas composition was analyzed every other day to avoid an influence on the catalyst performance.

The CO_x yield, Y_{CO_x}, was determined based on the following Eq. (1).

$$Y_{\text{CO}_x} = \frac{F_{\text{CO}}^{\text{out}} + F_{\text{CO}_2}^{\text{out}}}{12 \times F_{\text{C}_{12}\text{H}_{26}}^{\text{in}}} \quad (1)$$

where F_{CO}, F_{CO₂}, and F_{C₁₂H₂₆} are the molar flow rates of CO, CO₂, and dodecane, respectively.

Fig. 2 Temperature Profile of the Tubular Reactor before the Reaction

$n = \circ: 1, \Delta: 2, \square: 3, \nabla: 4, \diamond: 5$, and $\odot$: exit of the catalyst bed. Curves were calculated by Eqs. (8) - (11).

Fig. 3 Fractional CO_x Yield at Each Gas Sampling Point

To monitor the deactivation of the catalyst, the CO_x yield and the concentration of each gas component at each gas sampling point were continuously measured for 5000 h of time-on-stream.

2.3. Characterization

After the catalyst life test, the samples were taken from the catalyst bed along its length for BET analysis using nitrogen adsorption at 77 K (Quantachrome instruments, Autosorb1-MP), after degassing at 483 K for 10 h. The amount of carbon deposition on the catalyst was determined with a CHN analyzer (LECO, TruSpec CHN type).

3. Results and Discussion

3.1. Catalyst Durability

Figure 3 shows the CO_x yield from dodecane steam reforming over the $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst. The overall CO_x yield was very stable and nearly complete

$\times$: inlet of the catalyst bed, $n = \circ: 1, \Delta: 2, \square: 3, \nabla: 4, \diamond: 5$, and $\odot$: exit of the catalyst bed.

Fig. 4 Temperature of the Catalyst Bed at Each Gas Sampling Point

conversion of dodecane was sustained for as long as 5000 h, suggesting that $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst is a suitable candidate for the steam reforming catalyst for heavy hydrocarbons.

The change in the catalyst activity by time-on-stream was followed by the fractional CO_x yield determined by gas composition at each gas sampling port. The CO_x yield started to decrease from the inlet of the catalyst bed as reaction time increased. The CO_x yield at $n = 1$ and 2 decreased rapidly and the catalyst was almost deactivated within 500 h of time-on-stream. The CO_x yield at $n = 3$ was observed to decrease continuously over 5000 h. The CO_x yield at $n = 4$ started decreasing gradually at about 2000 h of time-on-stream, but the fractional CO_x yield at $n = 4$ remained at about 0.6 even after 5000 h. The CO_x yield at $n = 5$ and 6 near the outlet of the catalyst bed remained at nearly the same values during the reaction period. These results illustrate that the catalyst deactivation progresses from the inlet of the catalyst bed toward the outlet of the bed.

The temperature profiles at each gas sampling point are shown in Fig. 4. Steam reforming of dodecane is an endothermic reaction so the temperature of the catalyst bed where the reforming reaction proceeds may drop. Temperatures at $n = 1$ and 2, near the inlet of the catalyst, increased within a short period due to the loss of the catalyst activity near this region. Temperature at $n = 3$ decreased continuously as temperature at $n = 1$ and 2 increased, then started increasing at about 1000 h. Temperature at $n = 4$ started decreasing at about 1000 h and temperature at $n = 5$ started decreasing at about 3000 h. This behavior clearly corresponds to the changes in the activity of the catalyst as shown in Fig. 3.

Formation rates of CO , CO_2 , CH_4 , C_2H_4 , and C_2H_6 are shown in Fig. 5 as a function of the relative position of the catalyst bed. Both CO and CO_2 formation rates increased along the catalyst bed. As the reaction

○: CO, △: CO₂, □: CH₄, ▽: C₂H₆, and ◇: C₂H₄ formation rate.

