Supporting Information

Green and scalable synthesis of nitro- and amino-functionalized UiO-66(Zr) and effect of functional groups on oxidative desulfurization performance

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Table S1. N_2 sorption data and yield of various samples.

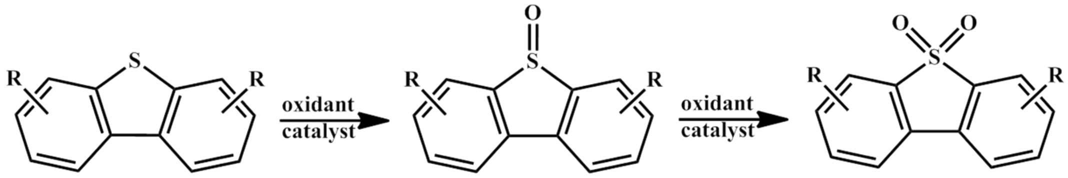
Samples	BET surface area (m^2/g)	Micropore volume (mL/g)[a]	Total pore volume (mL/g)	Yield (%)[b]
UiO-66(Zr)-NO_2-solvent	635	0.24	0.36	84.8
UiO-66(Zr)-NO_2-130-24	636	0.26	0.34	98.5
UiO-66(Zr)-NO_2-130-12 (UiO-66(Zr)-NO_2-green)	649	0.26	0.36	97.9
UiO-66(Zr)-NO_2-130-6	633	0.25	0.34	95.6
UiO-66(Zr)-NO_2-130-3	500	0.2	0.31	93.3
UiO-66(Zr)-NO_2-90-6	459	0.22	0.33	90.2
UiO-66(Zr)-NO_2-120-6	583	0.23	0.36	91.6
UiO-66(Zr)-NO_2-140-6	578	0.23	0.31	96.5
UiO-66(Zr)-NO_2-150-6	606	0.30	0.39	97.2
UiO-66(Zr)-NH_2-solvent	803	0.29	0.42	81.5
UiO-66(Zr)-NH_2-120-24	378	0.15	0.25	95.6
UiO-66(Zr)-NH_2-130-24	588	0.24	0.36	95.4
UiO-66(Zr)-NH_2-140-24	575	0.24	0.30	96.7
UiO-66(Zr)-NH_2-150-24	681	0.29	0.40	98.7
UiO-66(Zr)-NH_2-150-12 (UiO-66(Zr)-NH_2-green)	829	0.34	0.47	95.7
UiO-66(Zr)-NH_2-150-6	730	0.29	0.39	94.4
UiO-66(Zr)-NH_2-150-3	759	0.29	0.42	92.8
UiO-66(Zr)-NH_2-150-1.5	588	0.23	0.40	91.4
UiO-66(Zr)-NH_2-160-24	519	0.22	0.29	99.3

[a] HK method; [b] Calculated by the addition amount of BDC.

Table S2. Comparison of catalytic activities over several representative MOFs in ODS of DBT.

Catalysts	Dosage of catalyst (mg)	Metal content (wt %)	Sulfur content (ppmw)	Oxidant	Temp. (°C)	Time (min)	TOF[a] (h^{-1})	Ref.
TMU-10	100	15.0	500	TBHP	60	480	0.05	1
TMU-12	100	12.8	500	TBHP	60	480	0.13	1
MIL-125(Ti)	17	24.4	5000	TBHP	80	4320	0.28	2
MIL-47(V)	31	14.3	5000	TBHP	80	4320	0.56	2
MIL-125(Ti)	100	24.4	240	H_2O_2	60	30	0.20	3
UiO-66(Zr)	58.6	33.1	1500	H_2O_2	50	30	0.33	4
UiO-66(Zr)	50	32.9	1000	H_2O_2	60	120	0.44	5
UiO-66(Zr/Ti)	50	27.7/5.1	1000	H_2O_2	60	120	0.70	5
UiO-66(Zr)	100	33.1	500	H_2O_2	60	150	0.12	6
UiO-66(Zr)-free	50	32.2	1000	H_2O_2	60	120	0.88	7
UiO-66(Zr)-1h	50	33.1	1000	H_2O_2	60	60	2.32	8
UiO-66(Zr)-NH_2-green	52.6	30.7	1000	H_2O_2	60	90	0.8	This work
UiO-66(Zr)-green	50	32.2	1000	H_2O_2	60	90	1.1	This work
UiO-66(Zr)-NO_2-green	58.3	28.3	1000	H_2O_2	60	30	3.4	This work

[a]TOF (Turnover frequency): mole number of converted DBT per mole of metal active center in catalysts per hour.



