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Supplementary Materials

Article

Insight into the Acidity and Catalytic Performance on Butane Isomerization of Thermal Stable Sulfated Monoclinic Zirconia

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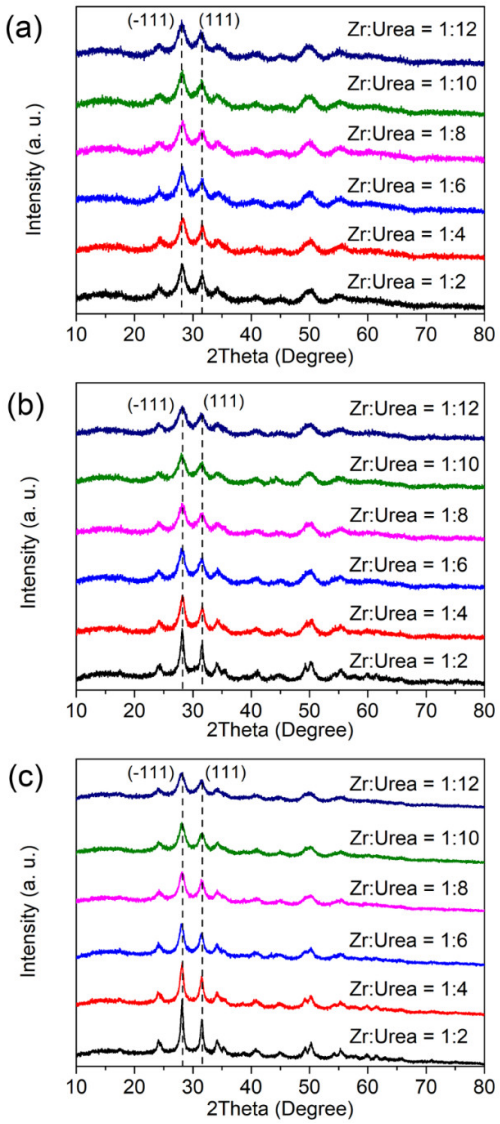

Figure S1. The XRD patterns of zirconia hydrothermally synthesized at (a) 393 K, (b) 433 K, and (c) 473 K with different Zr:Urea molar ratio.

Figure S1 shows the XRD patterns of samples obtained at different zirconium oxynitrate to urea ratios varying from 1:2 to 1:12 and different hydrothermal temperatures. The diffraction peaks of all samples are consistent with the monoclinic zirconia structure (JCPDS No. 37-1484). The main peaks of the XRD patterns which located at 28.2° and 31.5° are correspond to (-111) and (111) planes. The synthesis conditions have a significant effect on the particle size of the monoclinic zirconia samples. It can be observed that, with the increase of the urea ratio, the full-width-at-half-maximum (FWHM) for the related to (-111) and (111) planes increases, indicating that the particle size of monoclinic zirconia decreases with the increase of urea ratio. In addition, with the increase of the hydrothermal temperature, the FWHM decreases, indicating that the particle size of zirconia increases.

