Supporting Information

Carbon promoted ZrO_2 catalysts for aqueous-phase ketonization of acetic acid

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Energy consumption estimation

The estimation of the energy consumption between gas- and aqueous- phase ketonization is carried out below. Assuming that heat of water vaporization is 2435.0kJ/kg at 25 ºC, water formation enthalpy is 104.67kJ/kg and 1636.2kJ/kg at 25 and 340 ºC, respectively, and the heat capacity of water gas is 4.2 kJ/(kg K), the heating energy consumption of aqueous and gas phase reaction at 340 ºC is 1531.5 kJ/kg and 3758.0 kJ/kg, respectively.

Catalyst characterization

XRD patterns are measured on a D8 ADVANCE diffractometer using CuKα radiation (λ=0.1541 nm, 36 kV, 2 mA) with a scanning step = 2° min^{-1}. The diffraction patterns were recorded by scanning at an angle ranging from 5° to 80°.

TGA analysis is carried out on TA Instrument Q600 to estimate carbon content in catalysts. About 20 mg catalyst is heated to 700 ºC with a heating rate of 5 ºC/min under 100 mL/min air flow. The carbon content is defined as the weight loss between 105 and 600 ºC.

Raman spectra of the catalysts are acquired on a Horiba HR-800 spectrometer, using a 514 nm Ar^{+} laser at a spectral resolution of 1.76 cm^{-1}.

The X-ray photoelectron spectroscopy (XPS) analyses are performed on a Perkin Elmer PHI 5300 spectrometer. An X-ray source at 250 W (U = 15 kV) and Mg-K_{α} radiation (1486.6 eV) are used. Binding energies for catalysts without graphite carbon are corrected using the C 1s line at 284.6 eV, otherwise using graphite peaks at 284.4 eV.[39]

NH_3-TPD tests are carried out with a TP-5076 multifunctional automatic adsorption instrument (Xianquan Industry and Trade Development Co., Tianjin, China). 100 mg sample is pretreated at 350 ºC for 1 h in He stream (30 mL/min) before ammonia adsorption. After saturated absorption in the

stream of pure NH_3 for 30 min, the sample is purged by He at 100 ºC for 2 h to remove physisorbed ammonia. Then the TPD measurement is carried out from 100 to 350 ºC with heating rate of 5 ºC/min in He flow of 30 ml/min. The thermal conductivity detector is used for continuously monitoring the desorbed ammonia. Total acid sites are measured via external standard of pure NH_3. CO_2-TPD tests are the same with NH_3-TPD except using CO_2 to replace NH_3.

The morphological structure is identified using FEI Quanta 200F scanning emission microscope (SEM) and JEOL JEM 2010 LaB_6 transmission emission microscope (TEM) operating at 200 kV. The HRTEM is carried out with FEI Tecnai G^2 F20 field transmission emission microscope.

Calculation of acetone yield and acid conversion

The acid and acetone mole concentration in aqueous product, marked as [*Acid*] and [*Acetone*], respectively, is calculated via an external standard curve using the related peak area in GC analysis. The acetone yield and selectivity are calculated as follows:

$$Acetone\ yield(\%) = \frac{2\times[Acetone]}{[Acid]_{Initial}}\times 100\% \qquad \text{Equation S1}$$

$$Acid\ conversion(\%) = \left(1-\frac{[Acid]}{[Acid]_{Inital}}\right)\times 100\% \qquad \text{Equation S2}$$

where $[Acid]_{Initial}$ refers to the acid concentration in feed solution. The acid mole balance is calculated as follow.

$$Acid\ mole\ balance(\%) = \frac{2\times[Acetone]+[Acid]}{[Acid]_{Inital}}\times 100\% \qquad \text{Equation S3}$$

Table caption

Table S1. The comparison of ketonization activity under different conditions for the reaction at 340 ºC for 12 h.

Table S2. Crystallite size of ZrO_2-CA-600C, ZrO_2-UiO-600C and 30%ZrO_2-Hy-CNT-600C calculated from XRD results.

Table S3. Acetone yield and acid conversion of ZrO_2-CA-600C oxidized at different temperature.

Table S4. Acetone yield and average reaction rate of different catalysts at 340 °C.

Table S5. Average particle size and surface Zr atoms of different catalysts, obtained from TEM results.

Figure caption

Figure S1. XRD patterns of the synthetized UiO-66 materials. The peak positions agree well with reported values for UiO-66.

