Supplementary Information

Hierarchical porous carbon from PVC plastic wastes with efficient catalytic performance for acetylene hydrochlorination

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1 Experimental section:

1.1 Materials

1.2 Catalyst preparation

1.3 Catalyst characterization

1.4 Catalytic performance evaluation

2. Figure Captions:

Fig S1 TG and DTG curves of C-KOH(1:1) support under a nitrogen atmosphere.

Fig S2 XRD patterns of C-KOH(1:1) support.

Fig S3 HAADF-STEM image and the corresponding elemental mapping images of C, O and Pd elements of the fresh Pd/C-KOH(1:1) catalysts.

3. Table Captions:

Table S1 Physicochemical properties of C-KOH(1:1) support.

Table S2 The percentage of different carbon species in C-KOH(1:1) support.

Table S3 Comparison of acetylene hydrochlorination activity of the Pd/C-KOH(1:1) catalyst with other palladium -based catalysts in the literature.

Table S4 ICP results of the Pd/C-KOH(1:1) catalysts.

Table S5 Physicochemical properties of the Pd/C-KOH(1:1) catalysts before and after reaction.

1. Experimental section:

1.1 Materials:

Polyvinyl chloride (PVC) was purchased from Shenzhen Longgang district Shengshi home textile firm. Potassium hydroxide (KOH) was purchased from Tianjin Xinbote Chemical Co. Hydrochloric acid (HCl) solution was purchased from Sichuan Xilong Science Co. Palladium Chloride ($PdCl_2$), purity 59 %, was purchased from Shanghai Titan Scientic Co., Ltd. C_2H_2 gas (purity 99.99 %) and H_2 gas were purchased from Urumqi Xintiangyi Mining Co., Ltd. HCl gas (purity 99.9 %) was purchased from Beijing Malti Technology Co., Ltd. N_2 gas was purchased from Xinjiang Shanxia Mechanical Co., Ltd. All chemical reagents and materials were used as received without further purification.

1.2 Catalyst preparation

Preparation of C-KOH supports: Take the preparation method of C-KOH(1:1) as an example: 6 g of potassium hydroxide and 6 g of Polyvinyl chloride were evenly mixed and calcined at 5 °C/min to 700 °C for 2 h in a tubular furnace, then cooled down to room temperature naturally. The mixture was transferred to a beaker with 1 M HCl added and stirred for 8 h at room temperature. After filtration, it was rinsed several times with deionized water until neutral and vacuum dried at 70 °C for 12 h. C-KOH(1:1) was collected.

The series of C-KOH were prepared by the same method with 1:2 and 2:1 KOH with PVC mass rates were named C-KOH(1:2) and C-KOH(2:1).

Preparation of series Pd/C-KOH catalysts: The Pd-based catalysts were prepared by ultrasound-assisted impregnation method, and the Pd loading capacity of all catalysts was 0.5%. Take the preparation method of Pd/C-KOH(1:1) catalyst as an example: 0.033g palladium chloride ($PdCl_2$) precursor was dissolved in 32.65 mL hydrogen chloride aqueous solution and distilled water, and the mixed solution was stirred until completely dissolved. Then, the mixed solution was added into 4 g C-KOH(1:1) support, which was placed in the environment of ultrasonic bath for 1 h at room temperature. After standing about 25 °C for 12 h, and drying at 120 °C for 8 h, the Pd/C-KOH(1:1) catalyst was acquired.

When the mass ratio of KOH to PVC is 1:2 and 2:1, the catalysts prepared by the same method are named Pd/C-KOH(1:2) and Pd/C-KOH(2:1), respectively.