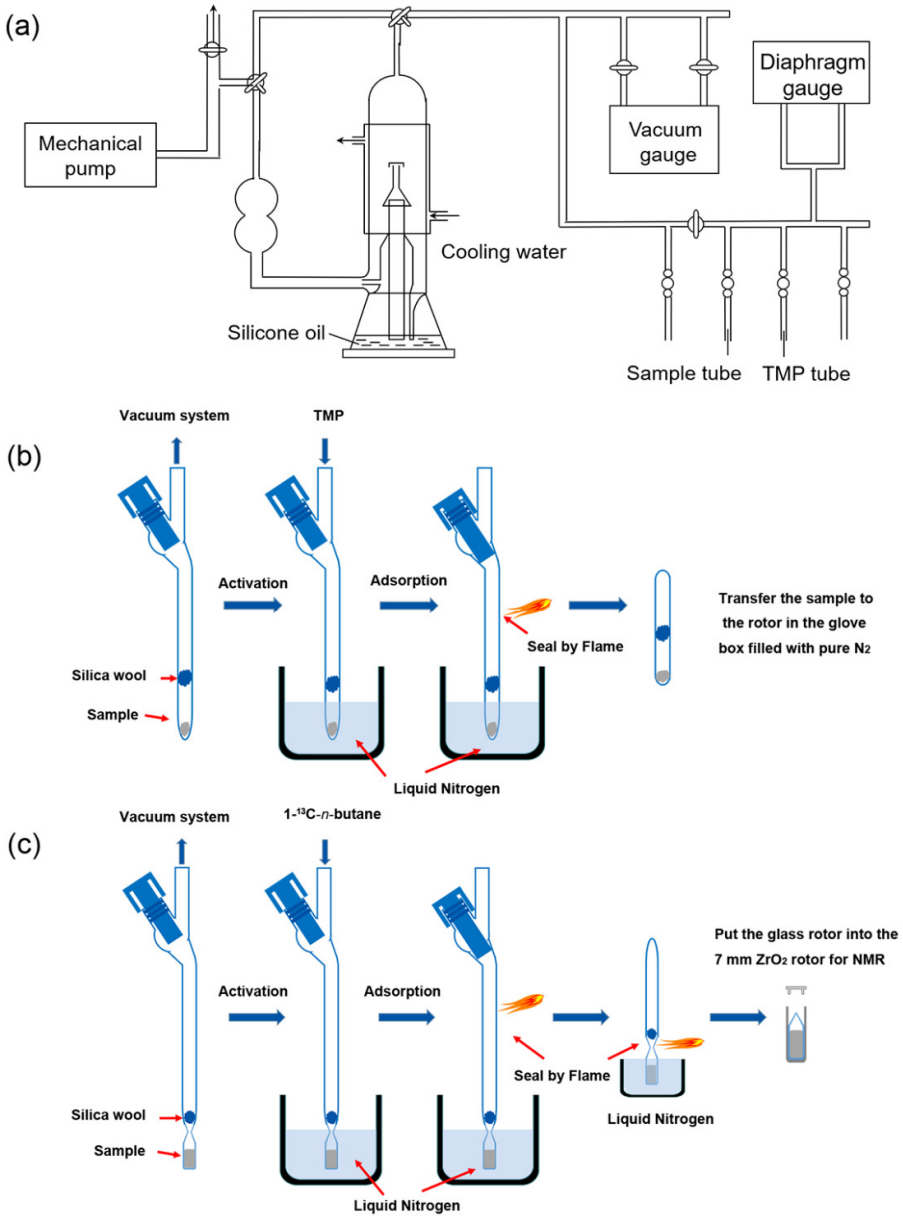

Figure S2. The apparatus for the sample treatment and reaction. (a) The vacuum system, (b) the preparation of the sample adsorbing TMP for acidity characterization, (c) the preparation of the sample adsorbing 1-^{13}C-*n*-butane for reaction.

