

新しいCO₂の水素化反応を 実現したパワフルな触媒

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二酸化炭素の水素化から：

- 1 飽和炭化水素（ガソリン、LPG）の合成
- 2 オレフィンの合成
- 3 芳香族、パラキシレンの合成
- 4 低温メタノールの合成

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大学院分子反応工学分野

個人履歴

1995 東大工応用化学専攻工学博士

1995-2001 同専攻 助手講師准教授

2001-現在 富山大工教授、サステナブル物質変換センター長

日本学術振興会賞2006年、日本エネルギー学会賞2017年、
触媒学会賞2019年、日本学術会議連携会員など;原著論文約
450報;特許約100件;引用数>1万;H-index 60.

J. Energy Chem., editor, board member.

椿研:企業駐在社員を含め、約50人のメンバー

C1 chemistry flow

Natural gas
Biomass
Coal
Garbage
Heavy oil

catalyst

Air
Water steam
Carbon dioxide

GTL
CTL
BTL
CO₂toX

FT合成
とMeOH
合成:
両大鍵
触媒反応

Synthesis gas (CO+H₂) /CO₂+H₂
normalized to carbon monoxide
and hydrogen

gasoline/diesel/
jet fuel/LPG

catalysts

alcohol

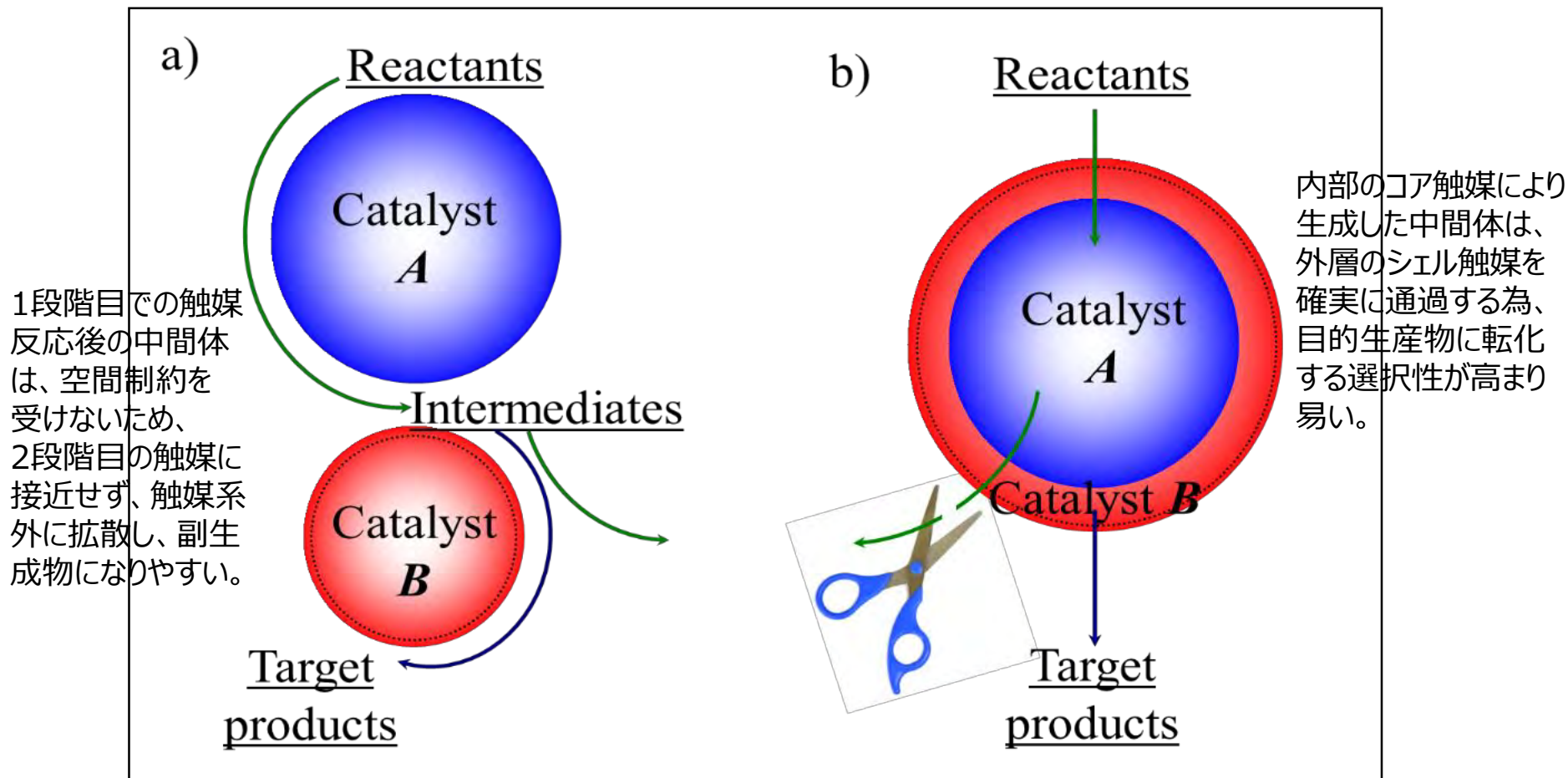
ester

organic acid

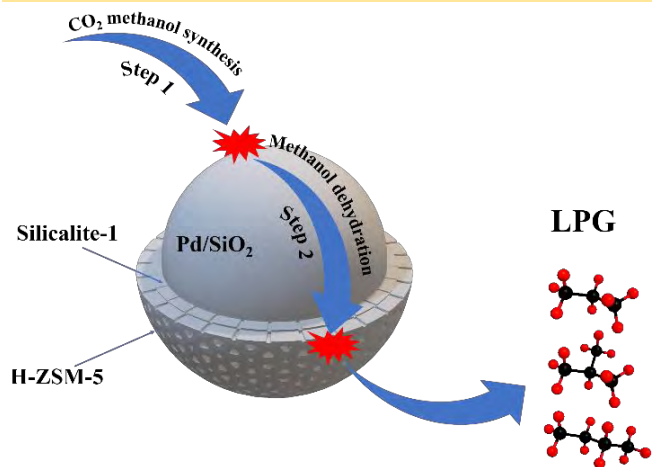
aromatics

olefin

C1化学とカプセル触媒の設計: 多段有機合成を一段にする新武器



物理混合触媒a)と新規カプセル触媒b)の比較
～カプセル触媒の空間規定性による中間生成物の抑制～



Scheme 1. Reaction scheme for CO₂ hydrogenation to LPG.

CO₂ hydrogenation to liquefied petroleum gas (LPG) can be realized via tandem reactions over well-defined capsule catalyst, as CO₂ hydrogenation to methanol over Pd/SiO₂ core catalyst (step 1), and subsequent dehydration of formed methanol into hydrocarbons over shell zeolite catalyst (step 2).



Figure 1. Images of Pd/SiO₂, Pd/SiO₂-S, Pd/SiO₂-SZ and Pd/SiO₂-SZP (from left to right side).

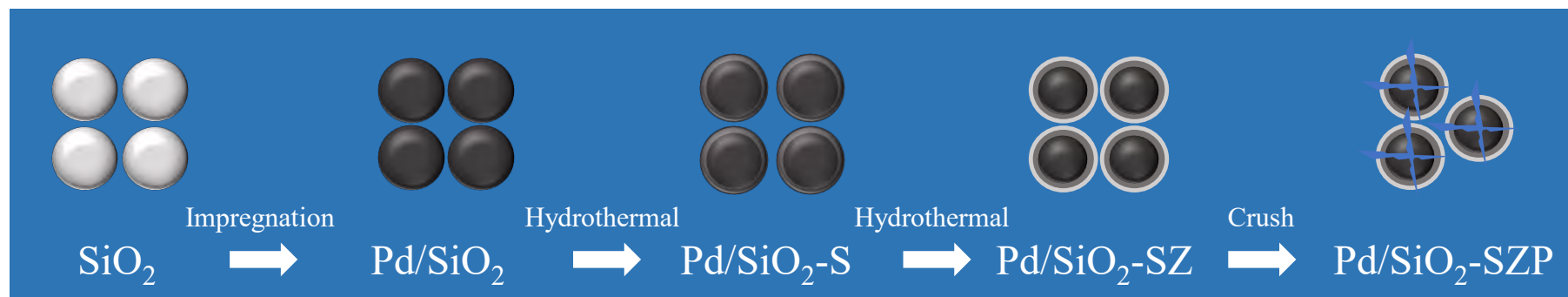


Figure 2. Catalyst preparation process of Pd/SiO₂, Pd/SiO₂-S, Pd/SiO₂-SZ and Pd/SiO₂-SZP.

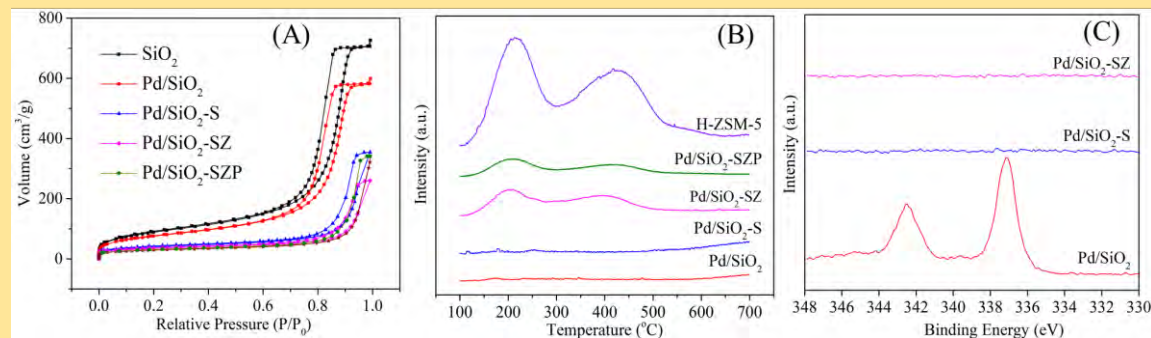


Figure 3. (A) N₂ adsorption-desorption isotherms, (B) NH₃-TPD, (C) Pd 3d XPS spectra.

All catalysts exhibit typical mesoporous structure with little micro pores, indicating that the structure of SiO₂ is well preserved during zeolite hydrothermal preparation process (**Fig. 3A**). Pd/SiO₂-SZ, Pd/SiO₂-SZP and H-ZSM-5 zeolite show two apparent desorption peaks, located at 220 °C and 450 °C, corresponding to weak acid sites and strong acid sites, respectively, responding for the dehydration of methanol to hydrocarbons (**Fig. 3B**). Pd 3d_{3/2} and Pd 3d_{5/2} centered at 342.5 eV and 337.5 eV are detected

only on Pd/SiO₂ catalyst, indicating that zeolite shells have completely coated the surface of core catalyst (**Fig. 3C**).