1.3 Catalyst characterization

The dispersity and crystallinity of the active component in samples were tested by X-ray diffraction (XRD, X'Pert PRO MPD) with Cu-Kα radiation (λ=0.15407 nm) in the scan range of 2θ between 10° and 80°. Field emission scanning electron microscopy (FESEM)and scanning transmission election microscopy (STEM) were carried out to observe the morphology and composition of the catalysts. The pyrolysis process of C-KOH(1:1) and carbon deposition of catalysts were analyzed by Thermogravimetric analysis (TGA, TA Q600) from 30 ℃ to 800 ℃ under nitrogen atmosphere and a heating rate of 10 ℃/min. Brunner-Emmet-Teller (BET, Quanta chrome Auto sorb iQ2) was measured to obtain the surface area and pore size of the carbon material and catalysts. About 50 mg samples were pretreated at 120 ℃ for 12 h and measured at liquid nitrogen temperature (77 K). Raman spectra were gathered by laser Raman spectrometer (Horiba Scientific, LabRAM HR Evolution). The excitation wavelength gratings were 532 nm. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250XI) was performed to analyze the elemental chemical states of catalysts and carbon, and the spectra was revised with standard C1s (284.8 eV). Inductively coupled plasma photoemission spectroscopy (ICP-OES, Agilent ICP-OEST30) was used to detect the true content of Pd in catalysts. In addition, the hydrogen chloride temperature-programmed desorption (HCl-TPD) and acetylene temperature programmed desorption (C_2H_2-TPD) test was performed using Auto Chem II 2920 adsorber to analyze the adsorption capacity of the reactants with the following procedure: the sample (0.75 mg) was mixed with C_2H_2 and HCl for 2 h at 180 ℃, followed by adsorption and sweeping from 25 ℃ to 800 ℃ in a gas stream of 100 mL/min Ar (purity, 99.9 %) and a heating range of 10 ℃/min.

1.4 Catalytic performance evaluation

The performance of all catalysts (4 g) was evaluated in a fixed-bed microreactor (tube 10 mm diameter, 40 mm length). After 15 minutes of nitrogen purging to remove impurities, the mixture of acetylene and hydrogen chloride was through 4 ml of catalysts at 160 °C for 40 min. The results of condition optimization show that the optimal reaction condition can be at 160 °C, a GHSV(C_2H_2) $=120^{-1}$ and V(HCl): V(C_2H_2) = 1.25 in acetylene hydrochlorination reaction. The acetylene conversion (XA) and vinyl chloride selectivity (Svc) were analyzed by a gas chromatography (GC 2010 Shimadzu, Kyoto, Japan) after eliminating unreacted hydrogen chloride or other effluent gases. Acetylene conversion (X_A) and selectivity to VCM (S_{VC}) can be calculated using the following equation:

$$X_A = \frac{\varphi_{A0} - \varphi_A}{\varphi_{A0}} \times 100\%$$

$$S_{VC} = \frac{\varphi_V}{1 - \varphi_A} \times 100\%$$

φ_{A0} is the volume fraction of C_2H_2 in the feed gas, φ_A is the residual volume fraction of C_2H_2 in the product gas, and φ_V is the volume fraction of VCM in the product gas, as determined by GC analysis.[1]

2. Figures Captions

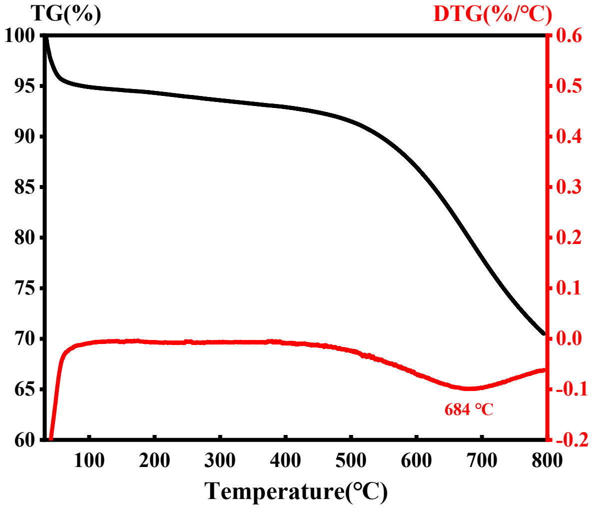

Fig S1 TG and DTG curves of C-KOH(1:1) support under a nitrogen atmosphere.

