Real-time Monitoring of the Surface Acetone Enolization and Aldolization

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Experimental

Bruker Tensor 27 FTIR spectrometer was used to record the Infrared spectra with a resolution of 4 cm^{-1} between 4000 cm^{-1} and 600 cm^{-1}. For the fast spectra collected during the pulsed acetone adsorption and reaction, an average of 32 scans (~20 S/spectrum) was used to better monitor the change of surface species. For each dose, the spectra experience an initial rapid change with time, and then stabilizes, after that an additional high resolution spectrum with an average of 128 scans was taken. After the high resolution of spectrum, another dose of acetone will be admitted followed by repeating the similar spectra recording process until the surface saturation of the catalysts. About 20 mg of the catalyst was loaded (Figure S1) and pretreated at 723 K for 30 min in flowing 10%Ar/He (50 SCCM). After that, the sample was cooled to 298 K, followed by the collection of background spectrum. The reactants (i.e. acetone, mesityl oxide) were injected into the *in-situ* cell using a 6-port-valve equipped with a 25 µL loop. This loop was filled with the mixture of gas-phase reactants and 10%Ar/He through a bubbler at room temperature. The flow rate of carrier gas (carrying the reactants in bubbler at 273 K to fill the loop) was low enough (5 SCCM) to ensure that the gas concentration reaches the state of saturation. During the adsorption, the amount of reactants (~2.04×10^{-7} mol/pulse for acetone, ~8.02×10^{-9} mol/pulse for mesityl oxide) is controlled to be much lower than that of monolayer coverage based on the Lewis acid sites on the catalysts loaded (20mg $Zn_1Zr_{10}O_z$, ~6.2×10^{-6} mol Lewis acid sites[1]). The reaction temperature is also reduced to room temperature (i.e., 25 °C) to slow down the rate of the elementary reaction during the surface enolization and aldolization. For the peak integration, due to the presence of both MSO satellite bands and water δ_{HOH} at ~1635 cm^{-1}, the region of 1630-1640 cm^{-1} was skipped by applying an OPUS baseline subtraction, resolving the ν(C=O) and ν(C=C) region separately.[2] Peak deconvolution for the C=O bands was done using Peak Analyzer Tool (Fit peaks (Pro) option) Gaussian function in the OriginLab9.0 software. It should be noted that, H-bonded acetone associated with surface hydroxyl groups (>1700 cm^{-1}) is barely observed on the $Zn_1Zr_{10}O_z$ catalyst, and a minor H-bonded acetone peak can only be deconvoluted in the 1st dose of acetone, after which adding the H-bonded acetone makes the deconvolution of acetone on Lewis acid sites and MSO very hard. Therefore, two Gaussian peaks were used for a better fitting of acetone and MSO for the spectra corresponding to the dose 2-5. The results are shown in Table S1. The evolution of deconvoluted C=O band for MSO (Figure S2) is also compared to that of C=C band, both of which show similar trend as a function of dose and time, suggesting the validity of the peak deconvolution. In Table S1, the wavenumber of MSO C=O peak keeps shifting to higher wavenumber with doses (from 1st dose to 5th dose), likely due to the increase of surface coverages, which is consistent with the observation in Figure S3.

The acetone adsorption enthalpies were experimentally measured using *in situ* vapor adsorption calorimetry at 25 °C. Experimental setup includes an integrated, custom-made system with a vapor dosing manifold (Micromeritics 3Flex) and a Calvet-type microcalorimeter (Setaram Sensys Evo). In each measurement, a sample pellet (~ 30 mg) was introduced in one side of a silica glass forked tube, the other side of which remained empty serving as a reference. The forked tube was inserted into the twin chamber of microcalorimeter and attached to the vapor dosing manifold. Before adsorption calorimetry measurement, the sample pellet was degassed under vacuum (<10^{-6} mmHg) for 12 hours at 250 °C to activate the surface of adsorbent. The vapor dosing manifold was programmed in incremental dosing mode with ~0.5 mmol per dose. Each dose was equilibrated for 2 hr. Calisto processing software (AKTS, Switzerland) was employed to obtain the differential enthalpies of adsorption (kJ per mol of acetone) as a function of acetone loading. Measurements on the same sample was triplicated to ensure reproducibility.

