

Communication

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Sai Zhang, Zhaoming Xia, Yong Zou, Fangxian Cao, Yuxuan Liu, Yuanyuan Ma, and Yongquan Qu J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b03217 • Publication Date (Web): 10 Jul 2019

Downloaded from pubs.acs.org on July 10, 2019

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Interfacial frustrated Lewis pairs of CeO₂ activate CO₂ for selective tandem transformation of olefins and CO₂ into cyclic carbonates

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Supporting Information Placeholder

ABSTRACT: Effective activation of CO_2 is a prerequisite for efficient utilization of CO_2 in organic synthesis. Precisely controlling the interfacial events of solids shows potential for activation. Herein, defect-enriched CeO_2 with constructed interfacial frustrated Lewis pairs (FLPs, two adjacent $Ce^{3+}...O^2$ -, Figure 1) effectively activates CO_2 via the interactions between C/Lewis basic lattice O^2 - and the two O atoms in CO_2 /two adjacent Lewis acidic Ce^{3+} ions. Selective cyclic carbonate production from a catalytically tandem protocol of olefins and CO_2 is used to demonstrate FLP-inspired CO_2 activation.

The catalytic transformation of CO_2 as a C1 building block into value-added chemicals has attracted increasing attention due to the potential for CO_2 reutilization.¹⁻⁵ However, the reactions of CO_2 are highly energy-intensive because of its chemical inertness and extremely high C=O bond energy of 806 kJ/mol. Thus, the effective activation of CO_2 under mild conditions is pivotal for practical applications. Among various strategies, homogeneous frustrated-Lewis-pairs (FLPs), the combinations of a sterically hindered Lewis acid and Lewis base, offer promising opportunities for CO_2 activation and conversion into CO, CH₄, CH₃OH and formamides.⁶⁻¹³ Inspired by the benefits of heterogeneous catalytic systems, including facile separation, elongated lifetime and scalable productivity, constructing heterogeneous FLP sites for CO_2 activation is fundamentally and practically attractive.

Recently, heterogeneous FLPs composed of Lewis acidic and basic block copolymers activated CO_2 for the *N*formylation of amines.¹⁴ FLP sites within metal organic frameworks with B-based ligands as Lewis acids catalyzed the conversion of diamines into benzimidazoles by using CO_2 as a C1 feedstock.¹⁵ To date, most homogeneous and heterogeneous FLPs have activated CO_2 through the respective interactions between Lewis basic sites/C and Lewis acidic sites/one O atom of CO_2 .^{14, 16-18} Recently, FLPs constructed on defective CeO_2 (lattice O as the Lewis base and two neighboring adjacent Ce^{3+} ions as Lewis acids, Figure 1) have been reported for hydrogen activation.¹⁹⁻²¹ Herein, we demonstrate that such interfacial FLPs exhibit the capability for CO_2 activation *via* the Lewis basic site of lattice O binding with the C atom and two Lewis acidic Ce^{3+} sites binding with both O atoms of CO₂. Such interfacial FLPs acting on defectenriched CeO₂ to achieve CO₂ activation is further demonstrated by the selective tandem transformation of olefins and CO₂ into cyclic carbonates.

CeO₂(110) instead of CeO₂(100) and (111) exhibits the highest possibility for FLPs construction due to the unique FLPs configuration and formation energy of oxygen vacancies on various surfaces.¹⁹ When two adjacent oxygen atoms were removed from CeO₂(110), adjacent reduced surface Ce atoms and lattice O atoms are independent Lewis acidic and basic sites at a proper distance, constructing the interfacial FLPs. However, FLPs cannot be created on CeO₂(111) due to its unique crystal structure and large oxygen vacancy formation energy.^{19, 22-24} Although CeO₂(100) exhibits the possibility of constructing FLPs, it is difficult to fix these surface Lewis acidic and basic sites due to the easily diffused oxygen atoms/vacancies on the less stable CeO₂(100) surface.^{19, 22-24}



Figure 1. Adsorption and activation of CO_2 on $CeO_2(110)$.

