2021年度　JPECフォーラム

「革新的石油精製技術のシーズ発掘」

減圧軽油(VGO)の
革新的変換プロセスの開発

2021年5月12日

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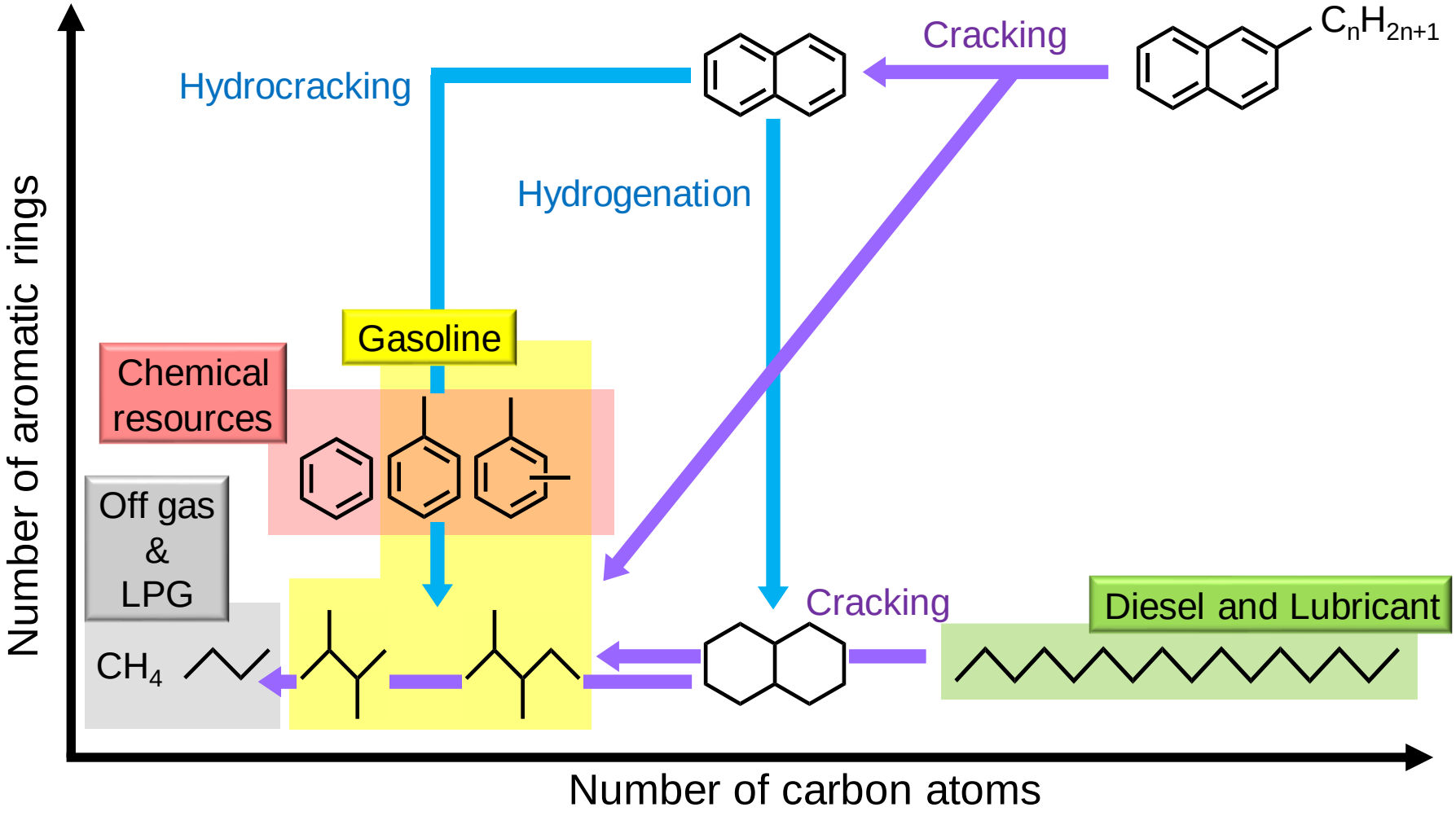
従来のVGO変換プロセス