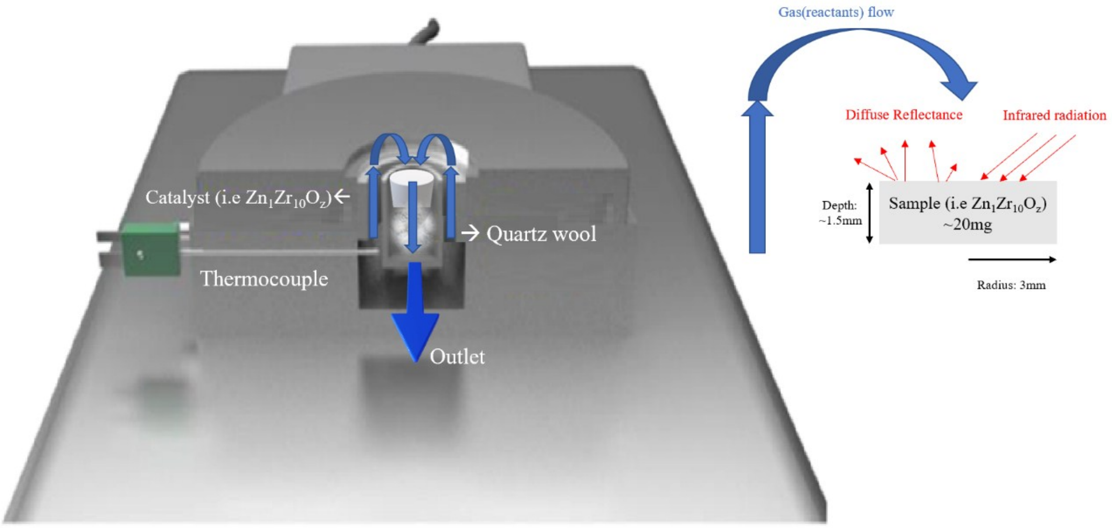

Figure S1. Schematic representation of DRIFT *in situ* cell. Blue arrows show the direction of gas flow.

Table S1. The deconvolution of C=O bands in Figure 1 and Figure S5-S8. Two representative deconvoluted spectra are shown in below (Figure S2).

Dose number	Time(s)	**Ace H-bond**		**Ace L-acid**		**MSO C=O**	
		peak area	peak position	peak area	peak position	peak area	peak position
1 st	20	0.122	1700	0.995	1691	0.043	1666
	66	0.223	1699	2.477	1690	0.372	1668
	100	0.315	1700	2.222	1690	0.480	1669
	132	0.233	1700	2.233	1690	0.538	1669
	169	0.271	1699	2.156	1689	0.472	1668
	216	0.221	1699	2.139	1689	0.421	1668
	263	0.170	1703	2.012	1689	0.539	1669
	387	0.154	1700	1.810	1689	0.657	1669
	618	0.114	1703	1.543	1689	0.638	1670
2nd	861			3.060	1695	1.080	1676
	898			5.054	1695	1.545	1675
	929			4.460	1694	1.985	1677
	1046			3.435	1693	2.058	1677
	1213			2.900	1694	2.050	1677
3rd	1451			4.730	1697	2.858	1678
	1488			5.087	1698	3.183	1679
	1538			4.156	1697	3.288	1679
	1614			3.566	1696	3.183	1679
4th	1761			4.383	1699	3.673	1680
	1783			4.997	1700	4.386	1681
	1819			3.110	1700	5.731	1684
	1869			2.625	1698	5.360	1683

	1940			2.249	1699	4.968	1684
5th	2052			2.585	1701	6.318	1685
	2136			2.306	1700	5.959	1687
	2180			1.783	1698	6.143	1684