Density functional theory (DFT) calculations were initially performed to explore the adsorption and activation of CO_2 on $CeO_2(110)$ (Figure 1, S1-S2). The most stable adsorption configurations on both ideal and defective CeO_2 were carbonate-like, consistent with previous reports.²⁵ On an ideal $CeO_2(110)$ surface, CO_2 is bent with an adsorption energy of -1.5 eV, where the O–C–O angle is 128.5° and the C=O bond

elongates from 1.177 to 1.284 Å. Upon introducing one oxygen vacancy (CeO₂(110)-10_v), the carbonate-like CO_2 configuration is such that one O of CO_2 falls into the oxygenvacancy-site and binds with Ce³⁺ and the C atom of CO₂ binds with lattice O^{2-} . Compared to CO_2 on an ideal $CeO_2(110)$ surface, the two C=O bonds of CO_2 elongate to 1.339 and 1.266 Å with similar adsorption energies (-1.5 eV), and the O-C-O angle is decreased to 119.1°. Thus, CO2 can be activated on defective CeO₂. FLPs can further enhance CO₂ adsorption (-2.2 eV), in which a C atom binds to a Lewis basic lattice 0^{2-} and the two 0 atoms of CO_2 bind to two Lewis acidic Ce^{3+} ions (Figure 1). Compared to CO_2 on $CeO_2(110)$ -10_V, in addition to the further decreased O-C-O angle (118.8°) and slightly elongated C=O bonds (1.339 and 1.267 Å), the more negatively charged O (-2.13 e) of CO₂ suggests its further activation on FLPs.3, 26

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Then, cyclic carbonate production from a catalytically tandem transformation of olefins and CO_2 was used to examine the capability of CeO_2 to promote CO_2 activation. Industrial production of cyclic carbonates is a two-step process of olefin epoxidation and subsequent CO_2 cycloaddition, which suffers from serious safety and environmental issues due to the sensitivity, combustibility and explosibility of epoxides during handling and transport. By using olefins as an inexpensive feedstock, the tandem conversion of olefins and CO_2 to cyclic carbonates provides a safe, environmentally friendly and economical strategy.²⁷



Figure 2. Catalytic performance of various CeO_2 catalysts. **Reaction conditions**: styrene (4 mmol), TBHP (0.65 mL, 70 *wt*% aqueous solution), TBABr (40 mg), CeO_2 (40/8 mg), 80 °C, 2 MPa CO_2 , 14 h.

To highlight the advantages of FLPs for tandem transformation, CeO₂ nanorods (NR-CeO₂) with FLPs and CeO₂ cubes (NC-CeO₂) and octahedra (NO-CeO₂) without FLPs were prepared with specific surface areas of 91, 15 and 18 m²/g, respectively (Figure S3-S4).28-29 Based on their X-ray photoelectron spectra (XPS, Figure S5-S6 and Table S1), NR- CeO_2 exhibited a similar surface Ce^{3+} fraction (20.8%) to NC-CeO₂ (20.6%) and NO-CeO₂ (20.9%).³⁰⁻³¹ Additionally, from the 0 1s profiles (Figure S6), the similar surface oxygen vacancy percentages of NR-CeO₂ (26.7%), NC-CeO₂ (24.4%) and NO-CeO₂ (23.1%) were consistent with their surface Ce^{3+} fractions (Table S2). The tandem reactions were optimized and assessed by using styrene as an olefin, tbutylhydroperoxide (TBHP) as an oxidant, tetrabutylammonium bromide (TBABr) as an initiator and CeO₂ as a catalyst for 14 h (Figure 2). Without catalysts, the reaction yielded a 23% conversion of styrene and a poor

selectivity of 47% to phenylethylene carbonates. Serious hydrolysis with 38% selectivity of diols was observed due to the presence of water in the catalytic solution. Next, 40 mg of CeO₂ catalyst was used under the same conditions. Styrene conversion was only slightly increased to 32% and 30% for *NC*-CeO₂ and *NO*-CeO₂, respectively. *NR*-CeO₂ delivered the highest styrene conversion of 69%. Importantly, the selectivity towards cyclic carbonates was >70% for all CeO₂, much higher than that without catalysts. Among the catalysts, *NR*-CeO₂ achieved the highest selectivity of >80% for cyclic carbonates.

