

Low Temperature Catalytic Methane Steam Reforming by Surface Protonics

Ryo Manabe¹,

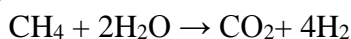
Shigeki Okada¹, Reona Inagaki¹, Shuhei Ogo¹
and Yasushi Sekine^{1*}

¹Department of Applied Chemistry, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan

*E-mail: ysekine@waseda.jp

Introduction

Conventional catalytic methane steam reforming (SR) is conducted at high temperatures (> 923 K) because of thermodynamic equilibrium and the stability of methane molecule, for industrial hydrogen production.



However, such high reaction temperatures raises some issues such as the necessity for heat-resistant materials, catalyst deactivation by coke deposition, and complex processes with multiple heat-exchangers. In addition, lowering the reaction temperatures can lead to more efficient heat and chemical energy conversion process because low-grade waste heat might be reused for hydrogen production. Our previous studies revealed that a steam reforming process in an electric field, *Electroreforming* (ER), shows a high activity even at 423 K with CeO₂-based catalysts [1]. To elucidate the detailed effect of electric field application on methane steam reforming, *operando*-DRIFTS measurements were conducted with Pd catalyst, in terms of the kinetic isotope effect (*KIE*).

Experimental

Pd supported catalyst (Pd/CeO₂) was prepared with an impregnation method. *Operando*-DRIFTS measurements were conducted using FT-IR at 473 K for ER and at 673 K for SR. Background measurements were taken under inert Ar gas, and subsequently reactant gases (CH₄: H₂O or D₂O: Ar = 1: 2: 62, total 65 SCCM) were supplied. Then the electric field was applied to the catalyst bed by imposing DC current, 5 mA. The activities were evaluated using a GC-FID for *operando* analyses.

Results and Discussion

We observed a peak assigned to the rotation of adsorbed water around 850 cm⁻¹, only when the electric field was applied to the catalyst bed with reactant gases at low temperature: 473 K [2]. This peak is regarded as having a strong relation to the Grotthuss mechanism, a principle mechanism of proton conduction. So it is suggested that the proton conduction via adsorbed water onto the catalyst surface occurred during electric field application: surface protonics.

To investigate the relation between surface protonics and catalytic activities in the electric field, *operando*-DRIFTS measurements were conducted using an isotope (D₂O). Figure 1 presents IR band intensities derived from gas phase methane at 3016.6 cm⁻¹ with or without the electric field. As shown in Fig.1, the amount of gas phase methane decreased more when D₂O was used instead of H₂O. These results indicate that methane is activated by proton collision derived from the Grotthuss mechanism, with the viewpoint of inverse *KIE* [3]. Because D⁺ is heavier than H⁺, methane is considered to be more easily converted into CO and CO₂. Therefore, we can conclude that surface protonics plays an important role in the enhancement of catalytic methane steam reforming at low reaction temperatures.

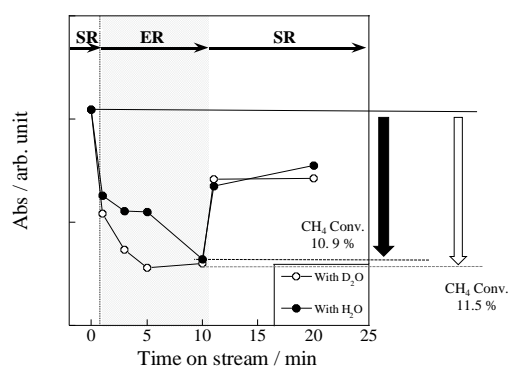


Fig.1 IR band intensities for CH₄ gas (3016.6 cm⁻¹) at 473 K in electric field [2].

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