

Hydrogen spillover on a non-reducible metal oxide comprising earth-abundant elements and its catalysis

<u>Kazuki SHUN</u>¹, Kohsuke MORI^{*,1}, Takumi KIDAWARA¹, Hiromi YAMASHITA¹ ¹ Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita Osaka 565-0871, Japan *mori@mat.eng.osaka-u.ac.jp

Significance and Relevance

Hydrogen spillover, the simultaneous diffusion of protons (H^+) and electrons (e⁻), were firstly achieved on a non-reducible MgO with heteroatom Al dopants (Al-MgO). This material exhibited more than 3 times larger of H^+ capacity compared with reducible metal oxides comprising rare elements, even though it is composed of only earth-abundant elements. Moreover, the spilled hydrogen on Al-MgO promoted the catalysis of Ni during CO₂ hydrogenation by a factor of 4.6. This work provides a new strategy for designing functional materials intended to hydrogen spillover for diverse application.

Introduction and Motivations

Hydrogen spillover, the simultaneous diffusion of protons (H⁺) and electrons (e⁻), is considered to be applicable to ubiquitous technologies related to hydrogen but limited to over reducible metal oxides composed of rare elements.^{1, 2} The present work demonstrates that a non-reducible MgO with heteroatom Al dopants (Al-MgO) allows hydrogen spillover in the same way as reducible metal oxides. Furthermore, a H⁺ storage capacity of this materials owing to hydrogen spillover is more than three times greater than those of various standard metal oxides based on H⁺ transport channels within its bulk region. Atomic hydrogen diffuses over the non-reducible Al-MgO produces active H⁺-e⁻ pairs, as also occurs on reducible metal oxides, to enhance the catalytic performance of Ni during CO₂ hydrogenation. The H⁺ and e⁻ diffusion pathways generated by the heteroatom Al doping is disentangled based on systematic characterizations and calculations.

Materials and Methods

 $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were firstly dissolved in distilled water. This solution was dropped to aqueous solution of Na_2CO_3 and NaOH and stirred overnight. Obtained white slurry was washed and dried. The resulting solid was calcined under air atmosphere for 1.25 h at 400 °C to obtain Al-MgO. Ru nanoparticles were deposited onto Al-MgO by the impregnation of $RuCl_3 \cdot nH_2O$ and following hydrogen reduction to yield Ru/Al-MgO (Ru = 2 wt%, Mg/Al=5). Ru/MgO was prepared in the same manner as Ru/Al-MgO.

Results and Discussion

The hydrogen spillover property of Al-MgO was comprehensively evaluated from the viewpoint of the H⁺ diffusion ability and e⁻ diffusion ability. In order to the evaluate the H⁺ diffusion ability of Al-MgO, thermogravimetry measurements under H₂-D₂ switching atmosphere were exhibited for Ru/MgO and Ru/Al-MgO, respectively. In response to switching between H₂ and D₂ flowing at 400 °C, the weight of Ru/Al-MgO rapidly changed compared with that of Ru/MgO (**Figure 1 (a)**). From these results, the H⁺ storage for Al-MgO was calculated to be 0.29 wt%, more than 3 times larger than that of various reducible metal oxide as well as MgO (**Figure 1 (a)**). A combination of *in situ* DRIFT and mass spectrometry under H₂-D₂ switching atmosphere revealed that H⁺ can diffuse both onto the surface and into the bulk of Al-MgO that extremely enhance the H⁺ storage of Al-MgO although it can migrate only onto the surface of MgO. In order to evaluate the e⁻ diffusion ability of Al-MgO, *in situ* UV-vis measurement under H₂ heating atmosphere was performed for the mixture of WO₃ and Ru/Al-MgO. As the results, WO₃ mixed with Ru/Al-MgO specifically absorbed visible light due to the mixed valence state of W⁵⁺ and W⁶⁺ over 200 °C indicating that e⁻ diffusion over Al-MgO (**Figure 1 (b)**). These results show that both of H⁺ and e⁻ diffusions were facilitated over non-reducible MgO by the addition of Al,



even though Mg²⁺ and Al³⁺ are both originally irreducible. The pathways of enhanced H⁺ and e⁻ diffusion on Al-MgO was further studied by systematic characterizations and calculations.

Hydrogen spillover on the Al-MgO was utilized for the promotion of catalytic CO_2 hydrogenation on Ni. The CO_2 conversion of Ni/Al-MgO increased by a factor of 4.6 by the physical mixture with Pt/Al-MgO, the initiator of hydrogen spillover. *In situ* XAFS measurements during H_2 - O_2 switching atmosphere elucidated the acceleration of the Ni reduction under the presence of Pt (**Figure2 (a)**). Therefore, the hydrogen spillover on Al-MgO readily removed poisoning oxygen on Ni evolved by CO_2 activation to enable effective catalysis during CO_2 hydrogenation (**Figure2 (b)**).

This material offers the design of functional materials based on hydrogen spillover as well as catalysts applicable to the ubiquitous hydrogen handling technologies for upcoming hydrogen society.³



Figure 1 Characterizations describing the enhanced H^+/e^- diffusion over Al-MgO. (a) The weight transition of Ru/MgO and Ru/Al-MgO under a H₂-D₂ switching atmosphere. (b) The transition in visible light absorption of WO₃ mixed with Ru supported each sample.



Figure 2 How hydrogen spillover on Al-MgO endows CO₂ hydrogenation on Ni. (a) The fraction of metallic Ni⁰ species in the (Pt + Ni)/Al-MgO, Ni/Al-Mg based on linear fitting for Ni K edge XANES at 350 °C. (b) A schematic diagram illustrating how hydrogen spillover on Al-MgO promotes the catalysis of Ni in CO₂ hydrogenation.

References

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