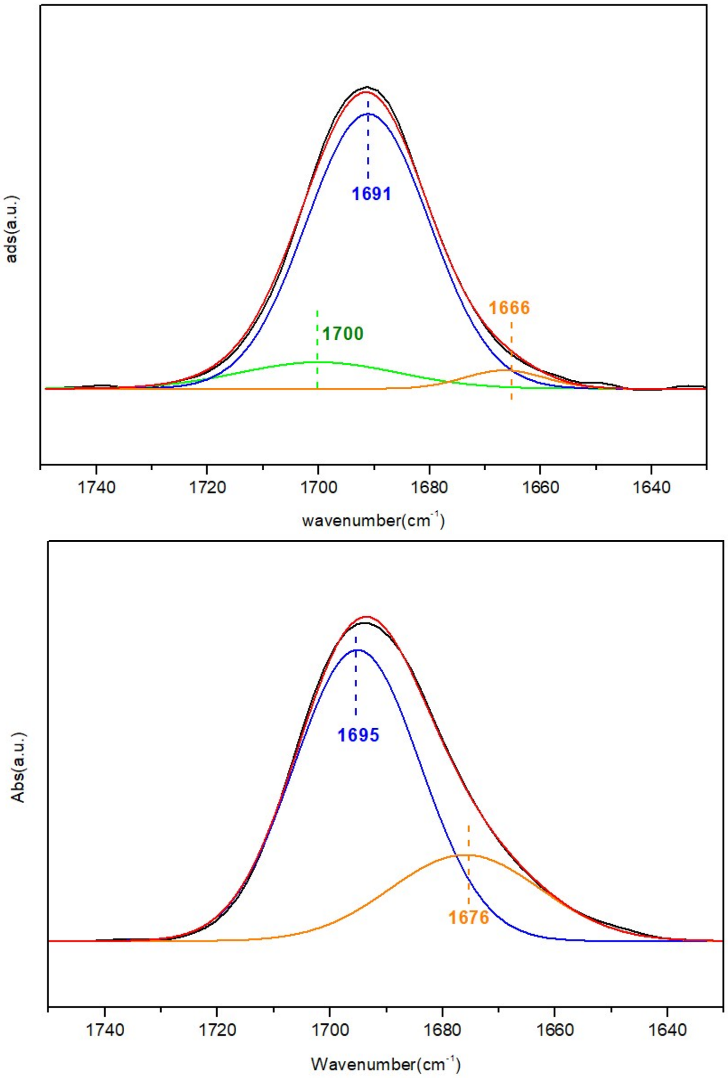

Figure S2. Deconvoluted spectra of 1st dose acetone adsorption on $Zn_1Zr_{10}O_z$ after 20 s (top) and 2nd dose acetone adsorption on $Zn_1Zr_{10}O_z$ after 861 s (bottom).