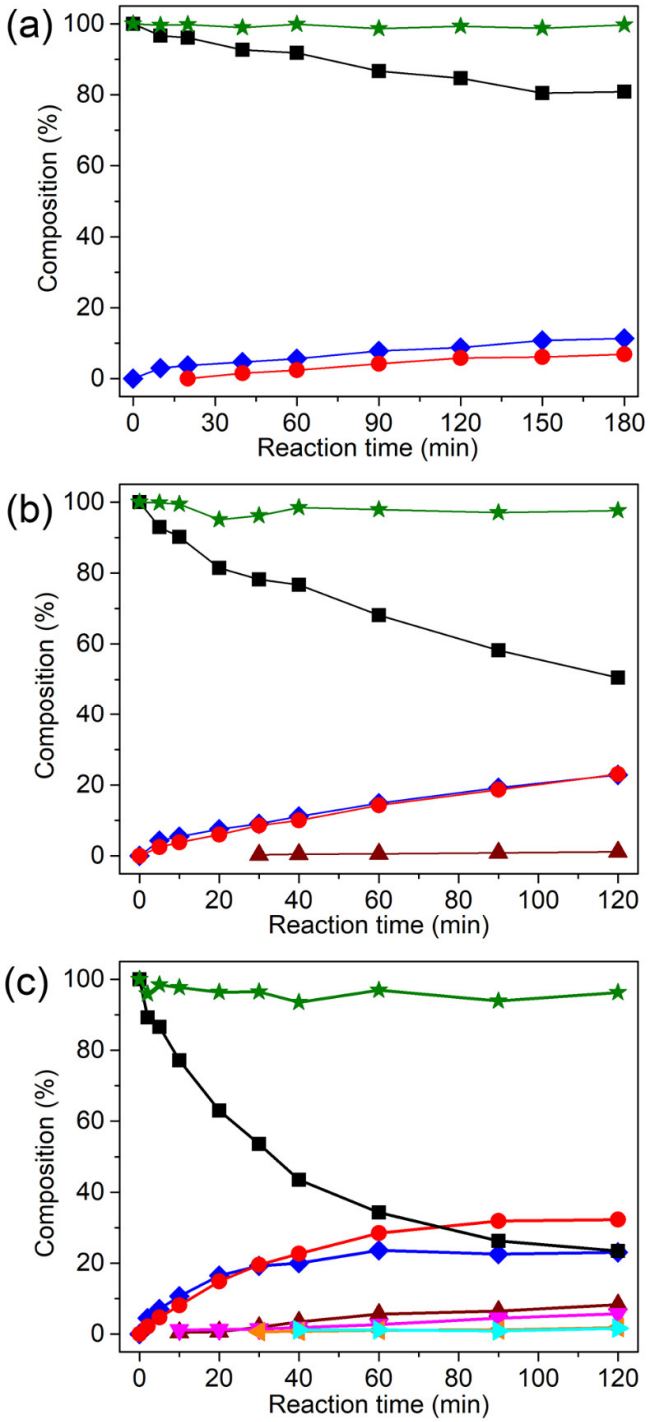

Figure S3. Butane isomerization catalyzed by M-SZ-1 at (a) 493 K, (b) 513 K, and (c) 533 K. (■) 1-^{13}C-n-Butane, (◆) 2-^{13}C-n-butane, (●) 1-^{13}C-isobutane and 2-^{13}C-isobutane, (▲) ^{13}C-isopentane, (▼) ^{13}C-propane, (◀) ^{13}C-pentane, (▶)^{13}C-hexane, and (★) the total amount of ^{13}C-labeled species.

