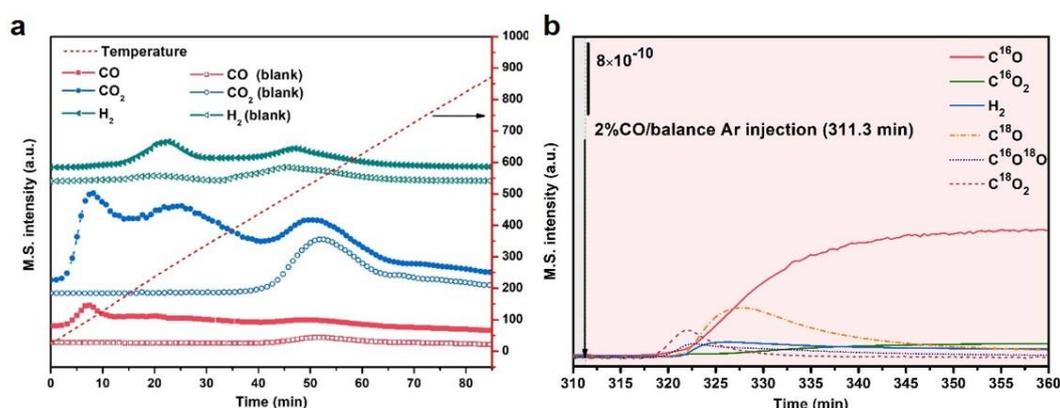


## Revisiting magnesium oxide to boost hydrogen production via water-gas shift reaction: Mechanistic study to economic evaluation

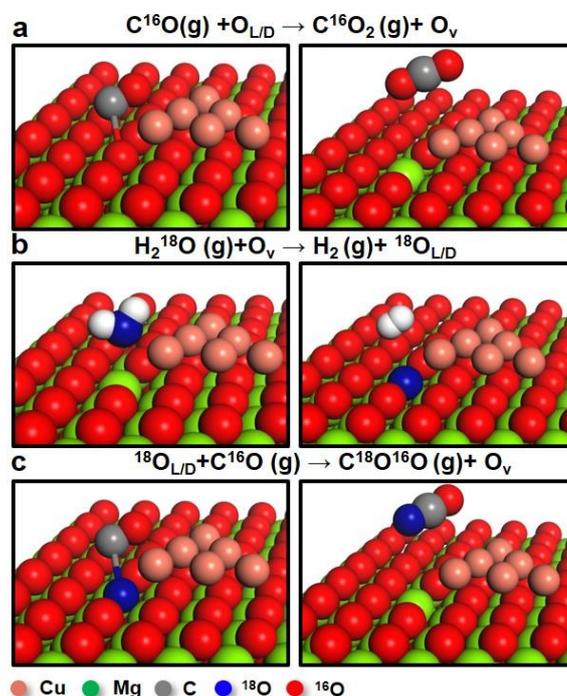
Although numerous defects can be generated on MgO by a novel synthesis route, research on MgO-supported catalysts is rare because the reported activities were not sufficient to replace other supports. We reported MgCeO<sub>x</sub>-supported Cu (MgCuCe) catalyst beads with several hundreds of micrometer size, featuring a unique macroscopic structure.



**Figure 1.** (a) CO-TPD-MS analyses and (b) TPSR result using oxygen isotope ( $H_2^{18}O$ ) for MgCuCe catalysts

The as-prepared catalysts showed unprecedented enhancements in the reaction activity in the water-gas shift (WGS) reaction, showing a significantly higher reaction rate of  $83 \mu\text{mol g}^{-1} \text{s}^{-1}$  at  $300^\circ\text{C}$  than that without MgO ( $30 \mu\text{mol g}^{-1} \text{s}^{-1}$ ). The underlying WGS reaction mechanism was illustrated by using an on-line mass spectrometer (Hidden HPR 20) coupled with other analyzers. CO-TPD-MS (Figure 1(a)) and *in situ* DRIFTS revealed that numerous defects in the MgCuCe catalysts promoted water dissociation and the subsequent associative mechanism. Numerous mono-coordinated and higher-coordinated OH groups were present on the MgCuCe catalysts because the dissociation of water was promoted by MgO with defects. And a large amount of carboxylate and formate species was formed by the adsorbed OH groups and CO on Cu<sup>+</sup>. The formation of the carboxylate species was dominant at low S/C ratios. On the other hand, a large quantity of the formate species was produced at high S/C ratios owing to the favorable interaction between the formate species and neighboring OH groups.

The TPSR experiments using isotope  $H_2^{18}O$  evidenced that the labile oxygen in MgO participated in the redox mechanism. When CO was introduced, the oxygen vacancy could be generated by the reaction between  $C^{16}O$  and labile  $^{16}O$  in the defect or lattice of MgO. The subsequent introduction of  $H_2^{18}O$  filled the oxygen vacancy by producing  $H_2$ . Then, introducing CO again, the  $^{18}O$  occupying the vacancy site reacted with CO. Accordingly, it was confirmed



**Figure 2.** A schematic for the redox mechanism on MgO-supported Cu catalyst.

that the oxygen replacement in the MgCuCe catalysts took place under the reaction conditions (Figure 1(b) and Figure 2).

At a low GHSV ( $125,000 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ), the temperature increase due to the bead catalyst was lower than that caused by the same powder catalyst although the conversion of the bead catalyst was higher by 15%. When the GHSV reached  $500,000 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , the temperature of the bead catalyst was eventually higher than that of the powder catalyst, showing 11% higher conversion. The highly porous bead structure also contributed to enhancing the reaction rate via the efficient dissipation of generated reaction heat.

The hydrogen production cost realised due to the use of MgCuCe catalysts was 0.63 USD/kg  $\text{H}_2$ , which is lower than that achieved by using commercial and  $\text{CeO}_2$ -supported catalysts. Lower  $\text{H}_2$  production cost of Mg-containing catalysts results from not only higher  $\text{H}_2$  productivity compared with commercial catalysts but also from lower catalyst production cost than that of  $\text{CeO}_2$ -supported catalysts. This study paves the route for exploiting earth-abundant MgO in developing efficient catalysts and contributes to reducing  $\text{H}_2$  production costs.



*The Hiden HPR-20 in the laboratory*

#### **Project summary by:**

Seongmin Jin and Chang-Ha Lee

Department of Chemical and Biomolecular Engineering, Yonsei University,  
Seoul, 03722, Republic of Korea



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#### **Hiden Product:**

[HPR-20](#)