Supporting Information

Electrocatalytic reduction of PhCH₂Br on Ag-Y zeolite modified electrode

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1. Materials and Instruments

All reagents were used as received.

XRD patterns were collected using a Rigaku Ultima IV diffractometer with nickel filtered Cu K α radiation at 35 kV and 25 mA.

SEM images were obtained on a Hitachi S-4800 field-emission scanning microscope.

TEM analyses were carried on a FEI TECNAI G2 F30 operating at 300 KV.

The amounts of Si, Al, Na and Ag etc. in zeolites were quantified by ICP on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HF solution.

Nitrogen adsorption—desorption isotherms at -196 °C were obtained on a BELSORP-max volumetric adsorption analyzer. The samples were out-gassed at 300 °C for 6 h before the adsorption measurement. The specific surface area was determined by the BET method using the data points of P/P₀ in the range of about 0.01-0.2 and the micropore surface area and the micropore volume of the samples were calculated using the *t*-plot method.

XPS was measured using a Thermo Fisher Scientific ESCALAB 250 spectrometer with Al K α radiation (1486.6 eV) as incident beam with a monochromator.

 H_2 -TPR and O_2 -TPO analysis was carried out with the Quantachrome Chem 3000 apparatus.

All electrochemical experiments were performed on a CHI 660D electrochemical work station (Chenhua, Shanghai, China) in an undivided cell.

2. General procedure

2.1 Prepare Ag-exchanged Y zeolite

Prior to Ag⁺ ion exchange, the impurity extraframework cations of NaY were removed by treatment in 0.1 M NaNO₃ for 2 h, followed by filtering, washing with distilled water and drying. The catalysts were prepared by impregnation of 0.5 g NaY in 50 mL 0.04 M AgNO₃ solution for 2 h under stirring in the dark at room temperature. After filtering, washing 3 times with distilled water and drying at 100°C for 1 h, a white powder was obtained. Then the samples were calcinated at 350°C for 3 h to obtain a little yellow powder, labeled Ag-Y.

2.2 Prepare Ag-Y/GC modified electrodes

Prior to the modification, GC electrode was polished with $0.5~\mu m$ alumina, and then sonicated for 5 min each in distilled water and acetone. 3 mg Ag-Y was adhered to the electrode surface with $10~\mu L$ POV as adhesive. The modified electrode, labeled Ag-Y/GC, was air dried.

2.3 Electrochemical process

Linear sweep voltammograms were carried out using a traditional three-electrode system with a GC (d = 2 mm), Ag (d = 2 mm), or Ag-Y/GC (d = 2 mm) as working electrode, a Pt wire as counter electrode and a Ag/AgI/I $^-$ as reference electrode, in MeCN – 0.1 M TEABF $_4$ – 5 mM PhCH $_2$ Br solution.

Potentiostatic electrolysis were carried out with a Ag, GC or Ag-Y/GC as working electrode, a Mg rod as sacrificial anode and a Ag/AgI/I as reference electrode, in MeCN – 0.1 M TEABF₄ – 0.1 M PhCH₂Br solution in the presence of N_2 or CO_2 . The products were extracted by diethyl ether and quantitatively analyzed by GC instrument (GC-2014, Shimadzu). For the electrocarboxylation carried out in the presence of CO_2 , the electrolyte should be esterified by addition of anhydrous K_2CO_3 and methyl iodide at 50-60°C for 5 h before the extraction.

3. N_2 adsorption-desorption isotherms

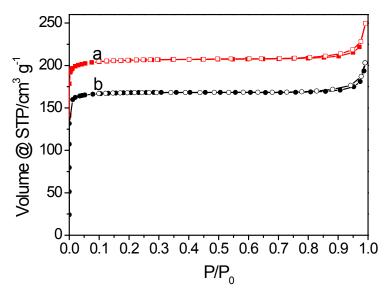


Fig. S1 N_2 adsorption-desorption isotherms of (a) NaY and (b) Ag-NaY

4. ICP data for Ag-Y

Table S1 Influence of concentration of AgNO₃ to exchange capacity

| Entry | Zeolite | C_{Ag^+} (mol L ⁻¹) | Ion concentration (g L ⁻¹) | | | | Exchange |
|-------|---------|-----------------------------------|--|-----------------|--------------------|------------------|----------|
| | | | Ag^+ | Na ⁺ | Si^{2+} | Al ³⁺ | capacity |
| 1 | NaY | 0 | | 82.9 | 319.9 | 104.8 | |
| 2 | Ag-Y-2 | 0.02 | 186.8 | 46.3 | 294.4 | 102.3 | 25 |
| 3 | Ag-Y-4 | 0.04 | 285.3 | 23.3 | 282.4 | 97.9 | 39 |
| 4 | Ag-Y-6 | 0.06 | 337.4 | 18.0 | 301.8 | 104.8 | 43 |
| 5 | Ag-Y-8 | 0.08 | 344.6 | 8.3 | 265.5 | 98.7 | 48 |