

***Supplementary Information for***

**Regulating oxygen vacancies by Zn atom doping to anchor and disperse promoter Ba on MgO  
support to improve Ru-based catalysts activity for ammonia synthesis**

Yuanjie Chen,<sup>a</sup> Junqiao He,<sup>a</sup> Haiyan Lei,<sup>a</sup> Qunyao Tu,<sup>a</sup> Chen Huang, Xiangwei Cheng,<sup>\*b</sup> Xiazhen  
Yang,<sup>a</sup> Huazhang Liu<sup>a</sup> and Chao Huo<sup>\*a</sup>

*a State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology and Key  
Laboratory of Green Chemistry-Synthesis Technology of Zhejiang Province.*

*Hangzhou 310014, China. E-mail: chaohc@zjut.edu.cn*

*a Modern Educational Technology Experimental Center, Zhejiang Police College.*

*Hangzhou 310053, China. E-mail: chengxiangwei@zjjcxy.cn*

Corresponding author *E-mail: chaohc@zjut.edu.cn*

The following are included as supporting information for this paper:

Total 12 Pages, 1 Text, 6 Figures, and 5 Table.

## **Text 1. Experimental section**

### *Characterization*

The phase and crystal structure of the catalyst were detected by Thermo ARL SCINTAG X'TRA X-ray diffraction analyzer (XRD). The emission source is Cu, the measured voltage is 40 kV, the current is 40 mA, the solid detector, the scanning rate is 5°/min, the scanning range is 10-80°.

The surface morphology of the samples was analyzed by using Zeiss type 500 field emission scanning electron microscope (FE-SEM) (accelerated voltage 15kV) to observe the surface micro/submicro morphology of the samples. The composition and distribution of the samples were analyzed qualitatively and quantitatively by using the Thermo NORAN energy spectrum (EDS) of the United States.

The catalyst H<sub>2</sub>-TPR was determined by Autochem 2910 automatic chemisorption instrument produced by Micromeritics. The sample was placed in a high purity H<sub>2</sub> (99.99) atmosphere of 20 mL/min and heated to 600 °C at a heating rate of 10 °C/min for detection. The final output is analyzed using a TCD detector.

The texture parameters of the prepared carrier were determined by BSD-PS1/2 automatic surface area porosity analyzer produced by Beijing BeiShiDe Company. The samples were degassed under vacuum at 160 °C for 6 h, and N<sub>2</sub>-adsorption desorption was performed at -196 °C. The specific surface area of the sample was determined by Brunauer-Emmett-Teller (BET) equation, and the pore volume and mean pore diameter were calculated by Barrett-JoynerHalenda (BJH) model.

The size and dispersion of active component Ru particles loaded on Ba-MgO carrier were

observed by Hitachi transmission electron microscopy (TEM) model 7700 with an acceleration voltage of 300 kV.

The analysis of CO<sub>2</sub>-TPD was performed on the AutoChem II 2920 automatic chemisorbed instrument. First, the sample was heated to 450 °C in a high-purity Ar atmosphere (20 ml/L) for 1 h; Then it was reduced to 50 °C and switched to CO<sub>2</sub> atmosphere (20 ml/L) for constant temperature adsorption for 1 h; Then switch to pure Ar atmosphere purge for 1 h, and finally heat up to 900 °C at a rate of 10 °C/min. The gas output is analyzed using a TCD detector.

H<sub>2</sub>-TPD was performed on the AutoChem II 2920 automatic chemisorbed instrument. First, the sample was heated to 450 °C in a high-purity Ar atmosphere (20 ml/L) for 1 h; Then it was reduced to 50 °C and switched to H<sub>2</sub> atmosphere (20 ml/L) for constant temperature adsorption for 2 h; Then switched argon as the carrier gas, and rises from 50 °C to 800 °C s at a rate of 10 °C per minute

X-ray photoelectron spectroscopy was measured on the Thermo Scientific K-Alpha instrument. The X-ray excitation sources are monochromated Al K $\alpha$ ( $h\nu= 1486.6\text{eV}$ ), the working voltage is 12 kV, 6 mA, and the working pressure of the analysis chamber is  $7.1 \times 10^{-5}$  Pa. The XPS sample preparation method is: The powder sample is fixed on the conductive carbon tape by pressing sheet for testing.