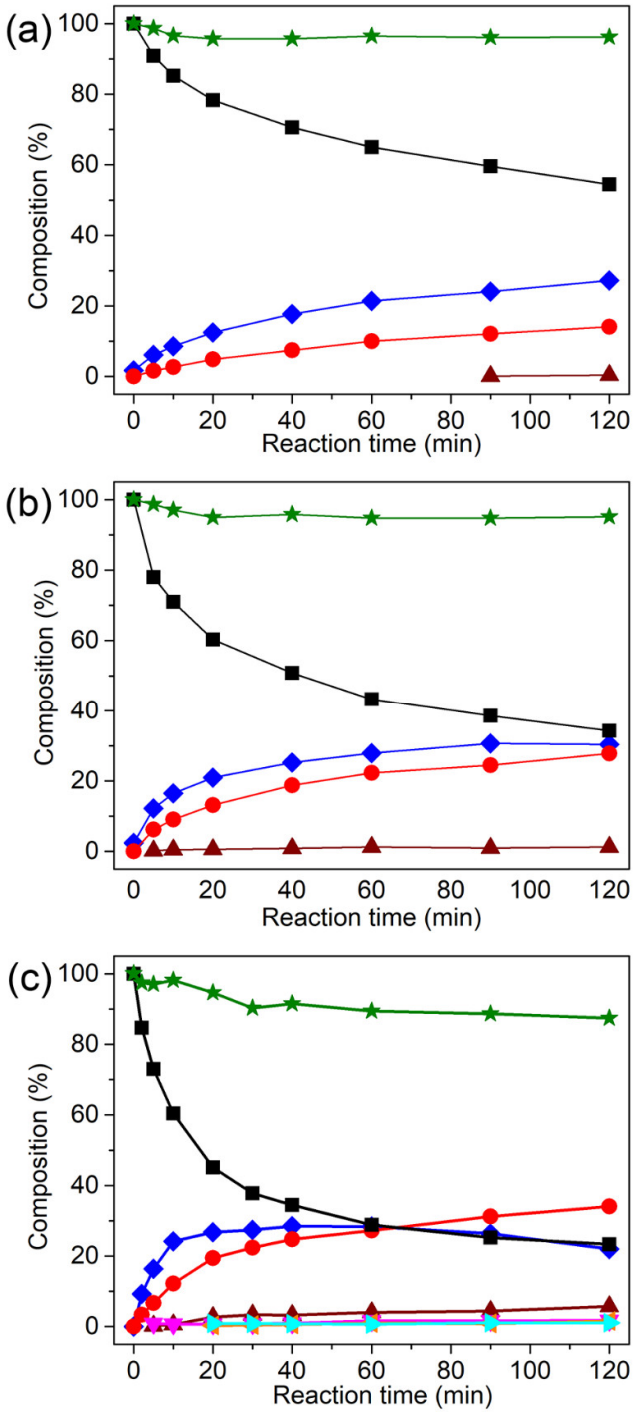

Figure S4. Butane isomerization catalyzed by M-SZ-3 at (d) 433 K, (e) 453 K, and (f) 473 K. (■) 1-^{13}C-n-Butane, (◆) 2-^{13}C-n-butane, (●) 1-^{13}C-isobutane and 2-^{13}C-isobutane, (▲) ^{13}C-isopentane, (▼) ^{13}C-propane, (◀) ^{13}C-pentane, (▶)^{13}C-hexane, and (★) the total amount of ^{13}C-labeled species.

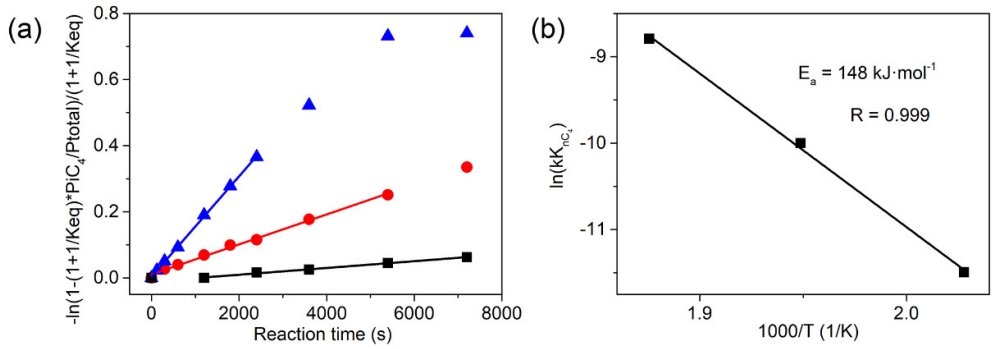

Figure S5. The kinetic study of butane isomerization at different temperatures catalyzed by M-SZ-1. (a) $-\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)\frac{P_{iC_4}}{P_{total}}\right]/\left(1+\frac{1}{K_{eq}}\right)$ vs. reaction time at (■) 493 K, (●) 513 K and (▲) 533 K, and (b) $\ln(kK_{nC_4})$ vs. 1000/T.

Table S1. The kinetic constant of butane isomerization catalyzed by M-SZ-1 at 493 ~ 533 K.

Reaction Temperature (K)	$kK_{nC_4}\times10^5$ (mol·g^{-1}·s^{-1})	R
493	1.19	0.998
513	4.54	0.998
533	15.20	0.998

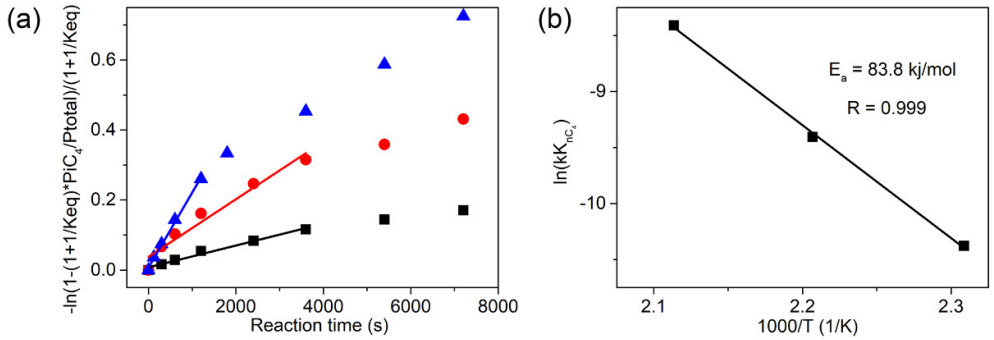

Figure S6. The kinetic study of butane isomerization at different temperatures catalyzed by M-SZ-3. (a) $-\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)\frac{P_{iC_4}}{P_{total}}\right]/\left(1+\frac{1}{K_{eq}}\right)$ vs. reaction time at (■) 433 K, (●) 453 K and (▲) 473 K, and (b) $\ln(kK_{nC_4})$ vs. 1000/T.