Figure S2 NH_3-TPD curves of differently synthetized catalysts (a), ZrO_2-CA-600C oxidized at different temperature in air (b), and CO_2-TPD curves of differently synthetized catalysts (c).

Figure S3. SEM of differently synthetized catalysts, a) ZrO_2-HT-600C, b) ZrO_2-Hy-600C, c) ZrO_2-UiO-600C, d) ZrO_2-CA-600C.

Figure S4. SEM (a1~d1) and TEM (a2~d2) of differently synthetized catalysts, a) ZrO_2-HT-600C, b) ZrO_2-Hy-600C, c) ZrO_2-UiO-600C, d) ZrO_2-CA-600C.

Figure S5. TGA (a) and XRD (b) of differently synthetized catalysts via carbonization of Zr-based MOF materials.

Figure S6. SEM (a1~b1) and TEM (a2~b3) of a) ZrO_2-UiO-FA-600C, b) ZrO_2-UiO-AA-600C.

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Figure S8. SEM-EDS analysis for Zr (green) and C (red) elements of ZrO_2-CA-600C catalyst.

Figure S9. TEM for measure the size distribution: a) ZrO_2-UiO-600C, b) ZrO_2-UiO-FA-600C, c) ZrO_2-UiO-AA-600C.

Figure S10. Ketonization activity comparison of carbonized and supported ZrO_2 catalysts.

Figure S11. Initial contact angles of fresh ZrO_2-CA-600C and 30%ZrO_2-Hy-CNT-600C.

Table S1. The comparison of ketonization activity under different conditions for the reaction at 340 ºC for 12 h.

Catalysts	Initial pressure (MPa)	Stirring (rpm)	Reactant volume (mL)	Reactor volume (mL)	Production (mmol/gcat.)
ZrO_2-CA-600C	0	0	30	50	38.09
ZrO_2-CA-600C	5	300	100	500	37.58999
ZrO_2-UiO-600C	0	0	30	50	23.72145
ZrO_2-UiO-600C	5	300	100	500	23.47905

Table S2. Crystallite size of ZrO_2-CA-600C, ZrO_2-UiO-600C and 30%ZrO_2-Hy-CNT-600C calculated from XRD results.

Catalysts	2sita of tetragonal (011)/ °	Crystallite size/nm
ZrO_2-CA-600C	30.207	2.3
ZrO_2-UiO-600C	30.028	3.0
30%ZrO_2-Hy-CNT-600C	30.323	26.0

Table S3. Acetone yield and acid conversion of ZrO_2-CA-600C oxidized at different temperature.

Oxidization	Acetone yield/ %	Acid conversion/ %	Acid mole balance[a]/ %
None	38.09	38.56	99.5
150Air	34.15	36.75	97.4
300Air	25.15	26.57	98.6
450Air	8.78	9.51	99.3
600Air	6.02	6.43	99.6

[a] Acid mole balance is calculated using the division of remained acid and double ketone by initial acid.

Table S4. Acetone yield and average reaction rate of different catalysts at 340 °C.

Catalysts	80 min reaction		12 h reaction	
	Acetone yield/ %	$R_{average}$[a]/ mmol gcat.$^{-1}$ h^{-1}	Acetone yield/ %	$R_{average}$/ mmol gcat.$^{-1}$ h^{-1}
ZrO_2-HT-600C	1.49	1.12	13.32	1.11
ZrO_2-Hy-600C	1.60	1.20	14.99	1.25
ZrO_2-UiO-600C	2.96	2.22	23.72	1.98
ZrO_2-CA-600C	4.22	3.17	38.09	3.17

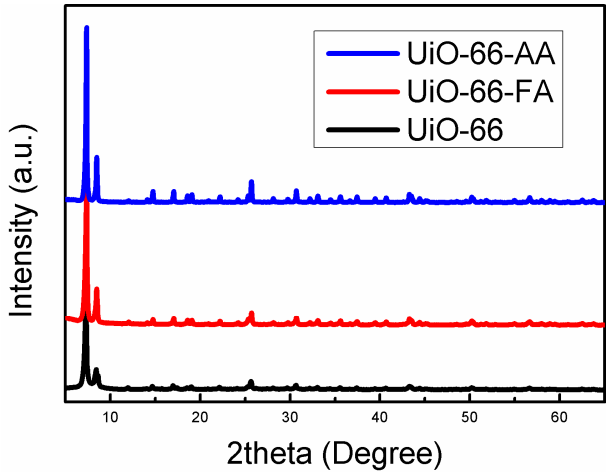
[a] $R_{average}$ means average reaction rate.