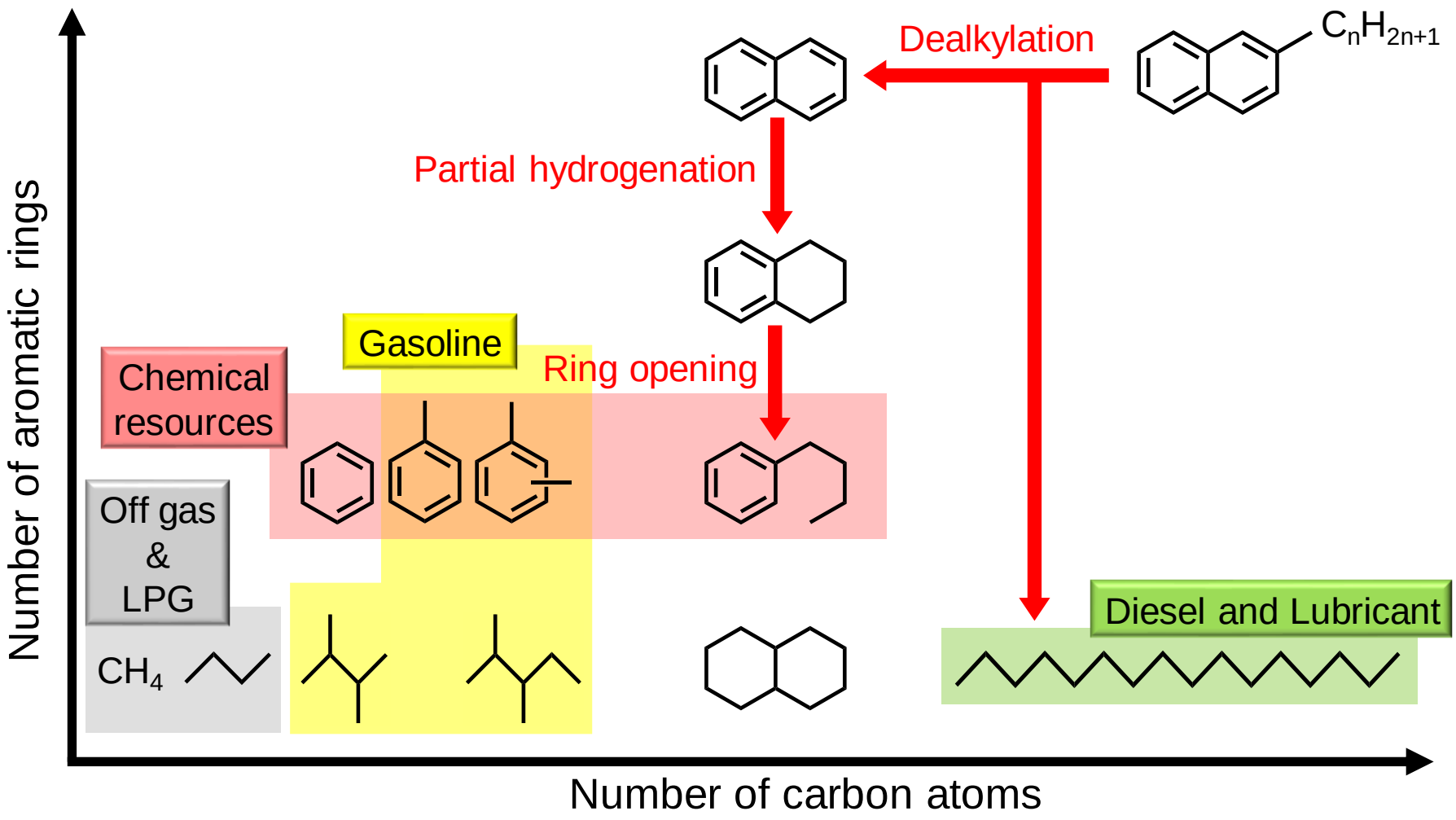
Cracking

分解軽油(LCO)の生成とアルカンの過剰分解

Hydrogenation/Hydrocracking

過剰な水素消費，ベンゼン誘導体生成量の減少

脱アルキル化によるVGO変換プロセス



需要が減少している低級アルカンの回収量は少ない．
需要が堅調に増加しているベンゼン誘導体，長鎖アルカンの回収量が多い．

本課題の開発ステップ

1st 阻害物質の除去

塩基性
含窒素化合物

2nd アルキル多環芳香族
脱アルキル化

3rd 生成物分離 → 多環芳香族

長鎖アルカン

4th 部分水素化

開環

ベンゼン誘導体

本課題の開発ステップ

1st 阻害物質の除去

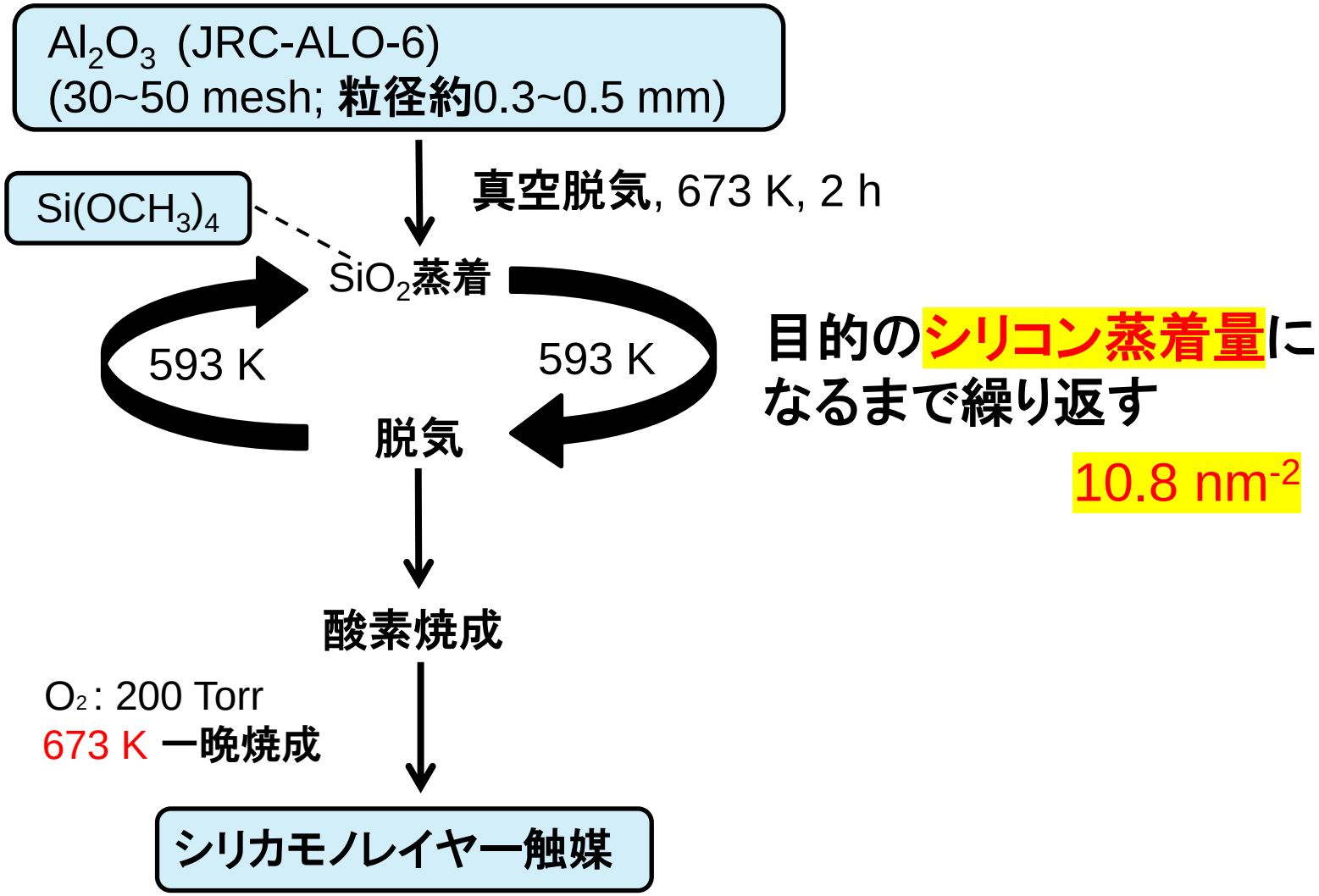
2nd アルキル多環芳香族 脱アルキル化

塩基性
含窒素化合物

