Electronic Supporting Information

Tert-Butyl Hydroperoxide (TBHP)-Mediated Oxidative Self-Coupling of Amines to Imines over α-MnO_2Catalyst

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Content:

1. Materials

β-MnO_2[1], δ-MnO_2[2], OMS[3], Mn_2O_3[4], Mn_3O_4[4], Co_3O_4[5], MoO_3[6]were prepared according to the literature procedures.Fe_2O_3, V_2O_5, CuO were obtained from Tianjin Kermel. $KMnO_4$ and $MnSO_4·H_2O$ were obtained from Tianjin Kermel and Sinopharm Chemical Reagent. Solvents were obtained from Tianjin Kermel, and substrates were obtained from J&K or Aladdin. TBHP was obtained from Sinopharm Chemical Reagent.

2. Preparation of α-MnO_2

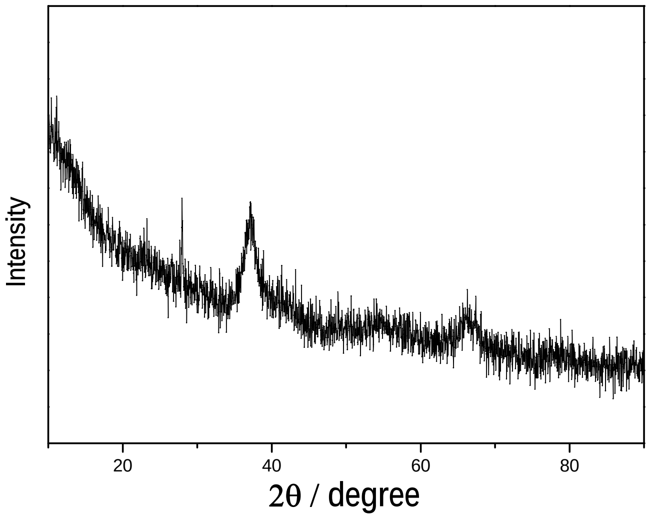
The α-MnO_2 was prepared as follows:[7] a 10 mL aqueous solution containing $KMnO_4$ (1 mmol) was mixed with 10 mL aqueous solution containing $MnSO_4$ (1.5 mmol) and stirred continuously for 6 h. A dark-brown precipitate thus formed and was collected by centrifugation, washed repeatedly with deionized water, and finally dried overnight at 70 °C.

3. Characterization of catalysts

Table S1 Surface area of different catalysts

Entry	Catalyst	Surface area m^2/g[a]
1	α-MnO_2	127.69
2	OMS-2	84.70
3	β-MnO_2	19.11
4	δ-MnO_2	68.57
5	Mn_2O_3	94.69
6	Mn_3O_4	50.47
7	Fe_2O_3	3.58
8	V_2O_5	12.13
9	CuO	2.58
10	Co_3O_4	3.29
11	MoO_3	9.14

[a] Surface area data were characterized using Quantachrome Instruments.



XRD pattern of α-MnO_2

4. Catalytic reaction

A general procedure for the synthesis of imines from amines was as follows: Amine (0.5 mmol), α-MnO_2 catalyst (10 mol%), TBHP (1 mmol) and solvent (2 mL) were placed in a pressure vessel with a magnetic stir bar. The reaction was carried out at room temperature. The product was analyzed by GC-MS using an Agilent 7890A/5975C instrument equipped with an HP-5MS column (30 m in length, 0.25 mm in diameter). The conversion was determined using internal standard method with dodecane as internal standard. The selectivity was determined using area normalization method. After the reaction was complete, used α-MnO_2 catalyst was separated by centrifugation, washed with ethanol and deionized water and dried at 70 ^oC prior to being recycled.

5. Filtration experiment and ICP analysis

The benzylamine oxidation mixture was quickly filtered through a Teflon-membrane filter after 2 h to another glass reactor, which was placed in the same oil-bath with the previous one. The reaction was then conducted with the filtrate for another 4 hour. Four samples were collected at 3 h, 4 h, 5 h and 6 h, and analyzed.