Fig. 5 Formation Rates of CO, CO₂, CH₄, C₂H₆, and C₂H₄ along the Catalyst Bed Length at (a) 230, (b) 1800, and (c) 4700 h of Time-on-stream

Table 1 Catalyst Characterization

		BET [m ² /g]	Carbon deposition [wt%]
Fresh		147	—
Spent	<i>n</i> = 1	108	13.0
	2	97	18.9
	3	92	16.2
	4	95	0.84
	5	89	0.39

period increased, the CO and CO₂ formation shifted toward the outlet of the catalyst bed due to the loss of the catalytic activity near the inlet of the bed. For example, almost no formation of CO and CO₂ was observed before *n* = 3 at 4700 h.

Relatively high CH₄ and C₂H₄ formation rates were also observed. Concentrations of CH₄ and C₂H₄ increased along the catalyst bed length, reached the maximum value, then decreased toward the outlet of the catalyst bed. As the reaction period increased, C₂H₄ tended to persist in the catalyst bed.

3.2. Carbon Deposition

BET surface area and amount of carbon deposited during the reaction are listed in Table 1. Reduction of BET surface area after the durability test was less apparent. BET surface area slightly decreased along the catalyst bed length. In contrast, very severe carbon deposition was confirmed after the durability test. More than 10 wt% of carbon deposition was observed at *n* = 1–3. On the other hand, carbon deposition at *n* = 4 and 5 was less apparent. The rapid deactivation of the catalyst at *n* = 1 and 2 may have been caused by the carbon deposition, which may block the active Ru sites on the surface.

3.3. Kinetic Study of Deactivation

Overall reaction of steam reforming of dodecane is given by

with simultaneous water-gas shift reaction,

On the catalyst surface, the reaction of dodecane with steam may proceed sequentially. In the initial stage, dodecane reacts with steam to form fragmental lighter hydrocarbons as well as H₂, CO, and CO₂. These lighter hydrocarbons further react with steam and finally form a mixture of H₂, CO, and CO₂ gases. The reaction may be written schematically as follows:

where $n < n'$ and $m < m'$.

As the hydrocarbons become lighter, the potential for carbon deposition may decrease gradually. The potential for carbon deposition may change sequentially along the catalyst bed length. In practice, the distribution of carbon number of hydrocarbons is difficult to determine continuously. In this study, as a first approximation, fragmental hydrocarbons were assumed to have similar potential for carbon deposition to dodecane irrespective of carbon number. Therefore, the decay kinetics could be analyzed based on the CO_x yield without considering the fragmental hydrocarbon.

The molar flow rate of steam can be expressed using the molar flow rate of dodecane, $F_{\text{C}_{12}\text{H}_{26}}$, and the ratio of steam to carbon, S/C , as $F_{\text{C}_{12}\text{H}_{26}}(1 + 12 \times S/C)$. According to Eq. (2), the molar concentrations of dodecane and H₂O can be expressed by the following equations:

$$C_{\text{C}_{12}\text{H}_{26}} = \frac{F_{\text{C}_{12}\text{H}_{26}} (1 - Y_{\text{CO}_x})}{F_{\text{C}_{12}\text{H}_{26}} (1 + 12 S/C + 24 Y_{\text{CO}_x}) RT/P} \quad (5)$$

and

$$C_{\text{H}_2\text{O}} = \frac{12 F_{\text{C}_{12}\text{H}_{26}} (S/C - Y_{\text{CO}_x})}{F_{\text{C}_{12}\text{H}_{26}} (1 + 12 S/C + 24 Y_{\text{CO}_x}) RT/P} \quad (6)$$

Table 2 Kinetic Parameters

A	55	$\text{mol} \cdot \text{s}^{-1}$
E_a	111	$\text{kJ} \cdot \text{mol}^{-1}$
α	1.3×10^{12}	h^{-1}
β	0.034	T^{-1}

respectively. Assuming that the steam reforming of dodecane is first order with respect to dodecane, the reaction rate can be expressed by the following Eq. (7):

$$-\frac{dF_{\text{C}_{12}\text{H}_{26}}}{dV} = k_{\text{SR}}^0 C_{\text{C}_{12}\text{H}_{26}} \quad (7)$$

where the rate constant of the steam reforming, k_{SR}^0 , is simply expressed by

$$k_{\text{SR}}^0 = A \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

Since the steam reforming of dodecane is restricted by the equilibrium limitation, Eq. (7) may be modified using the equilibrium concentration of dodecane as follows,

$$-\frac{dF_{\text{C}_{12}\text{H}_{26}}}{dV} = k_{\text{SR}}^0 (C_{\text{C}_{12}\text{H}_{26}} - C_{\text{C}_{12}\text{H}_{26}}^{\text{eq}}) \quad (9)$$

Integration of Eq. (9) from the inlet to any given position of the catalyst bed gives the fractional CO_x yield. The temperature profile of the catalyst bed before the reaction (Fig. 2) was used for the calculation.