Scheme S1. Reaction pathway about the ODS reactions of DBT and its derivatives.

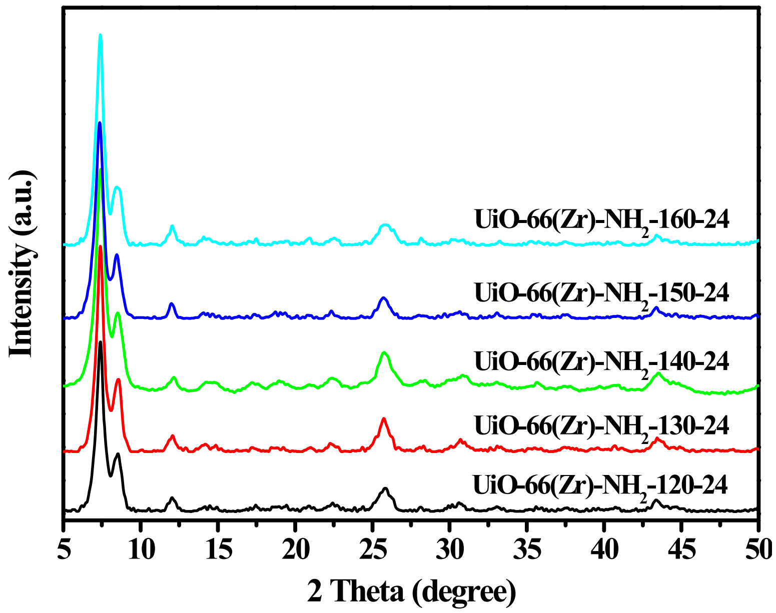


Figure S1. XRD patterns of various samples prepared under different crystallization temperatures.

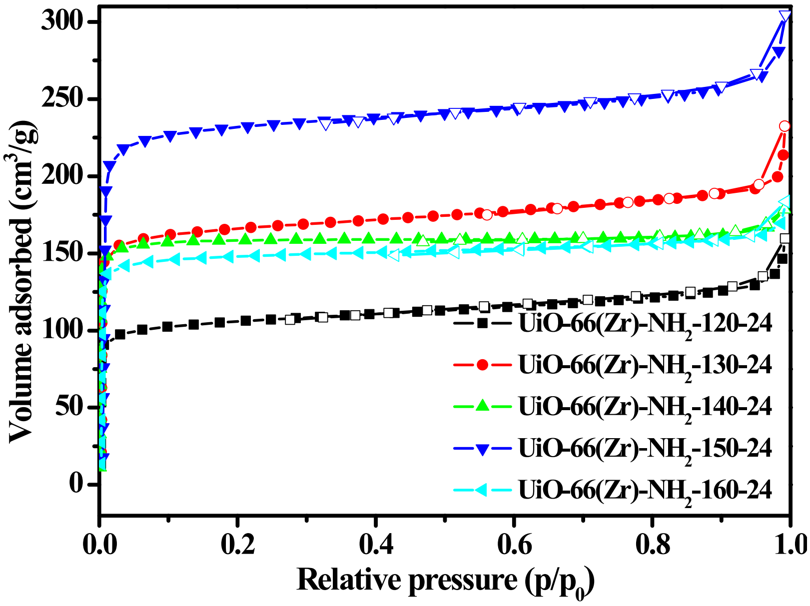


Figure S2. N_2 sorption isotherms of various samples prepared under different crystallization temperatures.