Table S2. The kinetic constant of butane isomerization catalyzed by M-SZ-3 at 433 ~ 473 K.

Reaction Temperature (K)	$kK_{nC_4}\times10^5$ (mol·g^{-1}·s^{-1})	R
433	3.11	0.991
453	8.23	0.979
473	21.41	0.997

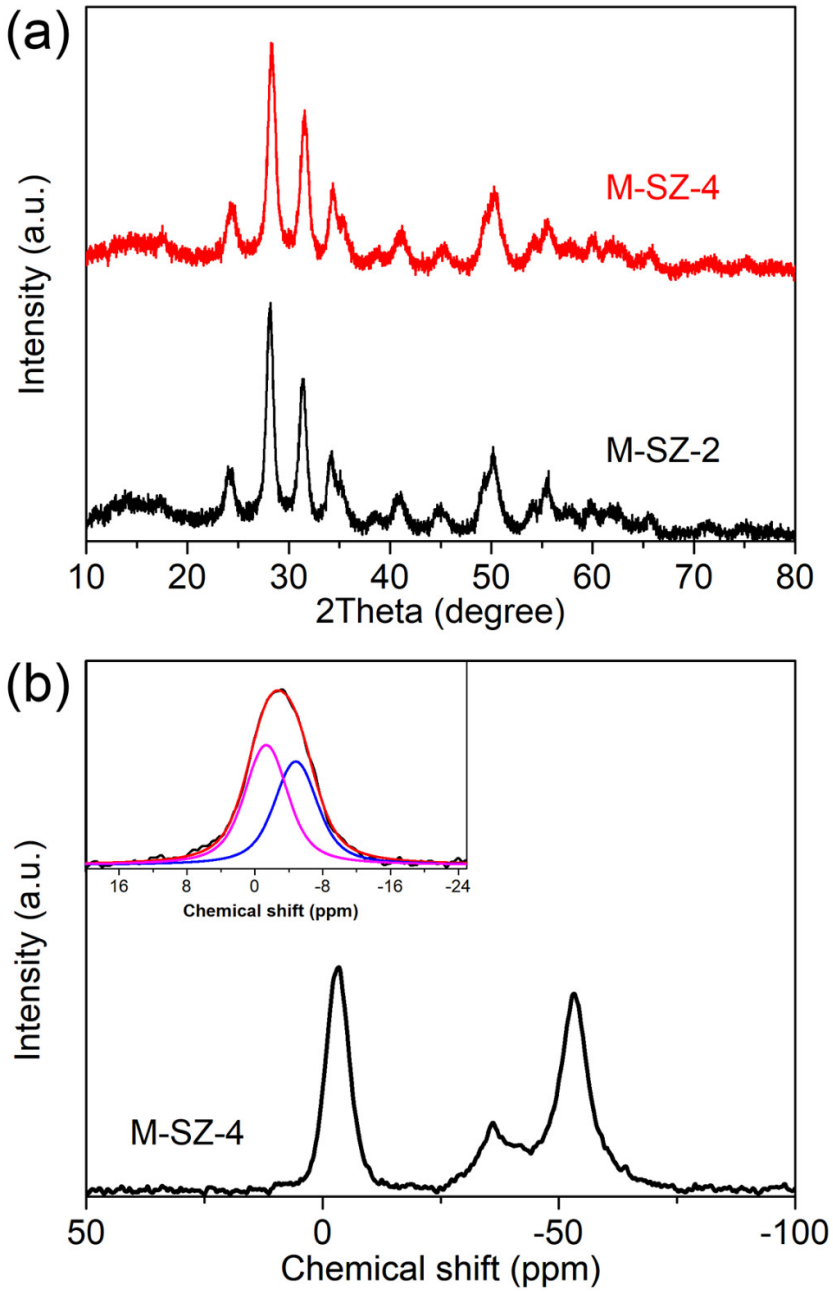

Figure S7. (a) XRD patterns of M-SZ-2 and M-SZ-4, (b) ^{31}P MAS NMR spectrum of M-SZ-4.

