Supporting Information

Bubble-template synthesis of $WO_3 \cdot 0.5H_2O$ hollow spheres as a high-activity catalyst for catalytic oxidation of benzyl alcohol to benzaldehyde

Huixiang Wang,[a] Xiaobo Ren,[ad] Zhong Liu,[bc] Dong Jiang*[a] and Baoliang Lv[a]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China.

*E-mail: jdred@sxicc.ac.cn; lbl604@sxicc.ac.cn

[b] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. Xining 810008, China.

[c] Key Laboratory of Salt Lake Resources Chemistry of Qinghai Province. Xining 810008, China.

[d] University of Chinese Academy of Sciences, Beijing 100049, China.

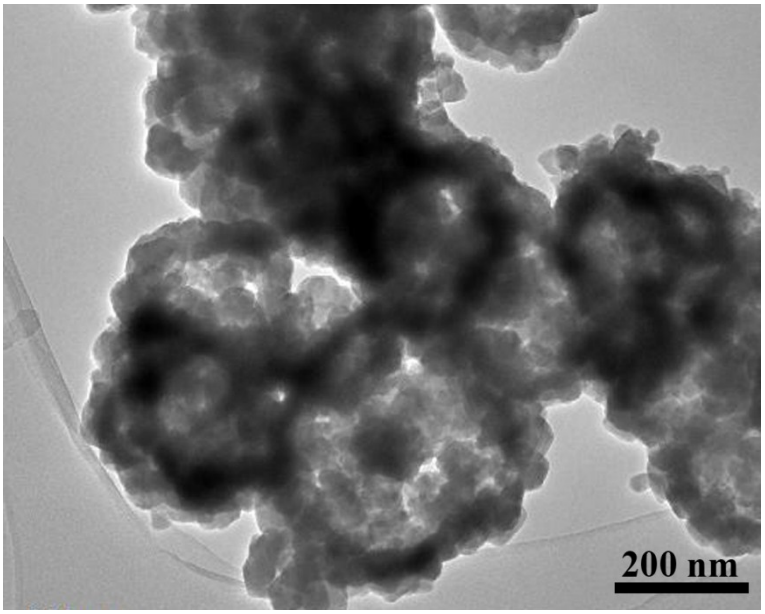

Fig. S1 The TEM image of $WO_3 \cdot 0.5H_2O$ hollow spheres obtained at 45 mM urea before 300 °C calcination in air atmosphere.

.

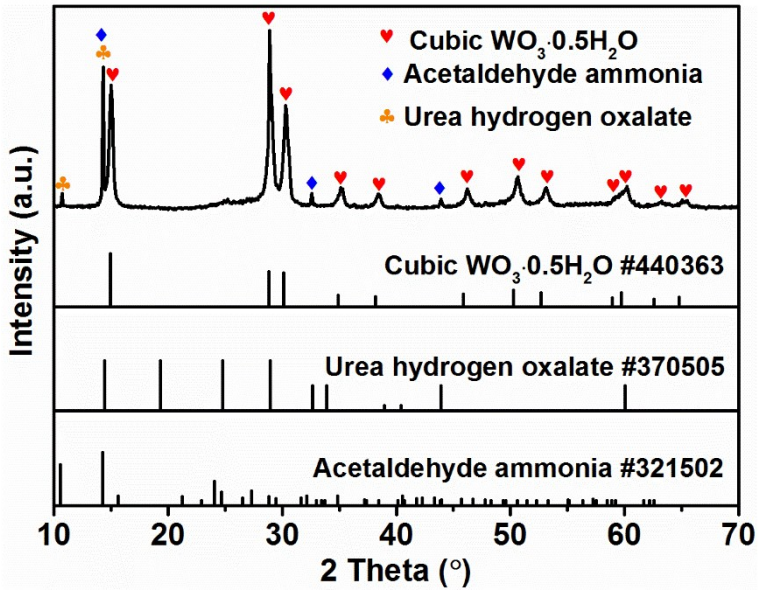

Fig. S2 The XRD pattern of WO_3 $0.5H_2O$ hollow spheres without calcination at 300℃in air atmosphere.

