

Electronic Supplementary Material (ESI) for ChemComm.

This journal is © The Royal Society of Chemistry 2020

Supporting Information

Highly efficient oxidation of 2,2'-hydrazobis-isobutyronitrile to 2,2'-azobis-isobutyronitrile over CrO_x/TiO₂ catalyst with hydrogen peroxide

Hu Zhang,^a Shengnan Yue,^a Xiujing Zou,^a Xueguang Wang,^{*a} Xingli Zou,^{*a} and

Xionggang Lu^{*a}

^a State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

Corresponding author. Email address: wxc228@shu.edu.cn; xinglizou@shu.edu.cn;

luxg@shu.edu.cn

Methods and Experiments

Chemicals

2,2'-hydrazobis-isobutyronitrile (HAIBN) was obtained from Daqing Langyuan Chemical Co., Ltd. Titanium dioxide (TiO_2) was supplied by Xuancheng Jingrui New Material Co., Ltd. Other chemicals of reagent grade including $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (analytical reagent (AR)), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (AR), H_2O_2 (30 wt.%) (AR), solvents and metal oxide supports (MgO , ZrO_2 , CeO_2 , La_2O_3 , $\gamma\text{-Al}_2\text{O}_3$) 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 $\text{MeO}_x/\text{support}$ (Me represents Cr, Co, Ni, Cu; support is TiO_2 , MgO , ZrO_2 , CeO_2 , La_2O_3 , $\gamma\text{-Al}_2\text{O}_3$) catalysts were prepared by the impregnation method. Typically, the required amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water (20 mL) at room temperature. TiO_2 powder (5.0 g) was added into the above solutions and then stirred for 1 h. After that, the suspensions were evaporated under stirring at $60\text{ }^\circ\text{C}$, then the solid products were dried at $100\text{ }^\circ\text{C}$ overnight, and finally the solid products were calcined in muffle furnace (air atmosphere) at the given temperatures for 6 h to generate the $\text{CrO}_x/\text{TiO}_2\text{-T}$ ($T = 300\text{ }^\circ\text{C}$, $400\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$) catalysts with 5.5% nominal Cr mass percentages.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200

diffractometer with Cu-K α radiation ($\lambda=0.1542$ nm) at a voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM) measurements were carried out using a FEI Nova NanoSEM 450 (Czech) to observe the morphology of the CrO $_x$ /TiO $_2$ -T catalysts. The chemical valence and ratio of Cr element were detected by an X-ray photoelectron spectrometer (XPS) on an ESCALAB 250Xi spectrometer with Al K α radiation ($h\nu = 1486.6$ 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 ($m_0 = 2.02$ g) and 20 mL of solvent were added into the flask. After the complete dissolution, 0.2 g of catalyst was added in 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 $_2$ O $_2$ was rapidly added into the reaction solution under stirring at a stirring rate of 500 rpm. As the same time, the reaction time was recorded from the first drop of hydrogen peroxide added into the reaction system. 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.

Note that the peaks of AIBN and HAIBN can be clearly seen in the spectrum of liquid

chromatography. Therefore, their peak areas can be integrated separately and recorded as S_{HAIBN} and S_{AIBN} , and the conversion in a certain time can be calculated as follow.

$$Conversion = \frac{S_{AIBN}}{S_{AIBN} \times S_{HAIBN}} \times 100\%$$

In particular, in order to increase the credibility of experimental, the data with error bars were obtained by repeated experiments.

Characterization of HAIBN and AIBN

In order to accurately detect the composition of HAIBN and the synthesis of AIBN. H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts (δ) were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($(CD_3)_2CO$, $\delta = 2.05$ ppm).