"Selective Dealkylation of Alkyl Polycyclic Aromatic Hydrocarbons Towards Innovative Upgrading Process of Practical Heavy oil"
Catal. Sci. Technol.(RSC), **11**, 239 - 249 (2020).

シリカモノレイヤー触媒の調製

CVD（Chemical Vapor Deposition：**化学蒸着**）**法**[1)]



1) N. Katada et al., *J. Phys. Chem.,* 98, (31) 7647-7652 (1994)

減圧軽油(VGO)

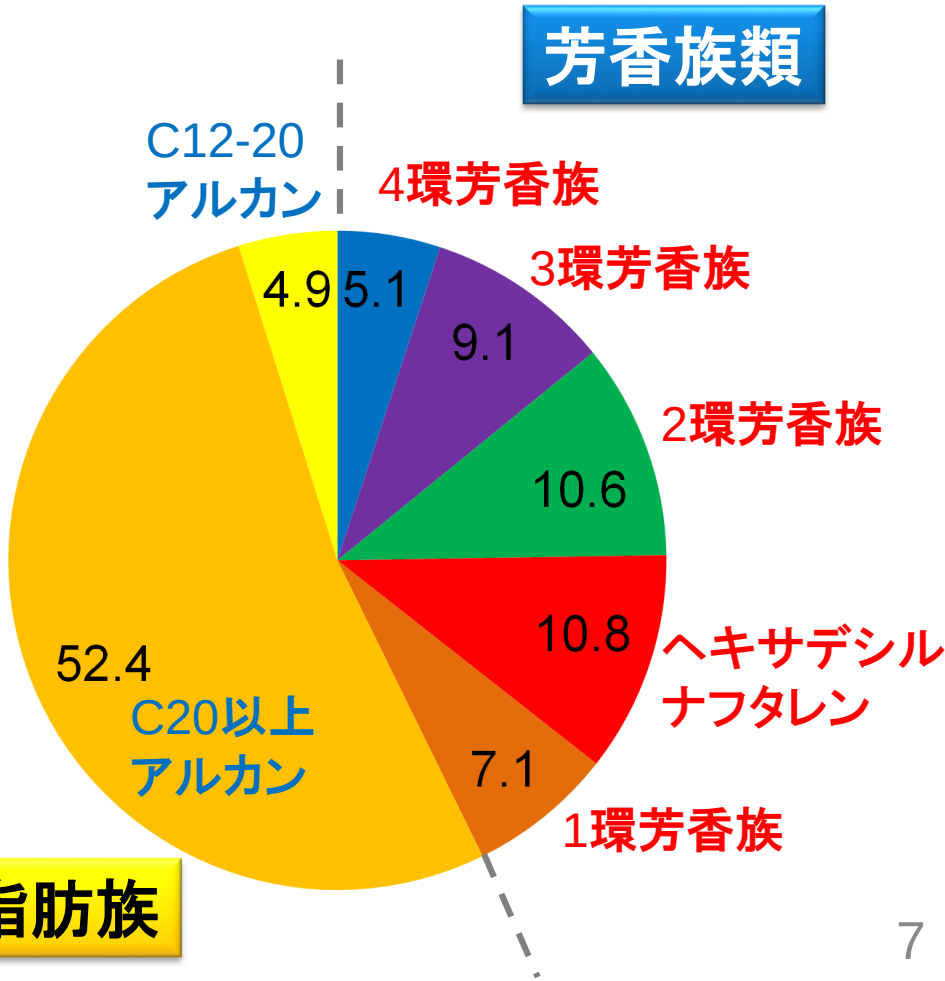
蒸留GC測定で最終沸点1008 KのVGO
- 流動化のためにベンゼン希釈
- 反応性評価のためにヘキサデシルナフタレン異性体混合物を添加
  (Synnestic 5, Exxon Mobil)

