Supporting Information

Ethylene production: process design, techno-economic and life-cycle assessments

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1. Catalyst Synthesis and Characterization

The boron-containing CHA zeolite was synthesized according to previously reported procedures.[1] First, a 17.2 g trimethyladamantylammonium hydroxide solution (TMAdaOH, 25 wt%) was added to 20.7 g deionized (DI) water. After that, 0.413 g boric acid ($B(OH)_3$) was dissolved in the solution with stirring for 30 min. Finally, 5.03 g Carbosil M-5 was added to the resulting solution while being stirred. The gel was transferred to a 45 mL Teflon-lined autoclave and heated at 160°C for 3 days under rotation. The zeolite product was washed with DI water and centrifuged, then dried at 80 °C overnight. The as-made zeolite was calcined at 580 °C in flowing air for 8 h with a ramping rate of 2°C min^{-1}. The powder product after calcination is denoted as B-CHA. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker powder diffractometer (D8 XRD) with a Cu Ka radiation (40 kV, 40 mA) as the X-ray source, in the range 2θ = 4-50° with a step size of 0.04° and 1 s per step. The morphology was determined using a scanning electron microscope (SEM, Auriga-60, ZEISS). Prior to the SEM measurement, the samples were coated with gold/palladium alloy. Textural properties were obtained by employing N2 physisorption experiments at -196.15°C on a 3Flex surface characterization analyzer (Micromeritics). Before the physisorption experiments, all the samples were degassed at 300°C overnight under vacuum. The micropore volume was determined using the t-plot method and the specific surface area was determined using the BET method. The boron and silica contents of the samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Galbraith Laboratories, TN).

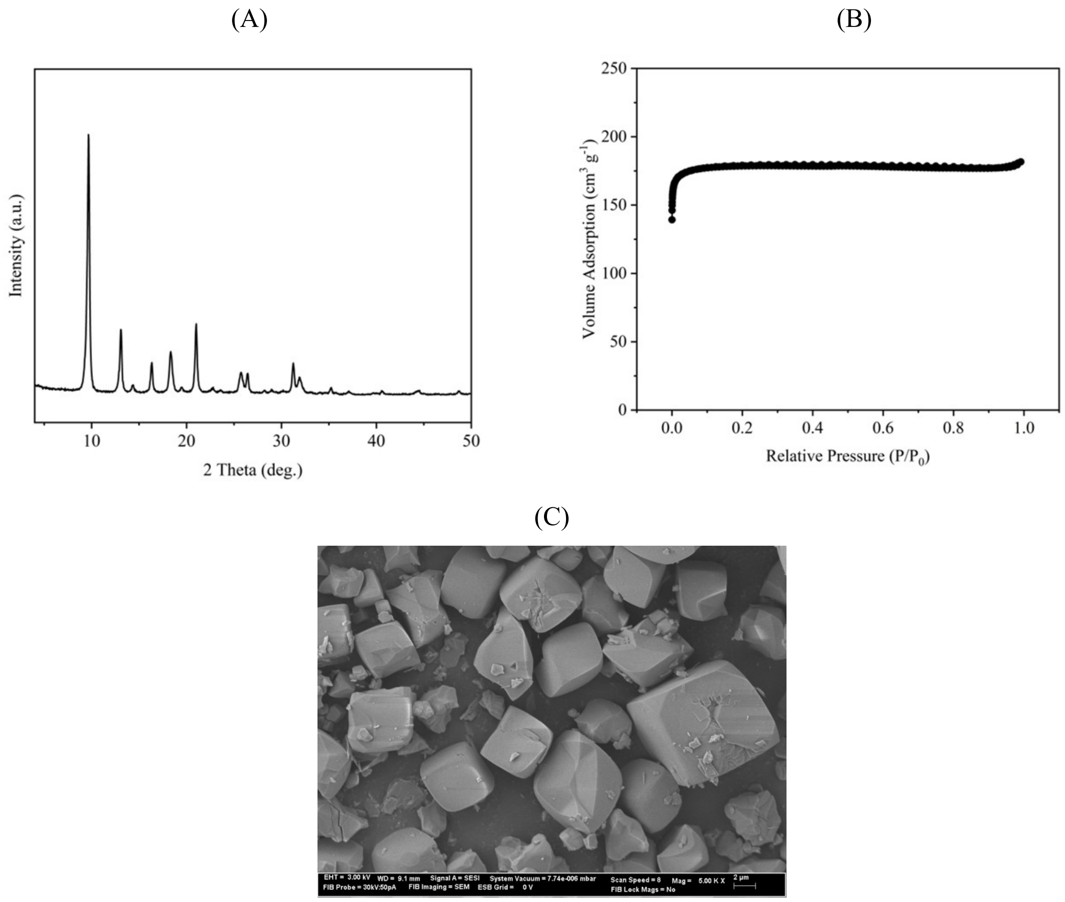

Figure S1. Characterization of B-CHA. (A) An XRD pattern, (B) N_2 physisorption, and (C) an SEM image.