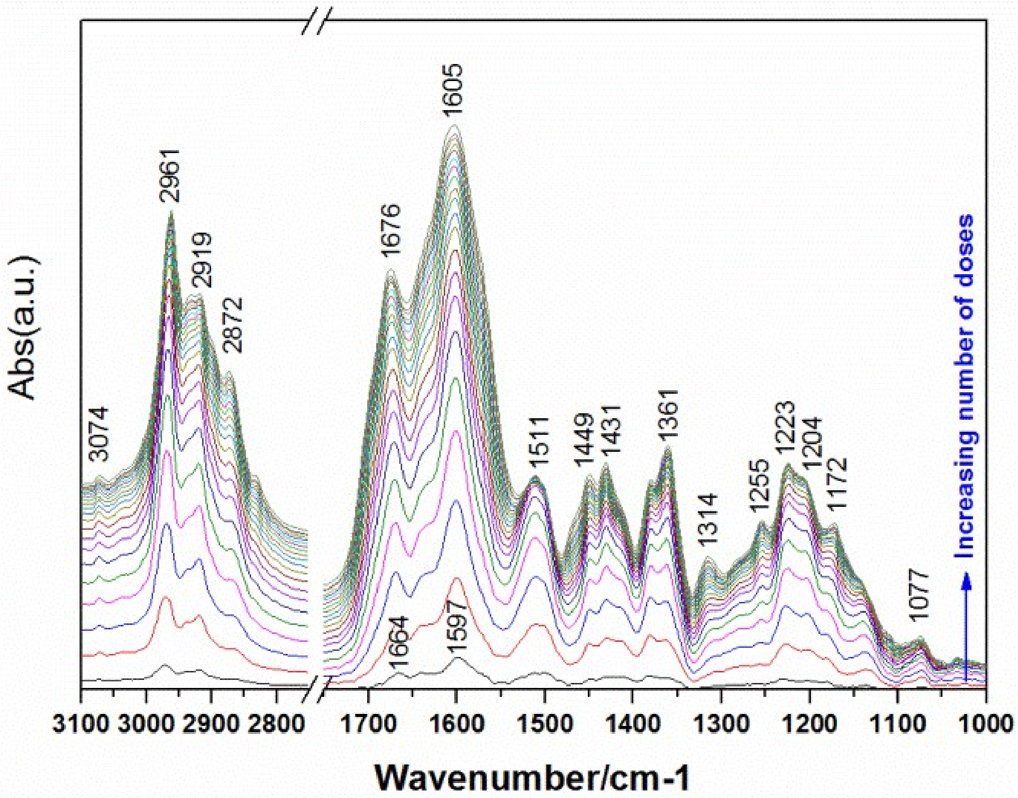

Figure S3. Infrared spectra of the adsorbed mesityl oxide (MSO) on $Zn_1Zr_{10}O_z$.

Peaks attributed to vibrations of mesityl oxide are at 1676 cm^{-1} (ν(C=O), 1664 cm^{-1} at low coverage) and 1605 cm^{-1} (ν(C=C), 1597 cm^{-1}at low coverage), 1450 cm^{-1}(ρ(C-H)), 1224 cm^{-1} and 1255 cm^{-1} (ν(C-C)).[3] The larger ν(C=C)/ν(C=O) intensity ratio of the adsorbed MSO than that in the gas phase ones[4] is likely due to the strong interaction between MSO and catalysts surface, which is also observed in literature.[2, 3] Noteworthy, a small amount of acetone is also identified in the mesityl oxide by our GC analysis (not shown), which should contribute the formation of small amount of acetone enolate (peaks at 1511 cm^{-1}, 1314 cm^{-1}, 1077 cm^{-1}, and shoulders at 1421 cm^{-1}, 1204 cm^{-1},and 1142 cm^{-1}). The fact that only traces amount of acetone is observed is due to the highly activity of the catalyst in the acetone activation and aldolization on $Zn_1Zr_{10}O_z$.