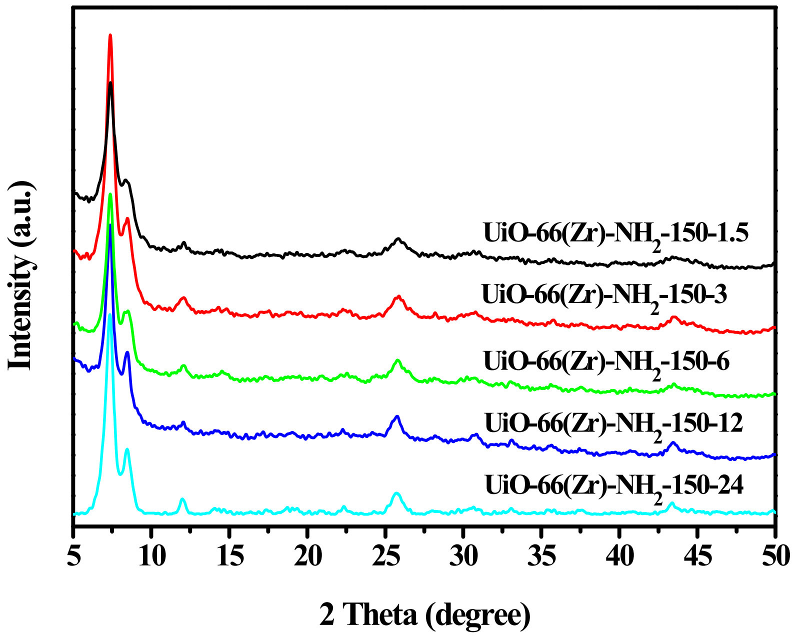


Figure S3. XRD patterns of various samples prepared under different crystallization time.

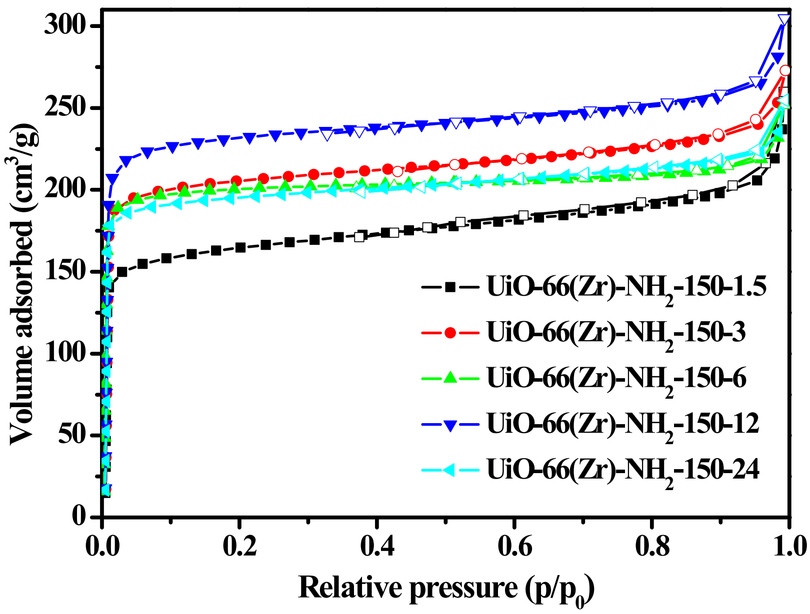


Figure S4. N_2 sorption isotherms of various samples prepared under different crystallization time.

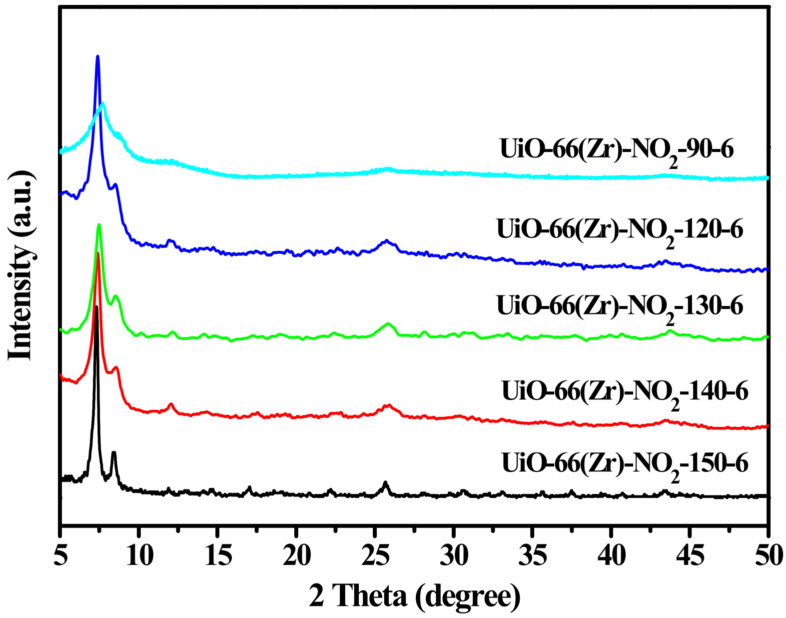


Figure S5. XRD patterns of various samples prepared under different crystallization temperatures.