ICP analysis was conducted after the reaction and the benzyl amine oxidation mixture was filtered through a Teflon-membrane filter.

6. Catalyst recycles

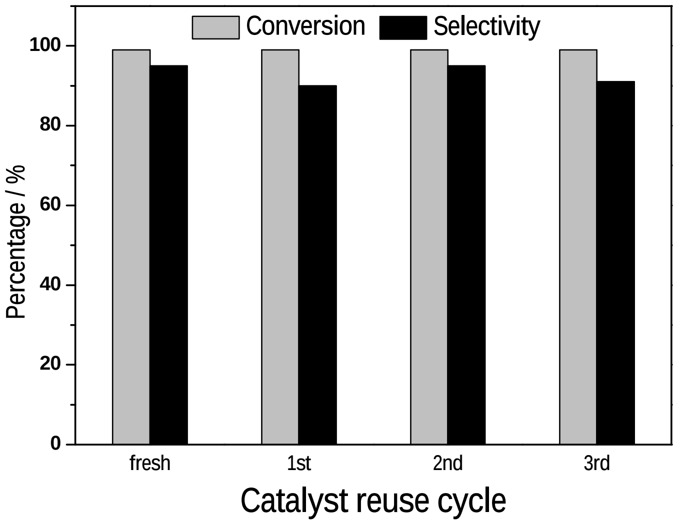
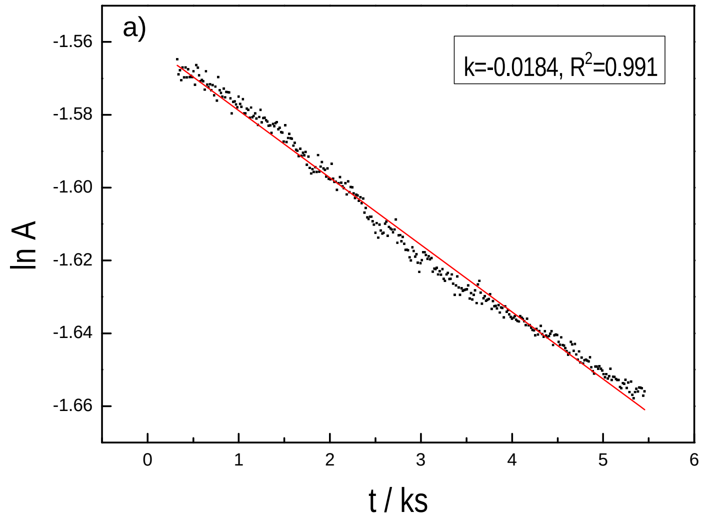
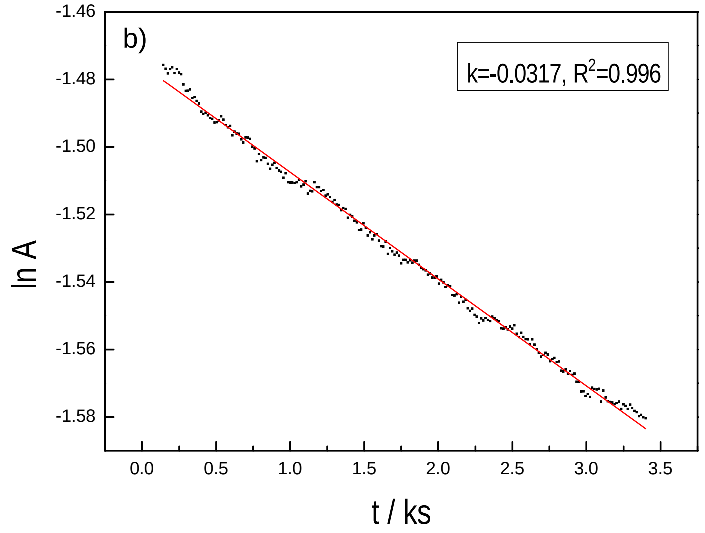
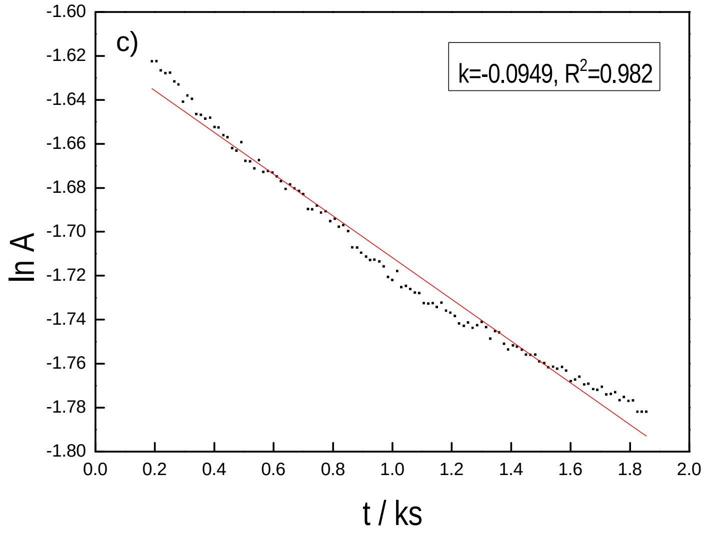