#### *Kinetic analysis*

The kinetic data were tested at 400°C and the performance data of each catalyst were tested three times and averaged

When measuring H<sub>2</sub> reaction order, the gas is composed of hydrogen nitrogen and argon. The

reaction rates of four groups of gases with different compositions were respectively measured. The flow rate of (H<sub>2</sub>, N<sub>2</sub> and Ar) is respectively (10%, 50% and 40%), (20%, 50% and 30%), (30%, 50% and 20%) and (40%, 50% and 10%) of the total flow rate.

When measuring N<sub>2</sub> reaction order, the gas is composed of hydrogen nitrogen and argon. The reaction rates of four groups of gases with different compositions were respectively measured. The flow rate of (H<sub>2</sub>, N<sub>2</sub> and Ar) is respectively (50%, 10% and 40%), (50%, 20% and 30%), (50%, 30% and 20%) and (50%, 40% and 10%) of the total flow rate.

When measuring NH<sub>3</sub> reaction order, the gas is composed of hydrogen nitrogen and argon. The reaction rates of four groups of gases with different compositions were respectively measured. The flow rate of (H<sub>2</sub>, N<sub>2</sub> and Ar) is respectively (42%, 14% and 44%), (48%, 16% and 36%), (54%, 18% and 28%) and (60%, 20% and 20%) of the total flow rate.

### *DFT*

In the model, it is difficult to achieve that the ratio of Zn/Mg molar ratio X is 0.03 in the theoretical calculation, so the ratio of Zn/Mg molar ratio X in the model is constructed below 0.1 to qualitatively explain the influence of Zn doping on the formation of oxygen vacancy. The two crystal planes were modeled respectively. When MgO (200) was constructed, the size of the supercell was 3 layers, the bottom layer was fixed, and the rest atoms relaxed. When MgO(111) is constructed, the size of the supercell is 5 layers, and the bottom two layers are fixed to relax with the atoms. Atomic substitution energy ( $E_{\text{sub}}$ ) is calculated by the following formula.

$$E_{\text{sub}} = (E_{\text{C}} + E_{\text{Mg}}) - (E_{\text{Zn}} + E_{\text{B}})$$

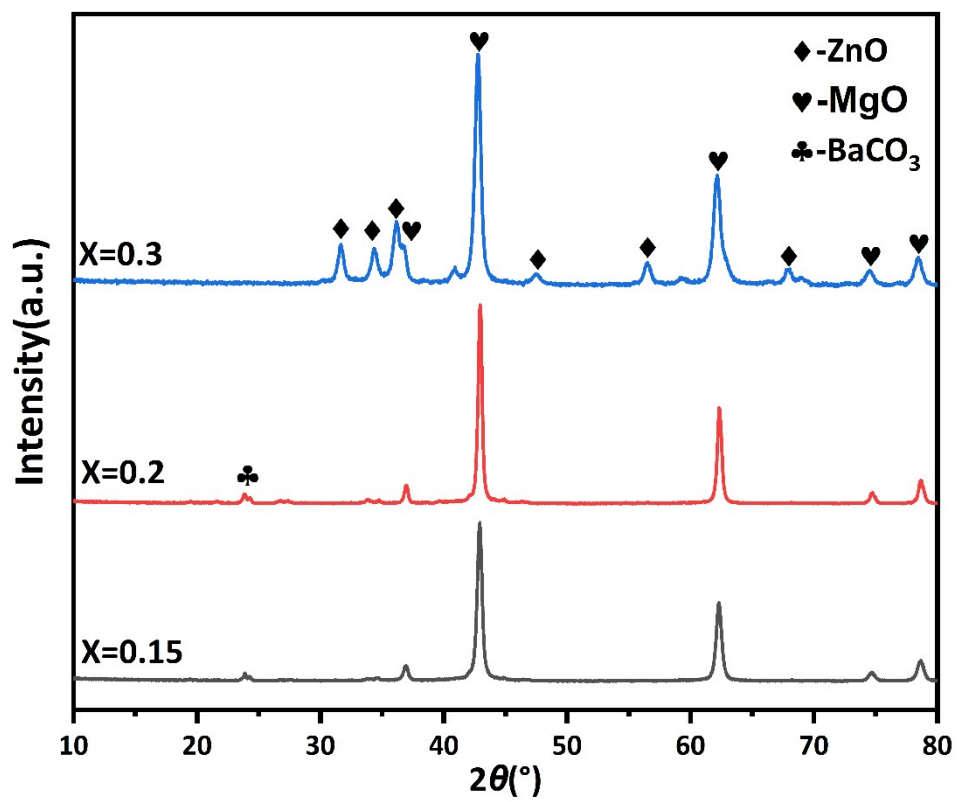
Where,  $E_{\text{sub}}$  is the atomic replacement energy,  $E_{\text{C}}$  is the catalyst surface energy after replacing

