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## Applied Catalysis B: Environmental

journal homepage: [www.elsevier.com/locate/apcatb](http://www.elsevier.com/locate/apcatb)Atomic Pd-promoted ZnZrO<sub>x</sub> solid solution catalyst for CO<sub>2</sub> hydrogenation to methanolKyungho Lee<sup>a,1</sup>, Uzma Anjum<sup>a,1</sup>, Thaylan Pinheiro Araújo<sup>b</sup>, Cecilia Mondelli<sup>b</sup>, Qian He<sup>c</sup>, Shinya Furukawa<sup>d,e</sup>, Javier Pérez-Ramírez<sup>b,\*</sup>, Sergey M. Kozlov<sup>a,\*</sup>, Ning Yan<sup>a,\*</sup><sup>a</sup> Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore<sup>b</sup> Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland<sup>c</sup> Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575, Singapore<sup>d</sup> Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan<sup>e</sup> Elements Strategy Initiative for Catalysis and Battery, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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## ABSTRACT

The development of efficient CO<sub>2</sub> conversion catalysts is a long-lasting desire. Herein, we introduce an atomic Pd-promoted ZnZrO<sub>x</sub> solid solution catalyst (Pd-ZnZrO<sub>x</sub>), which shows markedly enhanced rate of methanol production compared to bare ZnZrO<sub>x</sub>, as well as excellent stability over 100 h on stream. Up to 0.8 at% (*i.e.* 0.6 wt%), Pd can be atomically dispersed in ZnZrO<sub>x</sub>, leading to more oxygen vacancies on the mixed oxide that foster methanol production. Kinetic analysis and *in situ* DRIFTS reveal that hydrogen activation is limited on ZnZrO<sub>x</sub>, but Pd doping facilitates H<sub>2</sub> dissociation as well as the consequent formation of HCOO\*, thus boosting CO<sub>2</sub> conversion to methanol. DFT analyses suggest that the presence of atomic Pd enables a more exothermic H<sub>2</sub> dissociation, which increases the availability of surface H and facilitates CO<sub>2</sub> hydrogenation on adjacent Zn sites, providing rationale on the high activity and robustness of Pd-ZnZrO<sub>x</sub> in CO<sub>2</sub> hydrogenation.

## 1. Introduction

Taking steps forward to a circular carbon economy is a prominent global agenda. Anthropogenic CO<sub>2</sub> emissions have been identified as a major cause of climate change and ocean acidification [1,2]. Paradoxically, CO<sub>2</sub> can also be regarded as an abundant and sustainable carbon source when coupled to an efficient transformation technology. CO<sub>2</sub> hydrogenation to methanol has received a lot of attention because methanol is a useful platform chemical in the petrochemical industry, as well as its potential as an energy carrier in a broad range of applications [3,4]. For these reasons, various CO<sub>2</sub> valorization routes relying on methanol as a key intermediate are being widely explored [5–11].

CO<sub>2</sub> hydrogenation to methanol is thermodynamically favored at low temperature and high pressure [12]. However, since exceedingly low temperature limits the reaction kinetics, high pressure (>5 MPa) and moderate temperature (473–573 K) conditions are typically required [12,13]. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, commercially used for methanol synthesis from syngas, has been widely studied for CO<sub>2</sub> conversion to methanol, however, a rapid and permanent deactivation

through sintering of Cu, or segregation of Cu and ZnO species has been pointed out as a major drawback [14–16]. It is thus desirable to develop more efficient catalytic systems that simultaneously satisfy high methanol productivity and long-term stability.

Encouragingly, several oxide-based catalysts such as In<sub>2</sub>O<sub>3</sub>-based oxides [17–25] and MZrO<sub>x</sub> solid solutions (*M* = Zn, Cd, Ga, *etc.*) [26–31] have been identified as promising catalysts owing to their superior methanol selectivity and lifetime. Nonetheless, metal oxide catalysts show relatively poor activity compared to Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (which generally contains >60 wt% Cu), supposedly due to their inferior H<sub>2</sub> activation ability. Earlier literature indeed hints that the hydrogenation step over oxide-based catalysts is rate-determining. For example, Frei *et al.* observed that the reaction order of H<sub>2</sub> (0.3–0.5) is much larger than that of CO<sub>2</sub> (–0.1 to 0) for In<sub>2</sub>O<sub>3</sub>-based catalysts [20]. More recently, numerous reports demonstrated that metal promoters (*e.g.* Pt, Pd, Rh, Ru, Ir, Ni, Au, *etc.*) on oxide catalyst (especially In<sub>2</sub>O<sub>3</sub>) could substantially improve methanol yield [32–48]. A highly dispersed metal promoter can maximize the metal–oxide and/or metal–metal interfaces as well as provide a stronger H<sub>2</sub> splitting capability, accelerating methanol

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