☆VGO溶液（重量比）

• VGO	1
• ベンゼン	1
• ヘキサデシルナフタレン (HDN)	0.11

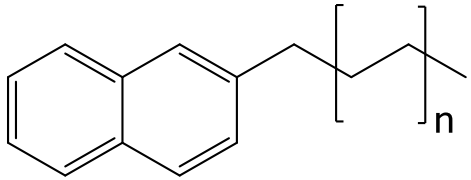
蒸留GC
- ✓ 36-170ºC: 0 %
- ✓ 170-350ºC: 19.5 %
- ✓ >350ºC: 80.5 %

VGO溶液の組成
(2D-GCで測定)
* ベンゼンは含まず



脱アルキル化反応

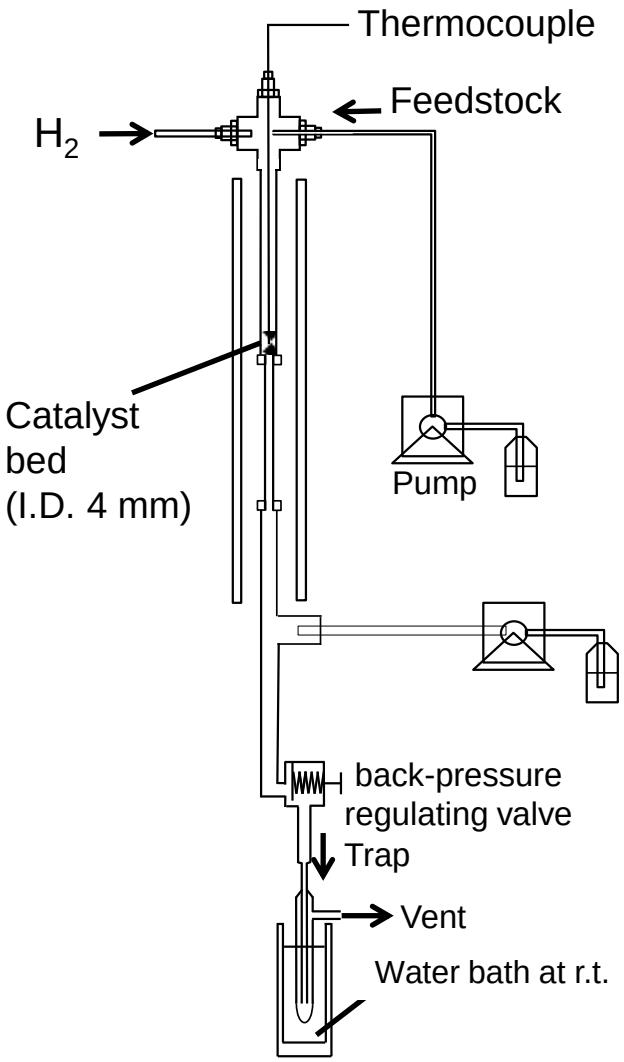
脱アルキル化の反応指標剤：
ヘキサデシルナフタレン（HDN）



n = 7

反応条件

- **触媒** 210 mg
- **反応温度** 723 K
- H_2 50 mL min^{-1} (0.12 mol h^{-1})
- **原料** VGO**溶液** 1.2 g h^{-1}
- **全圧** 1.0 MPa



反応後の分析条件

- 2**次元** GC **（液体）**

物理化学特性

Catalyst	Al_2O_3	Deposited Si atoms / nm^{-2}	Coverage / %	Surface area *1 / $m^2\ g^{-1}$	Pore size *2 / nm
SMA-1	Purchased sample *3	8.5	86	184 *4	6.2
SMA-2	ALO-9	8.1	90	182 *4	9.2
SMA-3	ALO-6	7.9	91	169 *4	24
SMA-4	ALO-7	8.7	95	147 *4	33