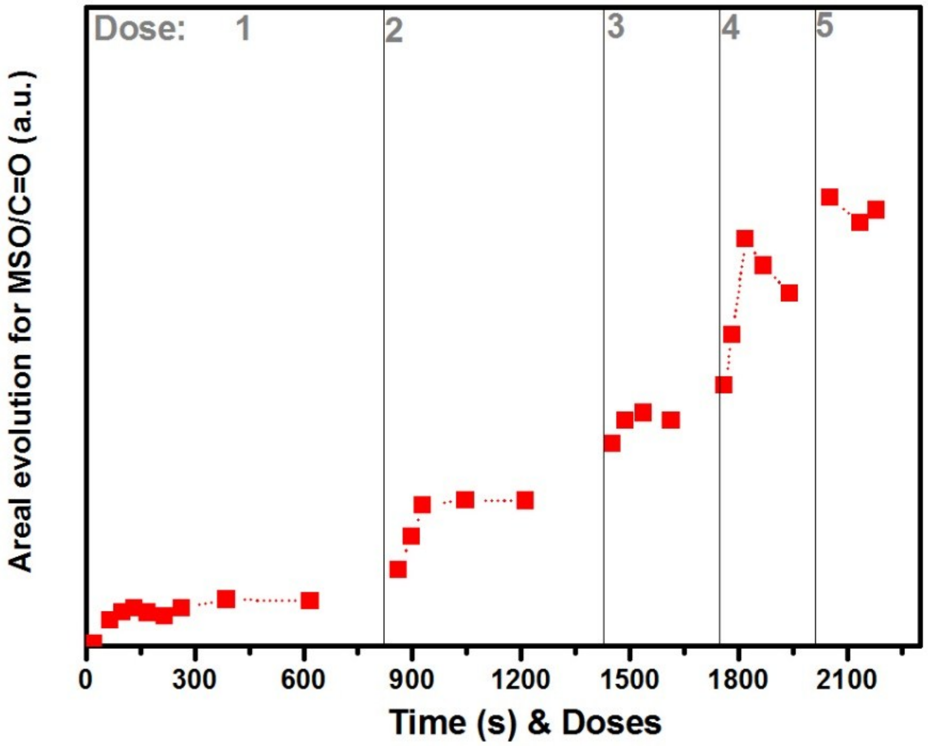

Figure S4. Evolution of deconvoluted C=O band of surface MSO. Note that the evolution of deconvoluted C=O matches that of C=C for MSO, suggesting the validity of the peak deconvolution.

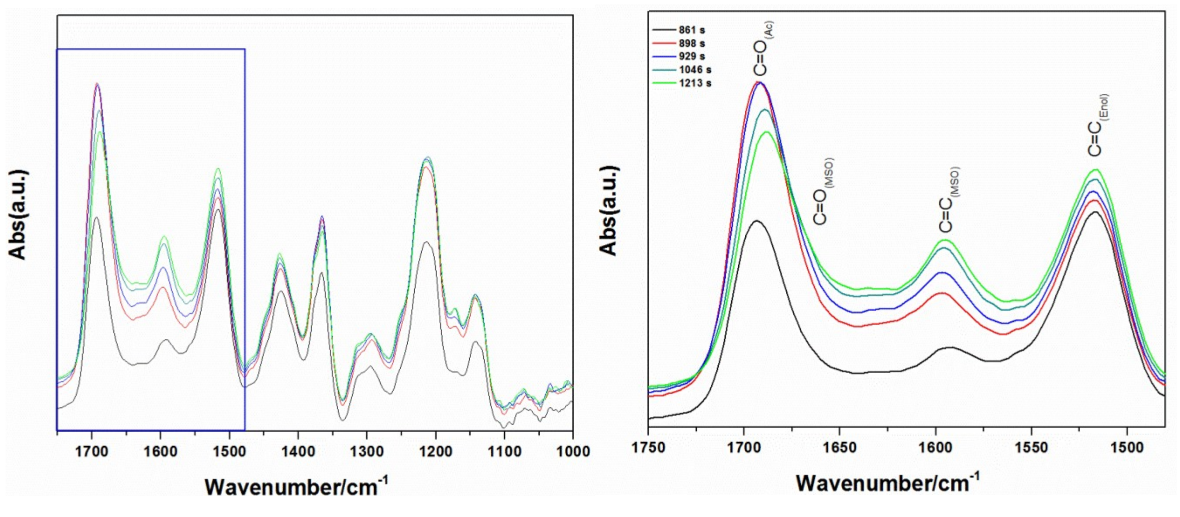

Figure S5. (left) Evolution of infrared spectra of adsorbed acetone on $Zn_1Zr_{10}O_z$ after 2nd dose; (right) Zoom-in spectra marked in the left spectra. Each spectrum takes ~20 s (32 scans).