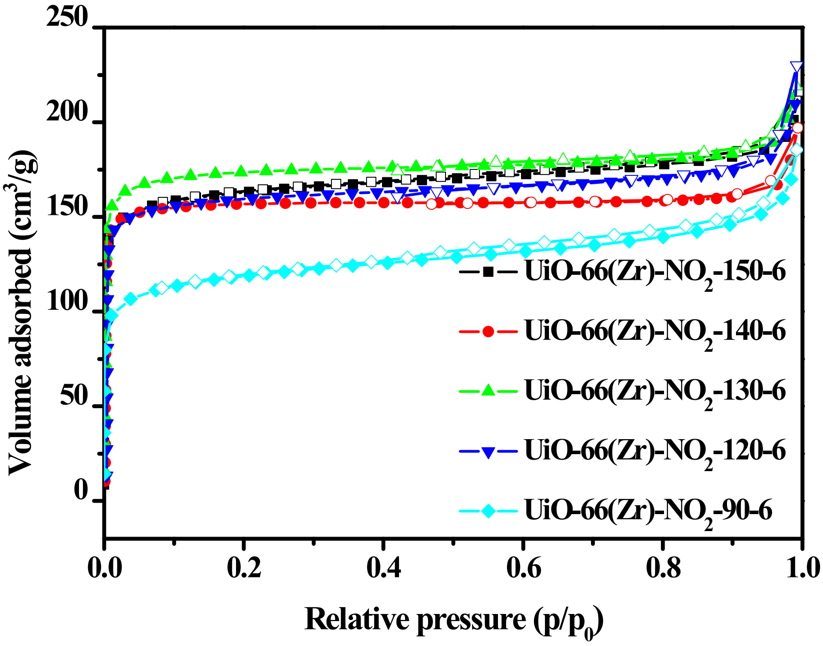


Figure S6. N_2 sorption isotherms curves of various samples prepared under different crystallization temperatures.

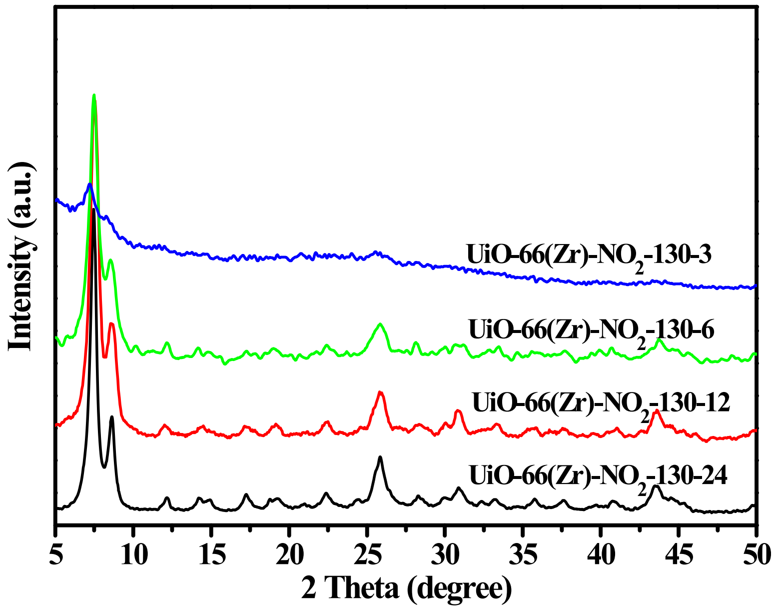


Figure S7. XRD patterns of various samples prepared under different crystallization time.

