Supporting Information

Electrocatalytic reduction of $PhCH_2Cl$ on Ag-ZSM-5 zeolite modified electrode

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1. Materials and Instruments

All reagents were used as received, except for acetonitrile which was dried over 4Å molecular sieves.

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

SEM measurements were achieved on a Hitachi S-4800 instrument.

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.

Nitrogen adsorption–desorption isotherms at 77K were obtained on a BELSORP-max equipment. Specific surface areas were calculated according to the BET-method using five relative pressure points in the interval of 0.01 - 0.1, and the external surface 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 Kα radiation (1486.6 eV) as incident beam with a monochromator.

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

The conductivity was determined by Four-Point Probes RST-8.

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

Electrocarboxylation yield was quantitative analyzed by Gas Chromatography (Shimadzu, GC-2014).

2. General procedure

2.1. General procedure for preparation of Ag-ZSM-5 zeolite modified electrode (Ag-ZSM-5/SS ZME)

The stainless steel substrates (SS-304) were polished by abrasive paper (400 grit), then cleaned with distilled water and acetone in an ultrasonic cleaner. The Ag-ZSM-5/SS zeolite modified electrodes were synthesized by a one-step process in a solution with a molar composition of Al:NaOH:TPAOH:TEOS:$AgNO_3$:H_2O = 0.0018:0.64:0.16:1.0:0.078:92.0. The clear solution was aged at room temperature for 4 h under stirring and then transferred to a 100 mL Teflon-lined Parr autoclave. The stainless steel substrates were fixed inside the synthesis solution. Crystallization was carried out in a convection oven at 175 ºC for 16 h. The samples were then removed from the autoclave and cooled.

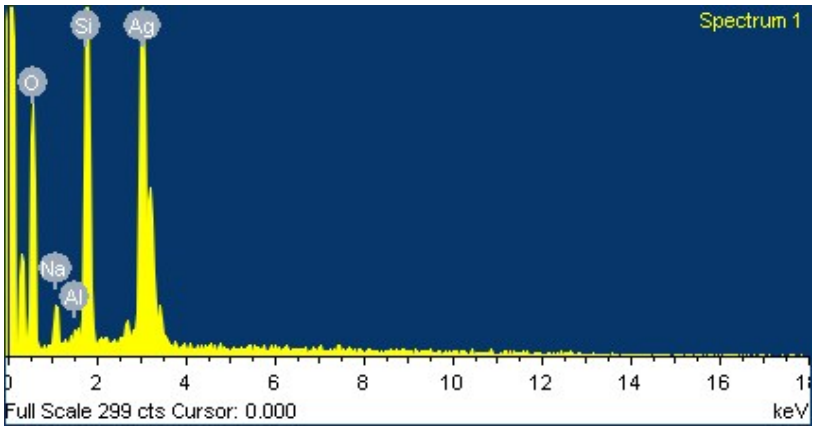
2.2. Electrochemical measurements of Ag-ZSM-5/SS

Cyclic voltammetry were carried out using a traditional three-electrode system with a Ag, or Ag-ZSM-5/SS as working electrode, a Pt wire as counter electrode and a Ag/AgI/I^- as reference electrode, in 2.6 mM $PhCH_2Cl$ – 0.1 M TEAP – MeCN solution.

Potentiostatic electrolysis were carried out with a Ag or Ag-ZSM-5/SS as working electrode, a Mg rod as sacrificial anode and a Ag/AgI/I^- as reference electrode, in 0.05 M $PhCH_2Cl$ – 0.1 M TEAP – MeCN solution in the presence of CO_2. After the electrolytsis, the electrolyte was esterified by addition of anhydrous K_2CO_3 and methyl iodide at 50-60^{o}C for 5 h. The solution was treated with aq HCl and extracted by diethyl ether. The organic layers were washed with H_2O, dried over $MgSO_4$, and evaporated before quantitatively analyzed by GC.