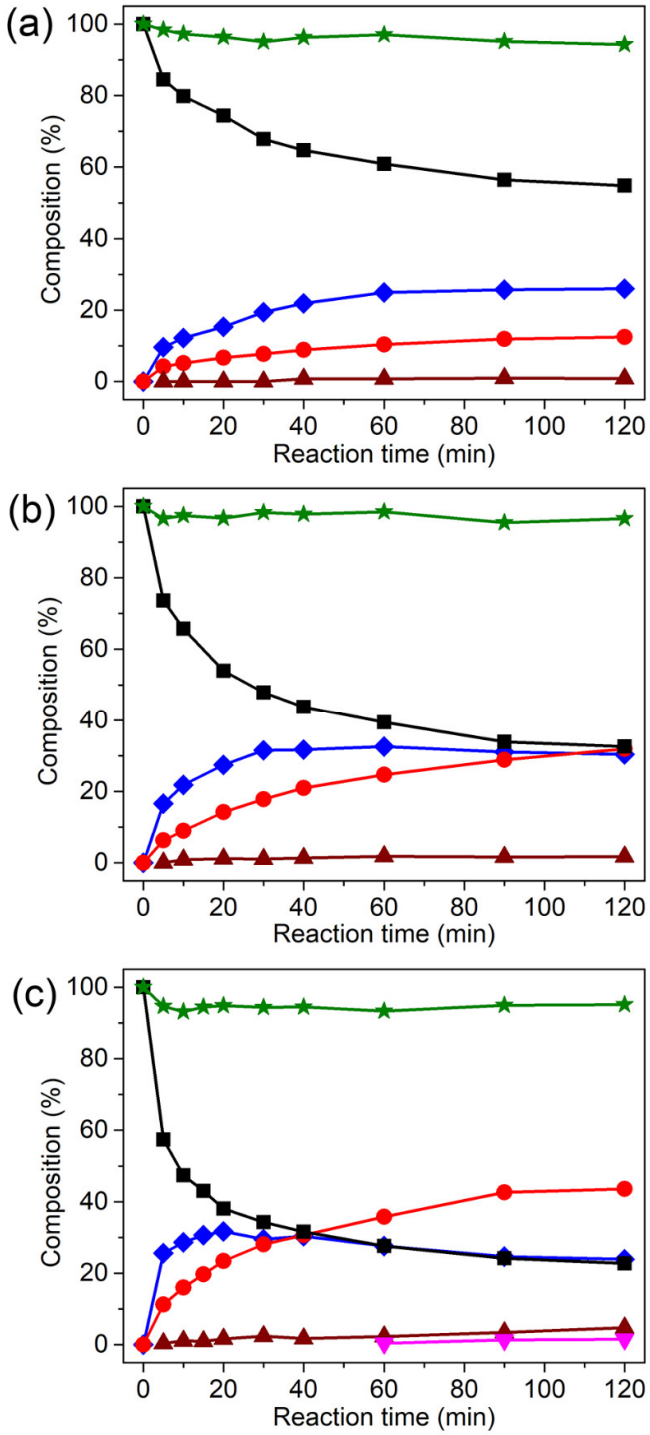

Figure S8. Butane isomerization catalyzed by M-SZ-4 at (a) 373 K, (b) 413 K, and (c) 433 K. (■) 1-^{13}C-n-Butane, (◆) 2-^{13}C-n-butane, (●) 1-^{13}C-isobutane and 2-^{13}C-isobutane, (▲) ^{13}C-isopentane, (▼) ^{13}C-propane, and (★) the total amount of ^{13}C-labeled species.

