Atomic-scale insights into nanostructured MgO for thermocatalytic CO_2-to-CO conversion

Hsin-Yu Chen[1,2], Shih-Yuan Chen*[3], Cheng-Hsi Yeh[2], Chien-Neng Liao[1,4], and Hsin-Yi Tiffany Chen*[1,2,4]

[1]*National Tsing Hua University, Department of Materials Science and Engineering, Hsinchu 300044, Taiwan.*
[2]*National Tsing Hua University, Department of Engineering and Systems Science, Hsinchu 300044, Taiwan.*
[3]*National Institute of Advanced Industrial Science and Technology (AIST), Energy Catalyst Technology Group, Energy Process Research Institute (EPRI), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.*
[4]*College of Semiconductor Research, National Tsing Hua University, Hsinchu 300044, Taiwan.*
*sy-chen@aist.go.jp (S.Y. Chen), hsinyi.tiffany.chen@gapp.nthu.edu.tw (H.-Y. T. Chen)

Significance and Relevance

Recently, global temperatures have risen by 1.5°C above pre-industrial levels, largely due to increased CO_2 in the atmosphere from burning fossil fuels, highlighting the need for CO_2 capture and conversion into high-value products as a key strategy for mitigating climate change and achieving a carbon-cycling society. This study reported a metal-free, thermocatalytic CO_2-to-CO conversion using nanostructured MgO(111), which, with its polar surface and terminal oxygen species, was active in converting CO_2 to CO at 450–500 °C, whereas conventional MgO(100) was not.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport, CO_2 utilization and recycling
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Introduction and Motivations

The global temperature has risen by 1.5°C above pre-industrial levels by 2024, surpassing the Paris Agreement target. This increase is largely attributed to the rapid rise in atmospheric CO_2 from burning fossil fuels, significantly impacting our environment and increasing vulnerability to climate change. To combat this, capturing and converting CO_2 into high-value products has emerged as a promising solution, using dual-functional materials with basic sites for capture and metallic sites for conversion[1]. These processes are vital for mitigating global warming, advancing a low-carbon society, and improving quality of life for future generations. However, Earth's limited metal resources are increasingly strained by rising demand for semiconductor-related applications essential to modern society. This study focused on a metal-free process for thermocatalytic CO_2-to-CO conversion, utilizing nanostructured MgO materials with either (111) or (100) facets. The structural properties of nanostructured MgO enriched with (111) facets (termed MgO(111)) and commercial MgO with (100) facets (termed MgO(100)) were systematically studied using atomic-scale microscopy, spectroscopy, temperature-programmed methods, and computational analysis. The results demonstrated that "metal-free" MgO(111), with its polar surface and terminal oxygen species, exhibited activity for the thermocatalytic conversion of CO_2 to CO—a key syngas component—at 450–500 °C, whereas MgO(100) did not.

Materials and Methods

MgO(111) was synthesized using a modified method[2]. $Mg(NO_3)_2$ was reacted with Na_2CO_3 to form white precipitates, which were washed with deionized water and ethanol, filtered, and calcined at 500–900 °C for 2 hours to produce nanostructured MgO(111). Commercial MgO(100) (99.9%, Wako) was used as a reference. The morphology and atomic structure of MgO(111) and MgO(100) were characterized by high-resolution transmission electron microscopy (HRTEM) with electron diffraction patterns (DP) and dark-field scanning transmission electron microscopy (DF-STEM). Their CO_2 capture and conversion capabilities were studied using in situ diffuse reflectance infrared Fourier transform spectroscopy and breakthrough curve analysis monitored by mass spectrometry (MS).

Results and Discussion

Figs. 1(a) and (c) present the HRTEM image with DP and DF-STEM image of MgO(111), respectively, compared to commercial MgO(100) as shown in **Figs. 1(b) and (d)**. The synthesized MgO(111) shows a