Since the catalyst deactivation is caused by carbon deposition, the number of active catalyst sites decreases continuously as the reaction time increases. Provided that the decrease in the number of active sites due to carbon deposition is irrelevant to the main reaction, the decay of the rate constant, k_{SR}^0 , may be written as

$$-\frac{dk_{\text{SR}}^0}{dt} = k_d \frac{C_{\text{C}_{12}\text{H}_{26}}}{C_{\text{H}_2\text{O}}} k_{\text{SR}}^0 \quad (10)$$

where the rate constant of deactivation, k_d , is simply defined as a function of temperature by the following Eq. (11):

$$k_d = \alpha \exp(-\beta T) \quad (11)$$

In Eq. (10), the decay of k_{SR}^0 is assumed to be proportional to dodecane concentration and inversely proportional to H_2O concentration because the carbon deposition may be accelerated by the presence of dodecane and suppressed by steam. The data shown in Fig. 3 were fit using Eqs. (8) - (11) by the least squares method with A , E_a , α , and β as parameters. The curves in Fig. 3 show the calculated results and the determined parameters are listed in Table 2.

The calculated results show good agreement with the observed values. The calculated k_d value was low, suggesting that the $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst is stable under these reaction conditions. According to the

temperature dependence of k_d , catalyst deactivation due to the carbon deposition is more severe at lower temperatures and becomes less significant as temperature rises.

The CH_4 steam reforming reaction proceeds by two steps, activation of CH_4 on the catalyst surface and subsequent reaction with adsorbed oxygen species⁶⁾. Similarly, steam reforming of higher hydrocarbons over Ni based catalyst starts with the adsorption of hydrocarbons and subsequent formation of their active species¹²⁾. By analogy with these reaction mechanisms, steam reforming of dodecane over $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst may proceed through the formation of active hydrocarbon species bound to the active catalyst site, $\text{C}_n\text{H}_\chi^*$. The active $\text{C}_n\text{H}_\chi^*$ species react with the surface oxygen species generated by steam to form the H_2 , CO mixture through the surface reaction.

Residual $\text{C}_n\text{H}_\chi^*$ left without further reaction with steam may form the deposited carbon.

As temperature rises, the reaction rate of $\text{C}_n\text{H}_\chi^*$ with steam becomes higher so carbon formation by residual $\text{C}_n\text{H}_\chi^*$ becomes less significant.

The reforming reaction was confirmed to proceed predominantly over the carbon deposition at higher temperature regions in this study. Therefore, one possibility to improve the catalyst life time is to increase the catalyst bed temperature moderately. However, excessive increase of temperature at the inlet of the catalyst bed may cause carbon deposition by intense thermal decomposition of hydrocarbons. Thus, careful control of the catalyst bed temperature is necessary during the reaction.

4. Conclusions

Durability of the $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst for steam reforming of dodecane was studied using the tubular reactor with multiple gas sampling ports. The $\text{Ru/CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst showed nearly complete conversion of dodecane to H_2 enriched gas and stable performance for as long as 5000 h of time-on-stream. The technique using multiple gas sampling port along the catalyst bed length allowed evaluation of the decay of the catalyst performance. The catalyst started to deactivate from the inlet of the catalyst bed, where severe carbon formation was observed. Assuming that the number of active catalyst sites was decreased by carbon deposition, kinetic analysis was performed to evaluate the decay of catalyst activity. Steam reforming of dodecane may proceed through the formation of active hydrocarbon species bound to the active catalyst sites. At lower temperatures, the activated hydrocarbons bound to the

active sites become less reactive and tend to form deposited carbon. As temperature rises, the reaction between the active hydrocarbon species and steam proceeds predominantly over the carbon formation.

