Supplementary Information

Bridging Molecular Mechanism and Industrial Process of Zeolite-catalyzed Methanol Conversion to Olefins and Ethanol by Advanced Solid-state NMR Spectroscopy

Jing Niu,†[a,b] Xinzhi Ding,†[a,b,c] Shutao Xu,*[a,b,c] Yingxu Wei [a,b,c] and Zhongmin Liu*[a,b,c]

a. National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
b. State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
c. University of Chinese Academy of Sciences, Beijing 100049, China.

Table S1 Elemental balance of device elements of DMTO plant[a]

Items			Material balance	Elemental balance		
				C	H	O
Input/(t/h)	methanol		224.78	84.29	28.1	112.39
Output/(t/h)	Coke	2.22wt%	4.99	4.71	0.28	
	Water	56.20wt%	126.33	0	14.05	112.29
	Methane	0.87wt%	1.95	1.46	0.49	
	Ethene	16.32wt%	36.69	31.45	5.24	
	Ethane	0.43wt%	0.96	0.77	0.19	
	Propene	15.66wt%	35.21	30.18	5.03	
	Propane	1.49wt%	3.36	2.75	0.61	
	C_4	4.72wt%	10.62	9.1	1.52	
	C_{5+}	1.73wt%	3.89	3.38	0.51	
	H_2	0.06wt%	0.14	0	0.14	
	CO	0.05wt%	0.12	0.05	0	0.12
	CO_2	0.01wt%	0.02	0.01	0	0.02
	Methanol	0.01wt%	0.02	0.01	0	0.03
	Acetylene	0.00wt%	0	0	0	
	Dimethyl ether	0.00wt%	0.01	0.01	0	
	Oils	0.21wt%	0.47	0.42	0.05	
	Output summation	100wt%	224.78	84.3	28.11	112.46
Material and Elemental Balance				100.01	100.04	100.06

[a]Table S1 are translated from Table 8.10 in the Chinese book "*Methanol to Olefins"* by Z. Liu *et al*., (Science Press: China, 2015). Oxygenated compounds such as acetaldehyde and acetone are in extremely low concentrations (each contributing less than 0.01wt%), so they are not listed in Table S1.

According to Table S1 based on the material balance data of DMTO industrial plant, approximately 50% of the hydrogen in the methanol feedstock is incorporated into water, 36.6% is incorporated into ethylene and propylene. When including butenes (assuming 95% olefin content), the total rises to 41.69%. The remaining hydrogen is distributed in the order: C_4 hydrocarbons > propane > C_5^+ hydrocarbons > methane > coke > ethane > hydrogen > oil. In terms of carbon distribution, 83.91% of the carbon in the feedstock is incorporated into main products (*i.e.*, ethylene, propylene, and C_4 hydrocarbons), while 10.50% goes into by-products (such as methane, ethane, propane, and C_5^+ hydrocarbons). Coke accounts for 5.59% of the total carbon. Over 99.9% of the oxygen from methanol feedstock is incorporated into water, with the rest is distributed in carbon monoxide.

Table S2 Abbreviations

Abbreviations	Full name
2D	Two-Dimensional
3Q	Three-Quantum
AIMD	Ab Initio Molecular Dynamics
AMTH	co-conversions of Acetone and Methanol-to-Hydrocarbons
APT	Atom Probe Tomography
BAPs	Brønsted Acid Pairs
BAS	Brønsted Acid Sites
C1	One-Carbon
CAVERN	Cryogenic Adsorption Vessel Enabling Rotor Nestling
CF	Continuous-Flow
CFM	Confocal Fluorescence Microscopy
CORD	Combined $R2_n^v$-Driven
COS	Correlation Spectroscopy
CP	Cross Polarization
CSA	Chemical Shift Anisotropy
CTO	Coal-to-Olefins
DFT	Density Functional Theory
D-HMQC	Dipolar-based Heteronuclear Multi-Quantum Coherence
DICP	Dalian Institute of Chemical Physics
D-INEPT	Dipolar-based Insensitive Nuclei Enhanced by Polarization Transfer
DME	DiMethyl Ether
DMTE	Dalian Methanol to Ethanol
DMTO	Dalian Methanol to Olefins
DNP	Dynamic Nuclear Polarization
DQ	Double Quantum
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EFAl	Extra-Framework Aluminum
FCC	Fluid Catalytic Cracking
FER	Ferrierite
FLP	Frustrated Lewis Pair
FT-IR	Fourier Transform Infrared spectroscopy
GC	Gas Chromatography

GC-MS	Gas Chromatography-Mass Spectrometry
HCPs	HydroCarbon Pool species
heptaMB$^+$	heptaMethylBenzenium cation
HETCOR	Heteronuclear Correlation
HP	HyperPolarized
HPLC	High Performance Liquid Chromatography
HTHP	High Temperature High Pressure
INADEQUATE	Incredible Natural Abundance DoublE QUAntum Transfer experiment
IR	Infrared Spectroscopy
J-HMQC	J-couplings comprise Heteronuclear Multiple-Quantum Coherence
J-RINEPT	J-couplings Refocused Insensitive Nuclei Enhanced by Polarization Transfer
LAS	Lewis Acid Sites
LPST	Low-Pressure $SiCl_4$ Treatment
MA	Methyl Acetate
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight
MAS	Magic Angle Spinning
MCP$^+$	MethylCycloPentenyl ion
MD	Molecular Dynamics
MQMAS	Multiple Quantum Magic Angle Spinning
MR	Membered Ring
MS	Mass Spectrometry
MTA	Methanol-To-Aromatics
MTE	Methanol-To-Ethanol
MTG	Methanol-To-Gasoline
MTH	Methanol-To-Hydrocarbons
MTO	Methanol-To-Olefins
MTP	Methanol-To-Propylene
NMR	Nuclear Magnetic Resonance
NPD	Neutron Powder Diffraction
OSDA	Organic Structure-Directing Agents
PAH	Polycyclic Aromatic Hydrocarbons
PARIS	Phase-Alternated Recoupling Irradiation Scheme
PDSD	Proton-Driven Spin Diffusion

PFG	Pulsed Field Gradient
PMBs	PolyMethylBenzenes
$R2_n^v$	second-order Rotary-resonance-recoupling
REAPDOR	Rotational Echo Adiabatic Passage Double Resonance
REDOR	Rotational Echo DOuble Resonance
RESPDOR	Resonance Echo Saturation-Pulse DOuble Resonance
RDG	Reduced Density Gradient
RINEPT	Refocused Insensitive Nuclei Enhanced by Polarization Transfer
SDAs	Structure Directing Agents
SEM	Scanning Electron Microscope
SEOP	Spin-Exchange Optical Pumping
SIM	Structured Illumination Microscopy
SMS	Surface Methoxy Species
SQ	Single Quantum
SRIPT	Sinopec Shanghai Research Institute of Petrochemical Technology
ssNMR	solid-state Nuclear Magnetic Resonance
STMAS	Satellite Transition Magic Angle Spinning
SXRD	Synchrotron X-Ray Diffraction
TEAOH	TEtraethylAmmonium hydroxide
TEM	Transmission Electron Microscope
TGA	ThermoGravimetric Analysis
TMACl	TetraMethylAmmonium Chloride
TMCS	TriMethylChloroSilane
TMO	TriMethylOxonium
TMP	TriMethylPhosphine
TOS	Time-On-Stream
TQ	Triple-Quantum
TRAPDOR	TRAnsfer of Population in DOuble Resonance
UOP	Universal Oil Products company
VT	Variable Temperature
WHSV	Weight Hourly Space Velocity
μMRI	Micromagnetic Resonance Imaging