Supporting Information

Impact of Water Removal Method on Tetraethyl Orthosilicate Direct Synthesis: Experiment and Process Assessment

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EXPERIMENTAL SECTION

TEOS Synthetic apparatus.

All the TEOS syntheses were carried out using the reaction apparatus shown in Figure S1. It is composed of a reaction vessel, a thermometer, a pressure gauge, and a mechanical stirrer. The temperature inside the apparatus was measured using the thermometer.



Figure S1. Reaction apparatus (30 mL autoclave) for TEOS synthesis

Additional Data of TEOS Synthesis.

The experimental results used for the further process evaluation are presented in Table 1 of the main text. Detailed results of the TEOS syntheses under various conditions are presented in Table S1. Although the TEOS yields are slightly varied with data; however, these results follow the same trend that of the data in Table 1. The optimal CaO/SiO₂ ratio is about 3 for the highest TEOS yield, while the TEOS yield is somewhat decreased for longer reaction time at the high CaO/SiO₂ ratio.

SiO ₂	CaO/SiO ₂	Reaction	Time	TEOS(0/)	Disiloxane	
(mmol)	(mol ratio)	temperature (°C)	(min)	1EOS (%)	(mmol)	
4.5	1	184	30	32.5	0.17	
9	1	189	20	25.9	0.29	
4.5	2	190	15	52.6	0.24	
4.5	2	190	20	51.8	0.21	
4.5	2	190	30	53.6	0.04	
4.5	2	190	60	55.6	0.10	
4.5	2	182	30	51.9	0.03	
9	2	189	20	48.8	0.63	
4.5	3	190	15	60.5	0.16	

Table S1. Results of TEOS synthesis with various reaction conditions

4.5	3	190	20	75.4	0.08
4.5	3	190	30	70.8	0.05
4.5	3	190	60	58.6	0.07
9	3	189	20	75.9	0.18
4.5	4	190	15	71.4	0.12
4.5	4	190	20	75.8	0.09
4.5	4	194	20	75.8	0.09
4.5	4	190	30	64.9	0.01
4.5	4	190	60	39	0.00
9	4	188	20	63	0.15
9	5	190	15	45.5	0.27
9	5	195	20	62.1	0.05
9	5	191	30	50.7	0.01

PROCESS DESIGN SECTION

Similarly to our previous study¹, we estimated the necessary thermodynamic and physical properties and the vapor–liquid equilibrium data using the available information.²⁻⁶ By inputting these new data to Pro/II, we could modify the component library and vapor–liquid equilibrium data of this process simulator. The process was designed and simulated using the non-random two-liquid (NRTL) thermodynamic model. The operation conditions of the main processing units, such as the number of stages, location of feed stage and reflux ratio of the distillation columns, were optimized using heuristic knowledge. Heat integration is applied where applicable. Suitable temperatures of the hot and cold output streams were selected for design of heat exchanger.

General description of MS process. The MS process is shown in Figure S2. More detail description can be found in ref 1. The raw materials (ethanol and silica) are mixed in mixer (a). The resulting stream (1) passes to the heat exchanger (b), where it receives heat transferred from the reaction-product stream 4. After further heated in the heater (c), it is transferred to the reactor (d). The reaction-product stream 4 passes through the heat exchanger (e) and the cooler (f), which lower its temperature. The water is removed in the water absorber (g), which is packed with 3A molecular sieve. Finally, the reaction-product mixture stream 9 is directed to the separation system including two distillation columns, which recovers the unconverted ethanol and purifies the TEOS to the desired purity.

General description of conventional process. The conventional process is shown in Figure S3. It is detailed in ref 1. This process has almost the same structure with that of MS process. However, metallurgical silicon (Si_{mg}) is used in replacing for silica. It is heated together with CuO at high temperature in a calcinator, before it can be used for TEOS synthesis.

The main process units and key parameters included in the considered processes are summarized in Table S2.

D rocoss units	Daramatara	Conventional	MS	CaO
Process units	Farameters	process	process	process
Heater	temperature (°C)	180	240	190
Reactor	temperature (°C)	180	240	190
	pressure (bar)	29	58	25
Heat exchanger c	hot product temperature (°C)	137	-	-
Heat exchanger f	hot product temperature (°C)	82	-	-
Heat exchanger b	hot product temperature (°C)	-	87	-
Heat exchanger e	hot product temperature (°C)	-	72	-
Cooler	temperature (°C)	25	60	-
Water absorber	pressure (bar)	-	1	-
Gas separator	pressure (bar)	1	-	-
	pressure (bar)	1	1	1
Ethanol	number of stage	10	16	17
recovery column	feed stage	4	10	11
	reflux ratio	0.3	0.2	0.2
	pressure (bar)	1	1	1
TEOS	number of stage	38	18	18
purification column	feed stage	14	6	8
	reflux ratio	12	0.3	0.3

Table S2. Main process units and key parameters

PROCESS EVALUATION AND DISCUSSION

The evaluation indicators were calculated as described in ref 1.

