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Supporting Information

Theoretical analysis and evaluation of reaction routes by the "three-parameter difference"

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Calculation details of parameters

(1) The reaction thermodynamics was computed by Aspen Plus software. The physical properties of substances not in the database were estimated by molecular structure, and the Gibbs free energy was calculated by the Equilibrium Reactor (REquil) module.

(2) The atom utilization (AU) is usually used to measure the atom economy of the chemical reaction process. Atomic utilization is the ratio of the sum of the atomic masses of the products to the sum of the atomic masses of all the reactants. It can be calculated by the following formula. The larger the AU, the fewer by-products. It does not refer to product selectivity but atom selectivity.

$$AU = \frac{v_i M_i}{\sum_{j=1}^{N} v_j M_j}$$

In the formula, v_i is the stoichiometric coefficient of the target product i; M_i is the molar mass of the target product i; v_j and M_j (j = 1, 2, ..., N) are the stoichiometric coefficient and molar mass of reactant j, respectively.

(3) The inherent safety was evaluated by the I-safe index method, which centers on the material properties and considers the basic reaction process conditions. Moreover, since this method requires less process information, it is particularly suitable for screening the reaction routes in the preliminary process design stage. The total index is divided into chemical and process inherent safety index. The previous is formed of subindices for reaction heats, flammability, explosiveness and toxicity. The latter is formed of subindices for process temperature, pressure and the safety of equipment and process structure. With reference to the definition of OSI, it is assumed that OSI' is the overall safety index of a reaction, which is used to reflect the safety of the reaction. The sub-indices (including the material safety index) and its value method are shown in the following table:

Symbol	Meaning	Calculation method
ICI	Individual Chemical Index	Nr + Nf + Nt + Ne
IRI	Individual Reaction Index	*R*t + *R*p + *R*y + *R*h
OSI'	Individual Safety Index	∑(ICI + IRI)
OCI	Overall Chemical Index	max(ICI)
ORI	Overall Reaction Index	∑IRI
OSI	Overall Safety Index	∑(OCI + ORI)

Notes: Nr: NFPA reactivity rating; Nf: Flammability; Nt: Toxicity;
Ne: Explosiveness; Rt: Temperature subindex; Rp: Pressure subindex;
Ry: Yield subindex; Rh: Heat of reaction subindex.

(4) According to the Gibbs free energy, atom utilization and inherent safety index of each reaction obtained above, the ΔR_i of was calculated according to the definition of "three-parameter difference".

Table S1 Material safety index of each reaction in the synthesis of DMC

Materials	Molecular formula	Nr	Flash point /°C	Nf	TLV /ppm	Nt	Explosiveness vol%	Ne
Methanol	CH_3OH	0	12	3	200	2	6~36.5	2
Phosgene	$COCl_2$	1	——	0	0.1	6	——	0
Dimethyl carbonate	$C_3H_6O_3$	1	17	3		1	4.22~12.87	1
Hydrochloric acid	HCl	0	——	0	2	4	——	0
Ethylene carbonate	$C_3H_4O_3$	0	143	1		1	3.6~16.1	1
Ethylene glycol	$(CH_2OH)_2$	0	111	1	25	3	3.2~15.3	1
Propylene carbonate	$C_4H_6O_3$	0	135	1		1	1.8~14.3	1
Propylene Glycol	$C_3H_8O_2$	0	99	1	150	2	2.6~12.6	1
Carbon monoxide	CO	0	-50	4	25	3	12.5~74.2	4
Oxygen	O_2	0	——	0	——	0	——	0
Water	H_2O	0	——	0	——	0	——	0
Methyl nitrite	CH_3NO_2	4	——	4	64.6	3	4.7-100[2]	4
Nitric oxide	NO	0	——	0	25	3	——	0
Urea	CON_2H_4	0	——	0		2	——	0
Ammonia	NH_3	0	——	4	25	3	15.7~25	2
Carbon dioxide	CO_2	0	——	0	5000	1	——	0
Propylene oxide	C_3H_6O	2	-37	4	2	4	1.9~36.3	2
Glycerol	$C_3H_8O_3$	0	199	1	10000	1	2.6~11.3	1
Cuprous chloride	CuCl	0	1490	1		1	——	0
Methoxy copper chloride	$Cu(OCH_3)Cl$	0	——	1		1	——	0
Ethylene oxide	C_2H_4O	3	-17.8	4		2	3~100	4
Cyclohexene oxide	$C_6H_{10}O$	3	27.2	2		2	1.15~12.36	1
Cyclohexanediol	$C_6H_{12}O_2$	0	114.3	1		1	——	0
Cyclohexenyl carbonate	$C_7H_{10}O_3$	0		0		1	——	0