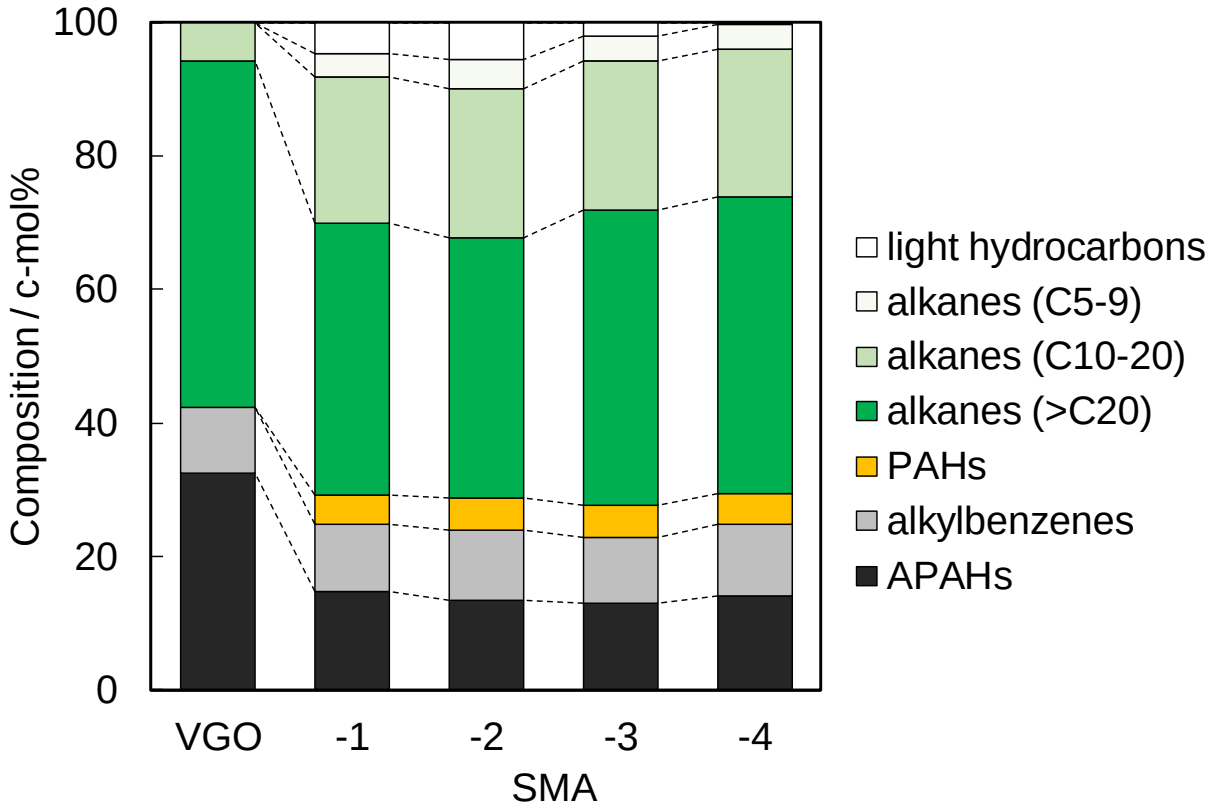
*1 calculated by BET equation, *2 mode value of pore size calculated by BJH method,
*3 sample purchased from FUJIFILM Wako Pure Chemical Corp., *4 normalized by catalyst weight,

酸性質

Catalyst	Brønsted acid amount / mol kg^{-1} (site nm^{-2}) *1	ΔH *2 / kJ mol^{-1}
SMA-1	0.11 (0.36)	116
SMA-2	0.08 (0.26)	116
SMA-3	0.10 (0.36)	116
SMA-4	0.06 (0.25)	116
N631-L	0.17 (0.21)	122
USY	0.34 (0.27)	136
ZSM-5	1.14 (2.23)	148

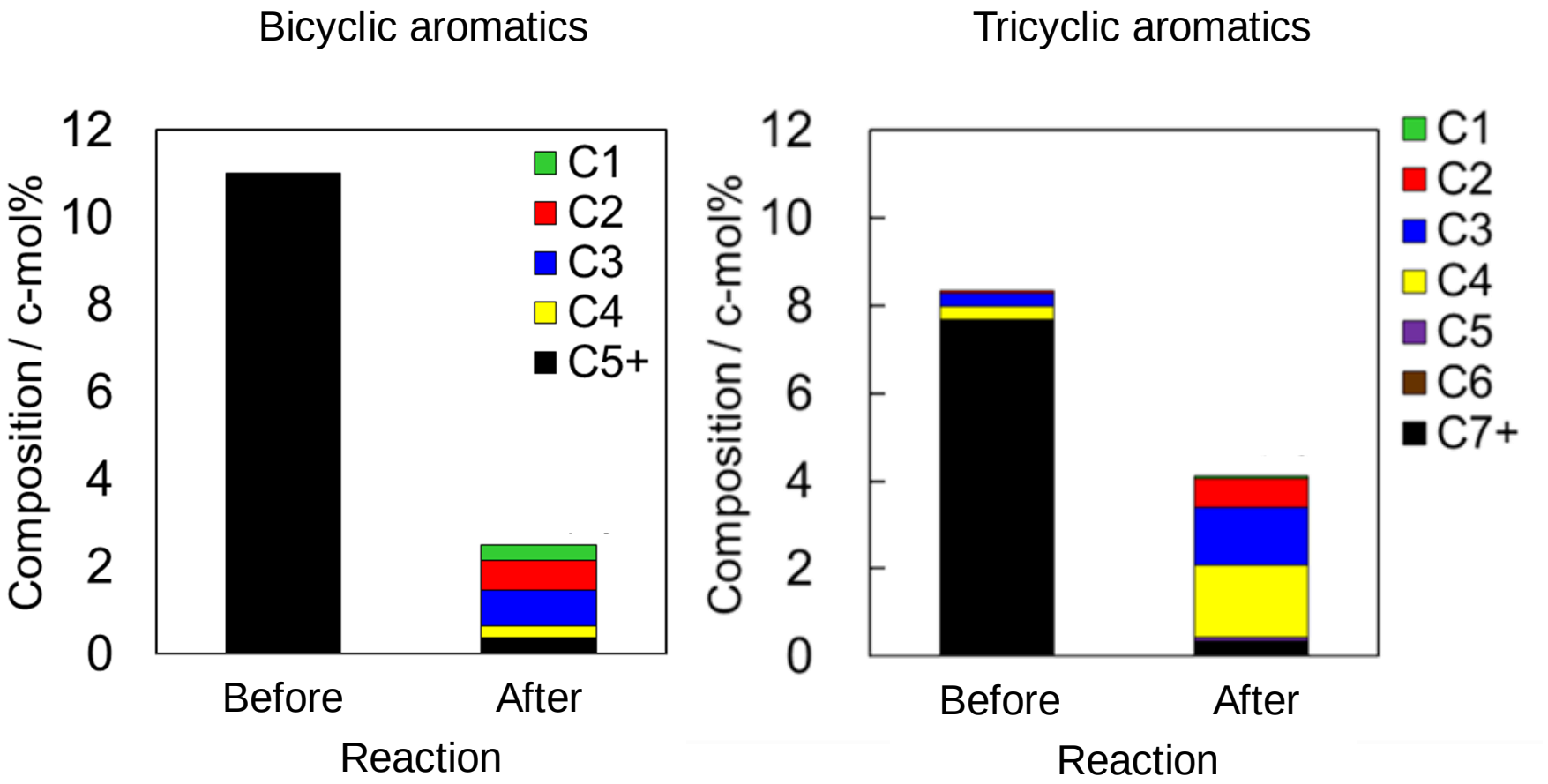
*1 Number of Brønsted acid sites normalized by BET surface area,
*2 mode value in enthalpy of ammonia desorption from Brønsted acid sites.