Even after normalizing to their surface area, 8 mg of NR-CeO₂ still delivered a much higher styrene conversion of 43% than 40 mg of NC-CeO₂ and NO-CeO₂. As determined by DFT calculations, the formation of interfacial FLP sites is critical for effective CO₂ activation and tandem reaction. The literature suggests that Lewis acids enable the epoxidation of olefins and Lewis bases to catalyze the cycloaddition of epoxides and CO₂.^{3, 32} Herein, the abundant defects on CeO₂ not only form the defect clusters for constructing the interfacial FLPs but also produce "isolated" Ce3+ sites.33-34 Based on that and the peroxidase-like activity of CeO_2 for peroxide activation by Ce^{3+,35} those "isolated" Ce³⁺ ions can catalyze styrene epoxidation. Hence, a catalytically tandem pathway is proposed: (1) olefin epoxidation on Lewis acidic Ce^{3+} ; (2) CO_2 activation on FLPs; (3) electrophilic attack of in situ-generated and released epoxides on the activated CO_2 (Figure 3a).



Figure 3. (a) Proposed catalytic process for the tandem transformation of olefins (propylene) and CO_2 into cyclic carbonates on FLPs. (b) H₂-TPR of *NR*-CeO₂-T. (c) Catalytic activity and (d) selectivity of *NR*-CeO₂-T *vs.* their surface Ce³⁺ fractions. **Reaction conditions**: styrene (2 mmol), TBHP (0.35 mL, 70 *wt*% aqueous solution), TBABr (50 mg), catalysts (40 mg), 80 °C, 2 MPa CO₂ and 14 h. (e) Adsorption energy of propylene oxide on defective CeO₂(110).

Generally, the abundance of CeO_2 defects benefits the formation of oxygen vacancy clusters, which can promote the creation of interfacial FLPs. The formation of oxygen vacancy

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clusters can be revealed from the oxygen migration or reducibility of CeO₂.³⁶ Then, H₂ temperature-programmed reduction (H₂-TPR) of various catalysts was recorded (Figure S7). The peak over 300 °C can be attributed to the reduction of surface lattice oxygen.³⁷⁻³⁹ The lowest reduction temperature of NR-CeO₂ over NO-CeO₂ and NC-CeO₂ indicated the most abundance of oxygen vacancy clusters on NR-CeO2 and thereby effective CO₂ activation, enabling the best catalytic performance of NR-CeO₂ for the tandem transformation.

Then, to eliminate the influence of morphology on the formation of FLPs, the surface defects of NR-CeO₂ were 10 modulated by calcination at 300 and 500 °C (NR-CeO₂-T) in air 11 with the preserved morphology and surface areas (Figure S8). Derived from their XPS profiles (Figure S9), the surface Ce³⁺ 12 fractions of NR-CeO₂-300 and NR-CeO₂-500 decreased to 13 15.5% and 11.3%, respectively. Derived from their 0 1s 14 spectra (Figure S10), the surface percentages of oxygen 15 vacancies were also reduced from 26.7% of NR-CeO₂ to 19.9% 16 of NR-CeO₂-300 and 12.5% of NR-CeO₂-500, consistent with 17 the changes in the surface Ce³⁺ fractions. These changes in 18 their surface properties can be further revealed by the Raman spectra (Figure S11). The intense band at 459 cm⁻¹ can be 19 ascribed to the Raman-active F_{2g} vibrational mode of the CeO₂ 20 fluorite-type structure. The weak band at 600 cm⁻¹ is 21 associated with oxygen vacancy.⁴⁰ At elevated temperatures, 22 the decreased values of the ratio of integrated peak areas at 23 600 and 459 cm⁻¹ (A_{600}/A_{459}) suggest a decrease in the surface 24 defect density of the thermal-treated catalysts. Similarly, NR-25 CeO₂ exhibits the lowest beginning temperature (250 °C) and the smallest reductive peak temperature (484 °C) compared 26 with NR-CeO₂-300 and NR-CeO₂-500, as determined from H₂-27 TPR analysis (Figure 3b). Thus, the defect-enriched NR-CeO₂ 28 exhibits the highest possibility for the formation of the 29 structural defect clusters³⁶, leading to the construction of 30 more surface FLP sites for CO_2 activation. As expected, in 31 terms of activity, the styrene conversions increased from 25% 32 to 32% and 69% for NR-CeO₂-500, NR-CeO₂-300 and NR-CeO₂, 33 respectively, indicating the benefits of the rich surface defect for FLP construction and thereby CO₂ activation (Figure 3c). 34