Figure S1 Reusability of α-MnO_2 in the transformation of benzylamine to *N*-Benzylidenebenzylamine.

7. ATR-IR


a)
k=-0.0184, R²=0.991
ln A
-1.56
-1.58
-1.60
-1.62
-1.64
-1.66
t / ks
0
1
2
3
4
5
6


b)
k=-0.0317, R²=0.996
ln A
-1.46
-1.48
-1.50
-1.52
-1.54
-1.56
-1.58
t / ks
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5


c)
k=-0.0949, R²=0.982
ln A
-1.60
-1.62
-1.64
-1.66
-1.68
-1.70
-1.72
-1.74
-1.76
-1.78
-1.80
t / ks
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

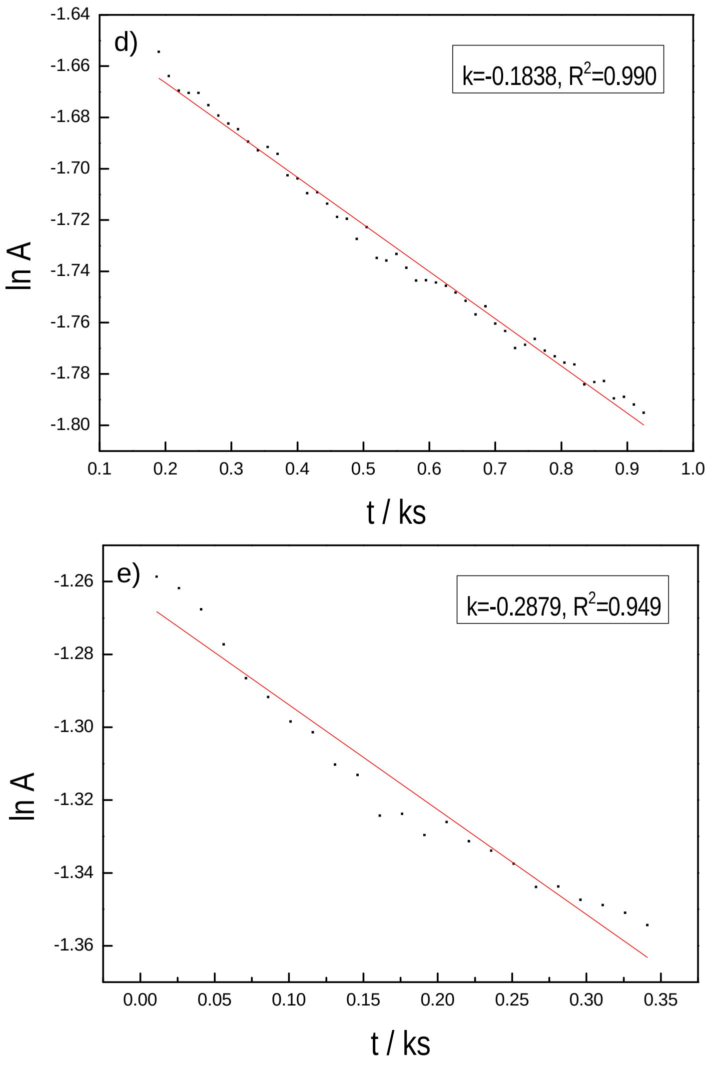
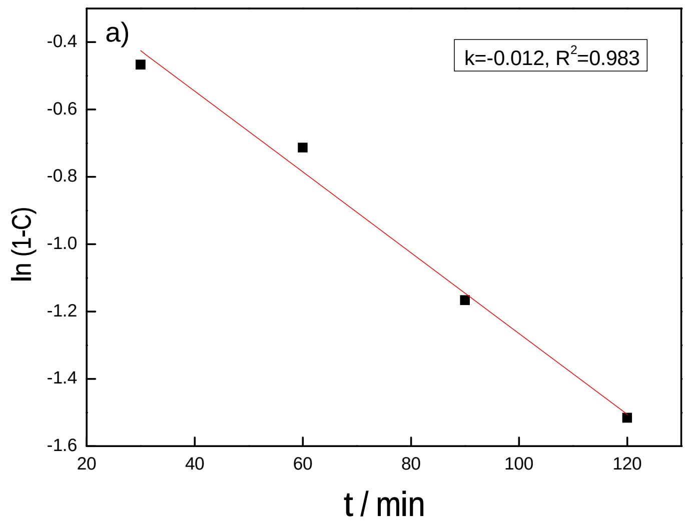
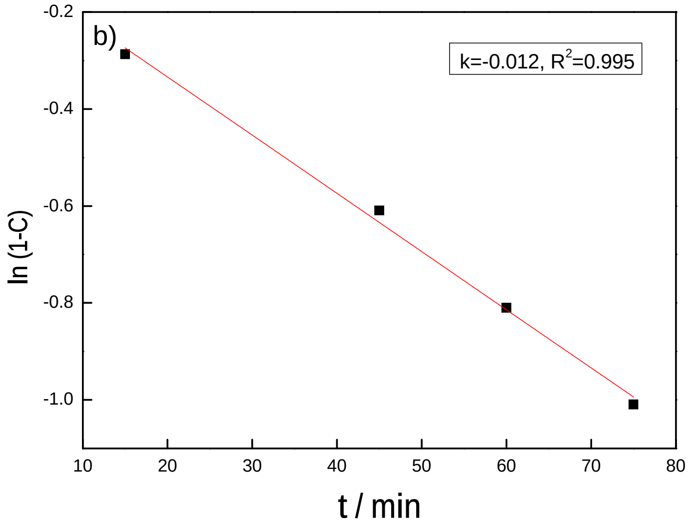
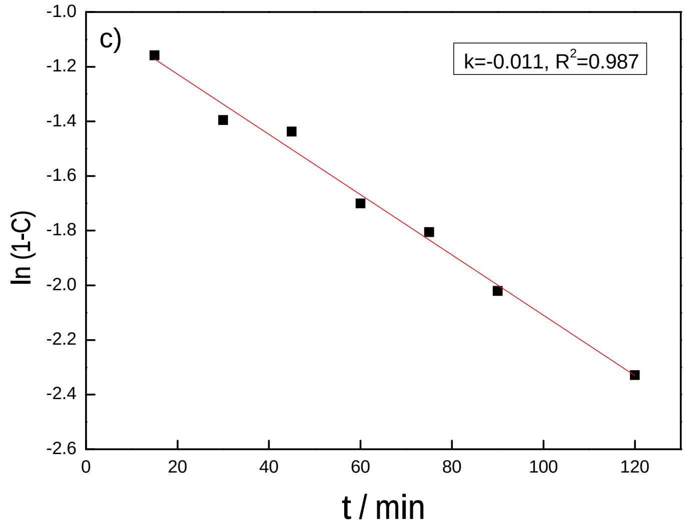


Figure S2 lnA (absorbance of 865 cm^{-1} band collected from ATR-IR) vs. time linear plot of a) 303 K, b) 313 K, c) 323 K, d) 333 K, e) 343 K.