Table S5. Average particle size and surface Zr atoms of different catalysts, obtained from TEM results.

Catalysts	Average particle size/ nm	Surface Zr atoms[b]/ μmol
ZrO_2-HT-600C	87	110
ZrO_2-Hy-600C	160	58.9
ZrO_2-UiO-600C	97	69.9
ZrO_2-CA-600C[a]	843	7.10

a The particle size of ZrO_2-CA-600C is quite large but less than 75 μm (200 mesh). Here, only the particles in TEM images are accounted, and the result is much less than the real average particle size from SEM images. However, The obtained value can present the typical size of ZrO_2-CA-600C to estimate surface Zr.

b Assuming spherical shape of different particles, the atoms in 1 nm surface layer is regarded as the surface atoms, and the total mass weight can be calculated using particle size. The weight percentage of Zr in surface layer is the same with that in the bulk catalysts. Thus, the mass of surface Zr can be calculated.



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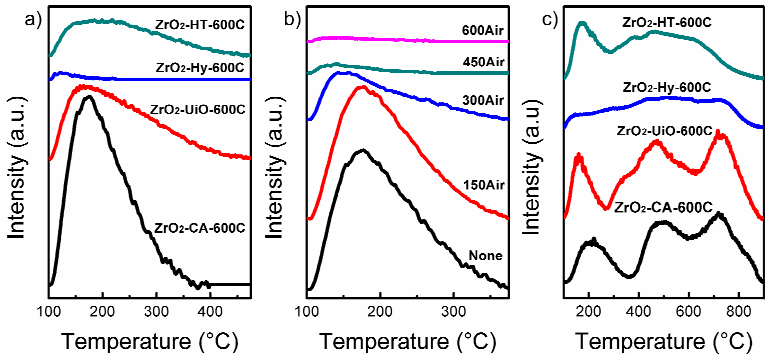
[1] X. L. Liu, N. K. Demir, Z. T. Wu, K. Li, *J. Am. Chem. Soc.* **2015**, *137*, 6999−7002.



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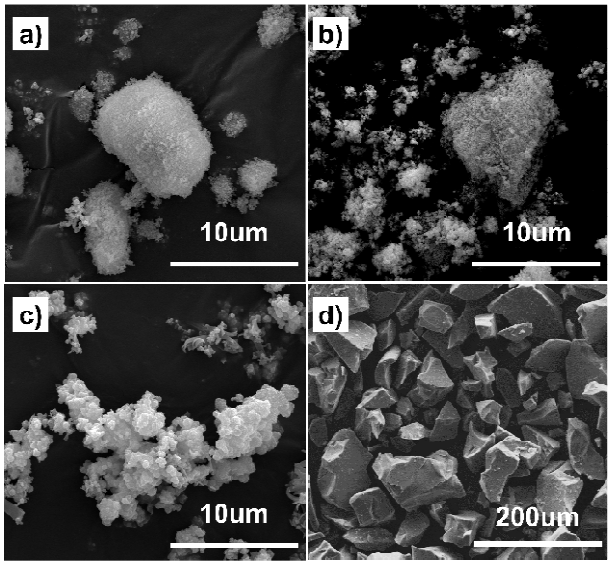

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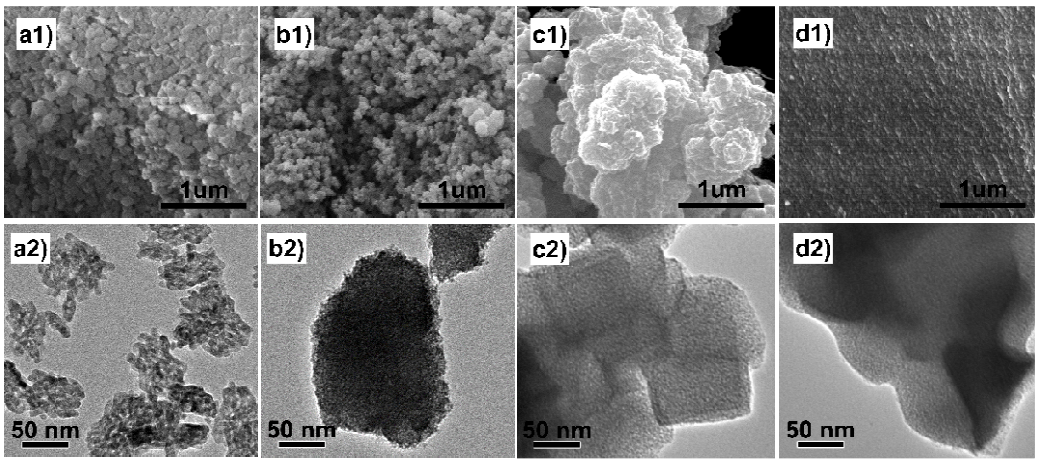