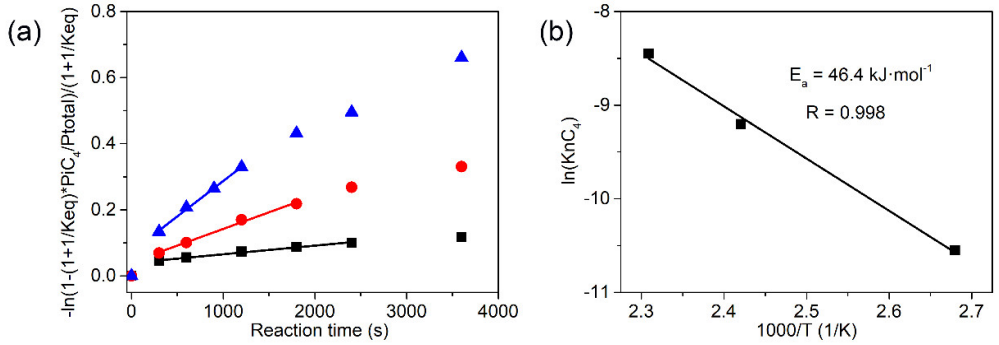

Figure S9. The kinetic study of butane isomerization at different temperatures catalyzed by M-SZ-4. (a) $-\ln\left[1-\left(1+\frac{1}{K_{eq}}\right)\frac{P_{iC_4}}{P_{total}}\right]/\left(1+\frac{1}{K_{eq}}\right)$ vs. reaction time at (■) 373 K, (●) 413 K and (▲) 433 K, and (b) $\ln(kK_{nC_4})$ vs. 1000/T.

Table S3. The kinetic constant of butane isomerization catalyzed by M-SZ-4 at 373 ~ 433 K.

Reaction Temperature (K)	$kK_{nC_4}\times10^5$ (mol·g^{-1}·s^{-1})	R
373	2.62	0.986
413	10.08	0.997
433	21.39	0.995

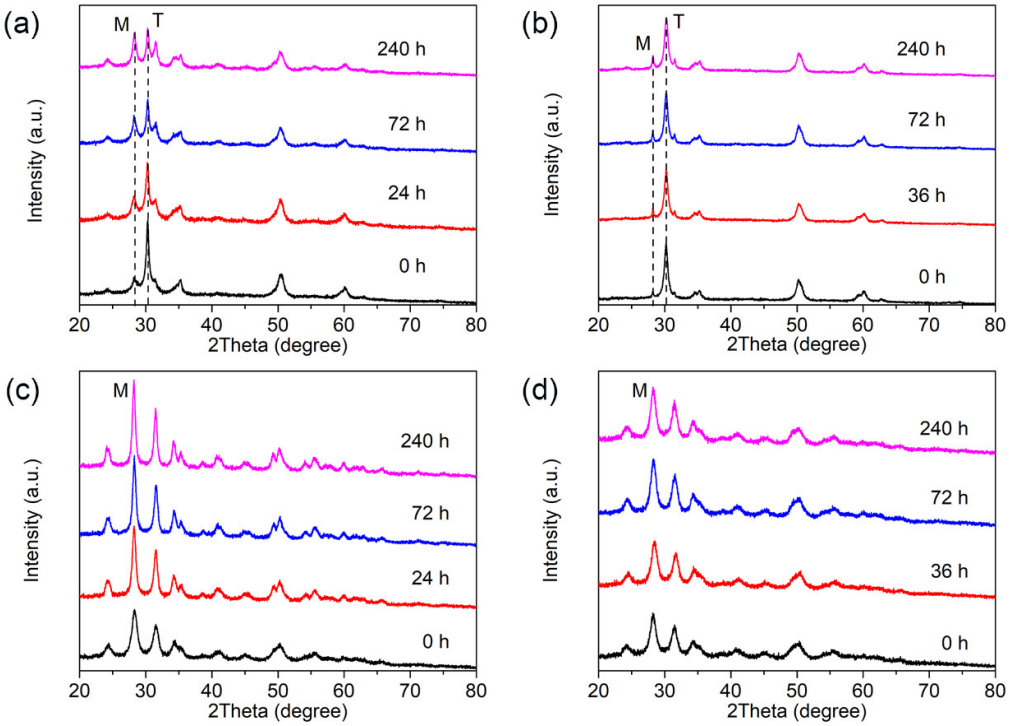

Figure S10. The XRD patterns of (a) T-ZrO_2-general, (b) T-SZ-general, (c) M-ZrO_2-2, and (d) M-SZ-2 calcined in air at 673 K for different time.