Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering

Supporting Information

Surface hydroxyl groups: the key to CrO_x/TiO_2 catalyst for efficient catalytic oxidation of 2,2'-hydrazine diisobutyronitrile

Hu Zhang,[a] Xingli Zou,[b*] Xueguang Wang,[b] Haijiao Xie,[c] Zheng Jiao[a*] and Xionggang Lu[b*]

[a] School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China.

[b] State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China.

[c] Hangzhou Yanqu Information Technology Company Limited, Zhejiang 310003, China.

Corresponding author. Email address: *xinglizou@shu.edu.cn; zjiao@shu.edu.cn luxg@shu.edu.cn*

Methods and Experiments

Chemicals

2,2'-hydrazobis-isobutyronitrile (HAIBN) was obtained from Daqing Langyuan Chemical Co., Ltd. Anatase (99.9 %) and rutile (99.9 %) was supplied by Xuancheng Jingrui New Material Co., Ltd. Other chemicals of reagent grade including $Cr(NO_3)_3\cdot 9H_2O$ (analytical reagent (AR)), H_2O_2 (30 wt.%) (AR), acetonitrile and so on were all purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals and solvents were used as received without further purification.

Catalyst preparation

A series of mCrO_x/TiO_2(a)-T and mCrO_x/TiO_2(r)-T catalysts were prepared by the impregnation method. Typically, the required amounts of $Cr(NO_3)_3\cdot 9H_2O$ were dissolved in deionized water (20 mL) at room temperature. Followed by addition of TiO_2 powder (5.0 g) into the above solutions and then stirred for 1 h. After that, the suspensions were evaporated under stirring at 60 °C, then the solid products were dried at 100 °C for 12 h, and finally the solid products were calcined in muffle furnace (air atmosphere) at the given temperatures for 6 h to generate the CrO_x/TiO_2-T (T = 300 °C, 400 °C, 500 °C, 600 °C) catalysts with m wt.% nominal CrO_x (m =1.3, 2.7, 4.1, 5.5, 6.8).

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200 diffractometer with Cu-Kα radiation (λ= 0.1542 nm) at a voltage of 40 kV and a current of 40 mA. Surface areas were obtained on an ASAP−2010 automatic surface analyzer (Micromeritics, America) by the Brunauer-Emmett-Teller (BET) method. The pore size distribution (D_p) was calculated using the BJH method and the desorption branch of the isotherm curve; the average pore size (D_a) was also calculated using the BJH formula, and the pore volume (V_p) was calculated using the single point value when the relative pressure was equal to 0.99. Fourier transform infrared spectroscopy (FTIR) spectrum of the surface hydroxyl groups of CrO_x/TiO_2 was measured using Bruker VERTEX7O Fourier transform infrared spectroscopy (Bruker Optics, Billerica, MA). The KBr and CrO_x/TiO_2 catalyst powder samples were dried overnight at 105 °C before sample determination. 0.2 mg CrO_x/TiO_2 catalyst sample and 80 mg KBr sample were mixed and thoroughly ground under infrared light irradiation. The disk containing the sample and KBr was pressed for 5 min under the pressure of 10 Mpa, and then put into the infrared spectrometer for analysis. The scanning range of the sample was 400-4000 cm^{-1}, the resolution was 4 cm^{-1}, and the scan was performed 64 times. Pure KBr was subtracted as blank sample. The chemical valence and ratio of Cr element were detected by an X-ray photoelectron spectrometer (XPS) on an ESCALAB 250Xi spectrometer with Al Kα radiation (hv = 1486.6 eV). The spectra were calibrated using the binding energy of C 1s peak at 284.6 eV.

Catalytic reaction

The catalytic oxidation of HAIBN was conducted in a 50 mL round-bottom flask with a water bath. In a typical experiment, 1 mmol of HAIBN (2.02 g) and 20 mL of solvent were added into the flask. After the complete dissolution, 0.2 g of catalyst was added into the solution under stirring, and kept at the set temperature of 30 °C with an accuracy of better than 0.2 °C for ~0.5 h. After that, 1.2 mmol of H_2O_2 was rapidly added into the reaction solution under stirring at a rate of 500 rpm. The solution was separated from the reaction mixture at appropriate reaction intervals with a filtering syringe in certain time, and the concentration of AIBN in this solution was analyzed by high-performance liquid chromatography (Agilent 1200) equipped with an Agilent ODS-C18 column stabled at 25 °C and a UV-detector set at 254 nm. The isocratic elution was a mixture of acetonitrile: water = 1:1 (vol/vol) with a flow rate of 1 mL/min.