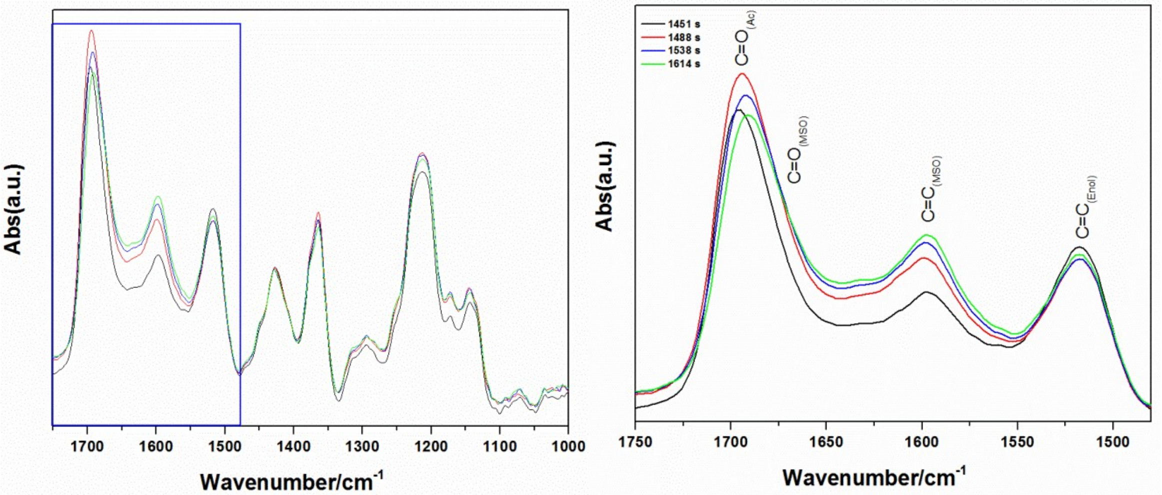

Figure S6. (left) Evolution of infrared spectra of adsorbed acetone on $Zn_1Zr_{10}O_z$ after 3rd dose; (right) Zoom-in spectra marked in the left spectra. Each spectrum takes ~20 s (32 scans).

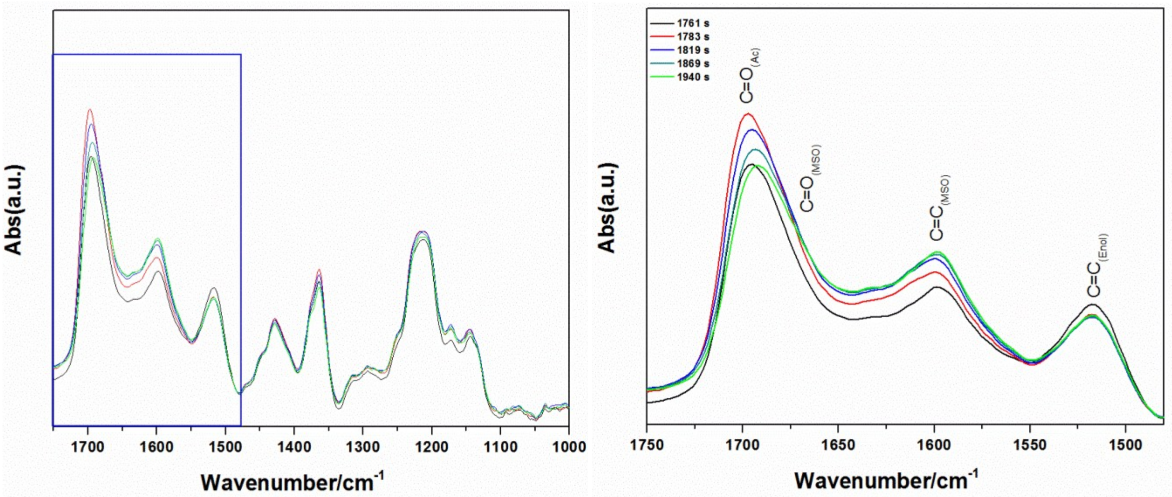

Figure S7. (left) Evolution of infrared spectra of adsorbed acetone on $Zn_1Zr_{10}O_z$ after 4th dose; (right) Zoom-in spectra marked in the left spectra. Each spectrum takes ~20 s (32 scans).