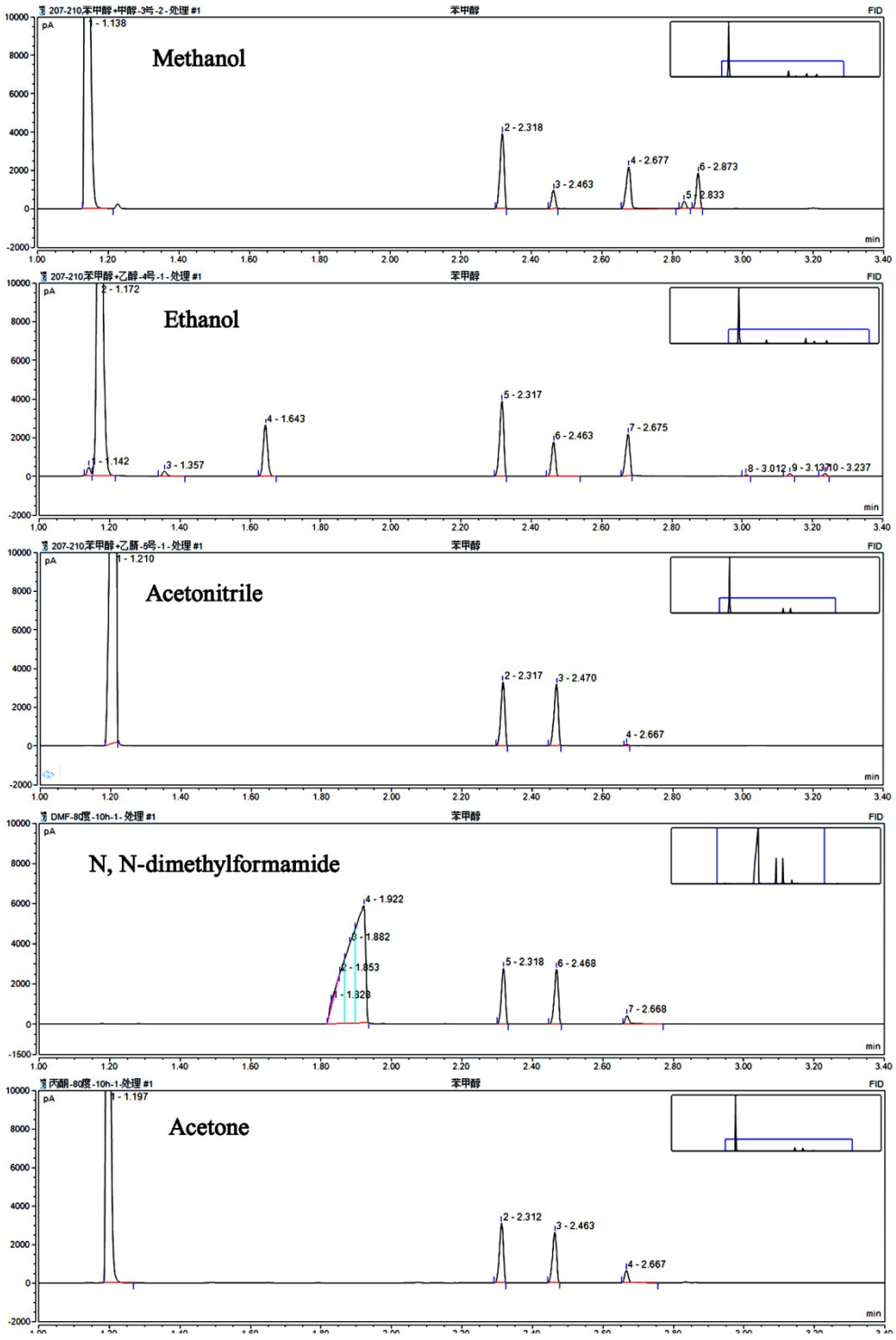

Fig. S3 Catalytic oxidation of benzyl alcohol on WO_3 $0.5H_2O$ hollow spheres with different solvents.