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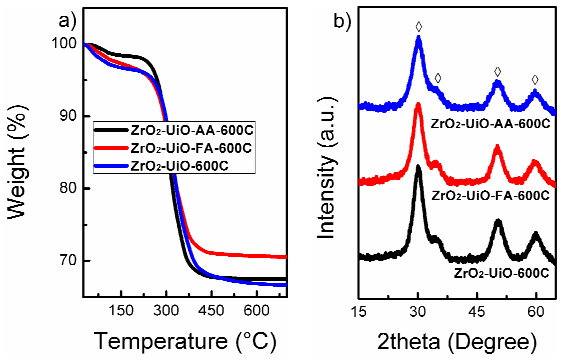

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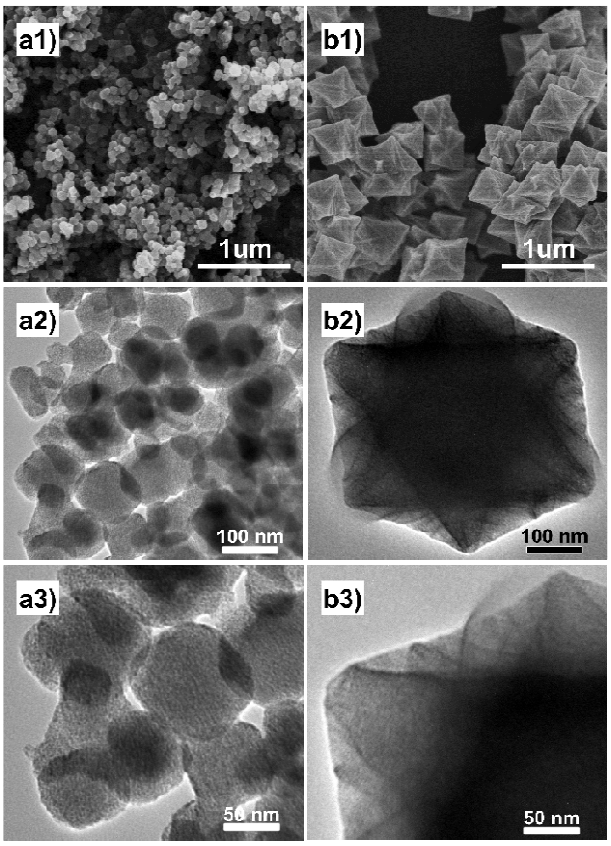

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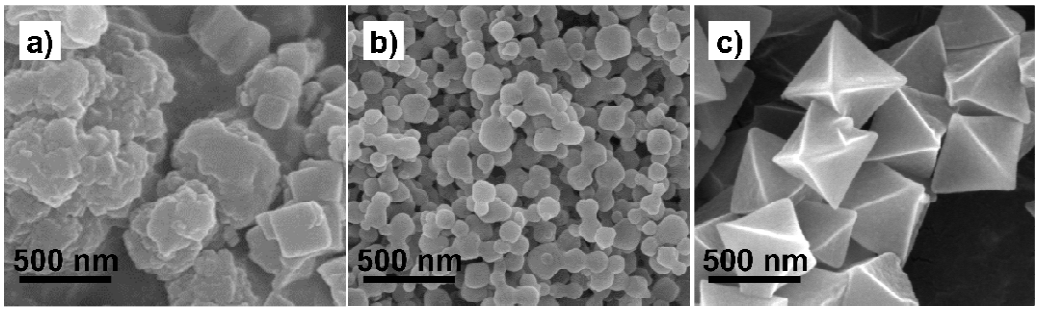