シリカモノレイヤー触媒による脱アルキル化



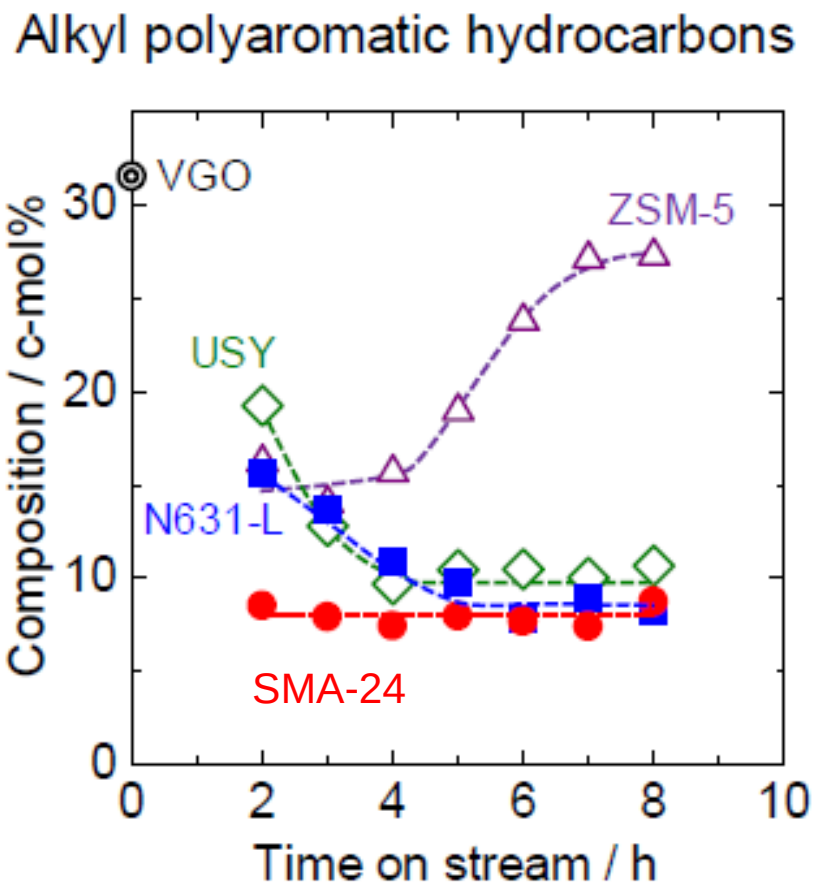
Compositions of outlet compounds averaged during 5-8 h on SMAs in the dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 $g_{VGO}\ g_{cat}^{-1}\ h^{-1}$.
The compositions in the original (fed) VGO are shown in a leftmost bar.