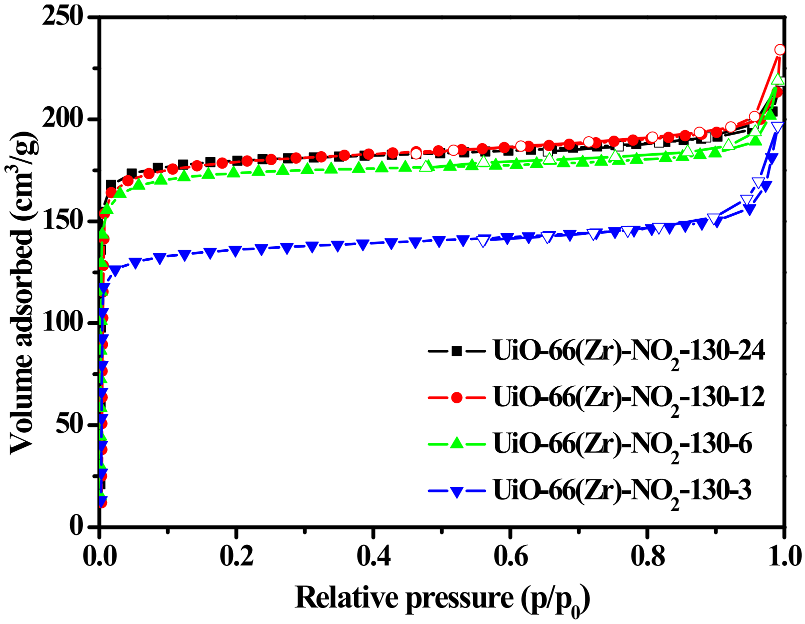


Figure S8. N_2 sorption isotherms of various samples prepared under different crystallization time.

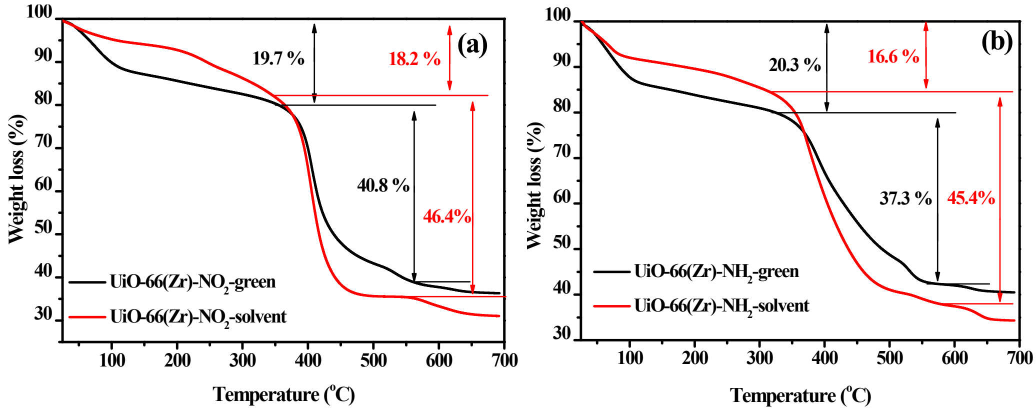


Figure S9. TGA curves of (a) UiO-66(Zr)-NO_2-green and UiO-66(Zr)-NO_2-solvent, (b) UiO-66(Zr)-NH_2-green and UiO-66(Zr)-NH_2-solvent under oxygen atmosphere.