Table S1. Boron contents and textural properties of B-CHA.

Catalyst	Boron content (wt%)	Micropore volume[a] ($cm^3\ g^{-1}$)	Mesopore volume ($cm^3\ g^{-1}$)	BET surface area[b] ($m^2\ g^{-1}$)
B-CHA	1.01[b]	0.26	0.02	538

[a]Determined by *t*-plot method.

[b]Determind by BET method.

2. Experimental Procedures

The catalyst samples in powder form were pressed, crushed, and sieved (20-40 mesh) to particle sizes ranging from 400 to 841 mm. The ODHE was measured in a fixed-bed quartz reactor (I.D. = 4 mm, O.D. = 6 mm, length = 536 mm). The catalyst bed was kept in place using silica glasswool plugs. A thermocouple was placed adjacent to the catalyst bed for temperature control and measurement. In each experiment, the reactor was first heated to the highest temperature (typically 600°C) with a ramping rate of 5°C min^{-1} under 20 vol% O_2/ 80 vol% He (total flow rate = 15 mL min^{-1}). After the temperature stabilized, the catalysts were treated with the reaction mixture with a composition of 20 vol% C_2H_6/ 12 vol% O_2/ 68 vol% He (total flow rate = 15 mL min^{-1}) until stable conversion was obtained as there is an activity induction period for boron-containing catalysts.[2-4] The temperature was then reduced to the desired temperature, and the reaction was run for predetermined time intervals. The average results over the interval were used to compute the results. The reactor effluent was injected into an online gas chromatograph (GC) (Agilent 7890) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID with an RT-Q-BOND column was used for CH4 analysis. The TCD had a HayeSep Q column and a Molseive 13X column in a series configuration and was used for C_2H_6, O_2, C_2H_4, CO, and CO_2 analysis. More details can be found in the reference.

3. Assumptions used in Techno-economic Analysis

The equipment and operating costs are estimated by Aspen Economic Analyzer® V12. The main assumptions applied in the economic analysis are as follows:

1. The plant capacity of the processes was controlled between 600,000-800,000 t ethylene production annually based on the communication with the industry. For the base scenario of oxidative dehydrogenation of ethane (ODHE) and the steam cracking processes, they are 733,000 t/y and 635,000 t/y, respectively.
2. A 20-year discounted cash flow rate-of-return analysis is executed to ascertain the minimum selling price (MSP) of ethylene, which renders the net present value (NPV) of the project as zero. These encompass a discount rate of 10%, a tax rate of 30%, the utilization of a straight-line depreciation method spanning 7 years, and an operational period of 8000 hours annually.
3. The furnace cost (56.7 MM$) is set five times higher than that of the reactor in the steam cracking process.
4. The market price of ethane is estimated as 200 USD/t[5] and of oxygen is 85 USD/t.[6]
5. The cost of triethylene glycol (TEG) is 1,320 USD/t,[7] of methyldiethanolamine (MDEA) is 2,660 USD/t.[8]
6. The boron-containing zeolite chabazite (B-CHA) catalyst cost is estimated at 165,000 USD/t, from which fumed silica contributes 6,470 USD/t,[9] boric acid 720 USD/t,[10] N,N,N-trimethyl-1-adamantyl ammonium hydroxid (SDA) solution (25%) 60,000 USD/t, deionized water 850 USD/t,[11] and the remaining costs come from the support and the catalyst manufacturing 11,000 USD/t.[12] The catalyst life is taken to be 12 months. The fact that B-CHA maintained high activity and the nearly unchanged characterization after ~60 h ODHE confirm the excellent stability of B-CHA. Therefore, after every 12 months only the cost of the reactivation of the catalyst would be required.
7. Heat integration was implemented for both the ODHE and steam cracking processes in the Aspen Energy Analyzer V12.
8. The cost of wastewater treatment is 1.0 USD/m^3.[13]
9. The minimum price of lubricants is calculated by keeping the selling price of high pressure (HP) steam, liquefied petroleum gas (LPG), and fuel gas generated are sold at 25 USD/ton, 550 USD/ton,[14] and 200 USD/ton,[15] respectively.

