

# Supporting Information for

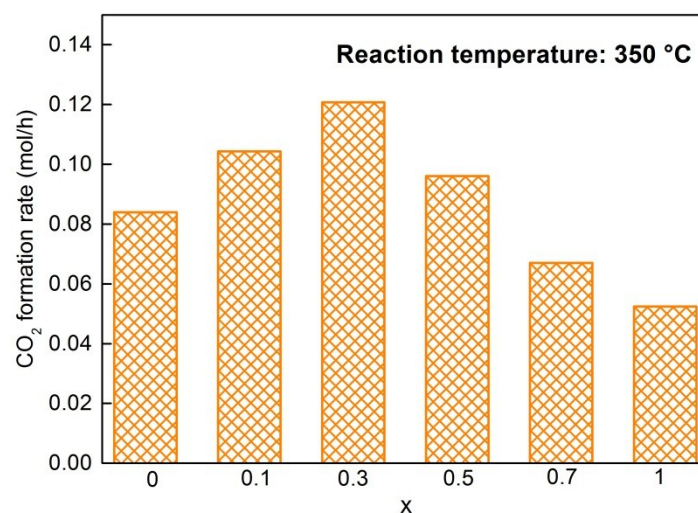
## Promotional Effect of Ti Doping on the Ketonization of Acetic Acid over CeO<sub>2</sub> Catalyst

Feipeng Lu<sup>a</sup>, BinBo Jiang<sup>a\*</sup>, Jingdai Wang<sup>a</sup>, Zhengliang Huang<sup>a</sup>, Zuwei Liao<sup>a</sup>, Yongrong  
Yang<sup>a</sup>, Jie Zheng<sup>b\*</sup>

<sup>a</sup>State Key Laboratory of Chemical Engineering, College of Chemical and Biological  
Engineering, Zhejiang University, Hangzhou 310027, P.R. China

<sup>b</sup>Department of Chemical and Biomolecular Engineering, The University of Akron, Akron,  
Ohio, USA 44325