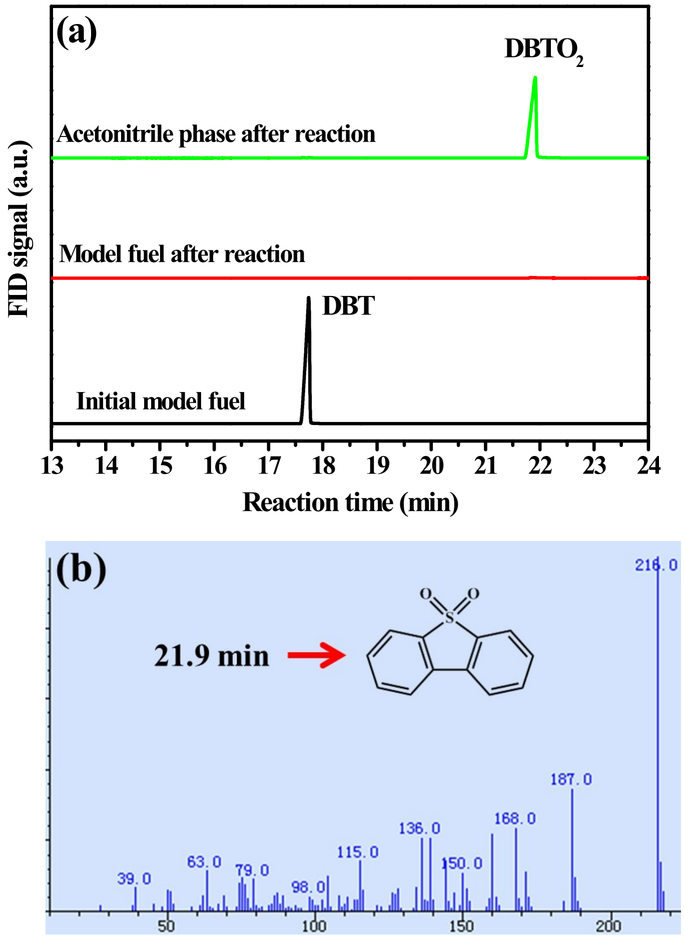


Figure S10. GC-FID chromatograms of initial model fuel, model fuel after reaction, acetonitrile phase after reaction over UiO-66(Zr)-NO_2-green (a) and mass spectroscopy of $DBTO_2$ in the acetonitrile phase (b).

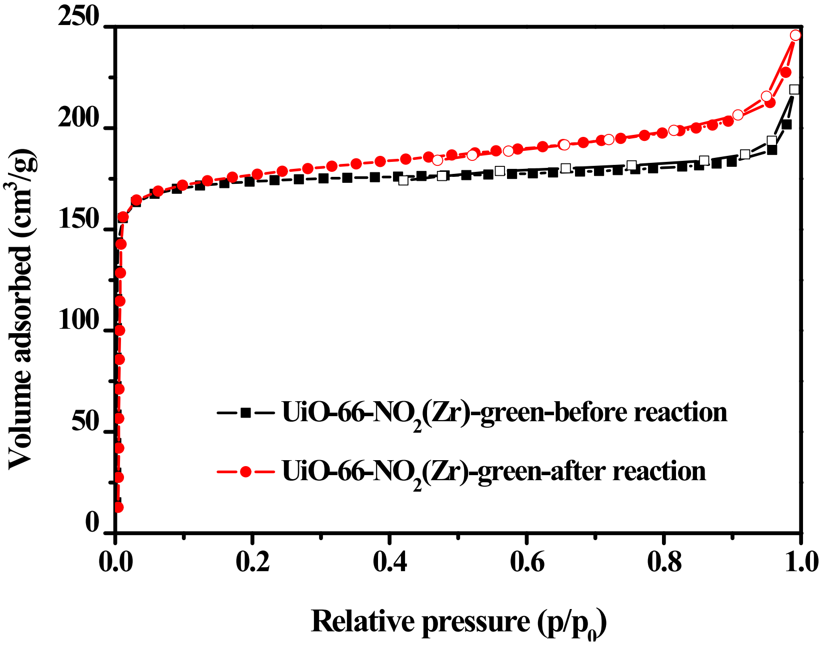


Figure S11. N_2 sorption isotherms of UiO-66(Zr)-NO_2-green before and after reaction.

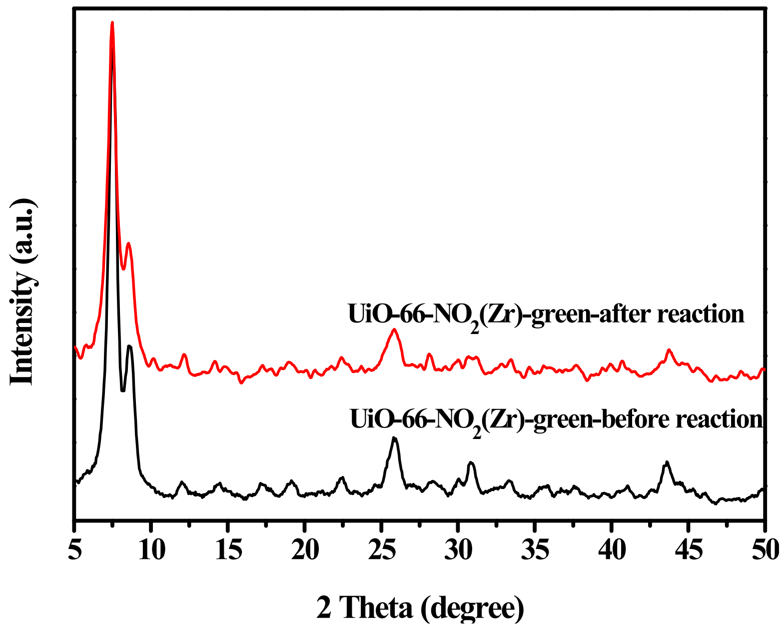


Figure S12. XRD patterns of UiO-66(Zr)-NO_2-green before and after reaction.