Retention time

1.138 min：Methanol；1.172 min: Ethanol; 1.197 min: Acetone; 1.210 min: Acetonitrile; 1.357 min: Ethyl acetate; 1.643 min: Acetal; 2.318 min: Anisole; 2.463 min: Benzaldehyde; 2.677 min: Benzyl alcohol; 2.833 min: Methyl benzoate; 2.873 min: Benzaldehyde dimethylacetal; 3.012 min: Benzoic acid; 3.137 min: Ethyl benzoate; 3.237 min: 3-Benzyloxy 2-butanol.

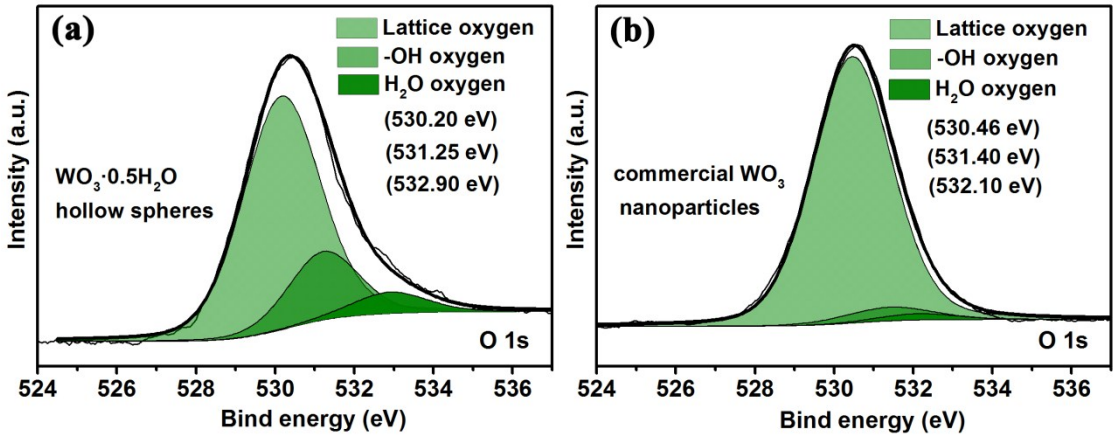

Fig. S4 The O 1s binding energy of WO_3 $0.5H_2O$ hollow spheres (a) and c-WO_3 (b).

Tab. S1 The performance comparison of WO_3 $0.5H_2O$ hollow spheres and reported catalysts in catalytic oxidation of benzyl alcohol to benzaldehyde

samples	BET ($m^2 \cdot g^{-1}$)	Catalyst (mg)	BzOH (mmol)	n(H_2O_2) / n(BzOH)	T (°C)	t (h)	Con. (%) (BzOH)	Sel. (%) (BzH)	TOF (BzH) ($mmol \cdot m^{-2} \cdot h^{-1}$)	Reference
MOR-HN	455.4	500	135	1:1	90	4	99.9	99.8	0.148	[1]
25ZSM(AT-0.5)	268	1000	99	1.3:1	90	4	52.0	70.0	0.034	[2]
20HPW/CeO_2	26.0	800	50	2:1	110	4	94.0	98.2	0.555	[3]
Cr(salen)/MCM-41	680.0	250	50	2.5:1	50	4	52.5	99.0	0.038	[4]
Fe_3O_4-AIP	31.3	200	40	2:1	100	1.5	40.0	85.0	1.448	[5]
Fe_3O_4-ECH-P-3g	28.0	200	40	2:1	100	1.5	39.2	84.8	1.572	[6]
Au/TS-1(0.3%)	372.0	300	29	1.3:1	80	24	79.0	75.0	0.06	[7]
SIL-$FeCl_3$	309.1	200	28.8	4:1	90	6	65.2	63.0	0.032	[8]
sulfated Ti-SBA-15(10)	594.0	500	10	4:1	60	2	62.0	96.0	0.010	[9]
RHAC-CoPor	114.0	80	10	1.5:1	70	5	97.1	97.7	0.208	[10]
$Ti(SO_4)_2$/GOF	119.8	400	6.5	3:1	75	4	91.3	99.0	0.031	[11]
$WO_3 \cdot 0.5H_2O$ hollow spheres	13.8	30	2	3:1	80	10	99.2	99.0	**0.474**	**This work**

