Electronic Supplementary Information

Enhanced Catalytic Activity of Cobalt Catalysts for Fischer–Tropsch Synthesis via Carburization and Hydrogenation and Its Application for Regeneration

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Detailed calculations of CO conversion and hydrocarbon selectivities

Ar was used as an internal standard for the quantitative analysis of flue gases reaching the GC detector. Conversions and selectivities reported herein were calculated from analysis of gas products as follows:

$$CO\ conversion\ (\%) = 100 \times ((n_{CO})_{in} - (n_{CO})_{out}) / (n_{CO})_{in}$$

$$CO_2\ selectivity\ (\%) = 100 \times (n_{CO2})_{out} / ((n_{CO2})_{in} - (n_{CO2})_{out})$$

Hydrocarbon selectivities (C_1-C_4)

$$S_{ij}\ (\%) = (100 \times (in_{ij})) / ((n_{CO})_{in} - (n_{CO})_{out} - (n_{CO2})_{out})$$

where S_{ij} is the selectivity of hydrocarbon species j containing i carbon atoms, n_{ij} is the molar flow of compound j in the gas phase, $(n_{CO})_{in}$ and $(n_{CO})_{out}$ are the molar flow rates of CO in and out of the reactor, and $(n_{CO2})_{out}$ is the molar flow rate of carbon dioxide out of the reactor.

The selectivity of C_{5+} hydrocarbons was calculated from the C_1-C_4 selectivities as:

$$S_{C5+}\ (\%) = 100 - (S_{C1} + S_{C2} + S_{C3} + S_{C4})$$

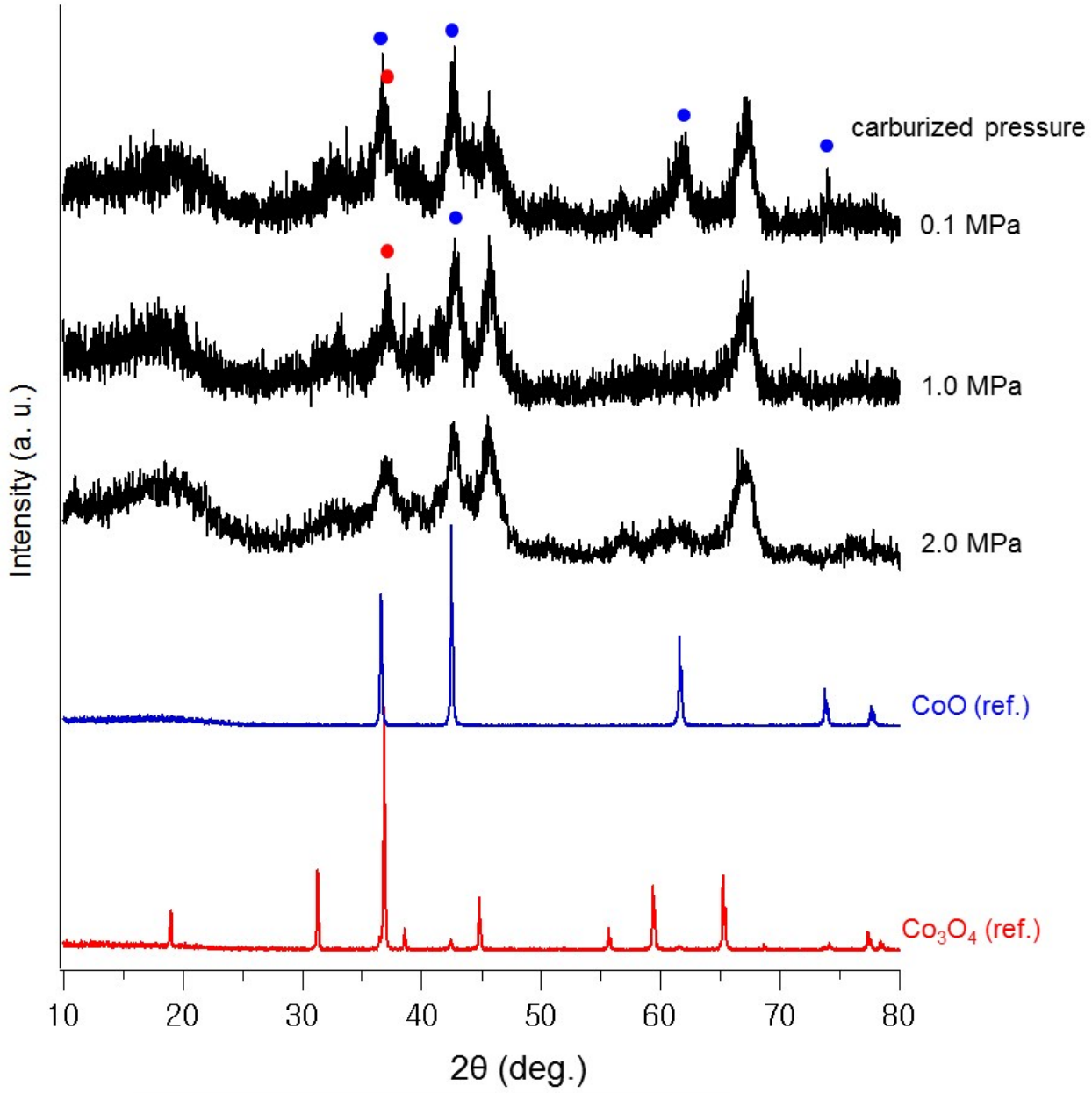

Figure S1. XRD patterns of catalysts carburized at different pressures after exposure to air.

The reduced cobalt catalysts carburized at lower pressures (0.1 and 1.0 MPa) were insufficiently transformed to Co_2C and partly oxidized with exothermicity in air. On the other hand, the well-developed Co_2C at 2.0 MPa maintained the presence of the Co_2C phase, in spite of air exposure.

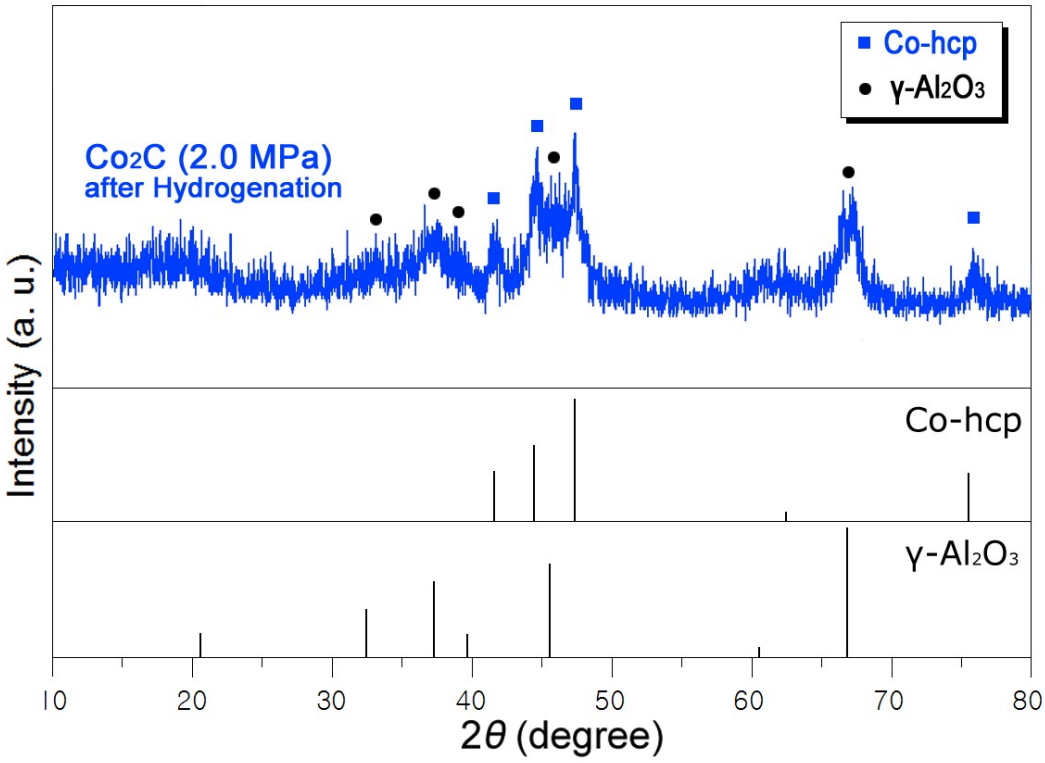

Figure S2. XRD pattern of the hydrogenated Co_2C (2.0 MPa).