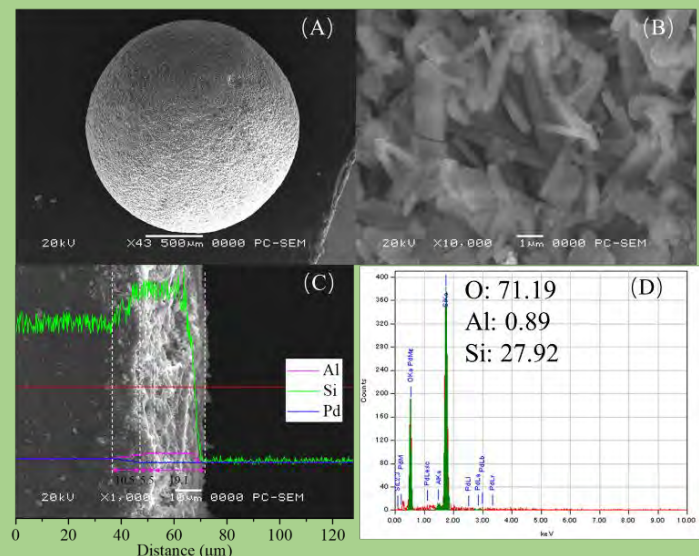


Figure 4. SEM images (A) and (B) of Pd/SiO₂-SZ, (C) EDS line scan of selected cross-section core-shell area, (D) Surface EDS analysis.

Pd/SiO₂-SZ catalyst presents a well-defined spherical structure and H-ZSM-5 zeolite crystallites of long hexagonal shape are clearly observed. The surface element of O:Al:Si molar ratio as 71.19:0.89:27.92, and no Pd signal is detected. From EDS line scanning results, the Silicalite-1 and H-ZSM-5 element zeolite shells with layers thickness of 5.5 μm and 19.1 μm are clearly observed.

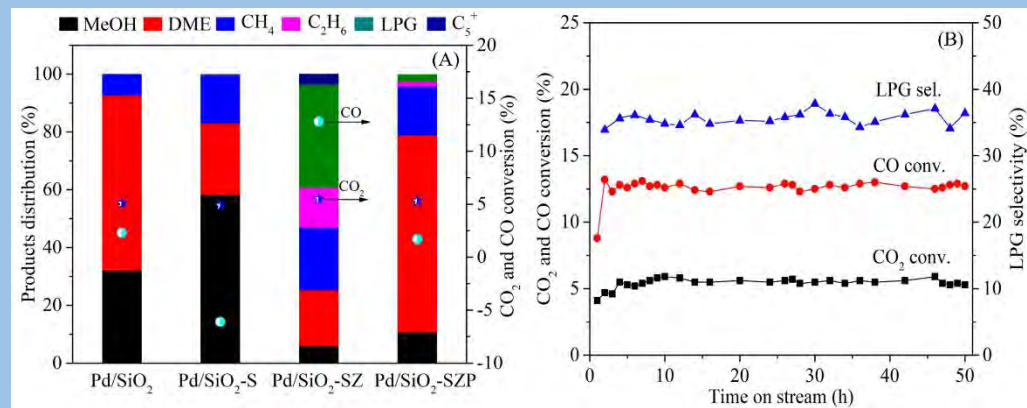
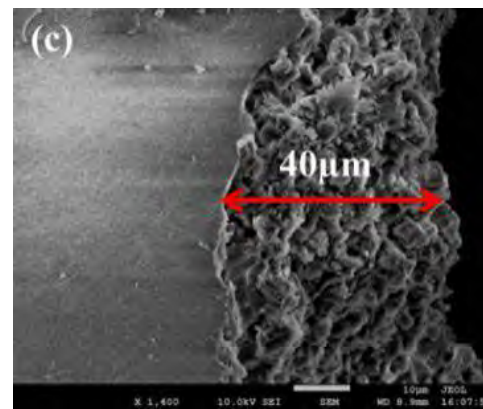
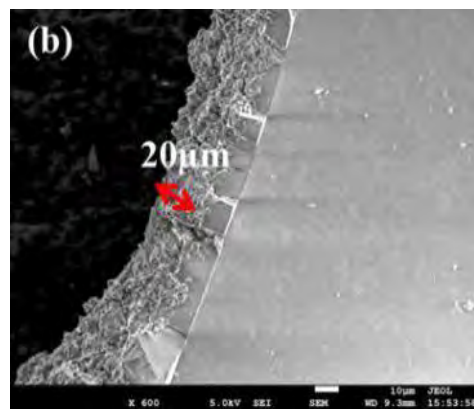
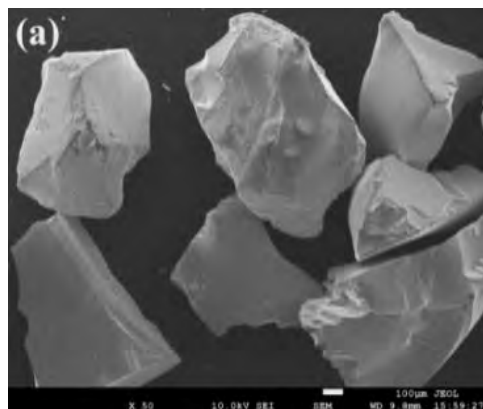
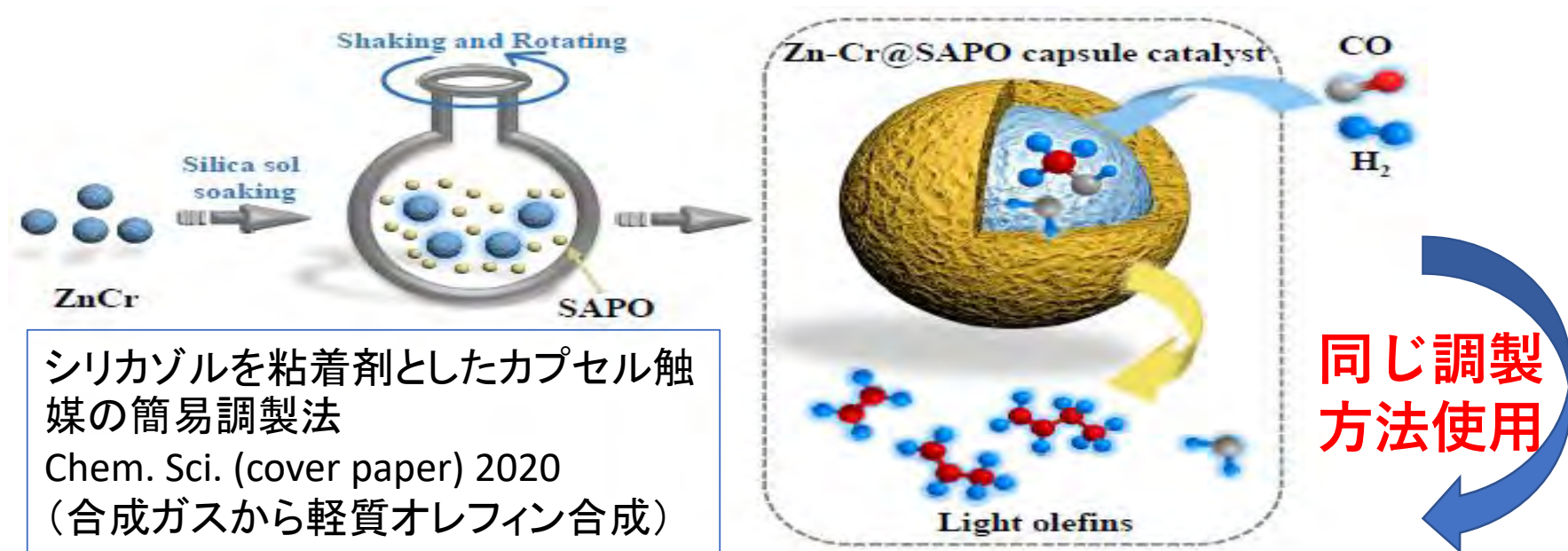


Figure 5. (A) Catalytic performance over different catalysts; (B) The catalytic performance of Pd/SiO₂-SZ as time on stream in 50 h. Reaction conditions: 4 MPa, 300 °C, W/F=10 g·h/mol, TOS=50 h.

Pd/SiO₂-SZ capsule catalyst exhibits LPG selectivity up to 35.6% by CO₂ and CO conversions of 5.5% and 12.8%, respectively. Furthermore, Pd/SiO₂-SZ presents highly stable catalytic performance in 50 h reaction.

1 - 2 カプセル触媒のガソリン合成; Catal. Sci. Tech., 2019



断面: Fe-Zn-Zr and HZSM-5 weight ratios: (b) 10:1, (c) 8:1, (a) Fe-Zn-Zr core。
Mapping も空間ゾーン分布を証明した。

1-2 カプセル触媒のガソリン合成

1-2-(1): カプセル触媒: プレミアガソリン (イソパラフィン*i*-C5-C11) の一段合成

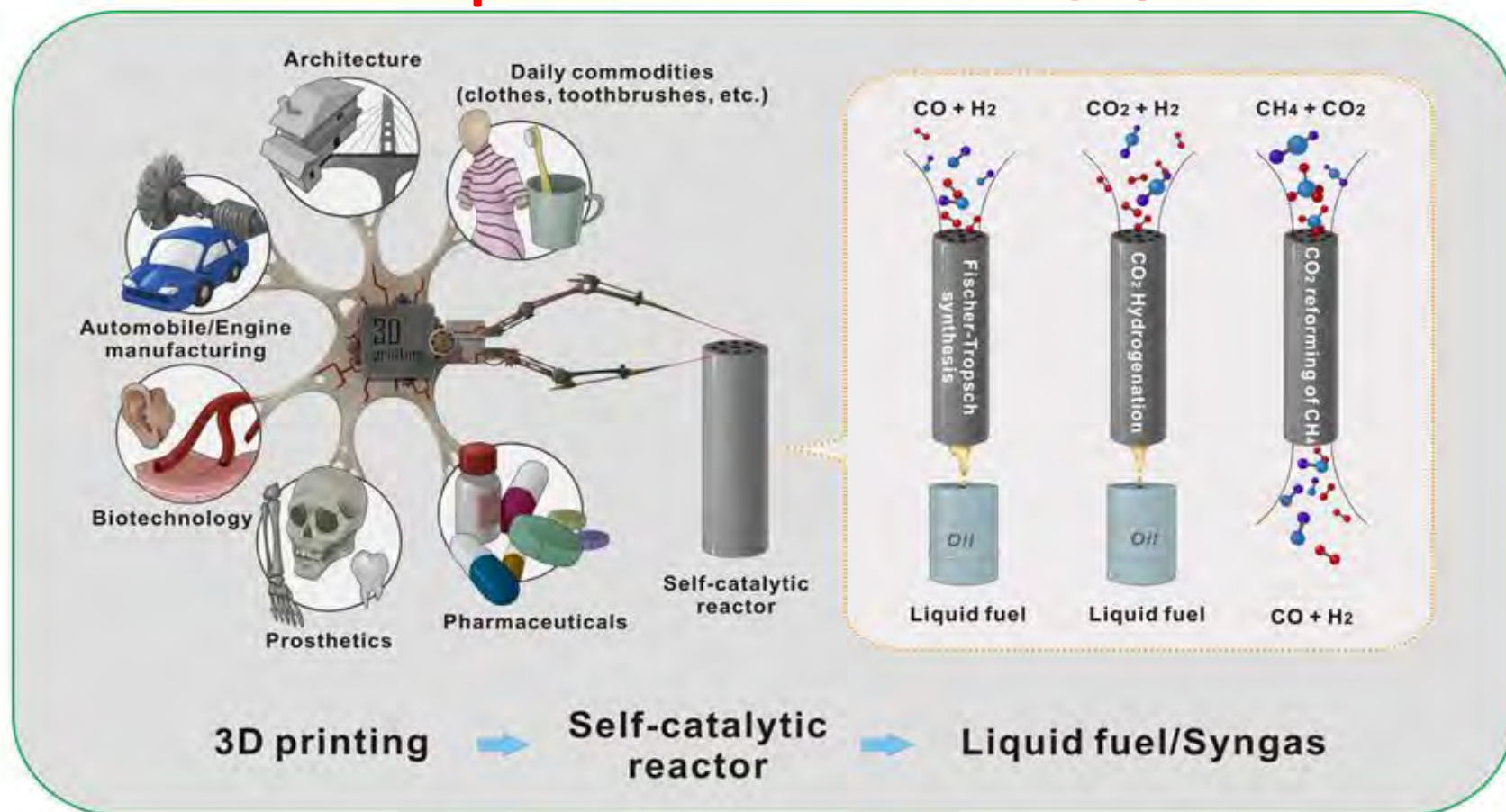
表 Fe-Zn-Zr@HZSM-5カプセル触媒のSi/Al₂モル比の考察、および物理混合触媒 granular-mixingに対する優位性