Mg atom;  $E_{\text{Mg}}$  represents the energy of one Mg atom;  $E_{\text{Zn}}$  represents the energy of the Zn atom;  $E_{\text{B}}$  stands for pre-catalyst energy.

Oxygen vacancy formation can be calculated by the following formula.

$$E_{\text{OV}} = E_{\text{defect}} + 1/2E_{\text{O}_2} - E_{\text{sur}}$$

Where  $E_{\text{OV}}$  is the energy of oxygen vacancy formation,  $E_{\text{defect}}$  is the energy of a supercell with an oxygen defect, and  $E_{\text{O}_2}$  is the energy of a gas oxygen molecule.  $E_{\text{sur}}$  is the surface energy of a complete supercell.



Supplementary figures

Figure S1. XRD results of Ru/Ba-Mg<sub>(1-x)</sub>Zn<sub>x</sub>O catalysts.

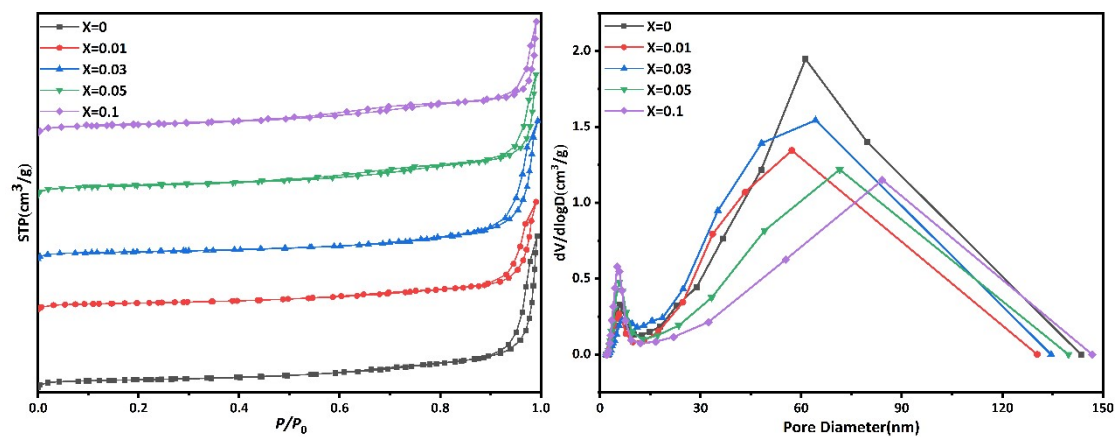


Figure S2. (a) Hydrogen adsorption-desorption (H<sub>2</sub>-TPD) curves of Ba-Mg<sub>(1-x)</sub>Zn<sub>x</sub>O supports.