8. Kinetics analysis







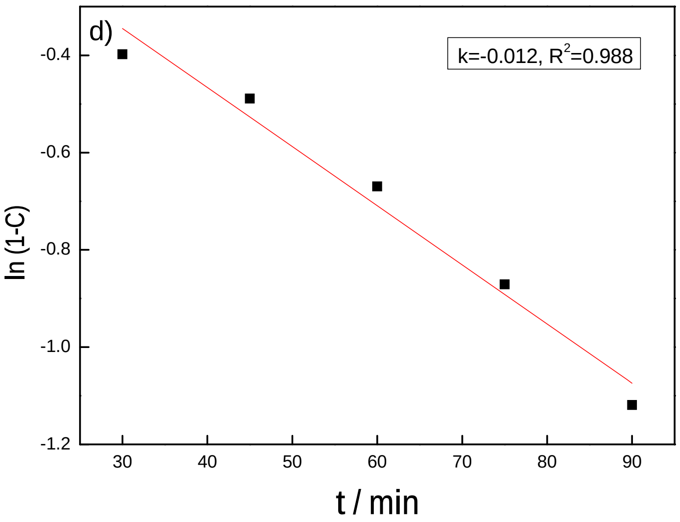
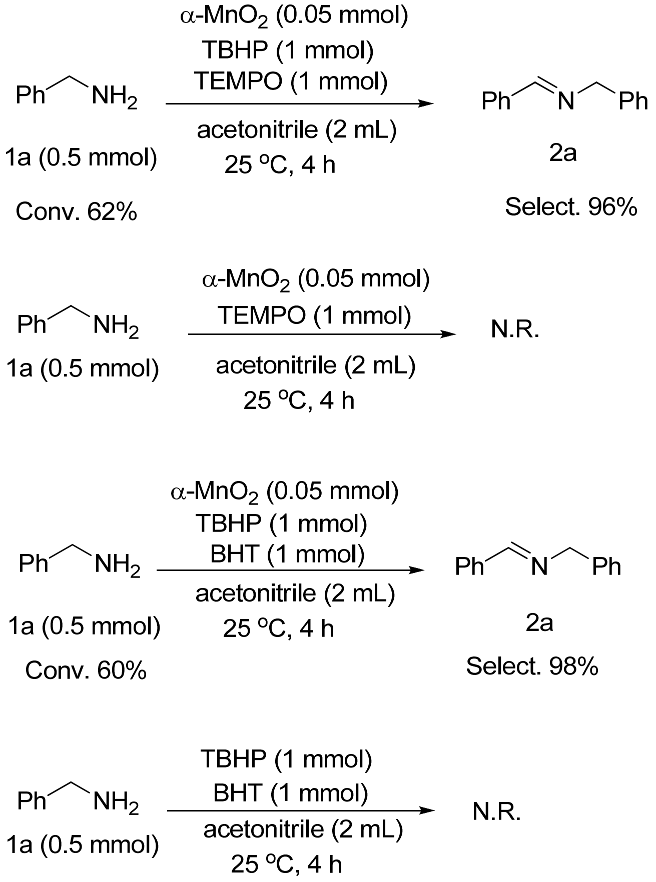


Figure S3 ln (1-C) vs. time linear plot for the oxidation of substituted benzylamine. a) *p*-F, b) *p*-Cl, c) *p*-OCH_3, d) *p*-H.