Table S2 Safety index of each reaction for DMC synthesis

Reactions	Temperature /°C	Rt	Pressure /bar	Rp	Yield/ %	Ry	Reaction heat /(J/g)	Rh
R1	100	1	1	0	99	1	882.72	2
R2	70~150	1	5~25	1	90~99	1	1380.98	3
R3	150~300	2	25~50	2	90~99	1	41.08	0
R4	150~300	2	25~50	2	90~99	1	116.80	0
R5	150~300	2	25~50	2	90~99	1	517.25	1
R6-1	160	2	30	2	99	1	682.59	2
R6-2	100	1	7	1	24	8	159.91	0
R7-1	150~185	2	105	3	95	1	931.84	2
R7-2	65	0	1	0	80	2	143.83	0
R8-1	150~300	2	25~50	2	90~99	1	599.66	1
R8-2	70~150	1	5~25	1	90~99	1	937.29	2
R9-1	100	1	1	0	90	1	608.99	2
R9-2	100	1	1	0	92	1	855.94	2
R10-1	70~150	1	5~25	1	90~99	1	43.64	0

Table S3 Inherent safety index of reactions for DMC synthesis from methanol as the initial raw material

Index	R1	R2	R3	R4	R5
Rt	1	1	1	1	1
Rp	0	1	1	1	1
Ry	1	1	1	1	1
Rh	2	3	0	0	1
IRI	4	6	3	3	4
max (Nr)	1	1	1	1	2
max (Nf)	3	4	4	3	4
max (Nt)	6	3	3	2	4
max (Ne)	2	4	2	2	2
ICI	12	12	10	8	12
OSI'	16	18	13	11	16
OCI	12	12	10	8	12
ORI	4	6	3	3	4
OSI	16	18	13	11	16

Table S4 Inherent safety index of transesterification with different epoxides as raw materials

Index	R6-1	R6-2	R7-1	R7-2	R8-1	R8-2
Rt	2	1	2	0	1	1
Rp	2	1	3	0	1	1
Ry	1	8	1	2	1	1
Rh	2	0	2	0	2	2
IRI	7	10	8	2	5	5
max (Nr)	3	1	2	1	3	1
max (Nf)	4	3	4	3	2	3
max (Nt)	2	3	4	2	2	2
max (Ne)	4	2	2	2	1	2
ICI	13	9	12	8	8	8
OSI'	20	19	20	10	13	13
OCI	13		12		8	
ORI	17		10		10	
OSI	30		22		18	

Table S5 Inherent safety index of oxidative carbonylation of methanol to DMC

Index	R9-1	R9-2	R2
Rt	1	1	1
Rp	0	0	1
Ry	1	1	1
Rh	2	2	3
IRI	4	4	6
max (Nr)	4	4	1
max (Nf)	4	4	4
max (Nt)	3	3	3
max (Ne)	4	4	4
ICI	15	15	12
OSI'	19	19	18
OCI	15		12
ORI	8		6
OSI	23		18

Table S6 Inherent safety index of reactions for DMC synthesis

Index	R10-1	R7-2	R3
Rt	1	0	1
Rp	1	0	1
Ry	1	2	1
Rh	0	0	0
IRI	3	2	3
max (Nr)	0	1	1
max (Nf)	4	3	4
max (Nt)	3	2	3
max (Ne)	2	2	2
ICI	9	8	10
OSI'	12	10	13
OCI	9		10
ORI	5		3
OSI	14		13