(b) Pore size distribution of Ba-Mg<sub>(1-x)</sub>Zn<sub>x</sub>O supports

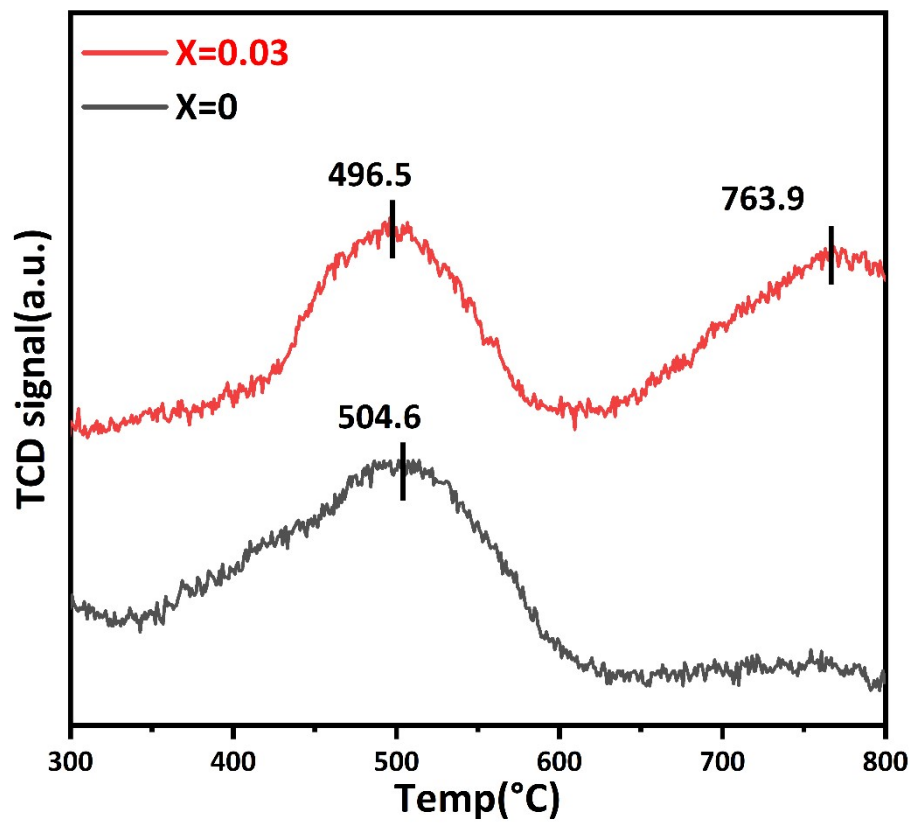


Figure S3. H<sub>2</sub>-TPD curves of Ru/Ba-Mg<sub>(1-X)</sub>Zn<sub>X</sub>O catalysts when X=0 and X=0.03