アルキル多環芳香族の組成比の変化



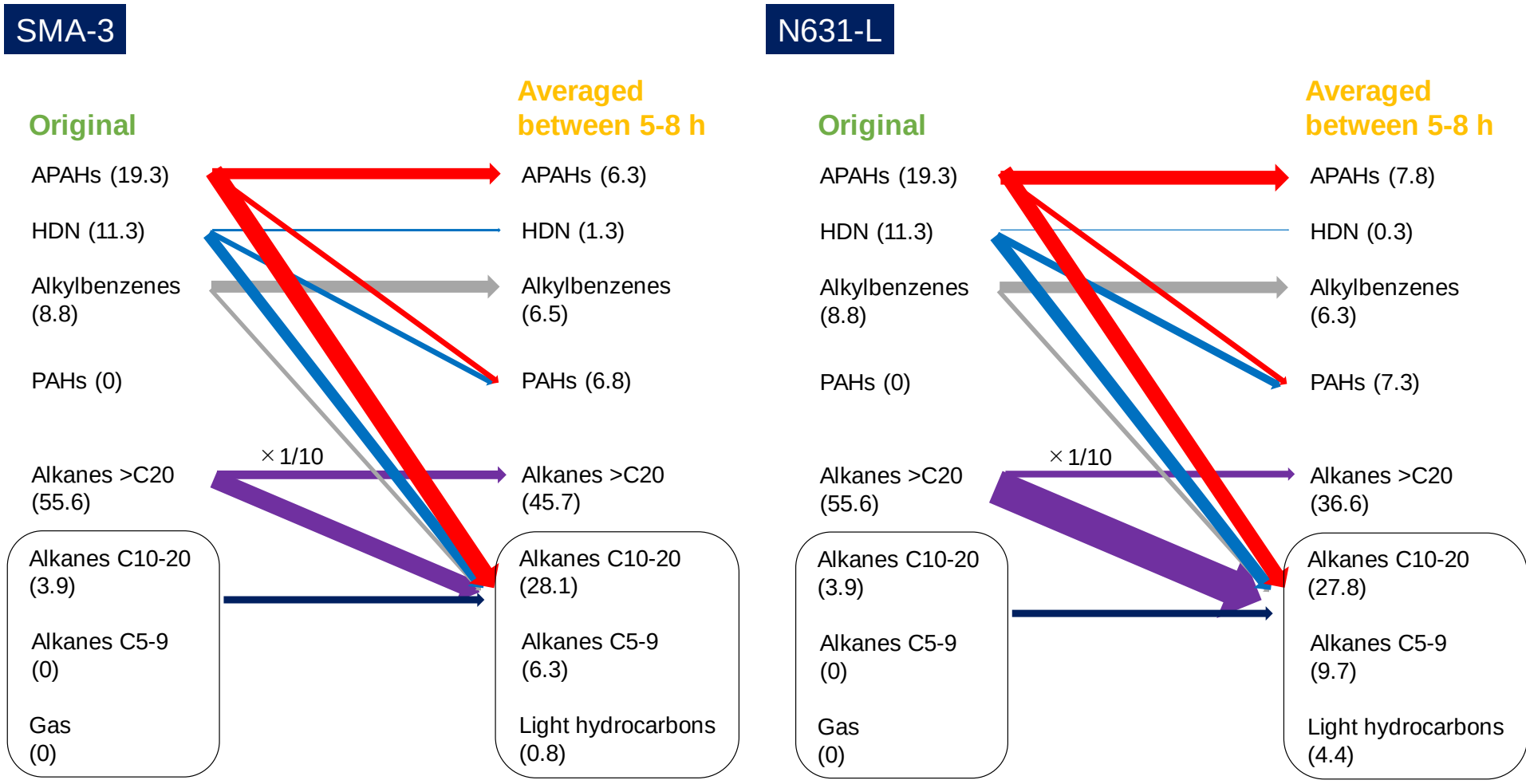
Composition averaged over 2-8 h of various carbon numbers of side chains in alkyl bicyclic and tricyclic aromatic hydrocarbons after the dealkylation over SMA-24.

アルキル多環芳香族の脱アルキル化



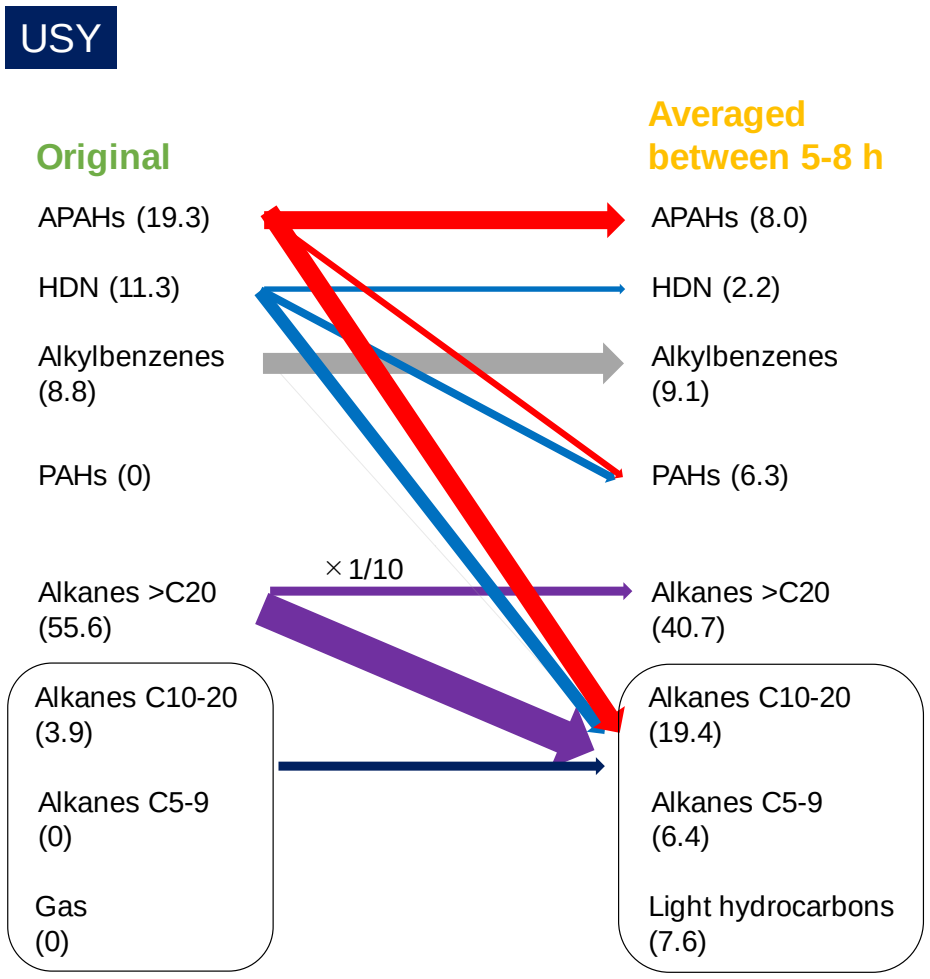
The dealkylation of APAHs in fed VGO at 723 K and LHSV = 5.7 $g_{VGO}\ g_{cat}^{-1}\ h^{-1}$. Double circle means the amount of APAHs in the original (fed) VGO.