nanosheet-like, single-crystal morphology with a 0.15 nm lattice fringe, corresponding to the exposed {111} surface and a {220} facet along the <111> viewing direction. In contrast, commercial MgO(100) exhibits a larger crystal size with a (100) facet structure. Breakthrough curve analysis was conducted to examine the CO2 adsorption and desorption behavior of prepared MgO(111) using a Belcat II instrument with an MS detector (**Figs. 1(e)**, **1(f)**, and **Table 1**). The curve illustrates CO_2 adsorption at 50 °C (light green area), representing total CO_2 uptake, and desorption under Ar flow at 50 °C (light yellow area) and 50–800 °C (light red area) during temperature-programmed desorption (TPD), corresponding to the release of physically and chemically adsorbed species, respectively. MgO(111) exhibits a high total CO_2 uptake of 1.40 mmol g^{-1}, including a small amount of physically adsorbed CO_2 and a large amount of chemically adsorbed CO_2. Notably, a considerable number of CO is produced during the TPD process of CO_2, indicating that the thermocatalytic conversion of CO_2 to CO can be catalyzed by "metal-free" MgO(111). In contrast, MgO(100) shows minimal uptake of physically adsorbed CO_2, and neither CO_2 nor CO is observed during TPD. These results clearly demonstrate that MgO(111) effectively captures CO_2 and converts it into CO, whereas MgO(100) does not.

Table 1. Breakthrough curve analysis of CO_2 adsorption and desorption on nanostructured MgO(111) compared to commercial MgO(100).

Material	Total CO_2 uptake at 50 °C (mmol g^{-1})	Physisorption (%)	Chemisorption (%)	CO/CO_2[a] (%)
MgO(111)	1.40	4.0	96	10
MgO(100)	0.11	100	0	0

a. Quantitative analysis of CO and CO_2 species at TPD region.

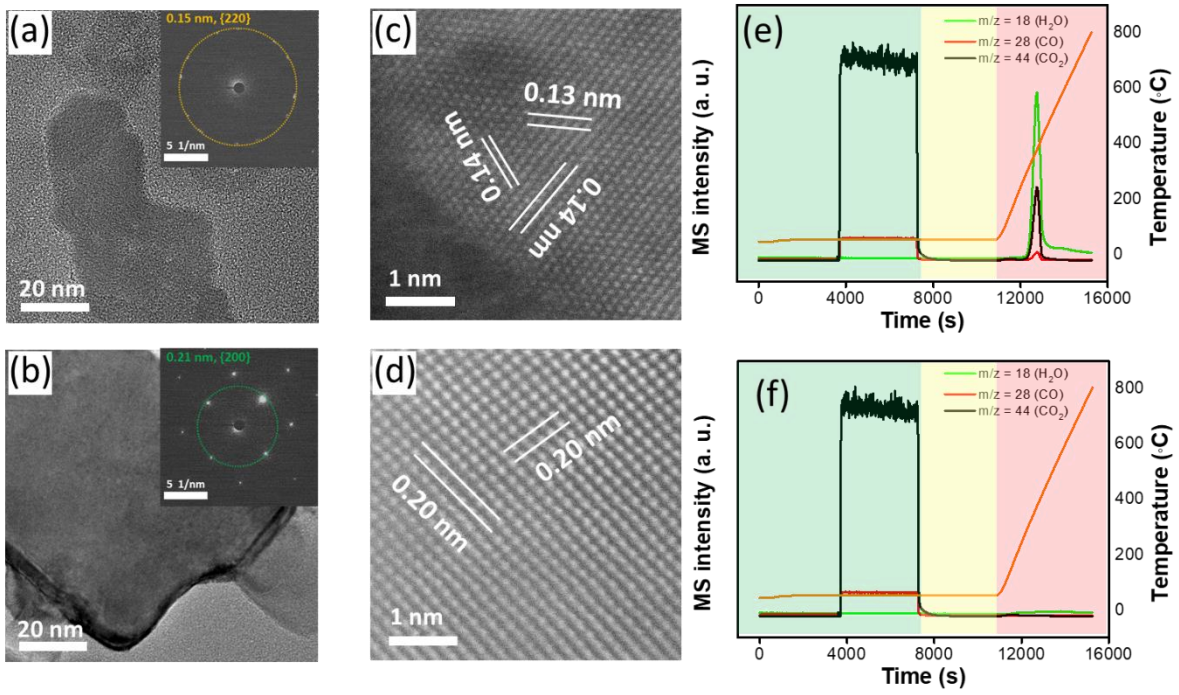

Figure 1 HRTEM images, diffraction patterns, DF-STEM images and breakthrough spectra (a, c, e) MgO(111) and (b, d, f) MgO(100).

References

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2. P. Liu *et al.*, *Angew. Chem. Int. Ed.* **2021,** 6, 3254-3260.

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