Catalysts	CO ₂ conv. (%)	Selectivity (C-mol%)			HC distribution (C-mol %)			I-C ₅₊ /C ₅₊ (%)	Aroma. /C ₅₊ (%)
		CO	Oxy.	HC	C ₁	C ₂₋₄	C ₅₊		
Fe-Zn-Zr@HZ5(38)	23.0	44.9	0.0	55.1	1.4	54.5	44.1	76.9	17.7
Fe-Zn-Zr@HZ5(50)	21.5	42.4	0.1	57.5	1.4	42.8	55.8	91.9	5.2
Fe-Zn-Zr@HZ5(100)	23.5	85.5	8.7	5.8	27.1	2.9	64.0	6.9	92.2
Fe-Zn-Zr/HZ5(50)	20.1	47.6	0.0	52.4	1.4	54.6	44.0	74.7	19.6

5.0 MPa; 340 °C; 6 h; 3000 ml/g/h; H₂/CO₂/N₂=72/24/4; Fe-Zn-Zr:HZSM-5=4:1 (weight ratio). Oxy=oxygen compounds; HC=hydrocarbon. I-C₅₊=C₅₊ isoalkanes; C₅₊=C₅₊ hydrocarbons.

酸点少ないと、イソ体が足りなく、ROHが炭化水素への速度も遅れる（CO選択率も上昇）。酸点が多いと、芳香族増加。Si/Al₂比50の膜は最適。比較例として、同じ重量比である物理混合触媒Fe-Zn-Zr/HZSM-5(50)もテストし、イソ体の減少および芳香族の増大が現れ、カプセル触媒によるランダムな副反応の抑制を証明できた。

MIRAI-inspired innovation for 未来

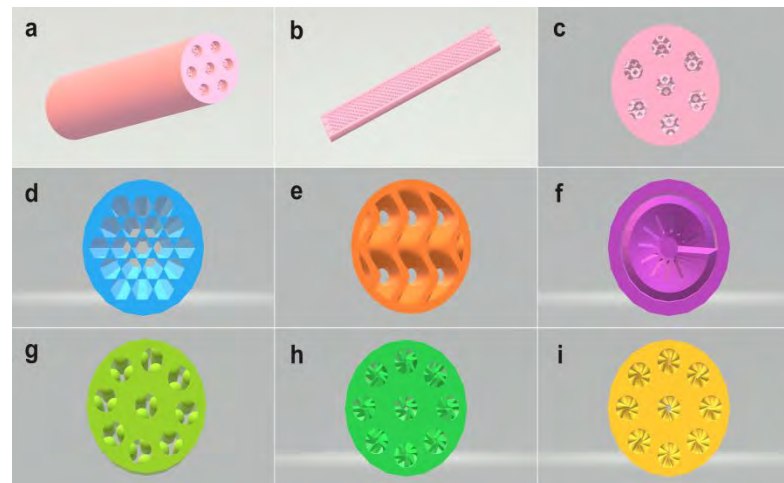
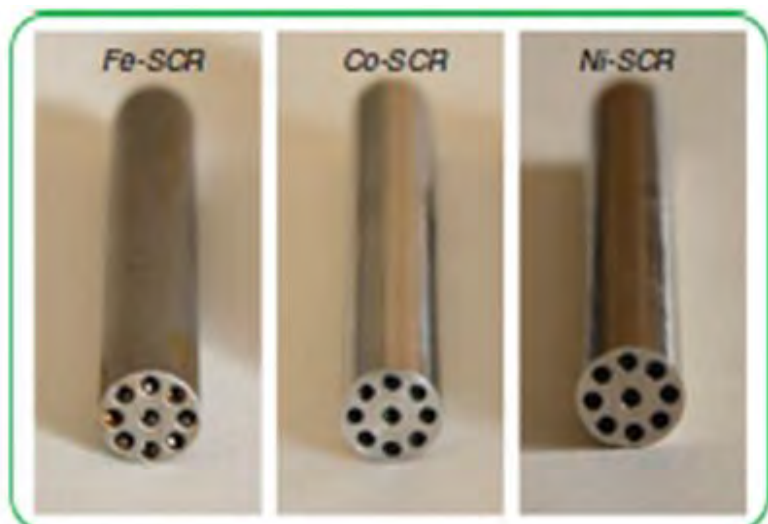


Ni系合金からの3D触媒反応器： $\text{CH}_4 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2$ 高温

Fe系、Co系合金からの3D触媒反応器：
 $\text{CO}_2 / \text{CO} + \text{H}_2 \rightarrow$ 液体燃料油 高温高压

3Dチューブ内表面
を化学処理、触媒化

1-3、金属3Dプリント自己触媒機能付き反応器



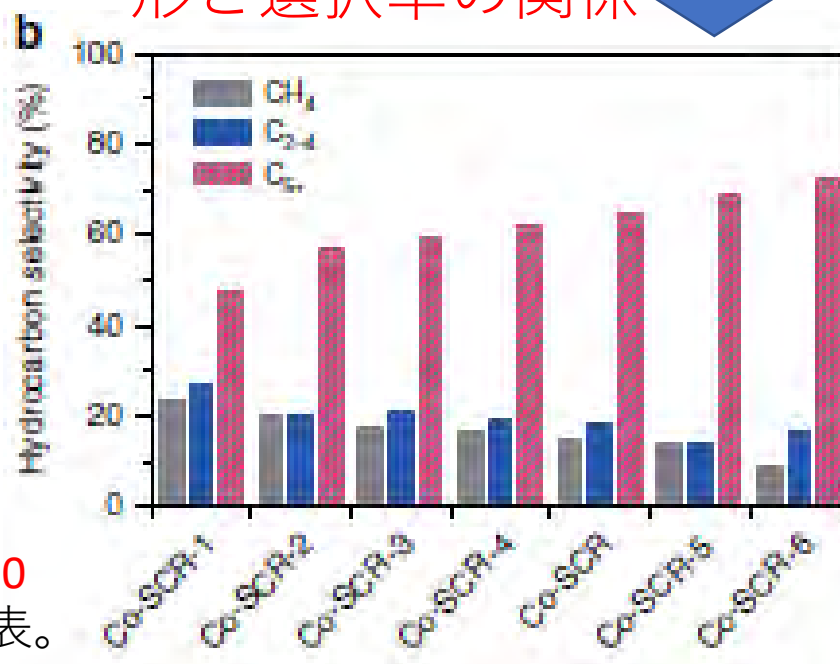
Movie at the web below

Nature Communications, Vol. 11, 4098, 2020

特願2020、富山大、日鉄；JSTプレス発表。

日経、朝日.....