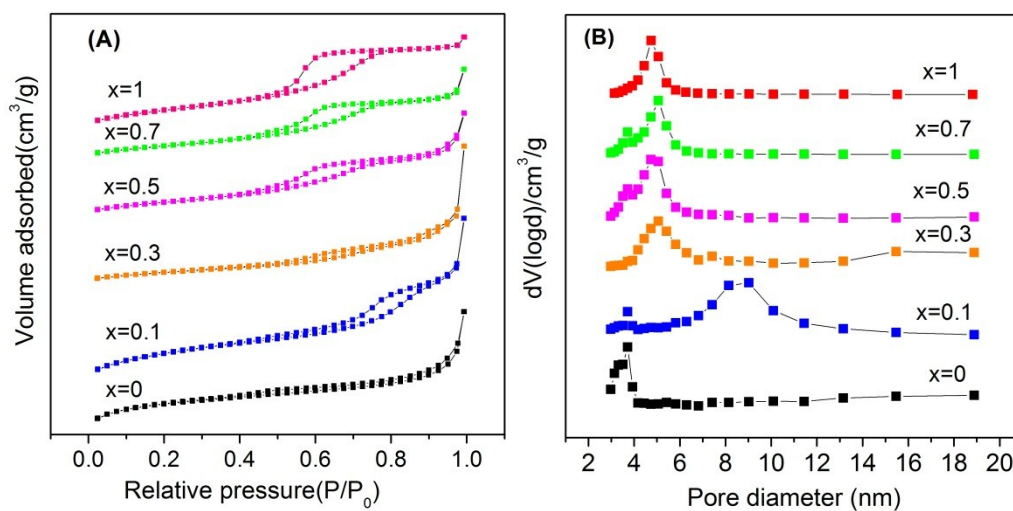
### Results



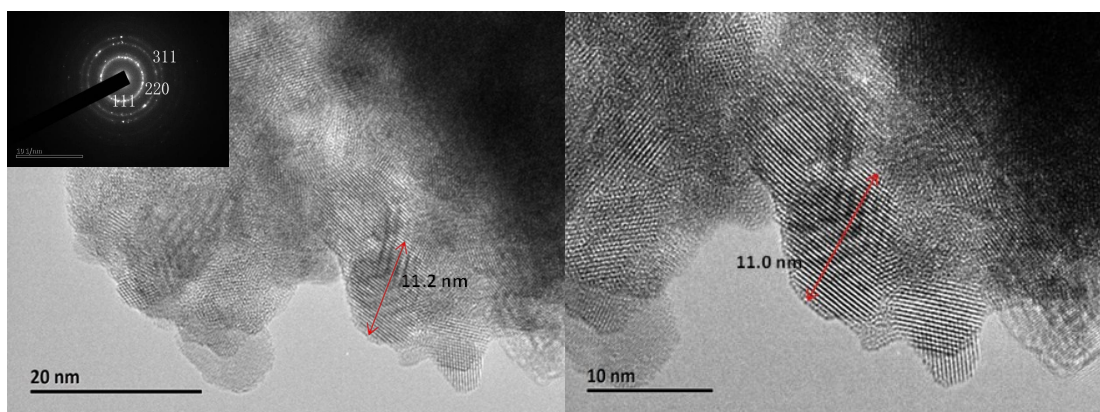
**Fig.S1.** CO<sub>2</sub> formation rate in the ketonization of acetic acid of Ce<sub>1-x</sub>Ti<sub>x</sub>O<sub>2-δ</sub> catalysts at 350 °C.

**Table S1** Ketonization activity of acetic acid into acetone over different catalysts.

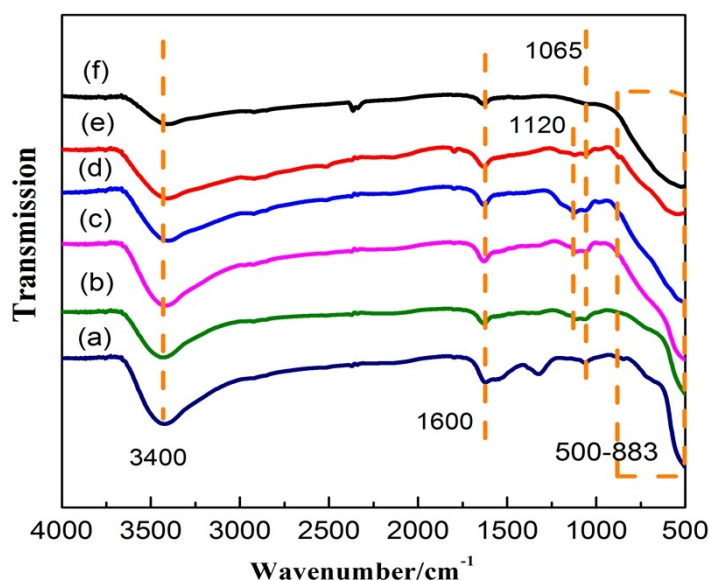
Entry	Catalyst	Conv./ %	Yield/ %	Select. /%	Reaction condition	Ref.
1	CeO <sub>2</sub>	51	51		350°C, WHSV=5.6 h <sup>-1</sup>	[1]
2	Pr <sub>6</sub> O <sub>11</sub>	80	80		350°C, WHSV=5.6 h <sup>-1</sup>	[1]
3	ZnO-Al <sub>2</sub> O <sub>3</sub> (3:1) <sup>a</sup>	89			350°C, WHSV=0.57 h <sup>-1</sup>	[2]
4	Zn-Cr (10:1)	86		100	350°C, W/F=4 h·g·mol <sup>-1</sup>	[3]
5	CeO <sub>2</sub> -ZrO <sub>2</sub>	95			450°C, WHSV=~146 h <sup>-1</sup>	[4]
6	CeO <sub>2</sub> -Mn <sub>2</sub> O <sub>3</sub>	72			450°C, WHSV=~146 h <sup>-1</sup>	[4]

<sup>a</sup> layered double hydroxides

**Fig.S2.**  $\text{N}_2$  adsorption-desorption isotherms (A) and pore size distributions (B) of  $\text{Ce}_{1-x}\text{Ti}_x\text{O}_{2-\delta}$  catalysts.



**Fig.S3.** TEM micrographs of the  $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_{2-\delta}$  sample.



**Figure S4.** FTIR spectra of  $Ce_{1-x}Ti_xO_{2-\delta}$  catalysts at (a)  $x=0$ , (b)  $x=0.1$ , (c)  $x=0.3$ , (d)  $x=0.5$ , (e)  $x=0.7$ , and (f)  $x=1$ .