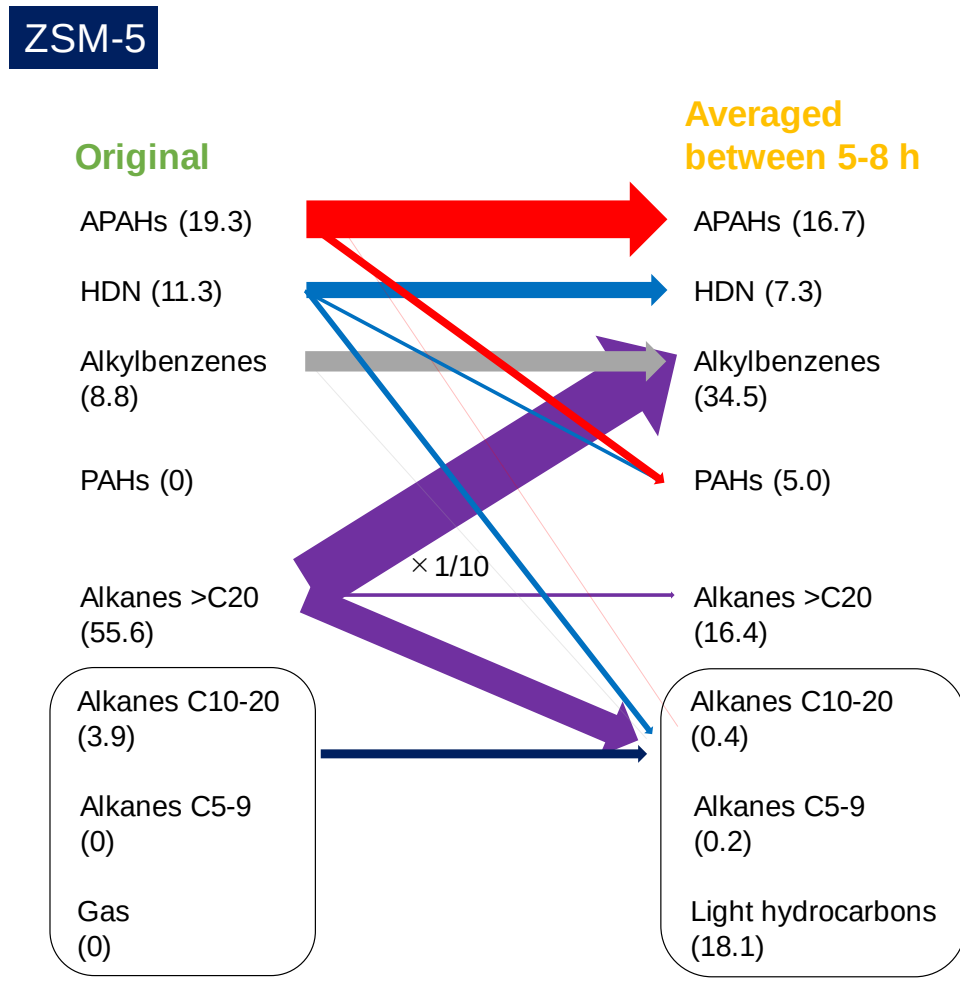
VGO中の組成比の変化



The bracketed values are composition of the components (C(carbon)-mol %) in original VGO (left side) and in the products averaged over 5-8 h (right side). APAHs and HDN were dealkylated into PAHs and alkanes (C10-20, C5-9, and light hydrocarbons), excluding alkanes (>C20). Alkyl groups in alkylbenzenes were cracked into alkanes (C10-20, C5-9, and light hydrocarbons). It is difficult to distinguish between alkanes (C10-20, C5-9, and light hydrocarbons) produced by the cracking of alkanes and alkyl groups in APAHs, HDN, and alkylbenzenes.

VGO中の組成比の変化





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まとめ

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3rd 生成物分離 ⇒ 多環芳香族

4th 部分水素化

開環

長鎖アルカン

ベンゼン誘導体

"Innovation of Catalytic Technology for Upgrading of Crude Oil in Petroleum Refinery", (Review), *Fuel Process. Technol.*, 208, 106518 (2020).