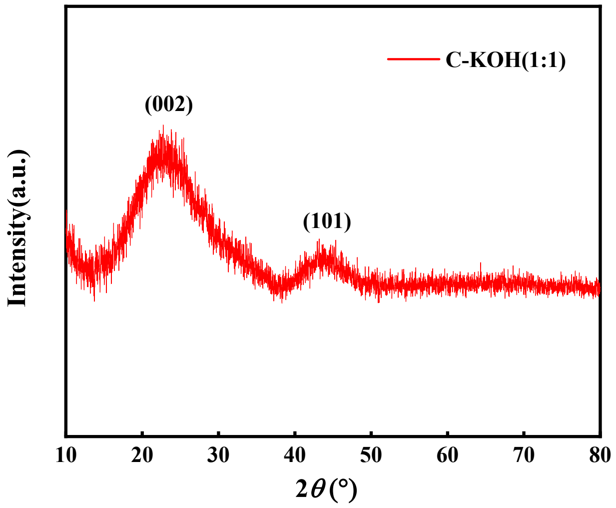

Fig S2 XRD patterns of C-KOH(1:1) support.

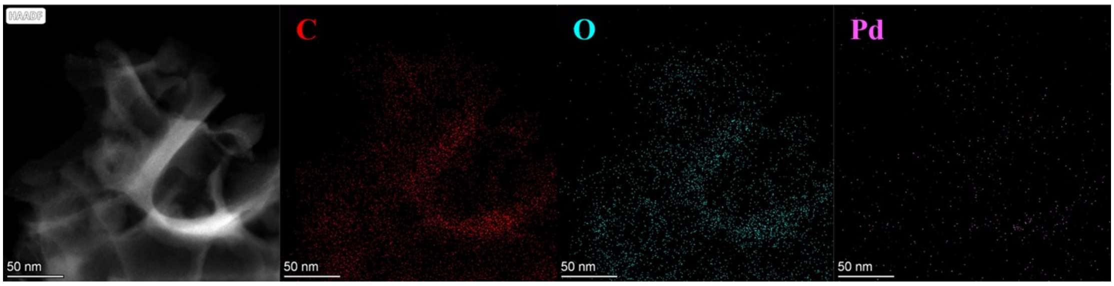

Fig S3 HAADF-STEM image and the corresponding elemental mapping images of C, O and Pd elements of the fresh Pd/C-KOH(1:1) catalysts.

3. Table Captions

Table S1 Physicochemical properties of C-KOH(1:1) support.

	Specific surface ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)
C-KOH(1:1)	652.5	1.66	12.66

Table S2 The percentage of different carbon species in C-KOH(1:1) support.

	sp^2-C	sp^3-C	C─O	C═O	COOH	π─π*
C-KOH(1:1)	42.9%	33.6%	7.2%	5.4%	4.9%	6.0%

Table S3 Comparison of acetylene hydrochlorination activity of the Pd/C-KOH(1:1) catalyst with other palladium-based catalysts in the literature.

Catalysts	GHSV(C_2H_2) (h^{-1})	C_2H_2 conversion (%)	VCM selectivity (%)	References
Pd/C-KOH(1:1)	120	90.2	97.8	This work
Pd/USY	120	74.8	99.4	[2]
Pd/UHNTs	150	90.0	94.0	[3]
Pd/AC	1000	42.0	99.0	[4]
0.5Pd/AC	740	43.6	99.8	[5]
Pd/SAC	120	95.0	99.9	[6]
Pd-[DBU][Cl]/AC	360	96.7	98.9	[7]
Pd/HY	110	99.0	99.0	[8]
$(NH_4)_2PdCl_4$/AC	100	99.7	99.5	[9]
Pd/7B2-HY	110	96	98	[10]

Table S4 ICP results of the Pd/C-KOH(1:1) catalysts.

Element	Catalysts	Content /(w·t%)	Loss of rate /%
Pd	Fresh Pd/C-KOH(1:1)	0.56	42.86
	Used Pd/C-KOH(1:1)	0.32	

Table S5 Physicochemical properties of the Pd/C-KOH(1:1) catalysts before and after reaction.

	Specific surface ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore size (nm)
Fresh Pd/C-KOH(1:1)	532.9	1.41	10.6
Used Pd/C-KOH(1:1)	105.1	0.89	34.0

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