Table S7 Material safety index of each reaction in the synthesis of TDI

Materials	Molecular formula	Nr	Flash point /°C	Nf	TLV /ppm	Nt	Explosiveness vol%	Ne
Toluene	C_7H_8	0	4	3	50	3	1.2~7	1
Nitric acid	HNO_3	0	——	0	2	4	——	0
Water	H_2O	0	——	0	——	0	——	0
Hydrogen	H_2	0	——	4	——	0	4~75	4
Phosgene	$COCl_2$	1	——	0	0.1	6	——	0
Toluene diisocyanate	$C_9H_6N_2O_2$	2	132	1	0.005	6	0.9~9.5	1
Hydrochloric acid	HCl	0	——	0	2	4	——	0
Carbon monoxide	CO	0	-50	4	25	3	12.5~74.2	4
Carbon dioxide	CO_2	0	——	0	5000	1	——	0
Methanol	CH_3OH	0	12	3	200	2	6~36.5	2
Oxygen	O_2	0	——	0	——	0	——	0
Dimethyl carbonate	$C_3H_6O_3$	1	17	3		1	4.22~12.87	1
Urea	CON_2H_4	0	——	0		2	——	0
Ammonia	NH_3	0	——	4	25	3	15.7~25	2
Ionic liquid hydroxylamine	H_3NO	3	——	0		1	——	0
2,4-Dinitrotoluene	$C_7H_6N_2O_4$	3	155	1		3	——	0
2,4-Diaminotoluene	$C_7H_{10}N_2$	1	149	1		2	——	0
Dimethyl 2,4-Toluenedicarbamate	$C_{11}H_{14}N_2O_4$	0	118	1		1	——	0

Table S8 Safety index of each reaction for TDI synthesis

Reactions	Temperature /°C	Rt	Pressure /bar	Rp	Yield/ %	Ry	Reaction heat /(J/g)	Rh
R11	60	0	1	0	94	1	1059.73	2
R12	100	1	20	1	100	0	4871.05	4
R13	100	1	20	1	90	1	154.46	0
R14	70~150	1	5~25	1	90~99	1	2872.69	3
R15	70~150	1	5~25	1	90~99	1	2720.41	3
R16	70~150	1	5~25	1	90~99	1	508.43	1
R17	70~150	1	5~25	1	90~99	1	1832.68	3
R18	150~300	2	25~50	2	90~99	1	241.87	1
R19	150~300	2	25~50	2	90~99	1	302.75	1
R20	150~300	2	25~50	2	90~99	1	232.43	1
R21	70~150	1	5~25	1	90~99	1	500	1

Table S9 Inherent safety index of reactions for TDI synthesis

Index	R_I			R_{II}			R_{III}			R_{IV}				R_V				R_{VI}				R_{VII}				R_{VIII}		
	R1	R12	R13	R1	R14	R11	R15	R16	R1	R12	R17	R16	R1	R12	R18	R16	R1	R12	R19	R16	R1	R12	R20	R16	R21	R19	R16
Rt	0	1	1	0	1	0	1	1	0	1	1	1	0	1	1	1	0	1	1	1	0	1	1	1	1	1	1
Rp	0	1	1	0	1	0	1	1	0	1	1	1	0	1	1	1	0	1	1	1	0	1	1	1	1	1	1
Ry	1	0	1	1	1	1	1	1	1	0	1	1	1	0	1	1	1	0	1	1	1	0	1	1	1	1	1
Rh	2	4	0	2	3	2	3	1	2	4	3	1	2	4	1	1	2	4	1	1	2	4	1	1	1	1	1
IRI	3	6	3	3	6	3	6	4	3	6	6	4	3	6	4	4	3	6	4	4	3	6	4	4	4	4	4
max (Nr)	3	3	2	3	3	3	3	2	3	3	1	2	3	3	1	2	3	3	1	2	3	3	1	2	3	1	2
max (Nf)	3	4	1	3	4	3	4	3	3	4	4	3	3	4	3	3	3	4	3	3	3	4	4	3	3	3	3
max (Nt)	4	3	6	4	6	4	3	6	4	3	3	6	4	3	2	6	4	3	2	6	4	3	3	6	3	2	6
max	1	4	1	1	4	1	4	2	1	4	4	2	1	4	2	2	1	4	2	2	1	4	2	2	1	2	2
ICI	11	14	10	11	17	11	14	13	11	14	12	13	11	14	8	13	11	14	8	13	11	14	10	13	10	8	13
OSI'	14	20	13	14	23	14	20	17	14	20	18	17	14	20	12	17	14	20	12	17	14	20	14	17	14	12	17
OCI		14			17		14			14				14				14				14				13	
ORI		12			9		13			19				17				17				17				12	
OSI		26			26		27			33				31				31				31				25	

