Supplementary Information

Halloysite nanotubes-supported bismuth catalysts for acetylene hydrochlorination

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1. Experimental Parts

1.1 Catalyst preparation

Bi/HNTs catalysts were prepared using an incipient wetness impregnation technique with the precursors of bismuth chloride ($BiCl_3$). Firstly, the raw material of halloysite nanotubes were dried at 120 ^oC for 1 h to remove the adsorbed water and the obtained halloysite nanotubes were denoted as HNTs used as the catalyst support. Then a $BiCl_3$ aqueous solution was added dropwise to the HNTs (5 g) under stirring and the obtained mixture was processed by ultrasonic treatment for 30 min. After drying at 120 ^oC for 10 h, the catalyst was prepared and denoted as the Bi /HNTs catalyst finally. Additionally, the serial Bi/HNTs catalysts were named in terms of the Bi loading (5 wt%,10 wt%, 15 wt%, 20 wt%), which were designated as 5Bi/ HNTs, 10Bi/HNTs, 15Bi/ HNTs, 20Bi/ HNTs, respectively.

1.2 Catalytic activity test

All catalysts (4 g) were tested on a fixed-bed microreactor (inner diameter of 10 mm) under the atmospheric pressure. Before reaction, nitrogen flow (15 mL min^{-1}) was injected to replace the impurities in the tube firstly and then a certain amount of hydrogen chloride flow (15 mL min^{-1}) was passed to activate the catalyst in the reactor. After the reactor was heated to preset temperature, hydrogen chloride and acetylene with a volume ratio of 1.15 were mixed and fed into the reactor. Finally, the effluent mixture was passed through a NaOH absorption solution and then injected to a gas chromatography (GC 2010, Shimadzu Co., LTD) for detecting the acetylene conversion and the VCM selectivity. In addition, the reaction conditions were: reaction temperature in the range of 120-220 ^oC and a C_2H_2 gas hourly space velocity (GHSV) of 120 h^{-1}.

1.3 Catalyst characterization

The morphologies of the samples were studied with Hitachi SU8220 field emission scanning electron microscope (SEM) at 10 kV. Brunauer-Emmett-Teller (BET) surface areas and pore parameters of the catalysts were measured by Quantachrome autosorb iQ2 equipment. Prior to analysis, approximately 0.15 g samples were degassed at 120 ^{o}C for 5 h and analyzed by liquid nitrogen adsorption at 77 K. The coke deposition of the catalysts was analyzed by thermogravimetric analysis instrument (TGA, TA Q600) under the air atmosphere flowing at 30 mL min^{-1}, and the test temperature was increased from ambient temperature to 800 ℃ at the heating rate of 10 ^{o}C/min. The crystallinities of the samples were analyzed by X-ray powder diffraction spectra (XRD, Bruker D8 ADVANCE) with Cu-Kα radiation at 60 kV and 50 mA over the scan range of 2θ from 10^{o} to 80^{o}. The morphologies of catalysts were observed by transmission electron microscope and high-resolution transmission electron microscope (TEM, HRTEM, Talos F200S) with 200 kV acceleration voltage respectively. The samples were dispersed uniformly in ethanol solution and dropped the resultant mixture onto a copper grid coated by a carbon film before the characterization of TEM. Surface chemical compositions and the valence states of elements were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Escalab Xi+) the spectral calibration detected on the basis of the C1s peak at 284.8 eV. The actual loading of bismuth species in the catalysts were detected by inductively coupled plasma-optical emission spectrometry (ICP-OES, PE Avio 200). The adsorption and desorption properties of reactants on catalysts were investigated by temperature-programmed desorption (TPD) techniques using Micromeritics Auto Chem II 2920.

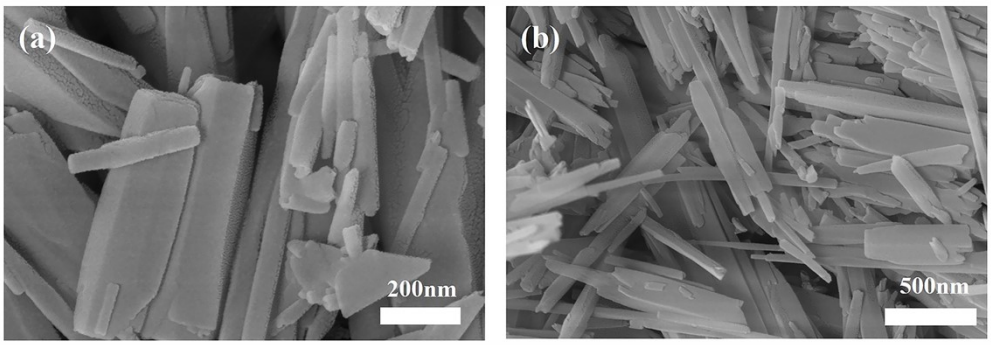

Fig S1 The SEM images of the HNTs (a and b).

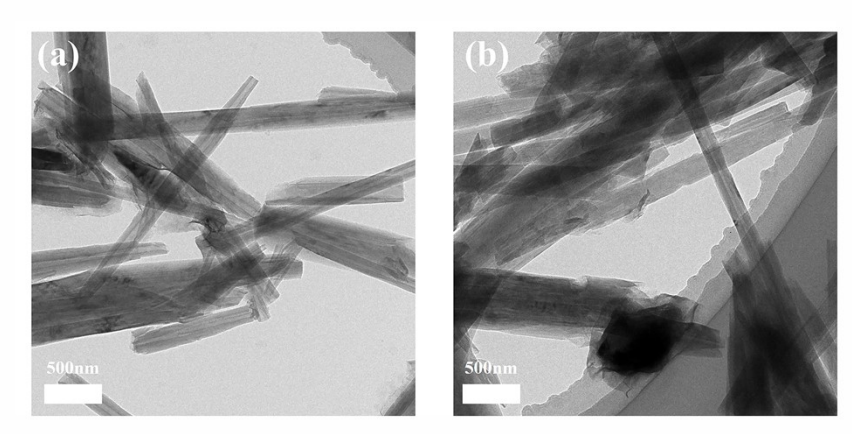

Fig S2 The TEM images of fresh (a) and used (b) 10Bi/HNTs catalysts.

Table S1 Textural properties of 10Bi/HNTs catalysts.

	S_{BET} (m^2/g)	V (cm^3/g^{-1})	D (nm)
HNTs	31.36	0.13	16.08
Fresh 10Bi/HNTs	16.52	0.17	43.14
Used 10Bi/HNTs	14.09	0.14	40.01

[a] S_{BET} specific surface area. [b] V Total pore volume [c] D Average Pore Size

Table S2 The actual Bi content determined by ICP.

Element	Catalysts	Element composition (wt%)	Loss ratio (%)
Bi	Fresh 10Bi/HNTs	9.39	18.74
	Used 10Bi/HNTs	7.63	