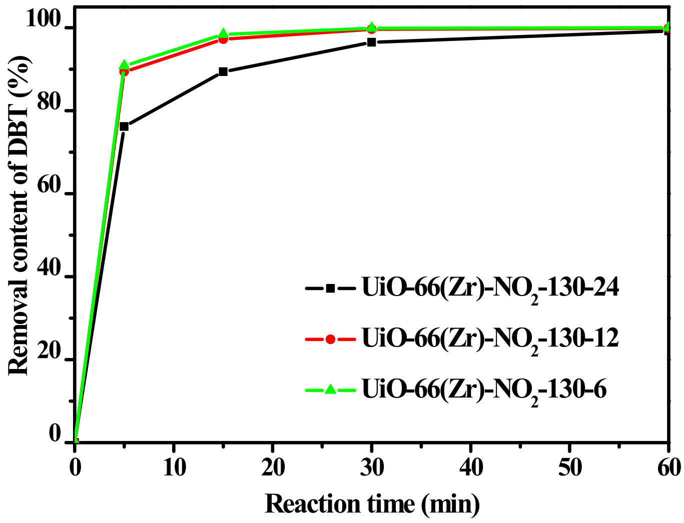


Figure S13. Removal content of DBT with reaction time over various catalysts.

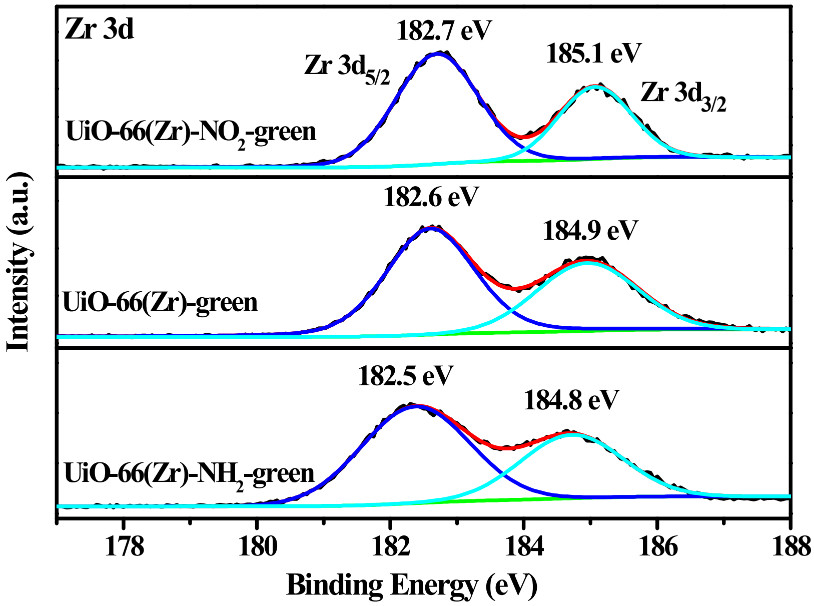


Figure S14. Zr 3d XPS spectra of various samples.