**Table S2** Hydrogen Consumption Estimated from Temperature-Programmed Reduction

x	H <sub>2</sub> consumption(mmol/g) <sup>a</sup>	Peak value
0	0.183	504.4
0.1	0.53854	507.7
0.3	0.62496	510.3
0.5	0.86899	553.1
0.7	0.77552	589.6
1	0.06781	--

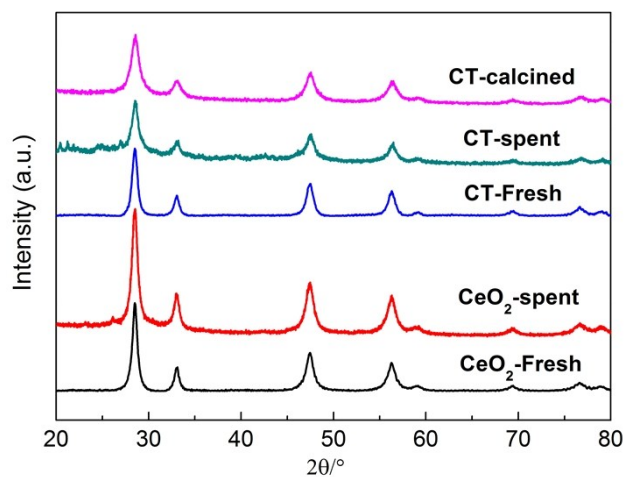
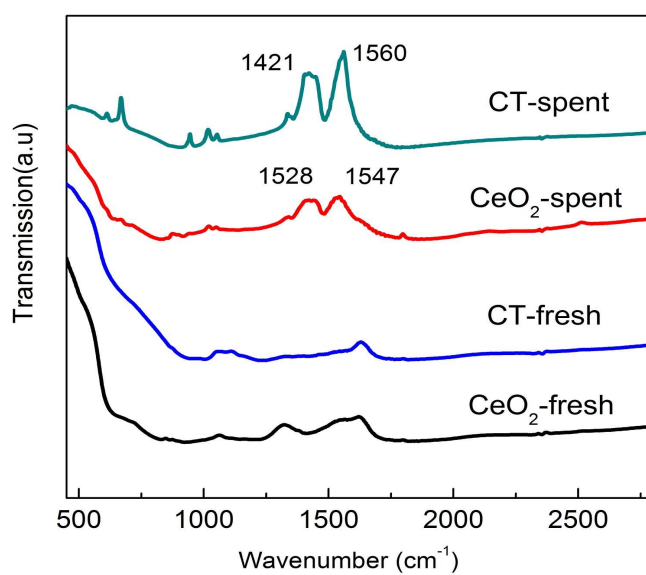
<sup>a</sup> The H<sub>2</sub> consumption was calculated from the integration of TPR area.

**Table S3** Acid sites distribution based on NH<sub>3</sub>-TPD data and basic sites distribution based on CO<sub>2</sub>-TPD data for  $Ce_{1-x}Ti_xO_{2-\delta}$  catalysts.