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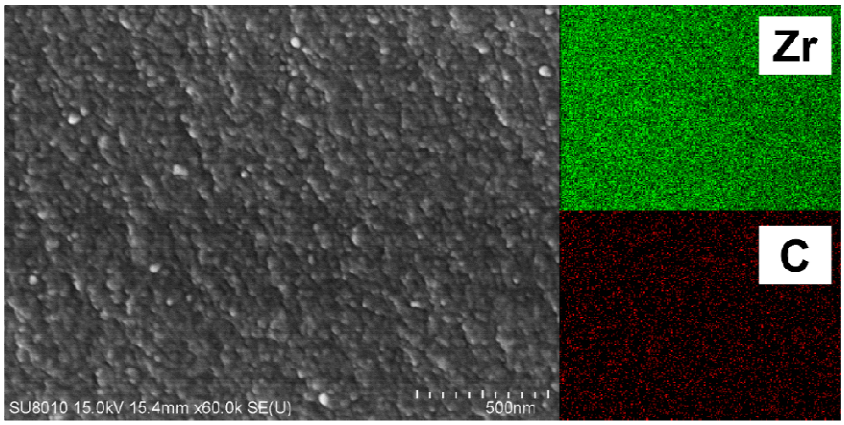

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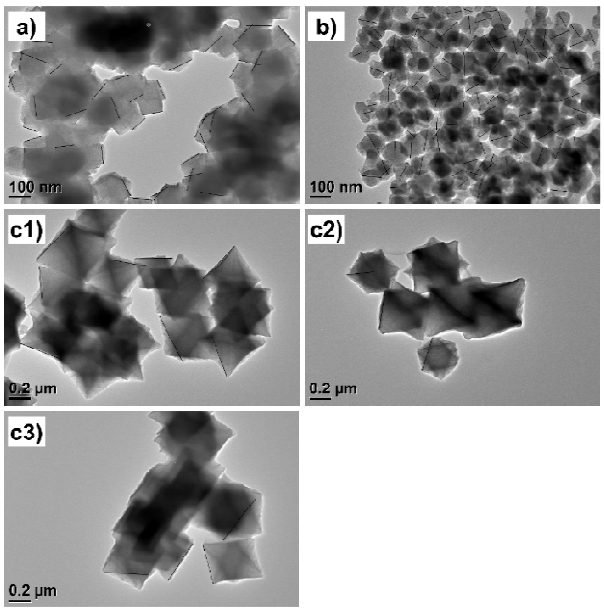

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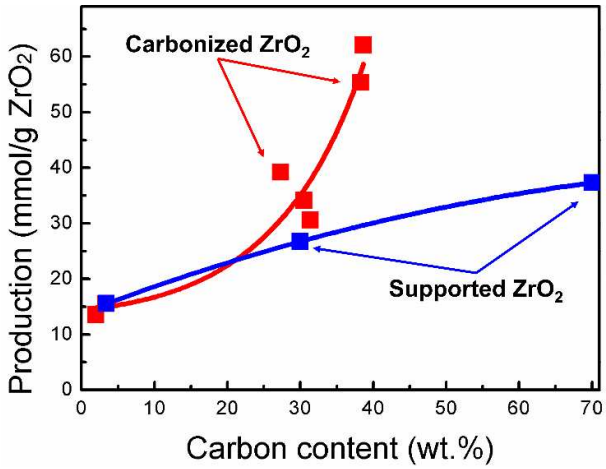

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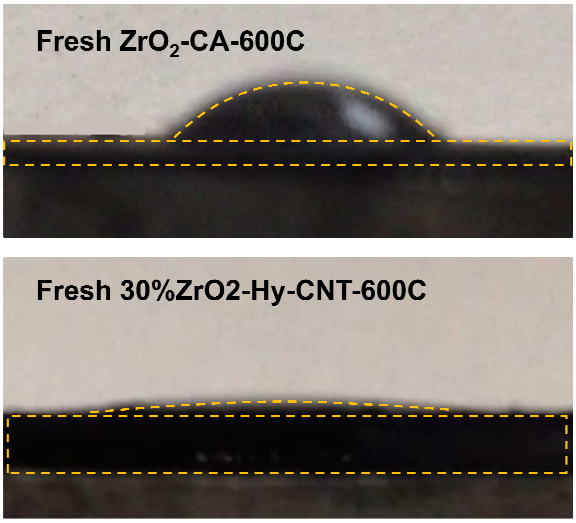

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