形と選択率の関係

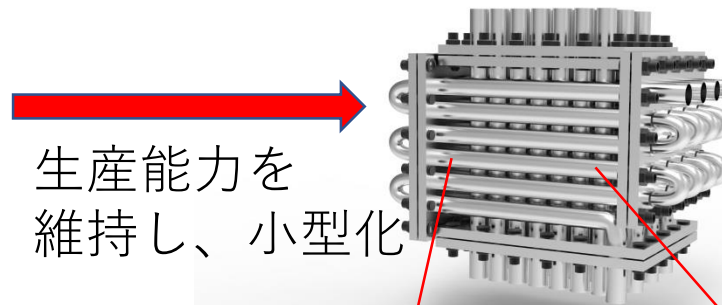


1-3、金属3Dプリント自己触媒機能付き反応器



従来の大型石油、化学、製薬工場

内壁はそのまま触媒として働く、
充填触媒不要。劇的に小型化。
メタンハイドレートなどの洋上
生産とGTL転換は可能



生産能力を
維持し、小型化

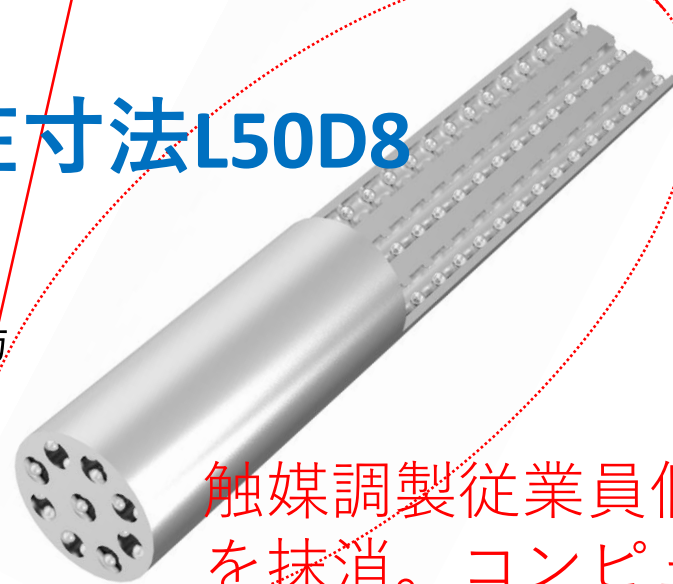
成形バインダー
不要

自己触媒機能付き
3Dプリント金属反応管

伝熱効果抜群

本数、
長さ
自由
配置

現在寸法L50D8



触媒調製従業員個人差
を抹消。コンピューター
で精密加工。再現性保証

1-3、金属3Dプリント自己触媒機能付き反応器

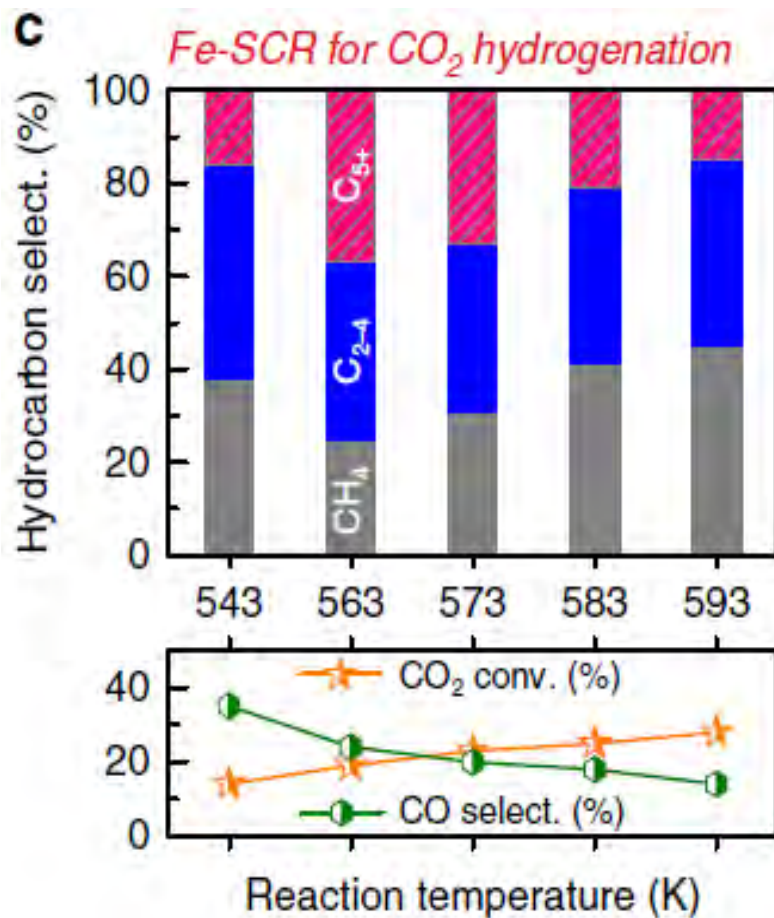
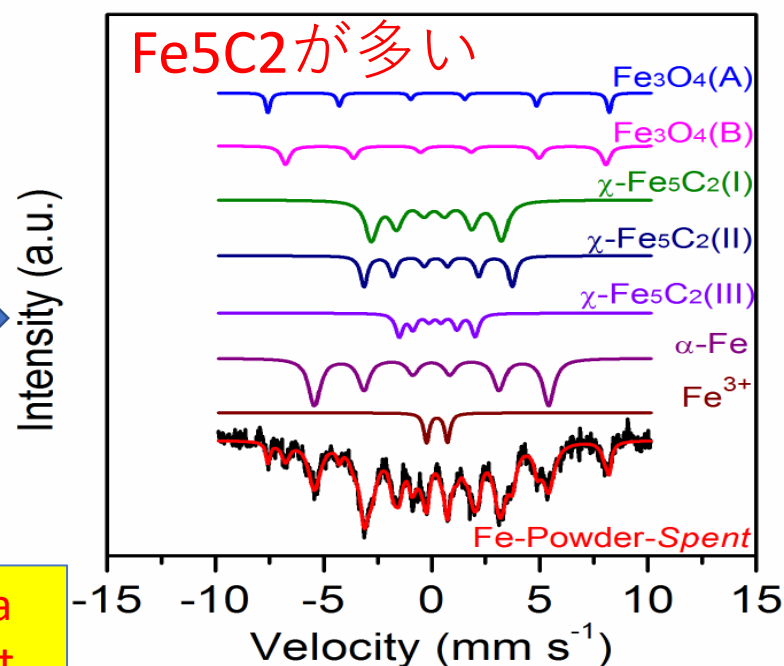
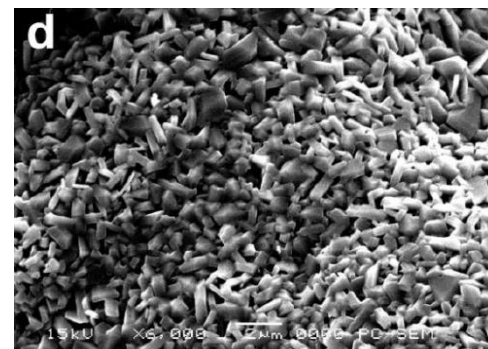


図 d : Fe-SCR
前処理後の
表面SEM



図c : 反応成績

⁵⁷Fe Mössbauer spectra
of the Fe-Powder-Spent

反応 : Fe-SCR (size: L50xD8) for CO₂ hydrogenation. Reaction conditions: P = 1.0

MPa; H₂/CO₂ = 3.0; flow rate, 20 ml min⁻¹; time on stream, 10 h.

前処理 : The Fe-SCR was calcined in air at 873 K for 60 h, and then reduced by H₂ at 673 K for 10 h with the H₂ flow rate of 40 ml min⁻¹

2 CO₂ 水素化によるオレフィン合成; Chem. Comm., 2020

Catalyst Preparation:

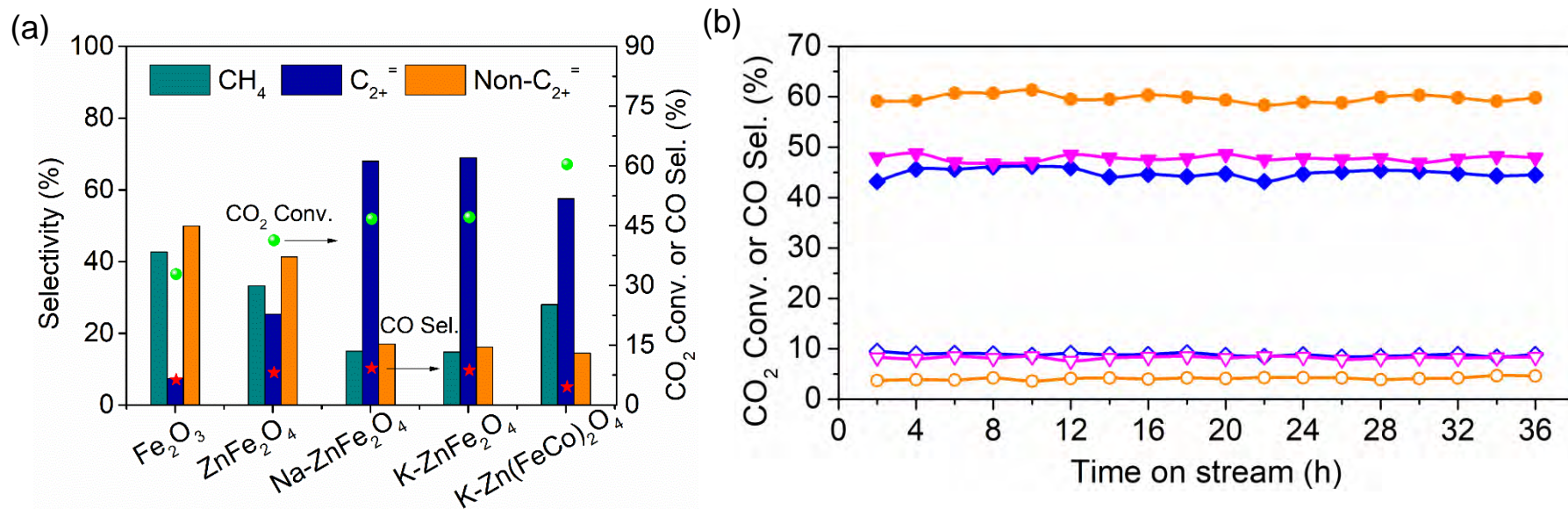
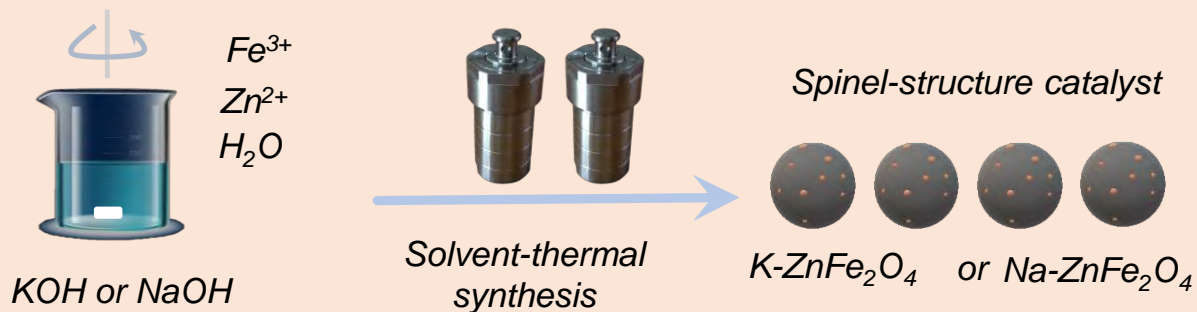
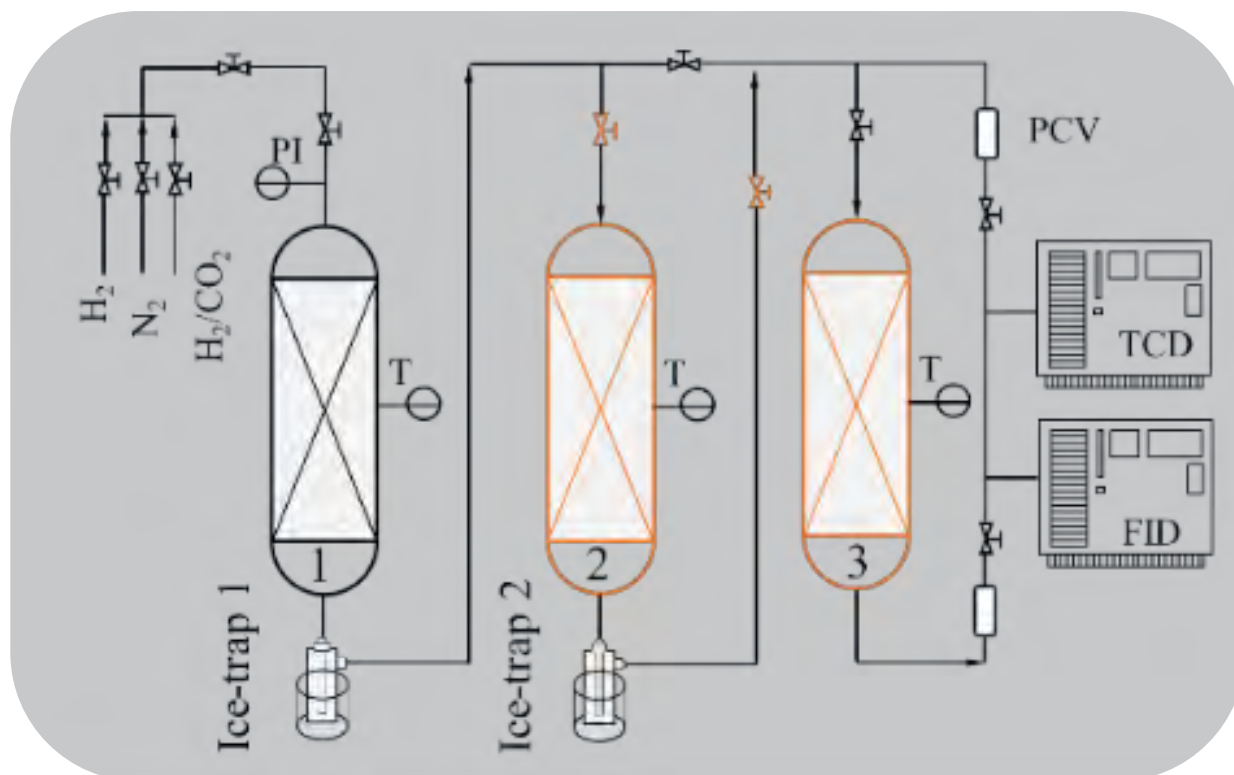


Figure . CO₂ hydrogenation performance. (a) Catalytic selectivities and conversions, (b) Catalytic stabilities.