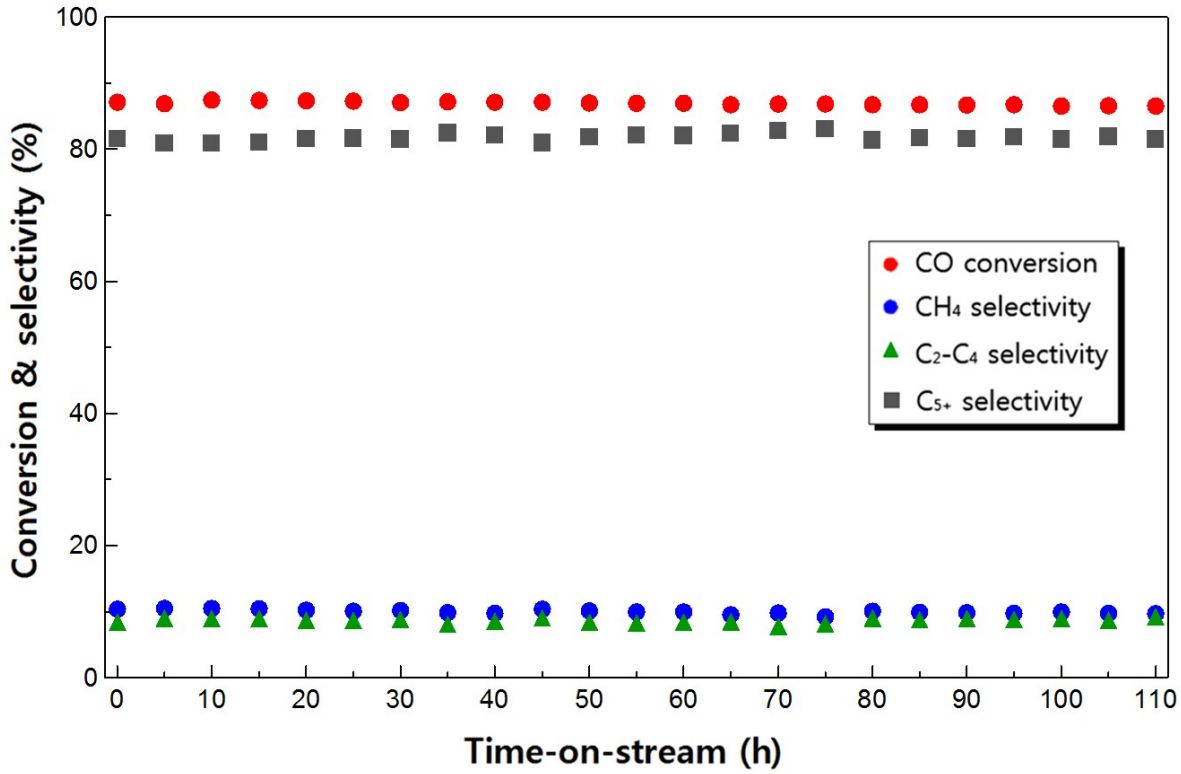

Figure S3. CO conversion and hydrocarbon (CH4, C2-C4, and C5+) selectivity with time-on-stream for regenerated catalyst after in situ carburization and hydrogenation at 220 °C.

Table s1. Catalytic activities of Co_2C depending on hydrogenation conditions in FTS.

Hydrogenation Conditions	CO conversion (%)	CTY[a] [10^{-5} $mol_{CO}/(g_{Co}/s)$]	Hydrocarbon Selectivity (%)		
			CH_4	C_2–C_4	C_{5+}
220 °C 2.0 MPa	80.04	9.82	6.82	6.09	86.95
220 °C 0.1 MPa	80.39	9.85	7.11	6.16	86.73
Without hydrogenation	39.72	4.87	15.82	8.91	77.10

GHSV: 8.0 $L_{syn}/(g_{cat}/h)$, *P*: 2.0 MPa, *T*: 220 °C, H_2/CO ratio: 2.0, feed composition: $H_2/CO/CO_2/Ar$ = 57.3/28.4/9.3/5.0 (mol%). Catalytic properties determined after 20 h on stream.

[a]Calculated from cobalt loading in catalysts, CO conversion, and GHSV.