Calculation of yield

All the yield data were obtained after HAIBN completely converted via extending the time. A typical post-treatment process of mixed solution after reaction includes the following steps, *i.e.*, the solid catalyst was separated from the reaction liquid by simple filtration and dried to participate in the catalytic reaction repeatedly. After that, the filtrate was distilled under reduced pressure at room temperature, wherein the distilled acetonitrile as the solvent for recycling. Finally, the remaining components (insoluble AIBN and a small amount of water and unreacted H_2O_2) were sequentially filtered, washed, and weighed to obtain crude AIBN. Then, dissolve the crude AIBN in 1 mL of hot ethanol at 50 °C for 30 seconds, and cool down quickly to 0 °C. Finally, filter the white crystalline powder crystallized from cold ethanol at low temperature, and dry it in a cool place and weigh it as m_{AIBN} . The yield of purified AIBN was calculated as

follow.

$$Yield = \frac{m_{AIBN} \times M_{HAIBN}}{M_{AIBN} \times m_0} \times 100\%$$

Where M_{HAIBN} is the molar mass of HAIBN, M_{AIBN} is the molar mass of AIBN, m_0 is the quality of the added substrate. In particular, in order to increase the credibility of experimental, the data of yield with error bars were obtained by repeated experiments.

Recycling of catalyst

In this reaction, AIBN is easy to decompose, which means that the yield of this reaction is a key indicator to measure the catalyst performance. After every reaction run, the catalyst was recovered by simple filtration of the reaction mixture, washing with acetonitrile, followed by drying for 24 h at 100 °C. Then, according to the weight of the recovered catalyst, the corresponding amounts of other materials added into the next cycle were reduced, respectively.

Table S1. The relationship between the content of Cr(III) and Cr(VI) in various types of CrO_x/TiO₂-T catalysts (the data calculated based on Fig. 1b).

Catalyst	The proportion of Cr(III)	The proportion of Cr(VI)
	in CrO _x (%)	in CrO _x (%)
CrO _x /TiO ₂ -300	80.4	19.6
CrO _x /TiO ₂ -400	73.8	24.2
CrO _x /TiO ₂ -500	82.6	17.4
CrO _x /TiO ₂ -600	93.7	6.3

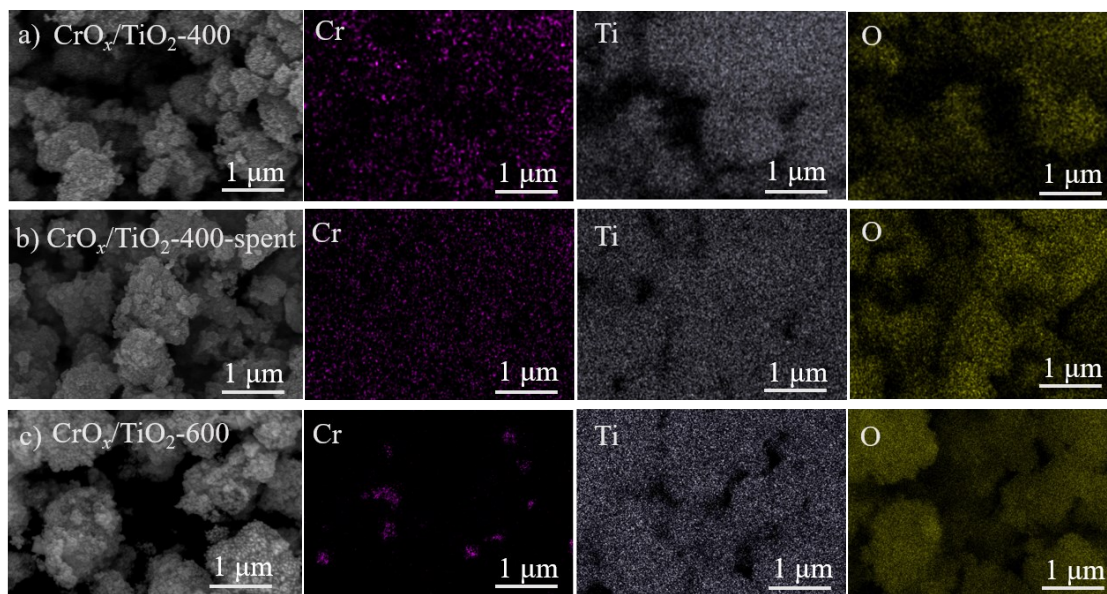


Fig. S1. Typical SEM images and their corresponding elemental mappings of Cr, Ti and O for (a) CrO_x/TiO₂-400, (b) CrO_x/TiO₂-400-spent and (c) CrO_x/TiO₂-600.