Spinel catalysts exhibit benign catalytic performance including product selectivities and catalytic stability.



Scheme *A homemade three-stage reactor system for CO₂ hydrogenation.*

To further enhance catalytic yield, a homemade three-stage reactor system was designed for removing formed water.

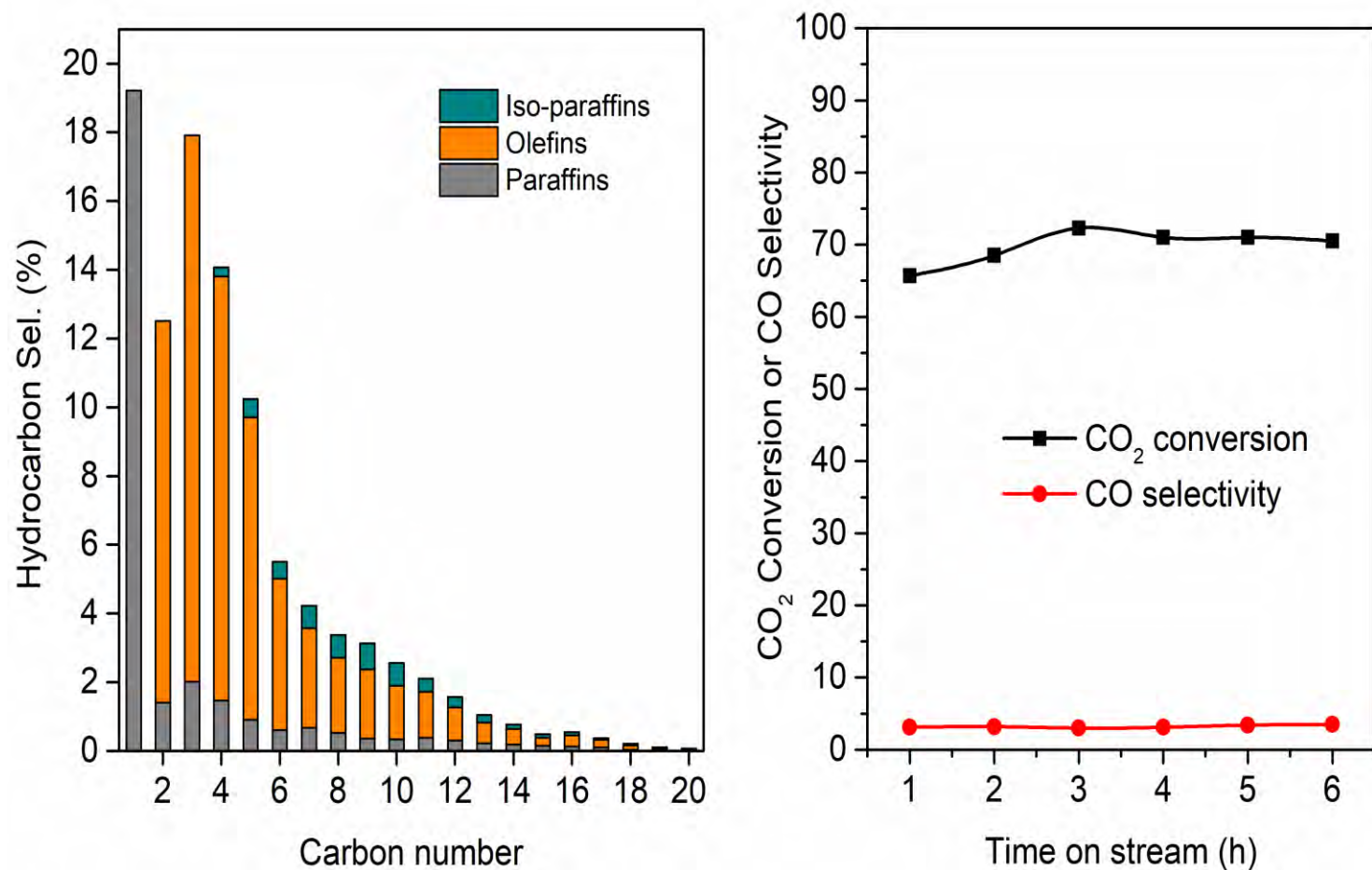


Figure . CO₂ hydrogenation performance of K-ZnFe₂O₄ over the three-stage reactor system. (a) Catalytic selectivities and conversions, (b) Catalytic stabilities. Conditions: 340 °C, 2.0MPa, GHSV = 24000 mL h⁻¹ g_{cat}⁻¹

High catalytic activity (70.8%) and ultra-low CO by-product selectivity (3.7%)

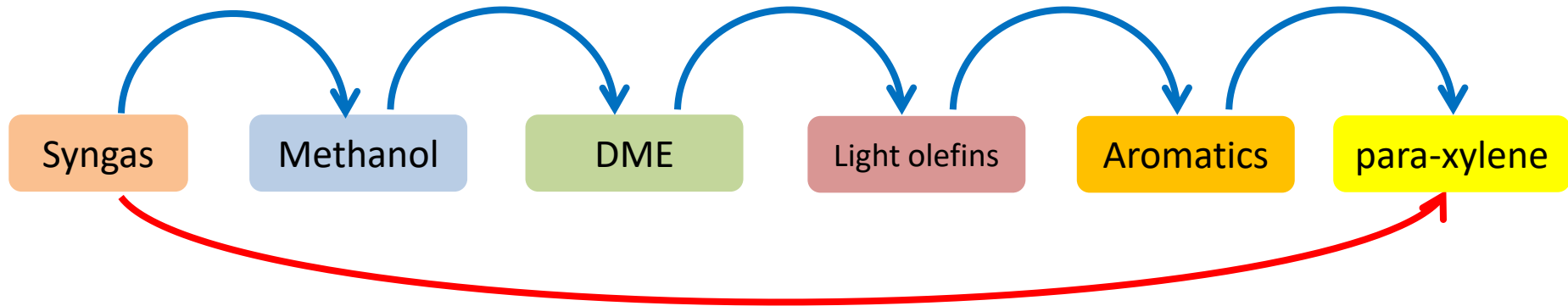
Catalytic yield of a spinel catalyst over a homemade multi-stage reactor system presents an ultra-high value.

3、二酸化炭素と水素から芳香族、あるいはPXの直接合成:c消費量大、水素消費少

世界初、CO,CO₂からPXの直接合成

The traditional **indirect** route for PX

synthesis from syngas

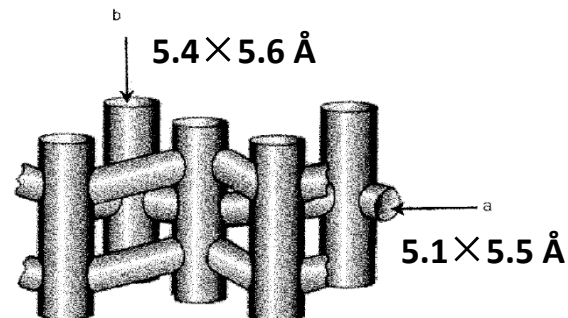
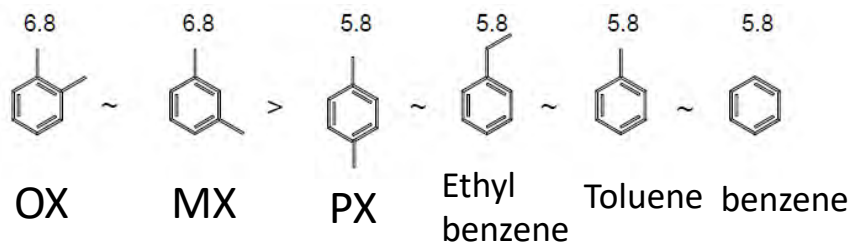


A new bifunctional catalyst for **direct**
synthesis of PX from syngas

- Generally, several steps and more catalysts are necessary for PX **indirect** synthesis from syngas.
- We had successfully developed a new bifunctional catalyst for PX **direct** synthesis from syngas. **PX年間5千万トン、市場大、価格高**

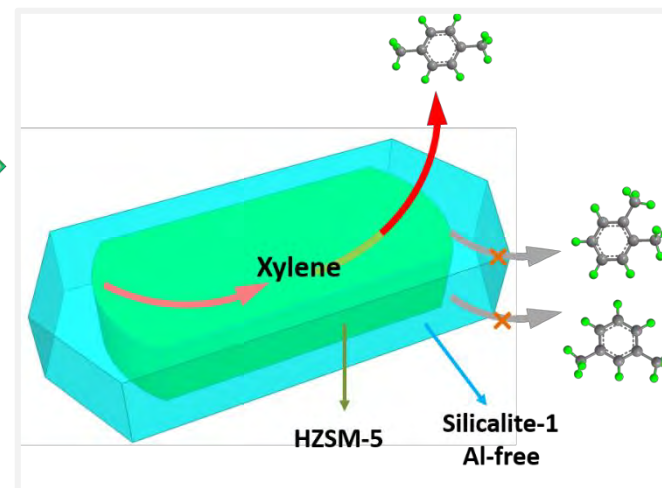
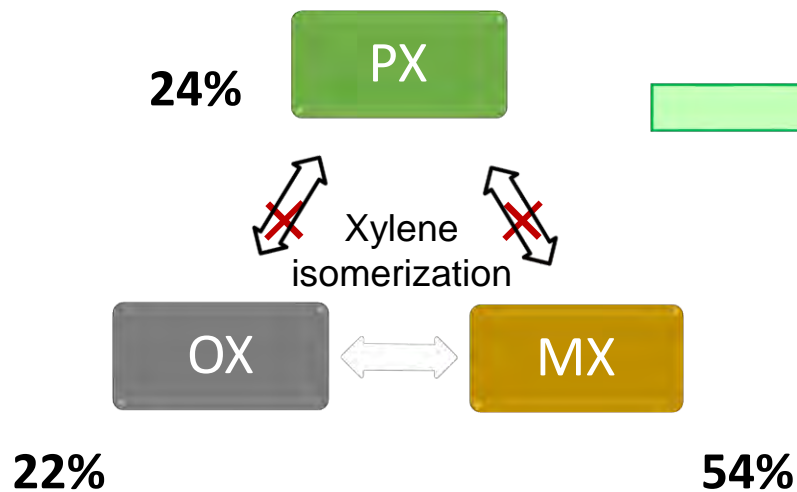
ZSM-5

