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journal homepage: www.elsevier.com/locate/apcatbAtomic Pd-promoted ZnZrO_x solid solution catalyst for CO₂ hydrogenation to methanolKyungho Lee^{a,1}, Uzma Anjum^{a,1}, Thaylan Pinheiro Araújo^b, Cecilia Mondelli^b, Qian He^c, Shinya Furukawa^{d,e}, Javier Pérez-Ramírez^{b,*}, Sergey M. Kozlov^{a,*}, Ning Yan^{a,*}^a Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore^b Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland^c Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575, Singapore^d Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan^e 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 CO₂ conversion catalysts is a long-lasting desire. Herein, we introduce an atomic Pd-promoted ZnZrO_x solid solution catalyst (Pd-ZnZrO_x), which shows markedly enhanced rate of methanol production compared to bare ZnZrO_x, 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_x, 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_x, but Pd doping facilitates H₂ dissociation as well as the consequent formation of HCOO*, thus boosting CO₂ conversion to methanol. DFT analyses suggest that the presence of atomic Pd enables a more exothermic H₂ dissociation, which increases the availability of surface H and facilitates CO₂ hydrogenation on adjacent Zn sites, providing rationale on the high activity and robustness of Pd-ZnZrO_x in CO₂ hydrogenation.

1. Introduction

Taking steps forward to a circular carbon economy is a prominent global agenda. Anthropogenic CO₂ emissions have been identified as a major cause of climate change and ocean acidification [1,2]. Paradoxically, CO₂ can also be regarded as an abundant and sustainable carbon source when coupled to an efficient transformation technology. CO₂ 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 CO₂ valorization routes relying on methanol as a key intermediate are being widely explored [5–11].

CO₂ 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/Al₂O₃ catalyst, commercially used for methanol synthesis from syngas, has been widely studied for CO₂ 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 In₂O₃-based oxides [17–25] and MZrO_x 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/Al₂O₃ (which generally contains >60 wt% Cu), supposedly due to their inferior H₂ 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 H₂ (0.3–0.5) is much larger than that of CO₂ (–0.1 to 0) for In₂O₃-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 In₂O₃) 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 H₂ splitting capability, accelerating methanol

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