Computational Methods

We have employed the first-principles [1] to perform all spin-polarization density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation. [2] We have chosen the projected augmented wave (PAW) potentials [4,5] to describe the ionic cores and take valence electrons into account using a plane wave basis set with 450 eV kinetic energy cutoff. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-4} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV·Å^{-1}. Finally, the adsorption energies (E_{ads}) were calculated as:

$$E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$$

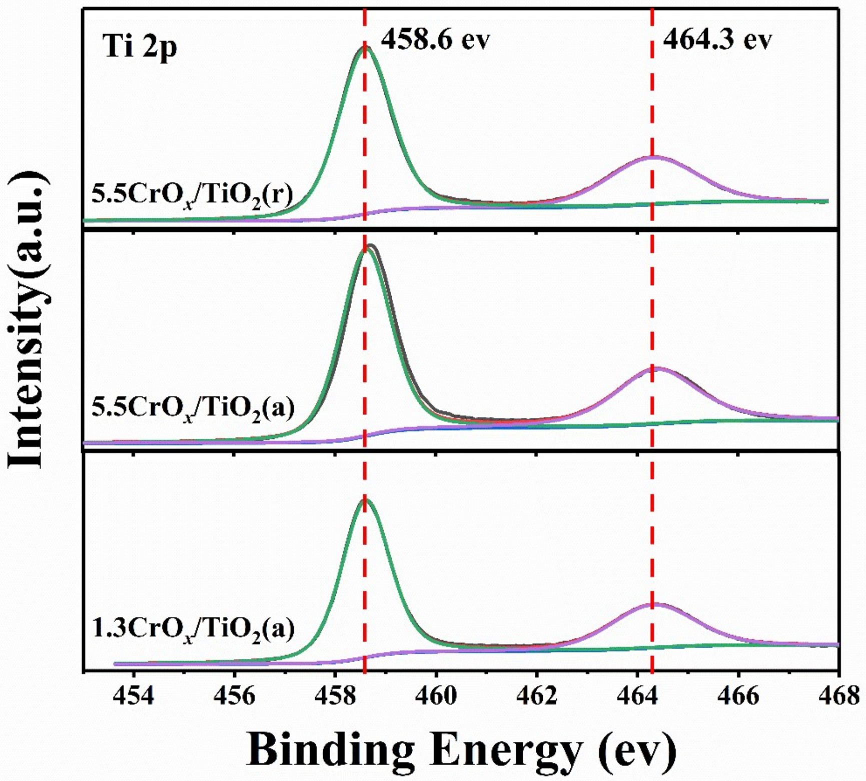
where $E_{ad/sub}$, E_{ad}, and E_{sub} are the total energies of the optimized adsorbate/substrate system, the adsorbate in the gas phase, and the clean substrate, respectively. The Brillouin zone integral uses the surfaces structures of 2×2×1 Monkhorst-Pack K point sampling for structures. The free energy (ΔG) for elemental reaction step was calculated as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where ΔE is the difference between the total energy, ΔE_{ZPE} and ΔS are the differences in the zero-point energy and the change of entropy, T is the temperature (T = 300 K in this work), respectively.