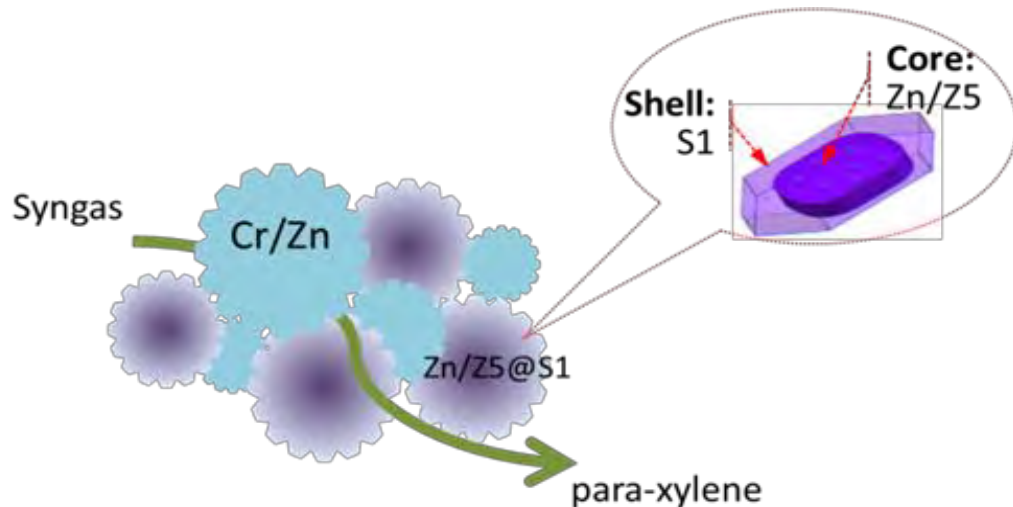
Kinetics diameter of aromatics close to the pore size of ZSM-5



Xylene isomerization

—Xylene at equilibrium





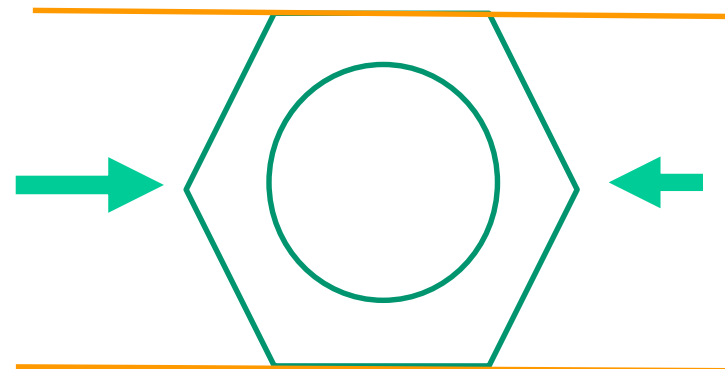
S-1 membrane erases zeo outside acid, stopping PX to MX/OX



Only 1- and 4- positions can be accessed by methanol. High PX selectivity.

Cr/Zn+Zn/Z5@S1 hybrid catalyst

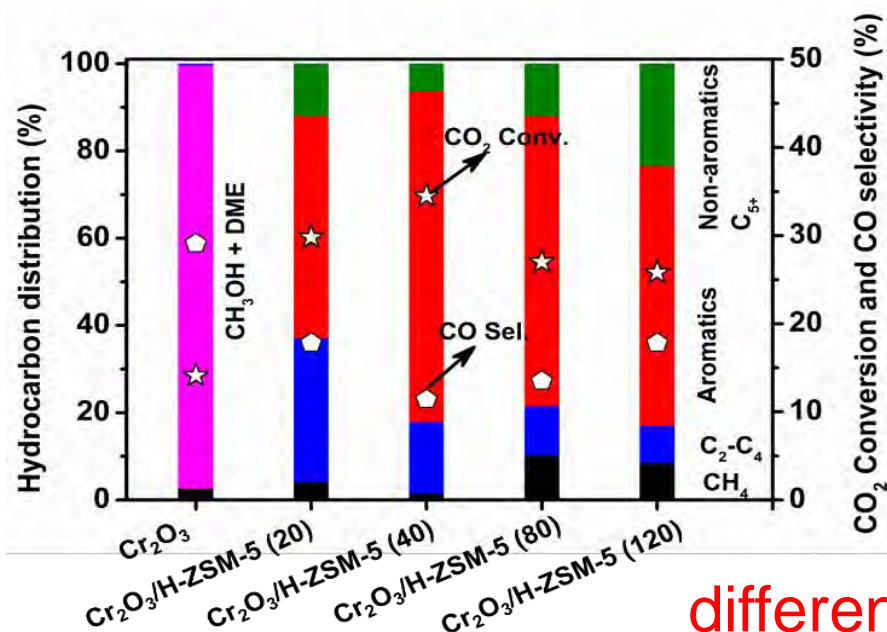
H-ZSM-5 zeolite channel



管内Friedel-Crafts合成、
ルイス酸触媒

Chemical Science (cover paper), 2017, 8, 7941-7946. 18

原料をCOからCO₂に切り替え、触媒も微調整



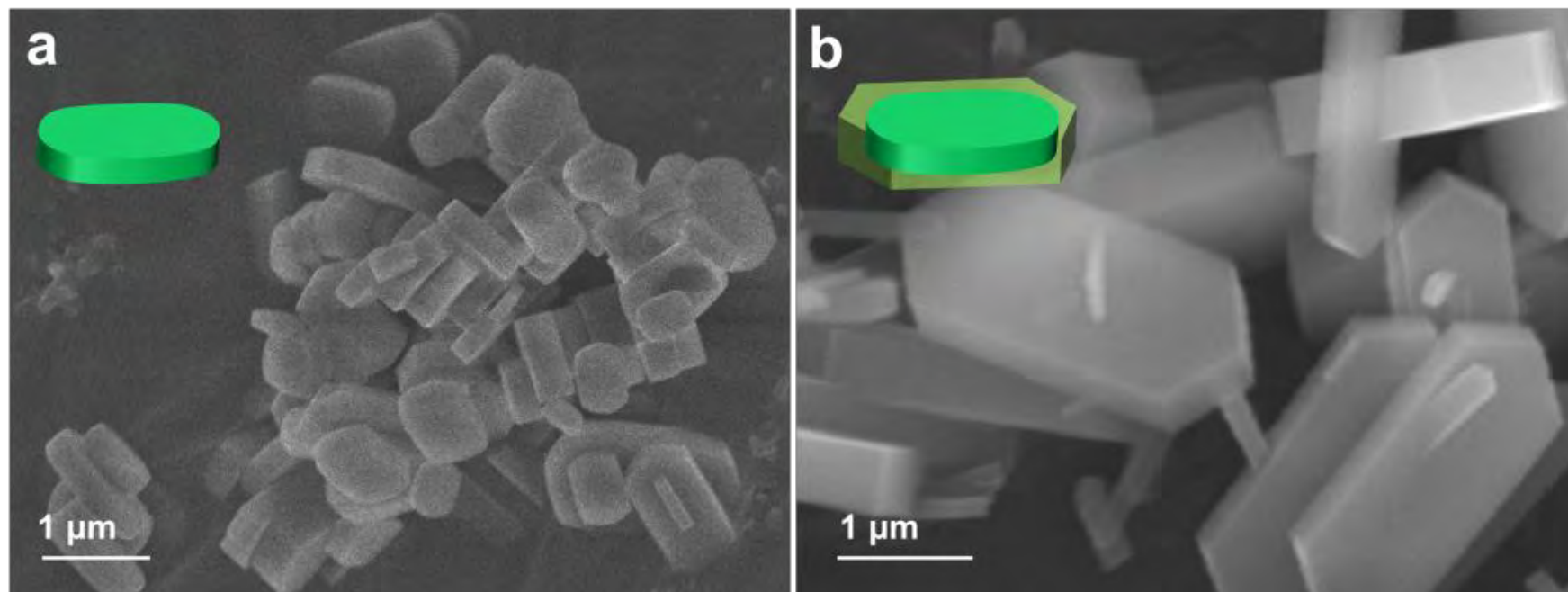
- ✓ 350 °C, 3 MPa, H₂/CO₂ = 3
(5.42 vol% CO in feed gas),
flow rate = 10 ml min⁻¹.
- ✓ 0.5 g Cr₂O₃/H-ZSM-5
(oxide/zeolite mass ratio 1);

different Si/Al ratio of ZSM-5 zeolite

Catalysts	CO ₂ Conv. (%)	CO Sel. (%)	Hydrocarbon distribution (%)						STY of A (g _{CH} kg _{cat} ⁻¹ h ⁻¹)
			CH ₄	C ₂₋₄ ⁰	C ₂₋₄ ⁼	CH ₃ OH +DME	C ₅₊	Aromatics	
Cr ₂ O ₃	14.1	29.1	2.6	0.1	0.2	97.1	0	0	0
Cr ₂ O ₃ /H-ZSM-5(20)	29.8	17.8	4.1	32.6	0.3	0	12.0	51.0	21.8
Cr ₂ O ₃ /H-ZSM-5(40)	34.5	11.4	1.5	14.9	1.5	0	6.2	75.9	40.4
Cr ₂ O ₃ /H-ZSM-5(80)	27.0	13.5	10.3	9.8	1.4	0	12	66.5	27.0
Cr ₂ O ₃ /H-ZSM-5(120)	25.8	17.8	8.5	5.4	3.1	0	23.5	59.5	22.0

Characterization

SEM images of H-ZSM-5 and H-ZSM-5@S-1



H-ZSM-5 crystals have been encapsulated by Silicalite-1

通路を有するS-1膜を通過したPXは酸点の無いS-1膜外表面において、異性化できない、PXの高選択率を達成.

ACS Catalysis, 2019; Chem. Euro. J., 2019; 富山大、日鉄特許

Catalytic performance

Table. Catalytic performance of tandem catalysis for CO₂ hydrogenation over Cr₂O₃/H-ZSM-5(40) and Cr₂O₃/H-ZSM-5@S-1.

Catalysts	CO ₂ Conv. (%)	CO Sel. (%)	Hydrocarbon distribution (%)					
			CH ₄	C ₂₋₄ ⁰	C ₂₋₄ ⁼	CH ₃ OH+ DME	C ₅₊	Aromatics
Cr ₂ O ₃ /H-ZSM-5	34.5	11.4	1.5	14.9	1.5	0	6.2	75.9
Cr ₂ O ₃ /H-ZSM-5@S-1	27.6	12.8	1.6	17.1	1.8	0	9.2	70.3

Table . Products distribution in aromatics.