9. Control tests



Scheme S1 Using TEMPO or BHT as additive for the oxidation of benzylamine

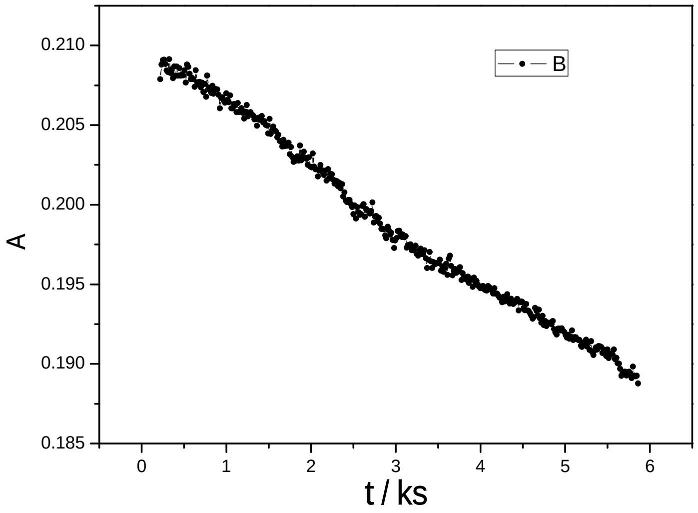


Figure S4 Absorbance of 865 cm^{-1} band collected from ATR-IR vs. time at 30^{o}C.

10. Influence of the amount of water

Anhydrous TBHP was prepared by extraction aqueous TBHP with dichloromethane, followed by drying over 4A zeolite. Acetonitrile was pretreated to remove water.

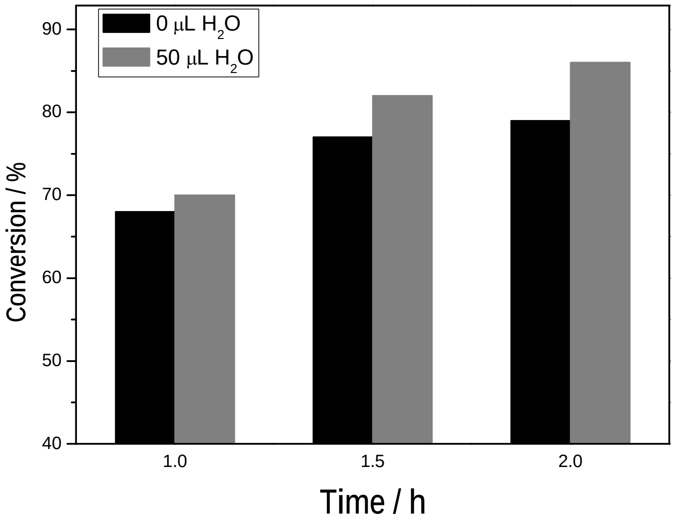


Figure S5 Influence of the amount of water on the catalytic oxidation of benzylamine.

11. Detection of NH_3

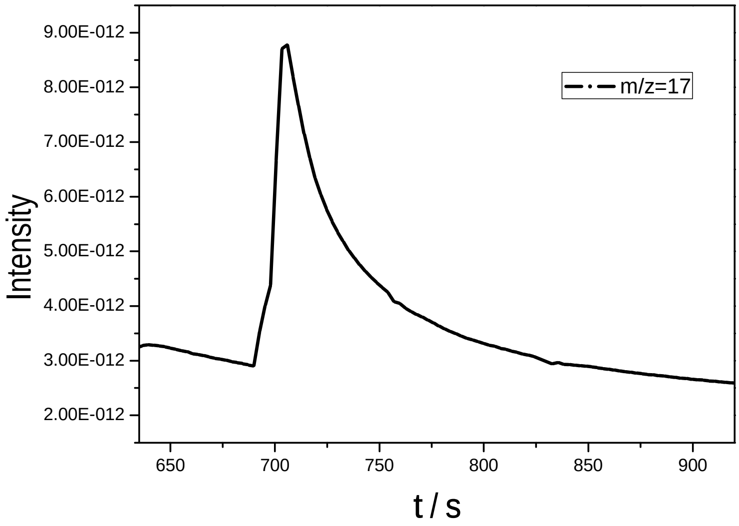


Figure S6 Detection of NH_3 after 4 h catalytic oxidation of benzylamine.

References:

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