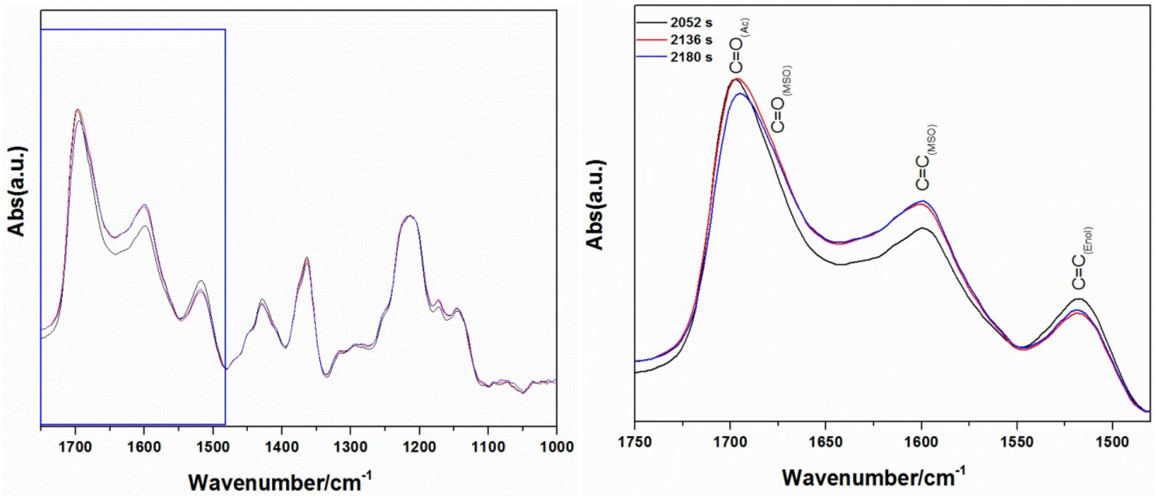

Figure S8. (left) Evolution of infrared spectra of adsorbed acetone on $Zn_1Zr_{10}O_z$ after 5th dose; (right) Zoom-in spectra marked in the left spectra. Each spectrum takes ~20 s (32 scans).