Catalysts	Selectivity of aromatics (%) ^b								Σ
	B	T	E	o-X	m-X	p-X	A(C ₉)	A(C ₁₀₊)	
Cr ₂ O ₃ /H-ZSM-5	0.3	1.8	-	3.1	0.4	7.6	40.1	22.6	75.9
Cr ₂ O ₃ /H-ZSM-5@S-1	0.9	7.4	1.3	3.8	6.2	25.3	18.1	7.3	70.3

Reaction conditions: 350 °C, 3 MPa, H₂/CO₂ = 3 (5.42 vol% CO in feed gas), flow rate = 10 ml min⁻¹, oxide/zeolite mass ratio = 1 (weight of bifunctional catalyst, 0.5 g).

B = Benzene, T = Toluene, o-X = *ortho*-xylene, m-X = *meta*-xylene, and p-X = *para*-xylene.

PART 4

Syngas/CO₂ to MeOH: new method development

FTと同様、もう一つC1化学の鍵反応
であるメタノール合成を革新する：
新規低温メタノール合成プロセスと触媒の開発

Background:

High-temp. ICI method, 300°C, 100bar, 20% max. conv.;

Conv. = 0% when <200°C STY=400 (cycled)

発熱反応：高温不利、低温進行せず。熱力学と速度論の

ジレンマ：素反応を含め、合成ルートの再設計が必要

*Low-temp. method until now (BNL, Mitsui, BASF,
Sintef et al.)*

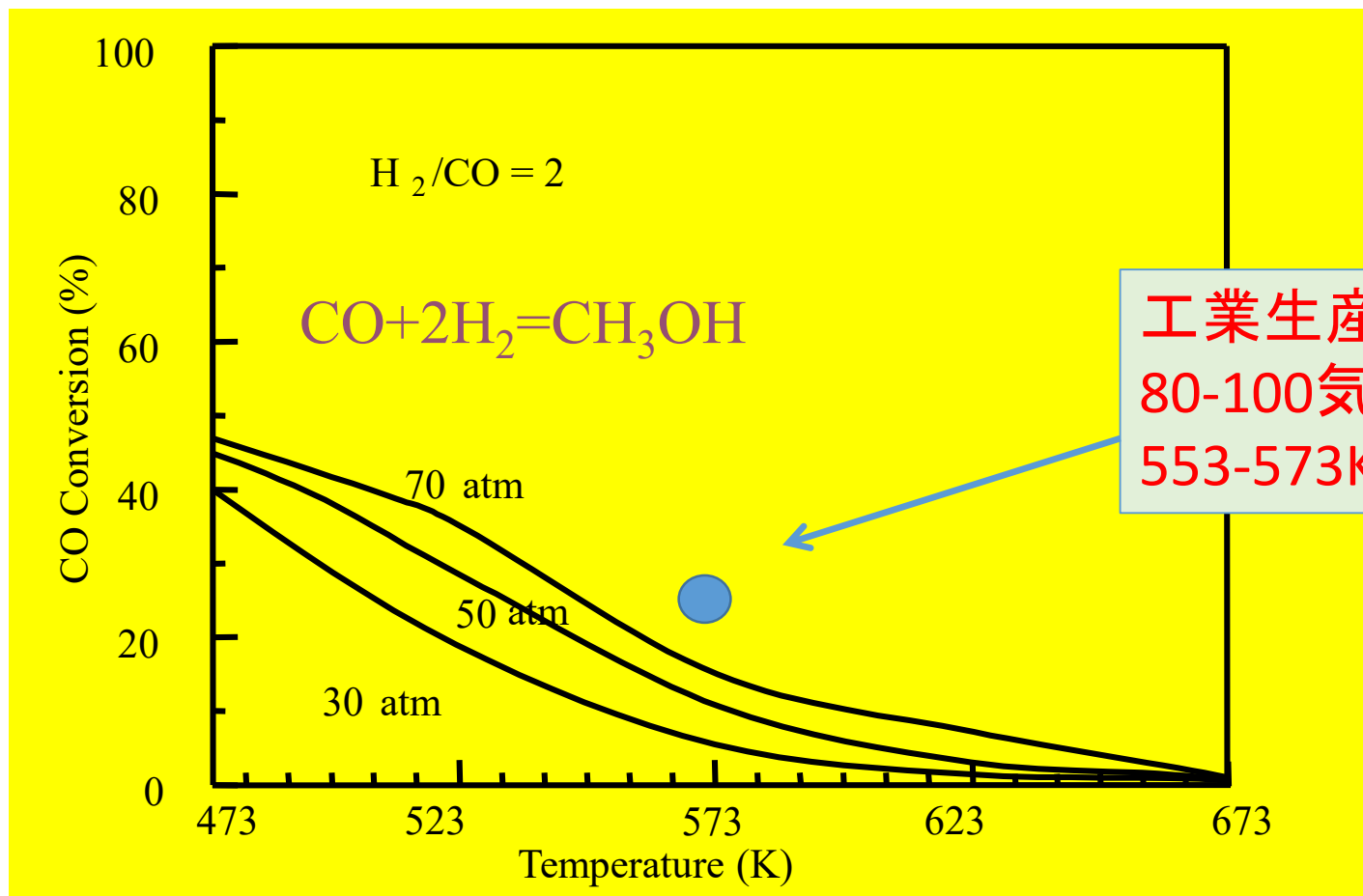


catalyst: CH₃ONa or CH₃OK + Raney Cu/Ni

Trace CO₂ and H₂O in syngas deactivate

発熱反応：
熱力学平衡
と速度論の
ジレンマ。

MeOH合成
とNH₃合成
両大著名
悪効率
合成プラント



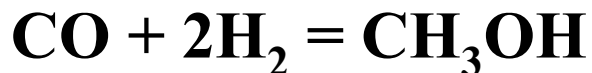
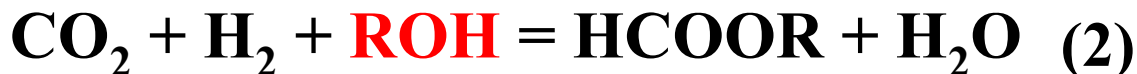
工業生産：
80-100気圧
553-573K

MeOH合成の最大平衡転化率計算。低温高压は有利

既存の高温型MeOH工業生産方法はNH₃合成と並び、エネルギー効率の悪い代表例である。

既存のすべての低温MeOH合成法は CH_3OK ,
 CH_3Na 使用、実用化不可

➤ New reaction path of methanol synthesis was proposed at low temperature by using **alcohol** as a catalytic solvent.



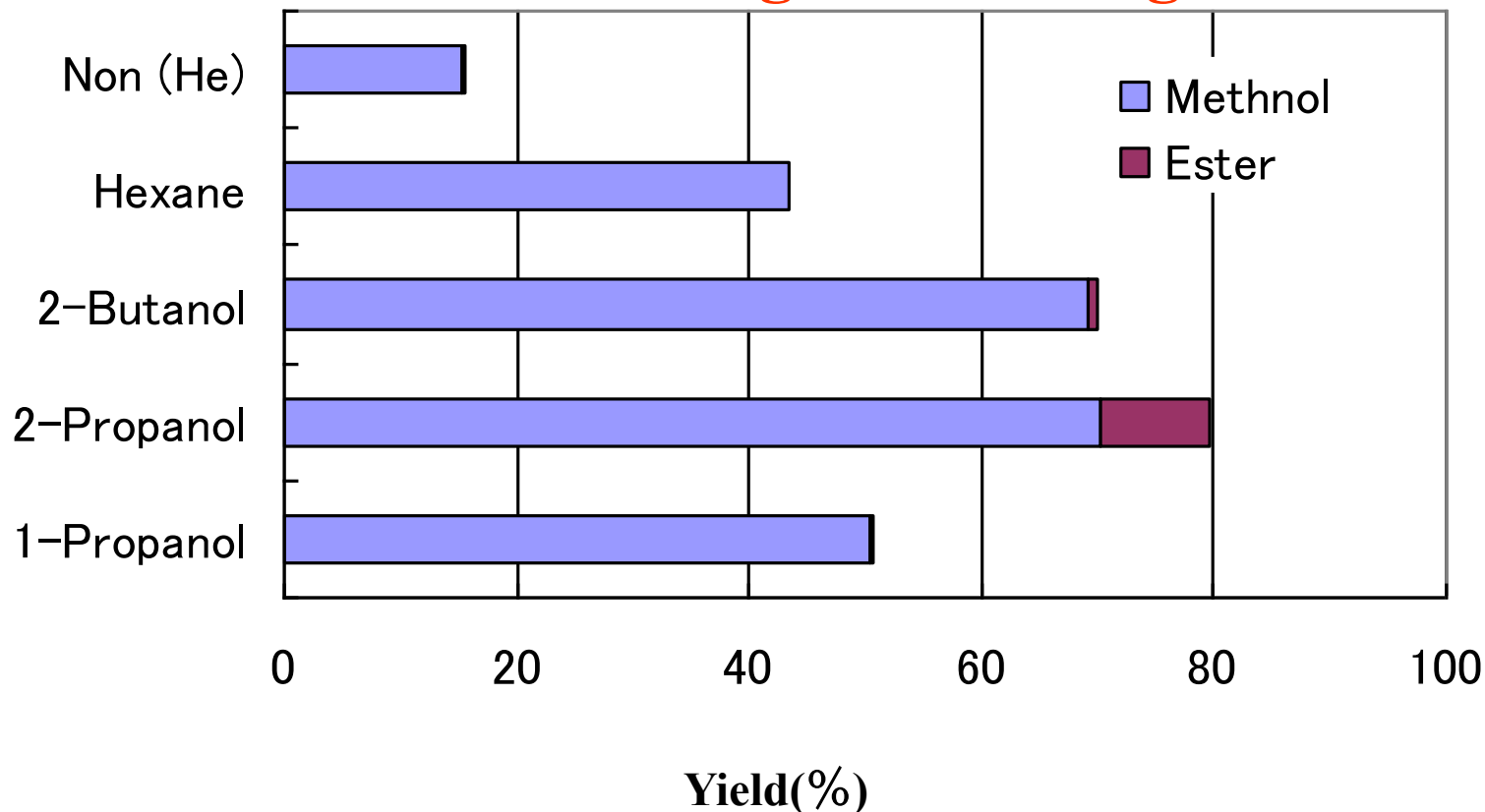
MeOHは触媒、溶媒、製品である(三つの役割)

➤ The effects of supercritical phase (SC) ROH on the new methanol synthesis are investigated.

➤ SC ROH also acting as a catalytic solvent in the catalytic cycle via reactions (1) - (3) will work more efficiently.