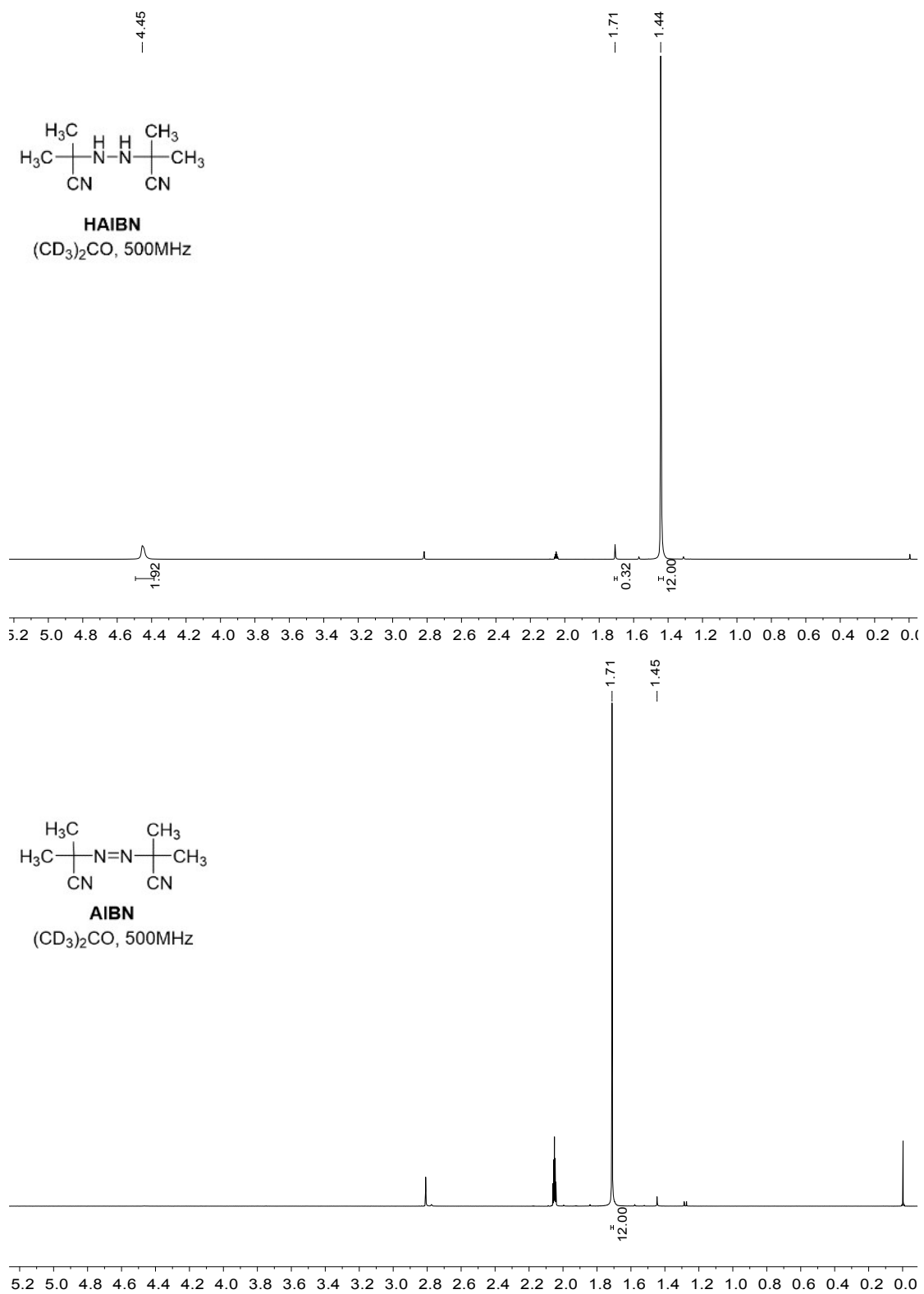


Fig. S2. ¹H NMR spectra of AIBN and HAIBN (**HAIBN**: ¹H NMR (500 MHz, (CD₃)₂CO): δ 1.44 (s, 12H), 4.45 (br, 2H); **AIBN**: ¹H NMR (500 MHz, (CD₃)₂CO): δ 1.71 (s, 12H)).