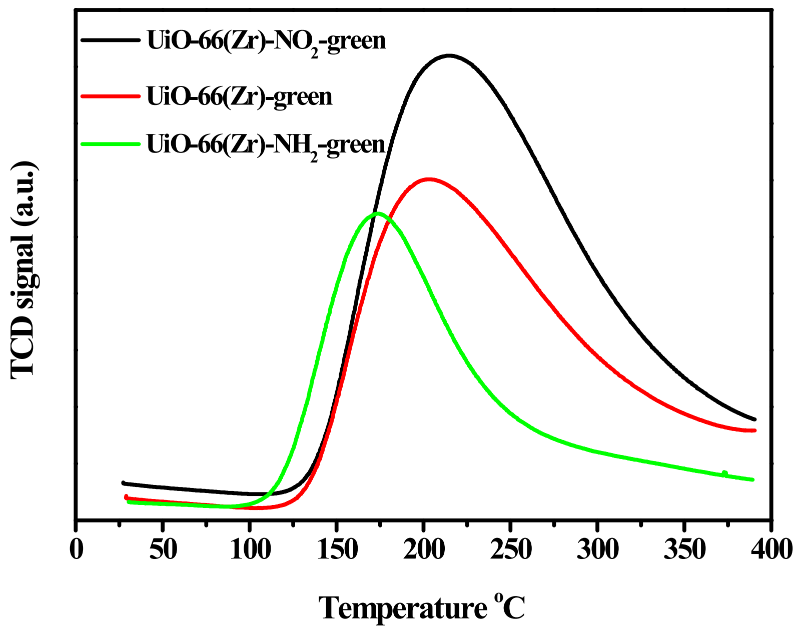


Figure S15. NH_3-TPD profiles of various samples.

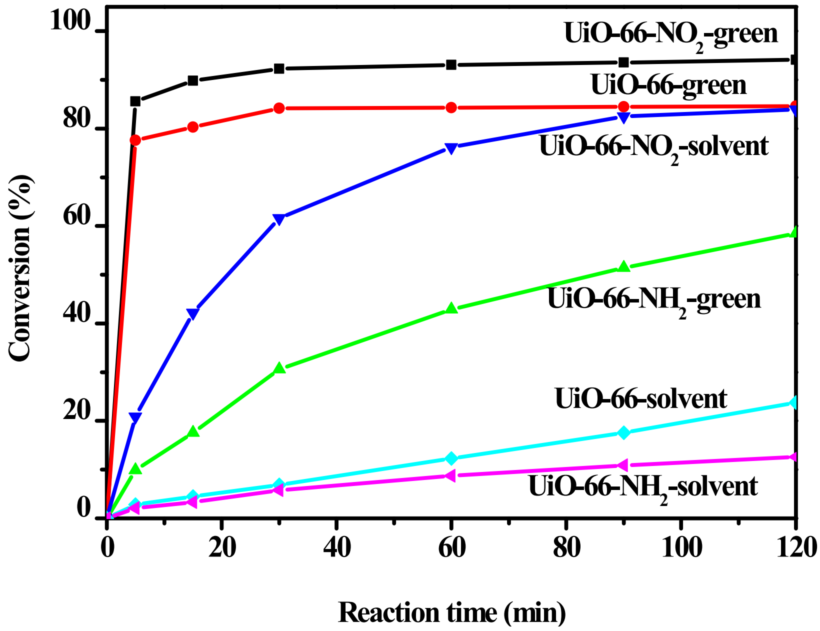


Figure S16. Catalytic performance of various catalysts in the acetalization of benzaldehyde with methanol.

References

[1] M. Y. Masoomi, M. Bagheri and A. Morsali, *Inorg. Chem.*, 2015, **54**, 11269-11275.

[2] D. Nicholas, M. Namara, G. T. Neumann, E. T. Masko, J. A. Urban and J. C. Hicks, *J. Catal.*, 2013, **305**, 217-226.

[3] Y. Zhang, G. Lia, L. H. Kong and H. Lu, *Fuel*, 2018, **219**, 103-110.

[4] C. M. Granadeiro, S. O. Ribeiro, M. Karmaoui, R. Valença, J. C. Ribeiro, B. de Castro, L. C. Silva and S. S. Balula, *Chem. Commun.*, 2015, **51**, 13818-13821.

[5] G. Ye, H. Qi, X. L. Li, K. Y. Leng, Y. Y. Sun and W. Xu, *ChemPhysChem*, 2017, **18**, 1903-1908.

[6] X. T. Zhang, P. C. Huang, A. L. Liu and M. Y. Zhu, *Fuel*, 2017, **209**, 417-423.

[7] G. Ye, D. Zhang, X. F. Li, K. Y. Leng, W. J. Zhang, J. Ma, Y. Y. Sun, W. Xu and S. Q. Ma, *ACS Appl. Mater. Interfaces*, 2017, **9**, 34937-34943.

[8] W. M. Xiao, Q. L. Dong, Y. Wang, Y. Li, S. J. Deng and N. Zhang, *CrystEngComm*, 2018, **20**, 5658-5662.