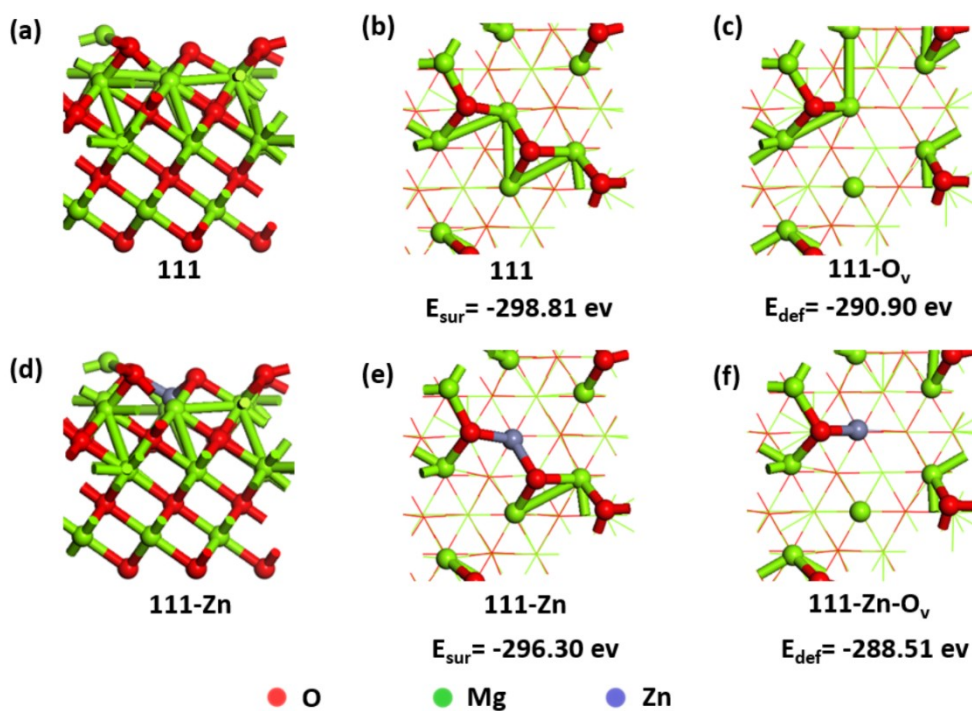


Figure S4. DFT calculation of the oxygen vacancy formation energy ( $E_{Ov}$ ) of (111) crystal planes before and after Zn atom doping

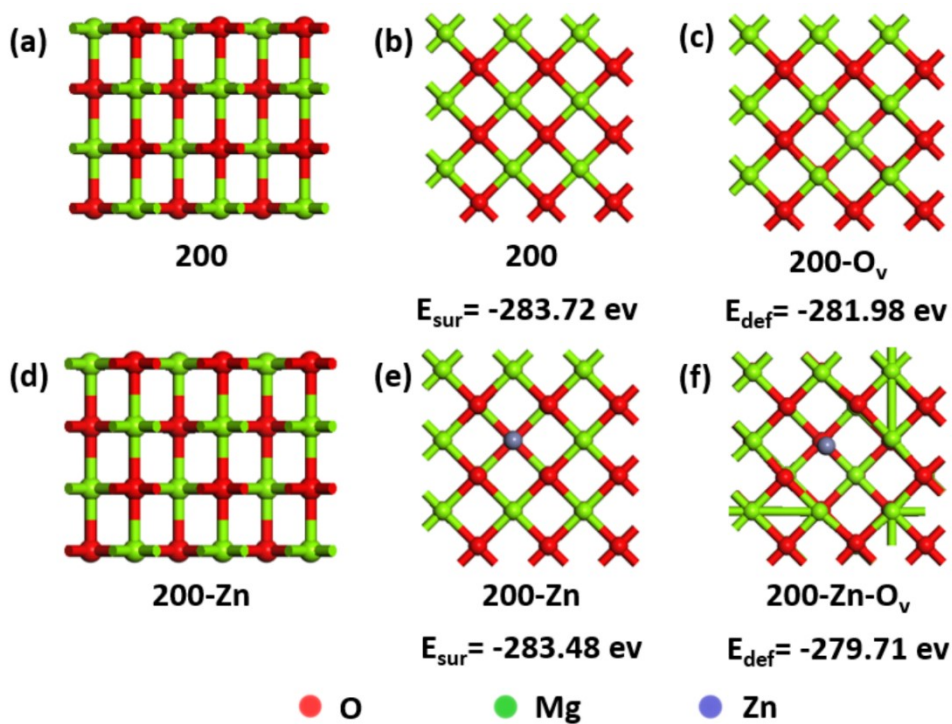


Figure S5. DFT calculation of the oxygen vacancy formation energy ( $E_{Ov}$ ) of (200) crystal planes before and after Zn atom doping