約半世紀以来
メタノール合成
の唯一の革新

STY:1200g – MeOH/kg-cat.h



Activity comparison

(Reaction conditions: Catalyst 0.5g, CO/H₂ (1:2), Reaction pressure

62atm (CO/H₂ : solvent=10 : 52) Reaction temperature 543K , Reaction time 6h)

J. Catal., 2001; J. Catal., 2004; Accounts of Chem. Res., 2013

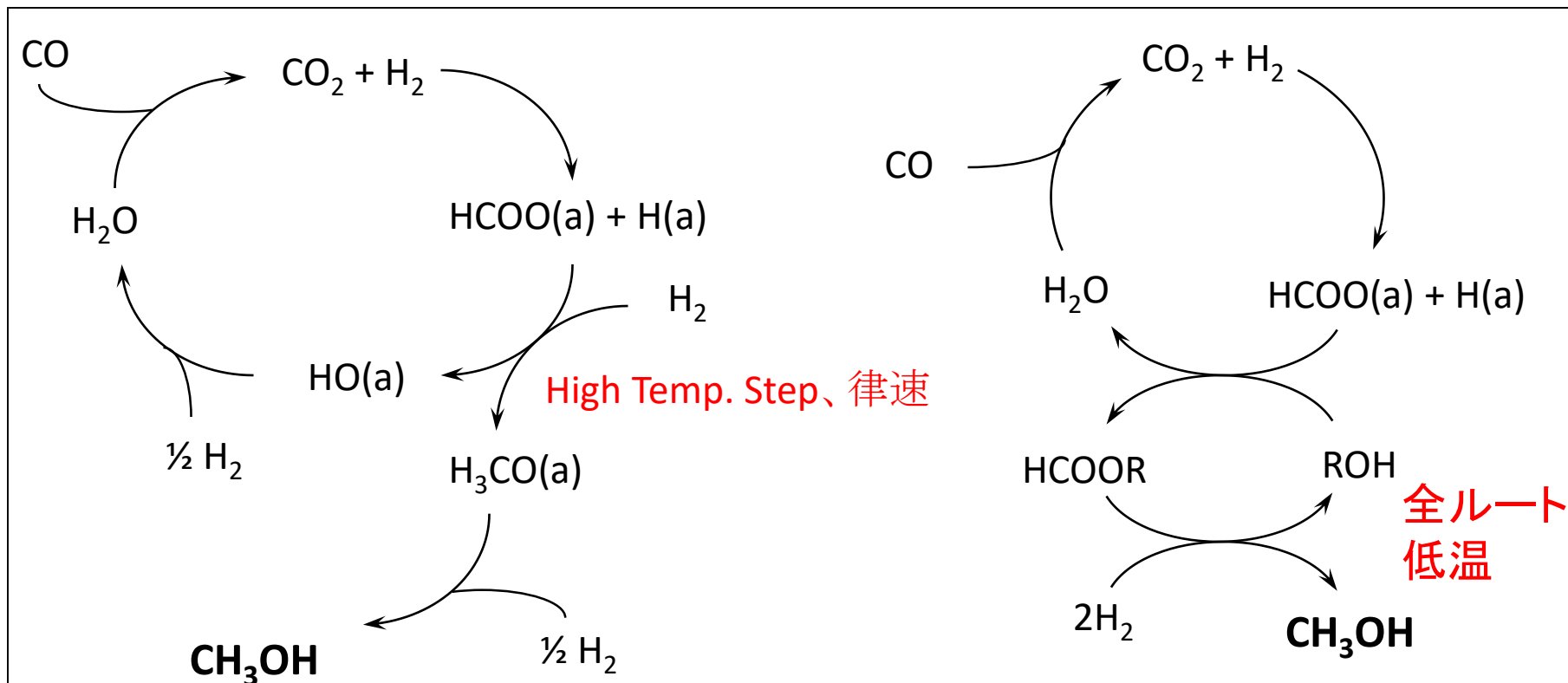
Reaction mechanism re-design

DRIFTSでin situ解明済み; J. Catal.

Addition of ROH as catalytic solvent alters the synthesis route.

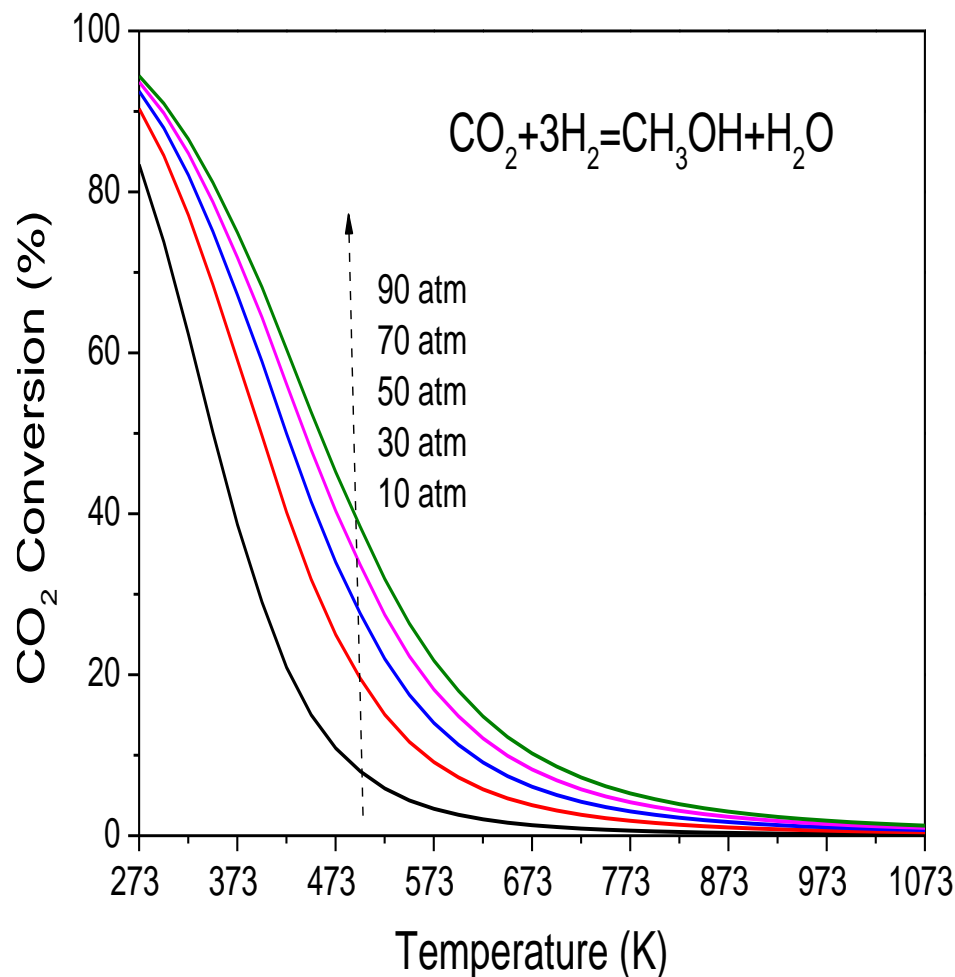
Surface formate hydrogenation to methoxy is a high temp. step and this

is avoided by ester cycle. MeOHの役割: 生成物 + 溶媒 + 触媒 R=Me

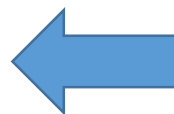


商業ICI法、水素大過剰、200°C停止

Our new method



CO₂からのMeOH:
熱力学平衡計算値
最大転化率: 低温有利



CO₂からのFT:
熱力学平衡計算値
平衡制限なし

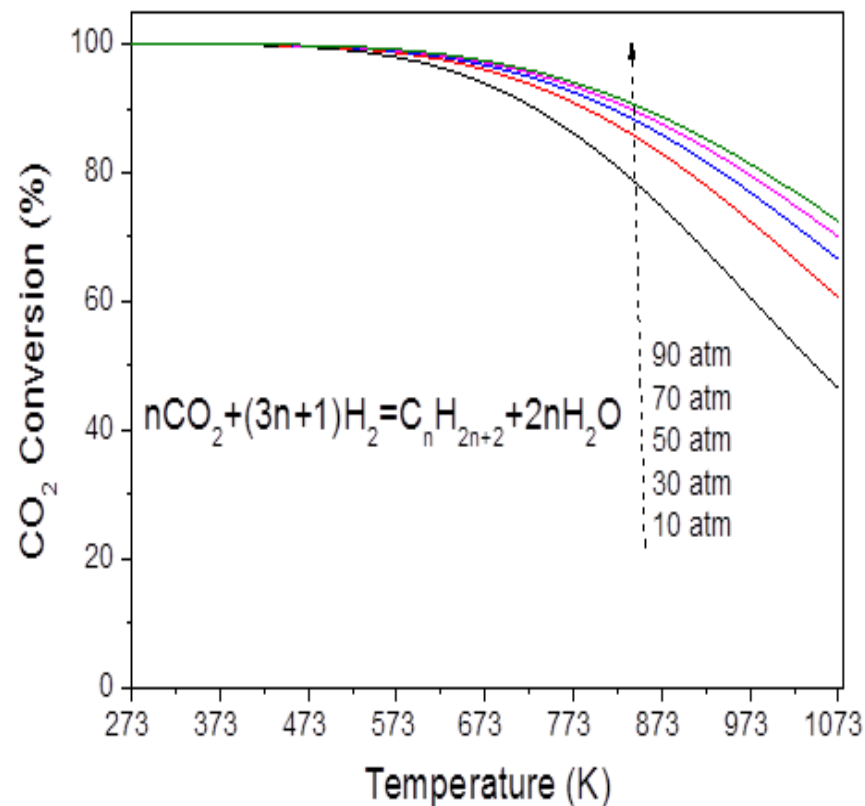


Table 1. The composition and preparation method of various catalysts

Catalyst label	Catalyst composition/mol % Cu/Zn/(Al)	Catalyst preparation method
CC	50/50	Conventional coprecipitation
OC01	50/50	Oxalate-gel coprecipitation
OC02	45/45/10	
OC03	60/30/10	
OC04	90/5/5	

Liu, Tsubaki, et al Chem. Letter, 2007

Table 2. The activities of methanol production on various catalysts^a

Catalysts	CO ₂ conversion ^b /%	Selectivity/%		
		CO	MeOH	Alkyl formate
ICI51-2	11.3	66.4	29.7	3.9
CC	5.2	85.4	11.9	2.7
OC01	14.3	45.1	54.8	0.1
OC02	16.9	29.2	70.7	0.1
OC03	25.9	27.1	72.9	0
OC04	15.7	21.3	78.7	0

^aReaction conditions: $T = 443$ K, $P = 5$ MPa, catalyst: 3 g, solvent: 2-octanol, reaction time: 20 h, feed gas: CO₂/H₂/Ar = 25.6/71.65/2.75, flow rate: 20 mL/min (STP), stirring speed: 2000 rpm.

^bCO₂ conversion was stable for all 20 h.

本CRFにおいて:

我々が発明した新規低温メタノール合成法を活かし、CO₂とグリーン水素から、あるいは石炭ガス化で得られた合成ガスから(CO+CO₂+H₂も)、従来の古典的な高温ICI法より高い効率でメタノールを合成する。

ご清聴ありがとうございました。

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基礎研究の共同研究者:中国科学院山西石炭化学研究所等。