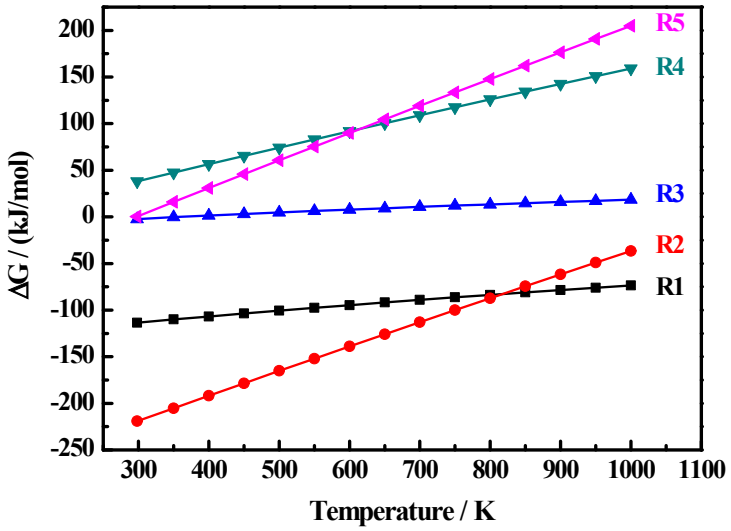

Fig. S1. The Gibbs free energy of reactions for DMC synthesis from methanol as initial raw material

R1: Phosgene process; R2: Gas-phase oxidative carbonylation of methanol by one-step process; R3: Gethanol-urea alcoholysis method; R4: Methanol-CO_2 method; R5: Methanol-propylene oxide-CO_2 method.

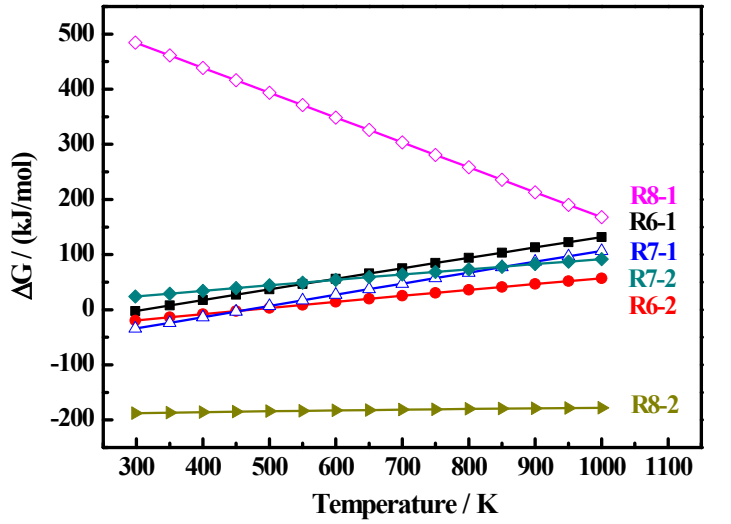

Fig. S2. The Gibbs free energy of DMC synthesis by transesterification with different epoxides as raw materials

R6-1: Ethylene oxide-CO_2; R6-2: Transesterification-ethylene carbonate; R7-1: Propylene oxide-CO_2; R7-2: Transesterification-propylene carbonate; R8-1: Cyclohexene oxide-CO_2; R8-2: Transesterification-cyclohexenyl carbonate.

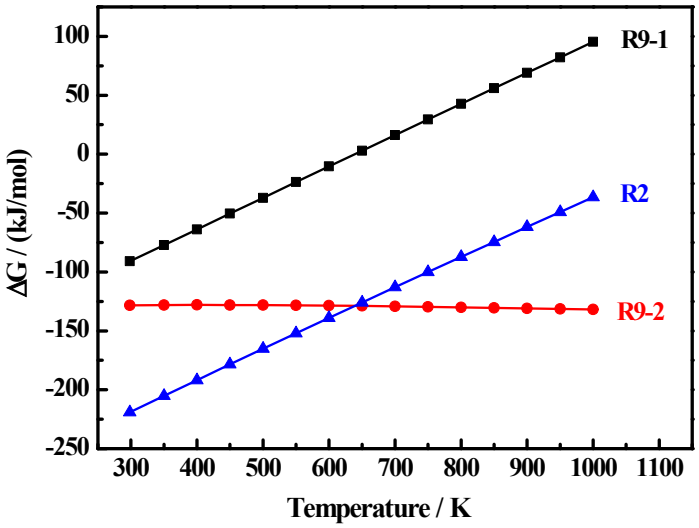

Fig. S3. The Gibbs free energy of gas-phase oxidative carbonylation of methanol to DMC

R9-1, 9-2: Gas-phase oxidative carbonylation of methanol by two-step;

R2: Gas-phase oxidative carbonylation of methanol by one-step.

