Supplementary data

**Kinetics of the catalytic oxidation of toluene over Mn,Cu co-doped Fe2O3: Ex Situ XANES and EXAFS studies to investigate mechanism**

Van Dien Danga,\*, Akhil Pradiprao Khedulkarb, Joemer Adorna Jrb, Van-Anh Thaic, Bidhan Panditd,\*, Xuan-Hoan Nguyena, Tan-Hiep Dange, Lavish Kansalf, N.K.Jhag, Mohd Ubaidullah.

a Faculty of Biology and Environment, Ho Chi Minh City University of Industry and Trade, 140 Le Trong Tan, Ho Chi Minh 700000, Vietnam

b Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu 30013, Taiwan

c Institute of Aquatic Science and Technology, National Kaohsiung University of Science and Technology, Kaohsiung City, 81157, Taiwan

d Department of Materials Science and Engineering and Chemical Engineering, Universidad Carlos III de Madrid, Avenida de la Universidad 30, 28911 Leganés, Madrid, Spain

e Department of Chemical Engineering, Ho Chi Minh City University of Industry and Trade, 140 Le Trong Tan, Ho Chi Minh 700000, Vietnam

f School of Electronics and Electrical Engineering, Lovely Professional University, Phagwara, India

g School of Engineering and Technology, Sharda University, Greater Noida 201310, India

h Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

**\*** Corresponding authors.

E-mail addresses: [diendv@hufi.edu.vn](mailto:diendv@hufi.edu.vn) (Van Dien Dang), [physics.bidhan@gmail.com](mailto:physics.bidhan@gmail.com) (Bidhan Pandit)

**Supplementary materials caption:**

Table S1. The reaction rate of Mn,Cu-Fe2O3 under various O2 and C7H8 concentration at 222 οC.

Table S2. Reaction rates of catalytic oxidation of toluene with fixed O2 concentration (10%)

Table S3. The mixed rate constants dependent on O2 concentration for the L-H model

Table S4. Reaction rates of catalytic oxidation of toluene with various inlet O2 concentrations at different temperatures

Table S5. The mixed rate constants dependent on toluene concentration for the L-H model

Table S6. The mixed rate constants dependent on toluene concentration for the L-H model

Table S7. The activation energy (Ea) based on various kinetic models

Fig. S1. (a) conversion rate as a function of C7H8 concentration at different temperatures (CO2 = 10%, Q = 200 mL min−1); (b) conversion rate as a function of O2 concentration at different temperatures, respectively (CC7H8 = 110 ppmv, Q = 200 mL min−1).

Fig. S2. Conversion rate fitting of C7H8 and CO2

Table S1. The reaction rate of Mn,Cu-Fe2O3 under various O2 and C7H8 concentration at 222 οC.

|  |  |  |
| --- | --- | --- |
| Concentration of C7H8 (mol cm−3) | Concentration of O2 (%) | Reaction rate (mol cm−3 s−1) |
| 4.29 x10-9 | 2.5 | 6.18 x10-11 |
| 4.29 x10-9 | 3.5 | 3.20 x10-10 |
| 4.29 x10-9 | 5.0 | 2.15 x10-9 |
| 4.29 x10-9 | 10.0 | 2.63 x10-9 |
| 4.29 x10-9 | 20.0 | 2.81 x10-9 |
| 4.29 x10-9 | 30.0 | 3.10 x10-9 |
| 1.94 x10-9 | 20.0 | 1.44 x10-9 |
| 6.59 x10-9 | 20.0 | 3.70 x10-9 |
| 9.10 x10-9 | 20.0 | 3.40 x10-9 |

Table S2. Reaction rates of catalytic oxidation of toluene with fixed O2 concentration (10%)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Initial C7H8 concentration  (10−9 mol cm−3) | Reaction rate (10−9 mol cm−3 s−1) | | | |
| 222 οC | 235 οC | 248 οC | 258 οC |
| 7.296 | 1.079 | 1.706 | 2.497 | 3.223 |
| 9.073 | 1.119 | 1.899 | 2.984 | 3.996 |
| 11.294 | 1.281 | 2.076 | 3.262 | 4.438 |
| 15.337 | 1.621 | 2.708 | 4.000 | 5.340 |

Table S3. The mixed rate constants dependent on O2 concentration for the L-H model

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Rate constants | | Heating temperature (οC) | | | |
| 222 | 235 | 248 | 258 |
| Fixed CO2 | K' | 0.191 | 0.298 | 0.477 | 0.590 |
| K'' | 0.024 | 0.018 | 0.038 | 0.042 |

Table S4. Reaction rates of catalytic oxidation of toluene with various inlet O2 concentrations at different temperatures

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Inlet CO2 (10−6 mol cm−3) | Reaction rate (10−9 mol cm−3 s−1) | | | |
| 222 οC | 235 οC | 248 οC | 258 οC |
| 8.93 | 4.85 | 3.76 | 2.67 | 1.67 |
| 6.70 | 4.50 | 3.46 | 2.43 | 1.57 |
| 4.47 | 4.34 | 3.26 | 2.25 | 1.39 |
| 2.23 | 4.39 | 3.20 | 2.01 | 1.08 |

(CC7H8 = 165 ppmv, Q = 200 mL min−1)

Table S5. The mixed rate constants dependent on toluene concentration for the L-H model

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Rate constants | | Heating temperature (οC) | | | |
| 222 | 235 | 248 | 258 |
| Fixed Ce | K1( | 3.395 | 2.370 | 1.399 | 0.718 |
| K1 | 0.176 | 0.161 | 0.136 | 0.110 |

Table S6. The mixed rate constants dependent on toluene concentration for the L-H model

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Rate constants | | Heating temperature (οC) | | | |
| 222 | 235 | 248 | 258 |
| Fixed Ce | K2( | 6.472 | 4.216 | 2.192 | 0.973 |
| K2 | 0.347 | 0.290 | 0.197 | 0.105 |

Table S7. The activation energy (Ea) based on various kinetic models

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Kinetic model | | Ea (kJ mol−1) | Frequency factor (s−1) | R2 |
| P-L | | 164.8 | 11.1 × 1012 | 0.943 |
| MVK | | 59.1 | 0.41 × 106 | 0.993 |
| L-H | O2 adsorption | 61.6 | 45.5 × 103 | 0.980 |
| O adsorption | 28.3 | 50.5 | 0.857 |



Fig. S1. (a) conversion rate as a function of C7H8 concentration at different temperatures (CO2 = 10%, Q = 200 mL min−1); (b) conversion rate as a function of O2 concentration at different temperatures, respectively (CC7H8 = 110 ppmv, Q = 200 mL min−1).



Fig. S2. Conversion rate fitting of C7H8 and CO2