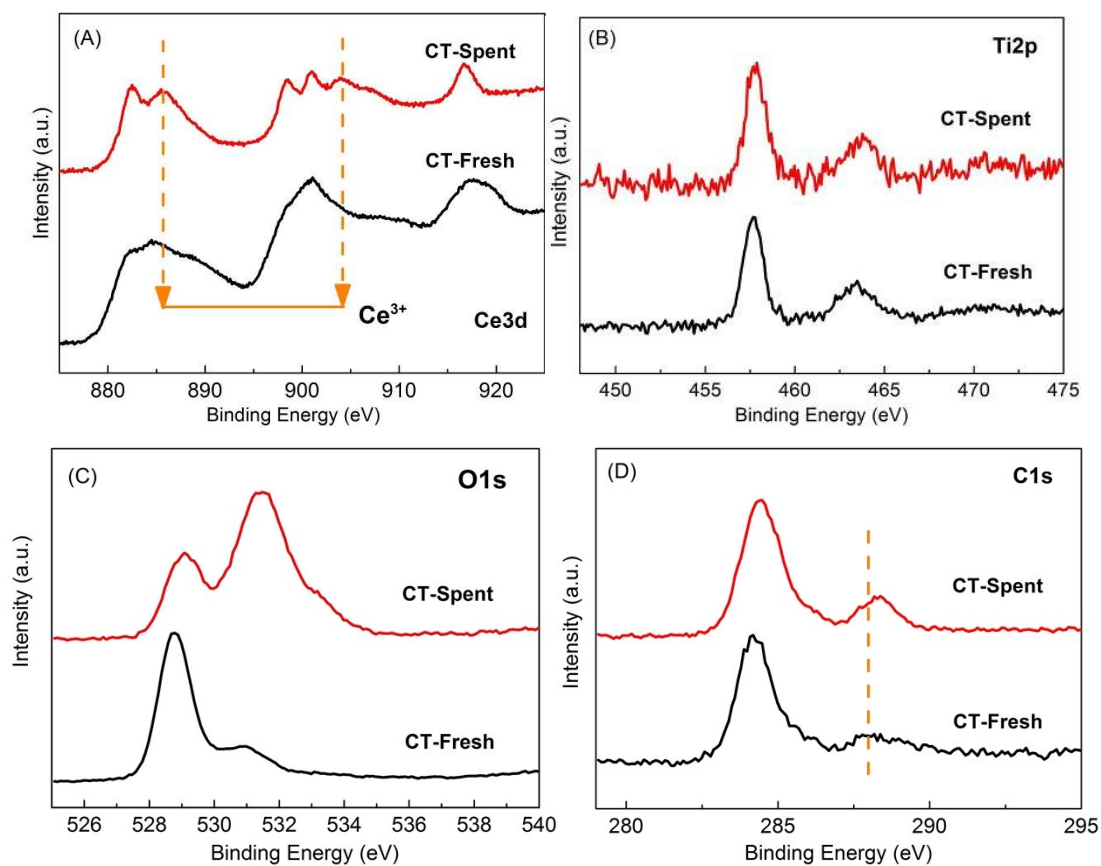
x	Acid sites/ $\mu\text{mol}\cdot\text{m}^{-2}$			Basic sites/ $\mu\text{mol}\cdot\text{m}^{-2}$		
	Weak (323-523 K)	Strong (523-773 K)	Tota l	Weak (323-523 K)	Strong (523-773 K)	Tota l
0	1.87	0.24	2.11	2.82	0.07	2.89
0.1	2.81	0.39	3.21	2.70	0.21	2.91
0.3	3.67	0.73	4.40	3.57	0.51	4.08
0.5	2.88	2.17	5.05	2.25	0.75	3.00
0.7	2.79	2.18	4.98	2.26	1.46	3.72
1	2.14	3.91	6.05	1.72	3.36	5.09

**Table S4** Ce3d XPS results of  $Ce_xTi_{1-x}O_{2-\delta}$  catalysts

Catalyst	BE, eV								Binding energy, eV		
	v	v'	v''	v'''	u	u'	u''	u'''	$O_\alpha$	$O_\beta$	$O_\gamma$
$CeO_2$	882.7	885.2	888.8	898.2	901.2	903.7	907.3	916.7	529.1	531.2	--
$Ce_{0.9}Ti_{0.1}O_{2-\delta}$	882.4	885.0	889.2	898.9	900.9	903.5	907.7	917.4	529.2	531.2	--
$Ce_{0.7}Ti_{0.3}O_{2-\delta}$	882.8	885.8	888.9	898.2	901.3	904.3	907.4	917.6	529.3	531.3	--
$Ce_{0.5}Ti_{0.5}O_{2-\delta}$	882.8	885.6	889.5	899.2	901.3	904.1	908.0	917.7	529.4	531.3	533.4
$Ce_{0.3}Ti_{0.7}O_{2-\delta}$	883.4	886.0	890.3	900.4	901.9	904.5	908.8	918.9	529.7	531.5	533.5

**Figure S5.** XRD results of postreaction catalysts.

**Figure S6.** FTIR results of postreaction catalysts.



**Figure S7.** XPS results of the spent and fresh  $\text{Ce}_{0.7}\text{Ti}_{0.3}\text{O}_{2-\delta}$  catalyst.

References:

- [1] Y. Yamada, M. Segawa, F. Sato, T. Kojima, S. Sato, *J. Mole. Catal. A: Chem.*, 346 (2011) 79-86.
- [2] J. Das, K. Parida, *React. Kinet. Catal. Lett.*, 69 (2000) 223-229.
- [3] H. Bayahia, E. F. Kozhevnikova, I. V. Kozhevnikov, *Appl. Catal. B*, 165 (2015) 253-259.
- [4] C. Liu, A. M. Karim, V. M. Lebarbier, D. Mei, Y. Wang, *Top. Catal.*, 56 (2013) 1782-1789.