The defect-enriched NR-CeO₂ also exhibited the highest selectivity for cyclic carbonates (Figure 3d). Generally, the strong interaction between in-situ generated epoxides and Ce³⁺ can impede epoxide release and lead to further hydrolysis of epoxides into diols on acidic Ce³⁺. Thus, weakening this interaction can suppress the hydrolysis sidereaction. DFT calculations were used to assess the defectdependent adsorption of epoxides on CeO2. To save computing resources, propylene oxide instead of styrene oxide was used (Figure 3e, S12-S13). Epoxide has an adsorption energy of -0.58 eV by forming a bond between 0 of epoxides and surface Ce on ideal $CeO_2(110)$. The adsorption energy of epoxide on $CeO_2(110)-1O_V$ is enhanced to -0.47 eV and further increased to -0.28 eV on FLPs, indicating its significantly weakened interaction on the defective CeO_2 (Figure 3e). Thus, the defect-rich CeO_2 leads to the easy release of in situ-generated epoxide from the catalyst, suppressed its hydrolysis and improved the yield of cyclic carbonates.

Based on the above understanding, further increases in surface defects might create more FLPs for CO₂ activation and weaker interactions between epoxide and catalyst for the improved selectivity of cyclic carbonates. Then, porous nanorods of CeO_2 (*PN*-CeO₂, Figure 4a) with a high surface Ce³⁺ fraction (28.2%, Figure S14a) delivered a styrene conversion of 63% and the highest selectivity of 95% to cyclic

carbonates within 14 h (Figure 4b).¹⁹ The tandem reaction continuously proceeded to reach 94% conversion of styrene after 24 h with a selectivity of 94% for cyclic carbonates. After recovery by centrifugation, *PN*-CeO₂ maintained its catalytic activity and selectivity for at least 3 cycles (Figure 4c). The unaltered morphology and surface Ce³⁺ fraction of the spent catalysts indicated their structural and catalytic stability (Figure S14).



Figure 4. (a) TEM image of PN-CeO₂; (b) styrene conversion and selectivity of cyclic carbonates vs. time; (c) recyclability at 20 h. Reaction conditions: styrene (4 mmol), TBHP (0.65 mL, 70 wt% aqueous solution), TBABr (40 mg), CeO₂ (40 mg), 80 °C and 2 MPa CO₂.

Table 1. Tandem conversions of olefins with CO₂.

Entry	Olefin	Product	Conv. (%)	Sel. (%)
1			97	92
2			80	93
3	\sim		99	85
4	$\bigcirc - / /$		64	86
5			99	92

Reaction conditions: substrates (4 mmol), TBHP (0.65 mL, 70 wt% aqueous solution), TBABr (50 mg), PN-CeO₂ (40 mg), 80 °C, 2 MPa CO₂.

PN-CeO₂ was then used for this tandem conversion with various olefins for 20 h (Table 1). For 4-methylphenylene and 4-t-butyl styrene, 97% and 80% conversions were achieved with 92% and 93% selectivity for cyclic carbonates, respectively (Entries 1-2). The conversion of α -methylstyrene reached 99% with 85% for cyclic carbonates (Entry 3). Also, 64% of vinylcyclohexane was converted into cyclic carbonates, with 86% selectivity (Entry 4). cis-Cyclooctene was converted to cyclic carbonates, with 99% conversion with 92% selectivity (Entry 5).

In summary, the constructed interfacial FLPs on CeO_2 effectively activate CO₂, which is demonstrated by the selective tandem conversion of olefins and CO₂ to cyclic carbonates. Defect-enriched CeO₂ benefits this tandem protocol by providing more FLP sites for efficient CO₂ activation for cycloaddition and weakening the adsorption of in situ-produced epoxides to suppress their hydrolysis. We anticipate that such CO_2 activation by solid FLPs can contribute to other catalytic CO₂ utilizations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental Procedures, Figure S1-Figure S15 and Table S1-S2.

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Author Contributions

S. Z. and Z. X. contributed equally to this work.

Notes

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The authors declare no competing financial interests.

ACKNOWLEDGMENTS

We acknowledge the financial support from the National Nature Science Foundation of China (21872109) and the China Postdoctoral Science Foundation (2018M640994; 2018T111034). Y. Qu is supported by the Cyrus Tang Foundation through the Tang Scholar program. S. Zhang is supported by the Fundamental Research Funds for the Central Universities (xjj2018033). The calculations were performed by using the HPC Platform at Xi'an Jiaotong University.

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