Simulation calculation process

On the one hand, from the perspective of the oxidation of hydrogen peroxide, the following four steps mainly occur on the CrO_x/TiO_2 catalyst. Firstly, hydrogen peroxide combines with Cr(III)-O-Ti through free electrons to realize the chemical adsorption of hydrogen peroxide on the catalyst surface. Next, the successfully adsorbed hydrogen peroxide was converted into two hydroxyl groups and attached to the same chromium atom, during which the electron transfer of Cr element to oxygen element was completed. Then the hydroxyl groups fall off from the catalyst surface successively into the reaction system, and water was formed in the process of reaction and collision, and the generated negative oxygen ions were adsorbed to the catalyst surface at the same time. The specific reaction process is shown in Fig. S2. On the other hand, during the catalytic oxidation of HAIBN, the hydrogen atoms on the aside continuously removed from the surface hydrogen element and form a nitrogen-nitrogen double bond, and the excess electrons were also transferred from the nitrogen



element to the chromium element. So the overall chemical equation of the reaction can be expressed as:

$$HAIBN + H_2O_2 \xrightarrow{CrO_x/TiO_2} AIBN + 2H_2O$$

Fig. S1 XPS spectra of the CrO$_x$/TiO$_2$-400 catalysts

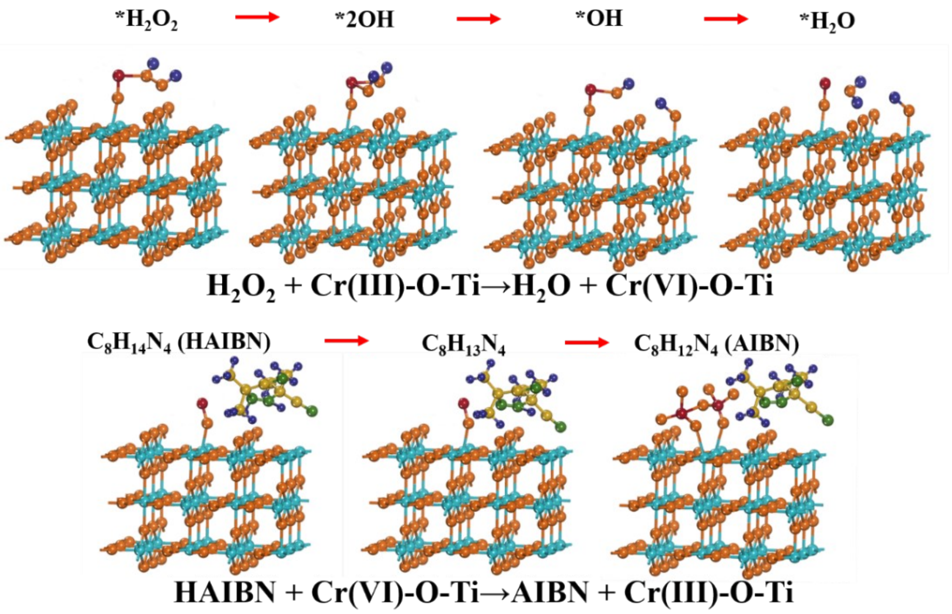


Fig. S2 Detailed step-by-step DFT simulation of this reaction

Table S1 Textural properties of the prepared catalysts

Catalysts	S_{BET}(m^2g^{-1})	V_p(cm^3g^{-1})	D_p(nm)	D_a(nm)
1.3CrO_x/TiO_2(a)-400	108.7	0.2	4.6	9.0
5.5CrO_x/TiO_2(a)-400	102.1	0.2	5.4	9.2
5.5CrO_x/TiO_2(r)-400	23.6	0.1	1.8	25.6

Table S2 The relationship between the content of Cr(III) and Cr(VI) in

CrO_x/TiO_2-T catalysts (the data calculated based on Fig. 1(d))

Catalysts	The proportion of Cr(III) in CrO_x (%)	The proportion of Cr(VI) in CrO_x (%)
1.3CrO_x/TiO_2(a)-400	86.6	13.4
5.5CrO_x/TiO_2(a)-400	73.8	26.2
5.5CrO_x/TiO_2(r)-400	92.6	7.4

References

1 (a) G. Kresse, J. Furthmüller. *Comput. Mater. Sci.* 1996, **6**, 15-50; (b) G. Kresse, J.

Furthmüller. *Phys. Rev. B* 1996, **54**, 11169-11186.

2 J. P. Perdew, K. Burke, M. Ernzerhof. *Phys. Rev. Lett.* 1996, **77**, 3865-3868.

3 (a) G. Kresse, D. Joubert. *Phys. Rev. B.* 1999, **59**, 1758-1775; (b) P. E. Blöchl. *Phys. Rev. B*. 1994, **50**, 17953-17979.