Production cost. The production cost includes the operation and investment costs, alongside other costs such as maintenance cost, labor cost, and property tax. These costs were calculated using the data in Table S3. The operation cost is the summed costs of the raw materials and utilities required for operating the synthesis process. The calculated consumption amounts of these inputs are based on the mass and heat balance data obtained in the process simulation, and their costs are determined from the estimated prices shown in Table S4. The investment cost sums the costs of all main equipment involved in the considered processes (the reactor, heater and distillation column). These apparatuses are sized and costed using Guthrie correlation⁷, and updated using the Chemical Engineering Plant Index 2016.⁸ Based on the total investment cost, the 10-year depreciation is calculated by the straight-line method. The calculated capital cost of the considered processes are summarized in Table S5.

Greenhouse gas (GHG) emissions. The GHG emissions (CO₂ equivalent) encompass all carbon dioxide, methane, and nitrous oxide emissions. In TEOS synthesis, GHGs are mainly released from the raw material production and the utilities required in the synthesis process. Thus, the total GHG emissions of the synthesis process are directly proportional to the consumed amounts of raw materials and utilities. To evaluate the GHG emissions, we extracted the life-cycle GHG emission data of the main raw materials and utilities from available source.⁹ These data are summarized in Table S4.

In this study, we compared the TEOS processes using in situ water removal by CaO and ex situ water removal by MS, and established common basis conditions for evaluating and comparing the two processes. The raw materials (ethanol and silica) of both processes originated from the same resources. To simplify the comparison, nonrenewable resources were used in the present study, although these can be replaced with renewable resources (such as ethanol derived from biomass and silica extracted from rice husk ash). Here, ethanol was obtained by hydrating ethylene, and silica was obtained by pre-treating quartz sand. High-grade silica can be obtained by different techniques of quartz-sand treatment. The GHG emissions of these different treatments range from 0.029 to 0.075 kg $CO_2/$ silica.¹⁰ When evaluating the GHG emissions of the CaO and MS processes, we adopted the average value of 0.053 kg CO_2/kg silica.

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Project lifetime	10 years
Working capital	15% process capital cost
Labor	10% operating cost
Maintenance	6% process capital cost
Supplies	2% process capital cost
Property tax	3% process capital cost
Depreciation	straight line

Table S3. Basic parameters in the production-cost evaluation

Table S4. Price and GHG emissions of main utilities and raw materials¹

Raw material/Utility	Price (\$/kg)	GHG emissions (kg CO ₂ /kg)	
Raw Material			
ethanol	0.7 ^a	1.67 ⁹	
silica	0.2^{a}	0.053^{10}	
Utility			
steam	0.02 ^a	0.17^{9}	
fuel oil	0.35 ^a	3.469	
cooling water (recycled)	0	0	

a Average estimated price as of 2016.¹

Table S5. Estimated capital costs (dollars) of main equipment in the alternative TEOS synthesis processes

Main aquinmont	MS process ¹ -	CaO process					
Main equipment		Alt.1	Alt.2	Alt.3	Alt.4	Alt.5	
Heat exchanger	153,136	-	-	-	-	-	
Heater	18,378	540,270	322,004	224,242	262,021	265,944	
Cooler	15,044	-	-	-	-	-	
Reactor	653,902	200,193	135,232	102,702	115,403	116,015	
Distillation columns	928,617	1,314,612	902,204	700,011	781,851	789,146	
Total	1,769,077	2,055,076	1,359,440	1,026,956	1,159,274	1,171,105	

(Alt.: alternative CaO-driven process; synthesis conditions detailed in Table 1)



Figure S2. TEOS synthesis process using molecular sieve as the water sorbent. Reprinted with permission from [Nguyen, T. T. H.; Fukaya, N.; Sato, K.; Choi, J.-C.; Kataoka, S. Technoeconomic and Environmental Assessment for Design and Optimization of Tetraethyl Orthosilicate Synthesis Process. Ind. Eng. Chem. Res. 2018, 57, 2192]. Copyright [2018, ACS Publications].

(a) Mixer; (b, e) heat exchangers; (c) heater; (d) reactor; (f) cooler; (g) water absorber; (h) ethanol recovery column; (i) TEOS purification column: TEOS: ethyl orthosilicate; DS:hexaethyldisiloxane



Figure S3. TEOS synthesis process from Si_{mg} (conventional process). Reprinted with permission from [Nguyen, T. T. H.; Fukaya, N.; Sato, K.; Choi, J.-C.; Kataoka, S. Technoeconomic and Environmental Assessment for Design and Optimization of Tetraethyl Orthosilicate Synthesis Process. Ind. Eng. Chem. Res. 2018, 57, 2192]. Copyright [2018, ACS Publications].

(a) Calcinator; (b) mixer; (c, f) heat exchangers; (d) heater; (e) reactor; (g) cooler; (h) gas separator; (i) ethanol recovery column; (j) TEOS purification column: TEOS: ethyl orthosilicate; TRES: triethoxysilane.

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