●BzOH: benzyl alcohol; BzH: benzaldehyde

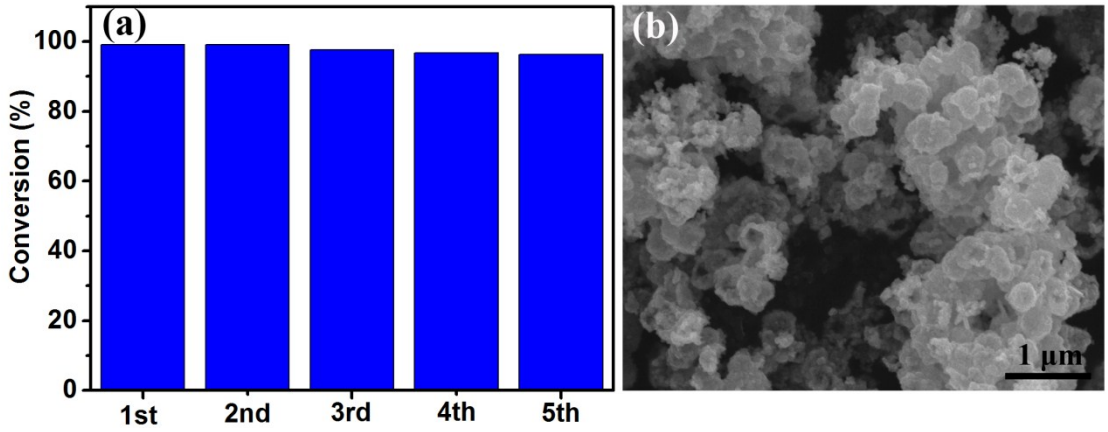

Fig. S5 (a) The conversion of five reactions on WO_3 $0.5H_2O$ hollow spheres. (b) The SEM image of WO_3 $0.5H_2O$ hollow spheres after the fifth reaction.

References

[1] S. K. Saxena, N. Viswanadham and A. H. Al-Muhtaseb, J. Porous Mater., 2016, 23, 1671-1678.

[2] A. Jia, L. L. Lou, C. Zhang, Y. Zhang and S. Liu, J. Mol. Catal. A, 2009, 306, 123-129.

[3] X. Han, Y. Kuang, C. Xiong, X. Tang, Q. Chen, K. Wang, C. T. Hung, L. L. Liu and S. B. Liu, J. Braz. Chem. Soc., 2018, 29, 88-98.

[4] X. Wang, G. Wu, J. Li, F. Xiao, W. Wei and Y. Sun, Chin. J. Catal., 2007, 28, 1101-1106.

[5] L. Xiong, R. Chen and F. Chen, RSC Adv., 2016, 6, 101048-101060.

[6] S. Xiao, C. Zhang, R. Chen and F. Chen, New J. Chem., 2015, 39, 4924--4932.

[7] G. Zhan, J. Huang, M. Du, D. Sun, I. Abdul-Rauf, W. Lin, Y. Hong and Q. Li, Chem. Eng. J., 2012, 187, 232-238.

[8] R. Cang, B. Lu, X. Li, R. Niu, J. Zhao and Q. Cai, Chem. Eng. Sci., 2015, 137, 268-275.

[9] R. V. Sharma, K. K. Soni and A. K. Dalai, Catal.Commun., 2012, 29, 87-91.

[10] F. Adam and W. T. Ooi, Appl. Catal. A, 2012, 445- 446, 252- 260.

[11] W. Ma, Q. Tong, J. Wang, H. Yang, M. Zhang, H. Jiang, Q. Wang, Y. Liu and M. Cheng, RSC Adv., 2017, 7, 6720-6723.