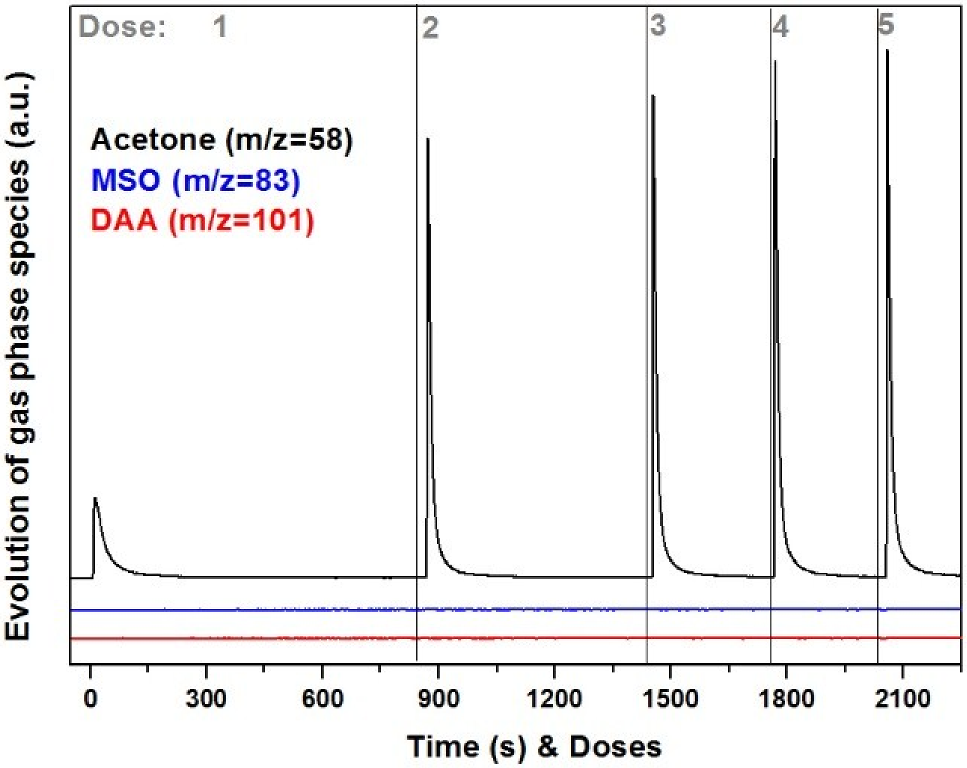

Figure S9. Evolution of gas-phase acetone, MSO, and DAA

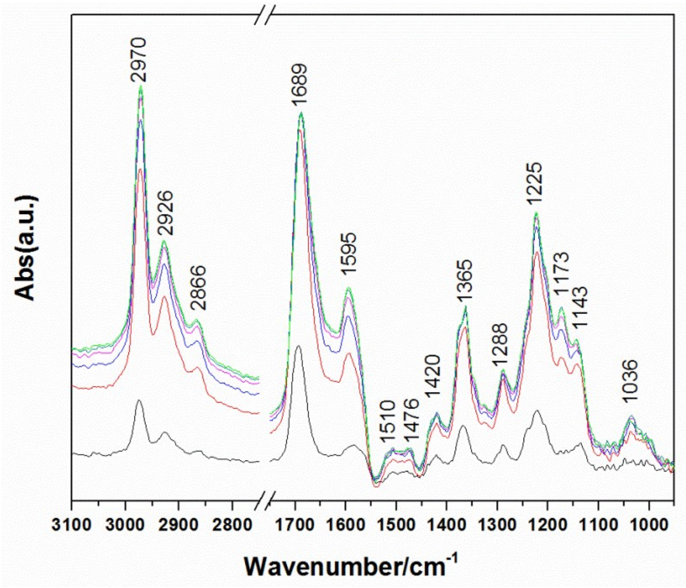

Figure S10. Evolution of infrared spectra of adsorbed acetone on ZrO_2 after one dose. Each spectrum takes ~20 s (32 scans).

Both acetone (peaks/shoulders at 2970, 2926, 1689, 1476,1437, 1374, 1225 and 1036 cm^{-1})[4] and mesityl oxide (peaks/shoulders at 2866, 1665, 1595, 1250, 1225 cm^{-1})[3] are observed. Note that, different from those on the $Zn_1Zr_{10}O_z$, although acetone aldolization occurs to form mesityl oxide, only minor acetone enolate is observed on ZrO_2 evidenced by the weak peaks or shoulders at 1510, 1420, 1300, 1204, and 1143 cm^{-1}. This result suggests that α-H abstraction might be the rate determining step on ZrO_2. The addition of zinc generated unique acid-base properties (i.e., new Zr-O-Zn identities) on the on the $Zn_1Zr_{10}O_z$, which in turn accelerated the enolization reaction via likely favorable hydrogen transfer [1] to form surface abundant acetone enolate on $Zn_1Zr_{10}O_z$. In addition, bands associated with isopropanol vibrations (ν(C-O) at 1173 cm^{-1} and δ(O-H) at 1288 cm^{-1})[5] are substantial on the ZrO_2, likely due to the presence of surface Brönsted acidity. This observation also matches with the formation of propylene products in the acetone reactions on ZrO_2.[1]

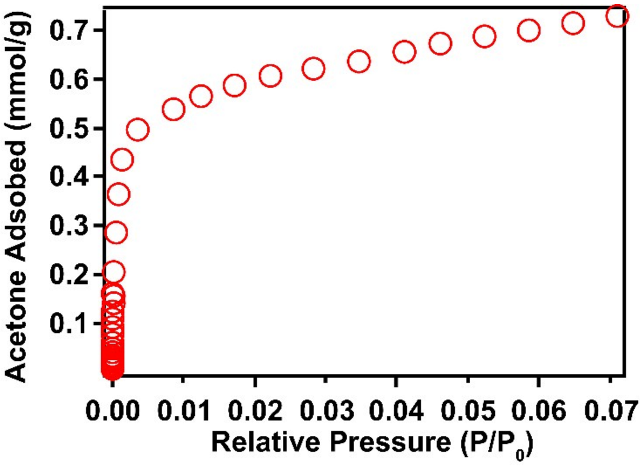

Figure S11. Acetone adsorption isotherms at 25 ºC on $Zn_1Zr_{10}O_z$

References

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