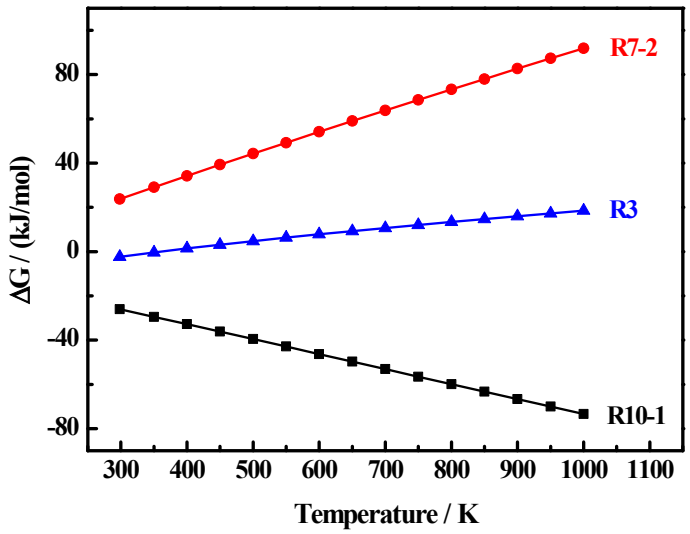

Fig. S4. The Gibbs free energy of each reaction for the synthesis of DMC

R10-1: Two-step method with propylene glycol as a circulating agent;

R7-2: Transesterification-propylene carbonate;

R3: Methanol-urea alcoholysis method.

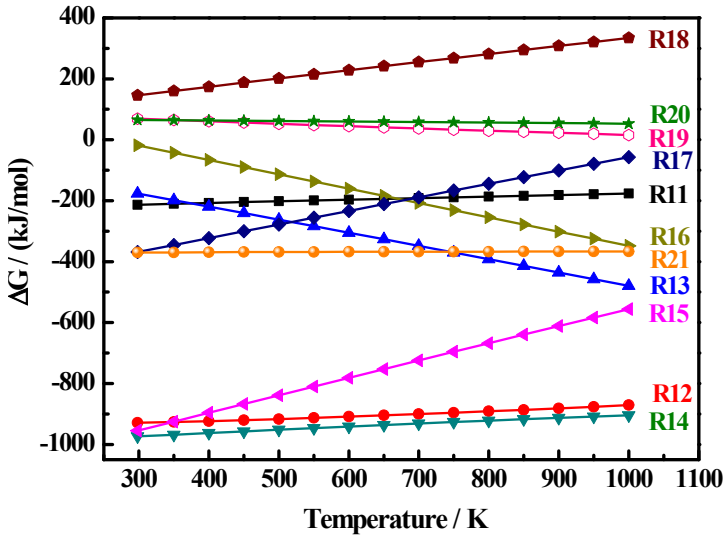

Fig. S5. The Gibbs free energy of reactions for TDI synthesis

R11: Toluene nitration; R12: Catalytic hydrogenation of 2,4-dinitrotoluene;R13: Phosgene process;

R14: Reduction carbonylation one-step method; R15: Reduction carbonylation two-step method;

R16: Catalytic decomposition of toluene dicarbamate; R17: Oxidative carbonylation method;

R18: Carbon dioxide method; R19: Dimethyl carbonate method; R20: Urea method;

R21: Dimethyl carbonate-ionic liquid hydroxylamine method.

Symbol Description

Symbol	Meaning
Nr	NFPA reactivity rating
Nf	Flammability
Nt	Toxicity
Ne	Explosiveness
Rt	Temperature subindex
Rp	Pressure subindex
Ry	Yield subindex
Rh	Heat of reaction subindex
ICI	Individual Chemical Index
IRI	Individual Reaction Index
OSI'	Individual Safety Index
OCI	Overall Chemical Index
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