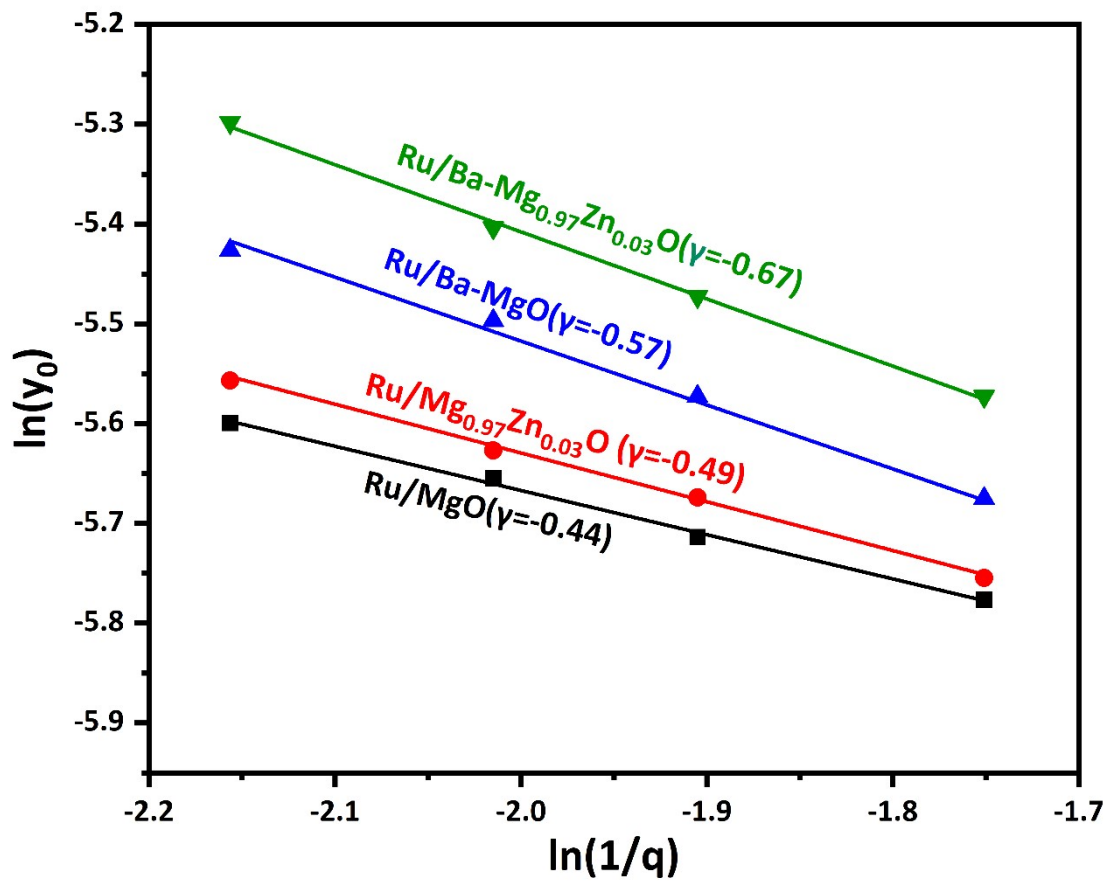


Figure S6. Reaction orders of  $\text{NH}_3$  for Ru/MgO, Ru/Ba-MgO, Ru/Mg<sub>0.97</sub>Zn<sub>0.03</sub>O and Ru/Ba-Mg<sub>0.97</sub>Zn<sub>0.03</sub>O catalysts.

**Table S1. Texture parameter of Ba-Mg<sub>(1-x)</sub>Zn<sub>x</sub>O supports.**

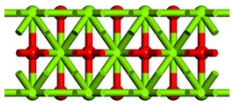
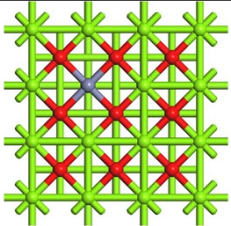
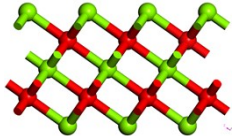
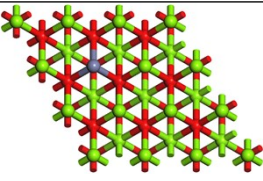
Sample	MgO Grain size(nm)	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Size (nm)
Ru/Ba-MgO	27.1	114.986	0.9644	23.4918
Ru/Ba-Mg <sub>0.99</sub> Zn <sub>0.01</sub> O	23.3	99.520	0.6989	19.4742
Ru/Ba-Mg <sub>0.97</sub> Zn <sub>0.03</sub> O	22.9	107.247	0.8704	23.5120
Ru/Ba-Mg <sub>0.95</sub> Zn <sub>0.05</sub> O	23.2	137.699	0.7753	16.7389
Ru/Ba-Mg <sub>0.90</sub> Zn <sub>0.10</sub> O	35.2	129.912	0.7145	14.7433