Nomenclatures

A	: pre-exponential factor for k_{SR}^0	[mol/s]
C_i	: molar concentration of component i	[mol/m ³]
C_i^{eq}	: equilibrium molar concentration of component i	[mol/m ³]
E_a	: activation energy for k_{SR}^0	[kJ/mol]
F_i	: molar flow of component i	[mol/s]
k_{SR}^0	: initial rate constant of dodecane steam reforming reaction	[mol/s]
k_d	: rate constant of catalyst deactivation	[h ⁻¹]
R	: gas constant (8.314)	[J/mol/K]
P	: reactor pressure (101, 300)	[Pa]
S/C	: molar ratio of steam to carbon	[—]
T	: temperature of catalyst bed	[K]
t	: catalyst operation time	[h]
V	: volume of catalyst bed	[m ³]
Y_{CO_x}	: CO _x yield	[—]
<Greeks>		
α	: pre-exponential factor for k_d	[h ⁻¹]

β : temperature coefficient for k_d

[T⁻¹]

References

- 1) Rostrup-Nielsen, J. R., *Catal. Today*, **63**, 159 (2000).
- 2) Trimm, D. L., *Catal. Today*, **37**, 233 (1997).
- 3) Trimm, D. L., *Catal. Today*, **49**, 3 (1999).
- 4) Yu, X., Zhang, S., Wang, L., Jiang, Q., Li, S., Tao, Z., *Fuel*, **85**, 1708 (2006).
- 5) Ishihara, A., Qian, E. W., Finahari, I. N., Sutrisna, I. P., Kabe, T., *Fuel*, **84**, 1462 (2005).
- 6) Rostrup-Nielsen, J. R., Bak Hansen, J.-H. *J. Catal.*, **144**, 38 (1993).
- 7) Suzuki, T., Iwanami, H., Yoshinari, T., *Inter. J. Hydrogen Energy*, **25**, 119 (2000).
- 8) Fukunaga, T., Katsuno, H., Matsumoto, H., Takahashi, O., Akai, Y., *Catal. Today*, **84**, 197 (2003).
- 9) Kobori, Y., Matsumoto, T., Anzai, I., Ueno, S., Oishi, Y., "Science and Technology in Catalysis 2002," Kodansha Ltd., Tokyo (2003), p. 477.
- 10) Wang, Y. H., Zhang, J. C., *Fuel*, **84**, 1926 (2005).
- 11) Birtill, J. J., *Catal. Today*, **81**, 531 (2003).
- 12) Christensen, T. S., Rostrup-Nielsen, J. R., "ACS symposium series 634," eds. by O'Connor, P., Takatsuka, T., Woolery, G. L., American Chemical Soc., (1996), p. 186.

要 旨

ドデカンの水蒸気改質反応における Ru/CeO₂/γ-Al₂O₃触媒の安定性

村本 知哉, 成相 健太郎, 大原 宏明, 鎌田 博之

(株)IHI 化学システム開発部, 235-8501 横浜市磯子区新中原町1番地

ドデカン水蒸気改質反応における Ru/CeO₂/γ-Al₂O₃触媒の安定性を、触媒層に沿って複数のガスサンプリングポートを備えた固定床流通型の管型反応器を用いて評価した。寿命試験前後の触媒は、BET 比表面積、炭素析出量測定を用いて分析した。触媒の長期安定性を調べた結果、Ru/CeO₂/γ-Al₂O₃触媒は5000時間にわたり安定した性能を示し、ドデカンをほぼ完全に水素リッチのガスに改質できることを確認した。管型反応器による寿命評価と分析の結果、触媒の性能低下は炭素析出量の多い触

媒層上流側から進行することが分かった。炭素析出により、触媒の活性サイト数が経時的に減少すると仮定して、触媒の劣化を速度論的に解析した。この結果より、ドデカンの水蒸気改質反応は、触媒表面に吸着した炭化水素の活性化を経て進行することが推察された。反応温度が低いと吸着した炭化水素の反応性が低いため、触媒表面での炭素化が進み易い。反応温度が高くなると、吸着した炭化水素の水蒸気による改質反応が炭素化に比べて優先的に進行するものと考えられる。