The electrochemically active surface areas (ECSA, cm^2) of Ag-ZSM-5/SS were measured by analyzing the charge associated with Pd under potential deposition stripping, associated with theoretical value of 400 $\mu C/cm^2$ for full coverage of Pb on Ag.[1]

3. Characterization of Ag-ZSM-5/SS



Element	Weight (%)	Atomic (%)
O K	49.51	76.52
Na K	2.81	3.02
Al K	0.09	0.08
Si K	14.53	12.80
Ag L	33.07	7.58
Totals	100.00	

Fig. S1 The EDX spectrum of Ag-ZSM-5

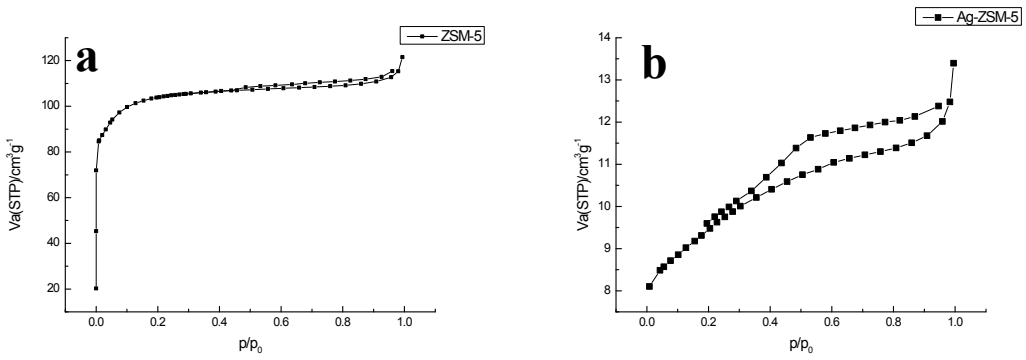


Fig. S2 N_2 adsorption–desorption isotherms for ZSM-5 (a) and Ag-ZSM-5(b)

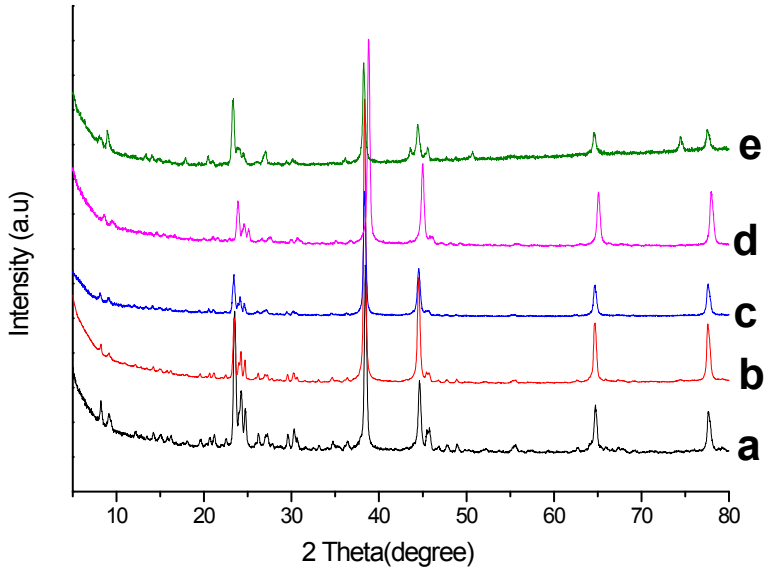


Fig. S3 XRD patterns of Ag-ZSM-5/SS electrodes prepared under different $AgNO_3$ concentration. a. Ag-ZSM-5/SS (0.0125 M), b. Ag-ZSM-5/SS (0.025 M), c. Ag-ZSM-5/SS (0.05 M), d. Ag-ZSM-5/SS (0.075 M), e. Ag-ZSM-5/SS (0.1 M).

4. Characterization of used Ag-ZSM-5/SS

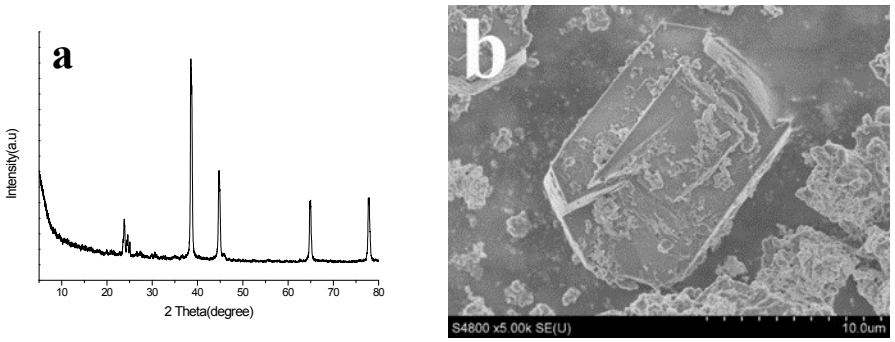


Fig. S4. XRD pattern (a) and SEM image (b) of Ag-ZSM-5/SS after bulk electrolysis.

Reference

1. E. Kirowa-Eisner, D. Tzur and E. Gileadi, *J. Electroanal. Chem.*, 2008, **621**, 146-158.