## 2. Supplementary tables

**Table S2. EDS analysis of the Ru/Ba-Mg<sub>(1-x)</sub>Zn<sub>x</sub>O catalysts.**

Sample	Relative content											
	C	C	O	O	Mg	Mg	Zn	Zn	Ru	Ru	Ba	Ba
	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%	wt%	atom%
Ru/Ba-MgO	3.32	5.50	42.40	52.73	50.16	41.06	0.00	0.00	2.18	0.43	1.93	0.28
Ru/Ba-Mg <sub>0.99</sub> Zn <sub>0.01</sub> O	2.61	4.43	40.40	51.41	51.30	42.98	1.25	0.39	2.48	0.50	1.96	0.29
Ru/Ba-Mg <sub>0.97</sub> Zn <sub>0.03</sub> O	2.95	5.15	36.93	48.44	51.34	44.33	3.55	1.14	2.55	0.53	2.68	0.39
Ru/Ba-Mg <sub>0.95</sub> Zn <sub>0.05</sub> O	2.71	4.82	36.17	48.26	50.05	43.96	6.46	2.11	2.41	0.51	2.19	0.34
Ru/Ba-Mg <sub>0.90</sub> Zn <sub>0.10</sub> O	2.57	4.73	34.68	48.00	46.58	42.44	11.75	3.98	2.37	0.52	2.05	0.33

**Table S3. Model configuration of on MgO (200) and MgO (111) planes with Zn substitution.**

Crystal plane	Model configuration	Top layer	Cell size	$E_{\text{sub}}$ (kJ/mol)
MgO(200)			3 Layers=1F+2R	322.0
MgO(111)			5 Layers=2F+3R	58.1

**Table S4. The energy of the defect formation energies ( $E_{\text{O}_V}$ ) of oxygen on MgO (200) and (110) planes before and after Zn doping.**

Crystal plane	Model configuration	Energy (eV)				
		$E_{\text{sur}}$	$E_{\text{defect}}$	$E_{\text{O}_2}$	$E_{\text{O}_V}$	$\Delta E_{\text{O}_V}$
(200)	undoped MgO	-431.34	-420.12		6.29	
	Zn-doped MgO	-428.33	-417.84		5.56	-0.73
(110)	undoped MgO	-298.81	-290.90	-9.86	2.98	
	Zn-doped MgO	-296.30	-288.51		2.86	-0.12

**Table S5. Peak area of CO<sub>2</sub> desorption derived from CO<sub>2</sub>-TPD results over Ru/Ba-Mg<sub>(1-</sub>****<sub>x</sub>)Zn<sub>x</sub>O catalysts.**

Sample	Peak area of CO <sub>2</sub> desorption		
	$\alpha$	$\beta$	Total
Ru/Ba-MgO	0.9143	8.5723	9.4866
Ru/Ba-Mg <sub>0.99</sub> Zn <sub>0.01</sub> O	1.1603	7.3748	8.5351
Ru/Ba-Mg <sub>0.97</sub> Zn <sub>0.03</sub> O	1.3349	8.9067	10.2416
Ru/Ba-Mg <sub>0.95</sub> Zn <sub>0.05</sub> O	1.1899	8.7757	9.9656
Ru/Ba-Mg <sub>0.90</sub> Zn <sub>0.10</sub> O	1.1060	8.9173	10.0233