Steam reforming of aromatic hydrocarbon in electric field at low temperature

Kent Takise,[a] **Keisuke Muraguchi**,[a] **Shuhei Ogo**,[a] **Yasushi Sekine**[a],*
[a]*Department of Applied Chemistry, Waseda University, Tokyo, 169-8555, Japan*
**Corresponding author: +81-3-5286-3114, ysekine@waseda.jp (Y. Sekine)*

Abstract: Toluene steam reforming was conducted on Ni supported catalysts in the electric field at low temperature as 473 K. Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$ and Ni/$La_{0.7}Ba_{0.3}AlO_{3-\delta}$ catalysts showed high catalytic activity and hydrogen yield. However, these catalysts showed low activity without the electric field in the low temperature range. These results might be attributable to the electric field promotes surface protonics in low temperature range according to partial pressure dependences. Application of electric field enables the Ni catalysts supported on perovskite-type oxides to produce hydrogen and carbon monoxide from aromatic hydrocarbons at such low temperature.

Keywords: Toluene steam reforming, Catalytic reaction in electric field, Hydrogen production.

1. Introduction

Steam reforming is a practical way for producing hydrogen and carbon monoxide from aromatic hydrocarbons. This reaction is an endothermic reaction, so that the reaction temperature generally must be high to proceed the reaction. Aromatic hydrocarbons have high C/H ratio, and are liable to form coke on a catalytic surface during a reforming reaction at high temperatures.[1,2] Therefore, large amount of steam is required for steam reforming of aromatic hydrocarbons to obtain stable catalytic activity with suppressing coke formation. Lowering reaction temperature is significant for suppressing the coke formation. In this study, toluene steam reforming was conducted at low temperature as 473 K in an electric field, in which metal supported catalyst shows catalytic activity even at low temperatures thanks to proton-coupled electron transfer and surficial proton hopping phenomena.[3]

2. Experimental

Regarding catalysts preparation, all oxide supports were prepared using the critic acid complex method. The obtained powder i.e. fluorite-type, perovskite-type and spinel-type oxide supports were impregnated with a solution of metal nitrates. Subsequently, it was dried and calcined at 773 K for 2 h. The size of the obtained catalyst was adjusted to 350-500 μm with sieving.

Catalytic activity tests were conducted in a tubular reactor, in which 200 mg of catalyst was charged in the fixed bed. Two stainless electrodes were contiguously set on upper-side and bottom-side of the fixed catalysts to charge electric field. Toluene steam reforming was conducted for 60 min at 473 K with charging a constant current of 3 mA. The reaction gas composition was $C_7H_8/H_2O/Ar = 3/42/155$ (vol%), with a 200 mL min^{-1} total flow rate. The product gas of this reaction was measured using GC-FID (GC-8A; Shimadzu Corp.) and GC-TCD (GC-8A; Shimadzu Corp.). Additionally, kinetic analysis was conducted to elucidate the effect of electric field charging.

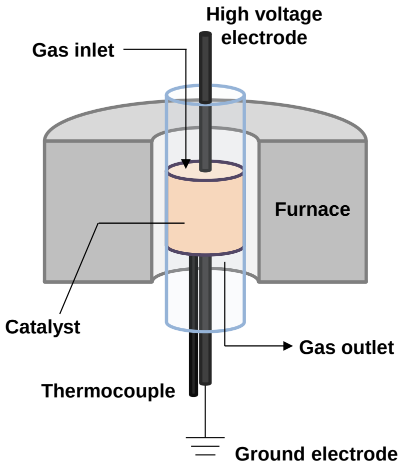

Figure 1 Experimental set-up for the reaction in the electric field.

3. Results and discussion

Toluene steam reforming reaction was conducted in the electric field at 473 K on 5 wt% Ni supported oxides such as fluorite-type, perovskite-type and spinel-type oxides. Among these catalysts, Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$ and Ni/$La_{0.7}Ba_{0.3}AlO_{3-\delta}$ catalysts showed higher activity and hydrogen yield than other catalysts. Subsequently, various metals were supported on these perovskite-type oxides, and Ni supported catalysts still showed the highest activity compared to other metals. Therefore, further investigations were conducted for these catalysts to elucidate the effect of added electric field on the catalyst. Furnace temperature was changed in a temperature range of 473 K and 873 K for both cases: with electric field and without electric field. Figure 2 shows toluene conversions on Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst in such temperature range with the electric field (ER) and without the electric field (SR). The Ni supported catalyst shows no activity at lower temperature without the electric field. The electric field charging enabled higher activity at lower temperatures. Then, kinetic analysis was implemented on Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst to clarify how the electric field promotes toluene steam reforming reaction at low temperature. Arrhenius plots revealed that the apparent activation energy was 71.5 kJ mol^{-1} without the electric field, while that was 21.0 kJ mol^{-1} with the electric field. Kinetic investigations revealed that toluene conversion rates can be described as follows, with the electric field (r_{ER}) and without the electric field (r_{SR}) according to partial pressure dependences.

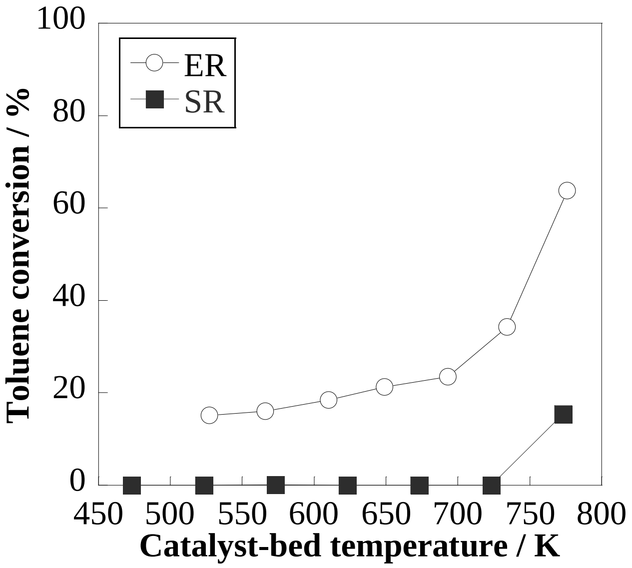

Figure 2 Toluene conversion over Ni/ $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst with the electric field (ER) and without the electric field (SR).

$$r_{ER} = k[P_{H2O}]^{0.29}[P_{C7H8}]^{0.95} \quad \text{eq.1}$$
$$r_{SR} = k[P_{H2O}]^{0.93}[P_{C7H8}]^{0.23} \quad \text{eq.2}$$

In the electric field, water pressure dependences decreased compared to conventional toluene steam reforming reaction. Mukai *et al*. reported that water dissociation could be the rate-determining step at low temperature.[4] It was considered that the electric field promoted adsorbed water dissociation from these results.

4. Conclusions

Ni/$La_{0.7}Sr_{0.3}AlO_{3-\delta}$ and Ni/$La_{0.7}Ba_{0.3}AlO_{3-\delta}$ catalysts showed toluene steam reforming activity stably at low temperature as 473 K in an electric field. Without the electric field, the catalysts showed no activity in such temperature range. These results were attributable to that the electric field promotes adsorbed water dissociation with the proton hopping in low temperature range according to partial pressure dependence.[3] Electric field charging enables the Ni supported perovskite-type oxides catalysts to produce hydrogen and carbon monoxide from aromatic hydrocarbons at such low temperatures.

References

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