It is worth mentioning that the assumptions linked to the prices of SDA solution (25%) and HP steam are derived from the personal communications with industry sources (Shanghai Maikelin

Biochemical Technology Co.,Ltd; Sinopec Energy Management Co., Ltd), as the bulk prices of these components are not available from public resources.

Table S2. Summary of the capital and operating cost of the steam cracking and ODHE processes

Route	ODHE	Steam cracking
	Cost (MM$)	
Total direct cost (Equipment, site development, and warehouse, along with additional expenses for the piping and instrumentation)	407.79	492.13
Total indirect cost (Portable and field expenses, project contingency costs, and home and office construction costs)	244.78	295.28
Working capital	32.64	39.37
Land	20.74	25.02
Total Capital Cost	706.13	851.81
	Cost per year (MM$)	
Raw materials	256.29	192.84
Utilities	115.42	66.13
Catalyst	9.69	0
Operating labor	55.32	66.73
General manufacturing cost	141.23	170.36
Total manufacturing cost	577.95	496.06

4. Assumptions used in Life-Cycle Assessment:

The LCA study in this work is an attributional LCA that only focuses on comparing two technologies that both produce ethylene, as opposed to the consequential LCA that analyzes future scenarios involving decision-making. The background data are taken from the Ecoinvent 3.9 database that includes comprehensive and regional data. The activities for conducting the life cycle impact assessment of ethylene production are outlined in Table S4.

Table S3. Inputs and outputs of the 1 kg ethylene production via steam cracking and ODHE processes. (Data are derived from rigorous process simulations in Aspen Plus V12)

Route	ODHE	Steam cracking
	Inputs	
Ethane (kg)	1.24	1.11
Oxygen (kg)	3.25	0.00
Water (kg)	0.00	72.14
Triethylene glycol (kg)	5.46E-05	4.16E-06
Low pressure steam (kg)	1.30	0.029

Refrigerant 1 (kg*day)	6.51	26.79
Refrigerant 2 (kg*day)	117.00	0
Refrigerant 5 (kg*day)	85.60	19.50
Electricity (kWh)	0.59	0.68
Outputs		
Ethylene (kg)	1.00	1.00
Wastewater (kg)	1.07	0.45
High pressure steam (kg)	3.18	0.00
Fuel gas (kg)	0.00	0.13
Liquefied petroleum gas (kg)	0.00	0.017

Table S4. Activities from the Ecoinvent 3.9 database for life-cycle impact assessment of ethylene production. (Activity refers to a specific process or operation within a product's life cycle that consumes resources or generates environmental impacts).

Product	Activity
Electricity	Electricity, high voltage {US-WECC} | heat and power co-generation, natural gas, combined cycle power plant, 400MW electrical | cut-off, S
Ethane	Ethane, {GLO} | market for ethane | cut-off, S
Refrigerant	Operation, reefer, cooling {GLO} | operation, reefer, cooling, 40-foot, high-cube, carbon dioxide, liquid as refrigerant | cut-off, S
Oxygen	Oxygen, {GLO} | market for oxygen | cut-off, S
Steam	Steam, in chemical industry {RoW} | steam production, in chemical industry | cut-off, S
Water	Water, tap water {GLO} | tap water production, underground water without treatment | cut-off, S
Triethylene glycol	Triethylene glycol, {GLO} | market for triethylene glycol | cut-off, S
Wastewater	Wastewater, average { RoW} | treatment of wastewater, average, wastewater treatment | cut-off, S

Other important assumptions for LCA include:

1) Most of the water condensate in flash unit in the ODHE process could be recycled, and no make-up water is needed as some additional waters are produced alongside with the ethylene product.

2) Because the buildings could be used for other purposes and catalysts are relatively stable during their life cycle, their contributions are not included in the life cycle assessment.

3) The "avoided burden" method is deployed to give credit for selling byproducts including LPG, fuel gas, and HP steam. Economic allocation is performed on the LPG and fuel gas generated in the steam cracking process. Meanwhile, system expansion is performed on the HP steam produced in the ODHE process. Based on Econivent v3.9 HP steam data, it is estimated that 1 kg HP steam production will lead to 0.612 CO_2 reduction in the market.

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