Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary material

Effect of ordered meso-macroporous structure of Co/SiO_2 for an enhanced activity of CO hydrogenation to hydrocarbons

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Supplementary **Figure S1** represents the pore size distribution of the fresh (A) MMS support, (B) Co/MMS and (C) Co/SiO_2 catalysts.

Supplementary **Figure S2** represents the FT-IR spectra of the adsorbed CO molecules on the fresh Co/MMS and Co/SiO_2 catalysts.

Supplementary **Figure S3** represent the long-term catalytic stabilities of the Co/MMS and Co/SiO_2 catalysts at the following reaction conditions; T = 230 °C, P = 2.0 MPa, weight hourly space velocity (WHSV) of 12000 $L/(kg_{cat}\bullet h)$, and the feed syngas composition of $H_2/CO/N_2$ = 63.1/31.5/5.4 for 60 h, where N_2 was used as an internal standard gas by using 0.2 g catalyst with 2.0 g of inert material of SiC.

Supplementary **Figure S4** represents the full range FT-IR spectra of the fresh and used (A)

Co/MMS and (B) Co/SiO$_2$ catalysts.

Supplementary **Figure S5** represents the Raman spectra of the used Co/MMS and Co/SiO$_2$ catalysts.

Supplementary **Figure S6** represents the catalytic activity on the Co/MMS, Co/SiO$_2$ and Co/SBA-15 catalysts for 20 h on stream at the reaction conditions of T = 230 ^{o}C, WHSV = 4000 L/(kg$_{cat}$•h), P = 2.0 MPa, and H$_2$/CO = 2.0 by using 0.2 g catalyst with SiC inert material of 2.0 g. The Co/SBA-15 catalyst was prepared by using similar methods with the Co/SiO$_2$ with the composition of 20wt%Co-0.1wt%Pt/79.9wt%SBA-15, where Co/SBA-15 has a surface area of 670 m^2/g and a particle size of Co$_3$O$_4$ of around 11.7 nm measured from N$_2$ sorption and XRD analysis [**1**].

Supplementary **Table S1** represents the summary of the respective TPR and FT-IR of adsorbed CO molecules calculated from the results of **Figure 2** and **Figure S2**.

Supplementary **Table S2** represents the results of in-situ regeneration of the Co/MMS and Co/SiO$_2$ by introducing liquid octane with a flow rate of 1.65 ml/min for 20 minutes at the reaction conditions of T = 230 ^{o}C, WHSV = 4000 L/(kg$_{cat}$•h), P = 2.0 MPa, and H$_2$/CO = 2.0 with 0.1 g Co/MMS and 0.2 g Co/SiO$_2$ without using inert material of SiC, respectively.

[1] J. M. Cho, C. I. Ahn, C. Pang, J.W. Bae, *Catal. Sci. Technol.*, 2015, **5**, 3525-3535.

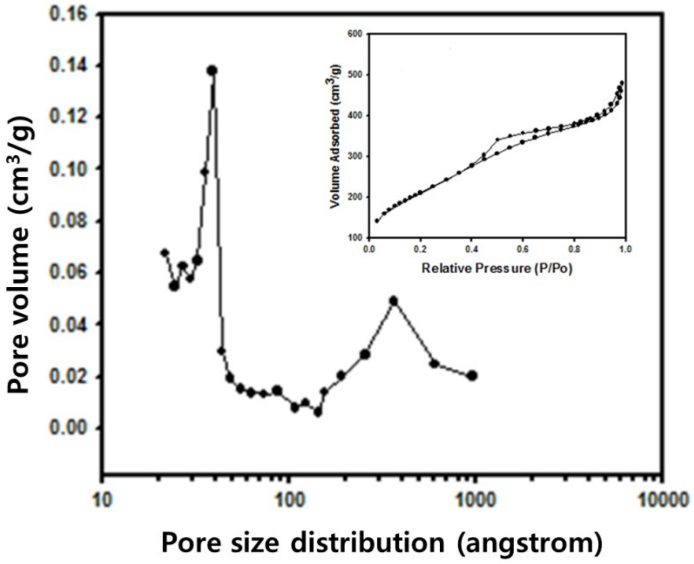

Figure S1(A). Pore size distribution of MMS support

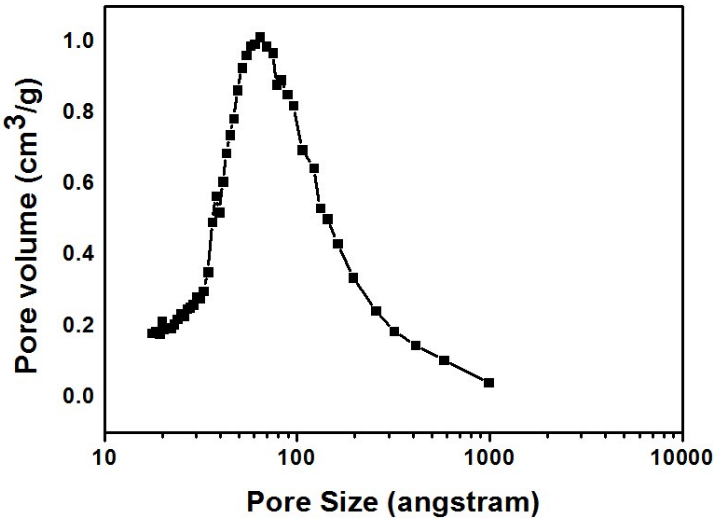

Figure S1(B). Pore size distribution of Co/MMS catalyst

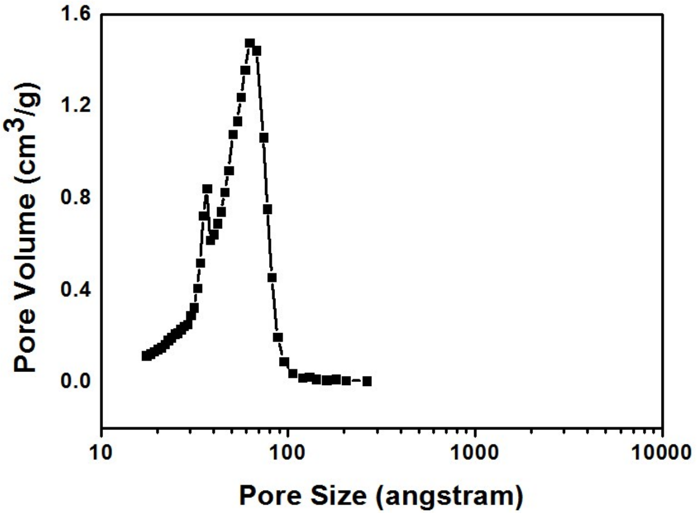

Figure S1(C). Pore size distribution of the fresh Co/SiO_2 catalyst

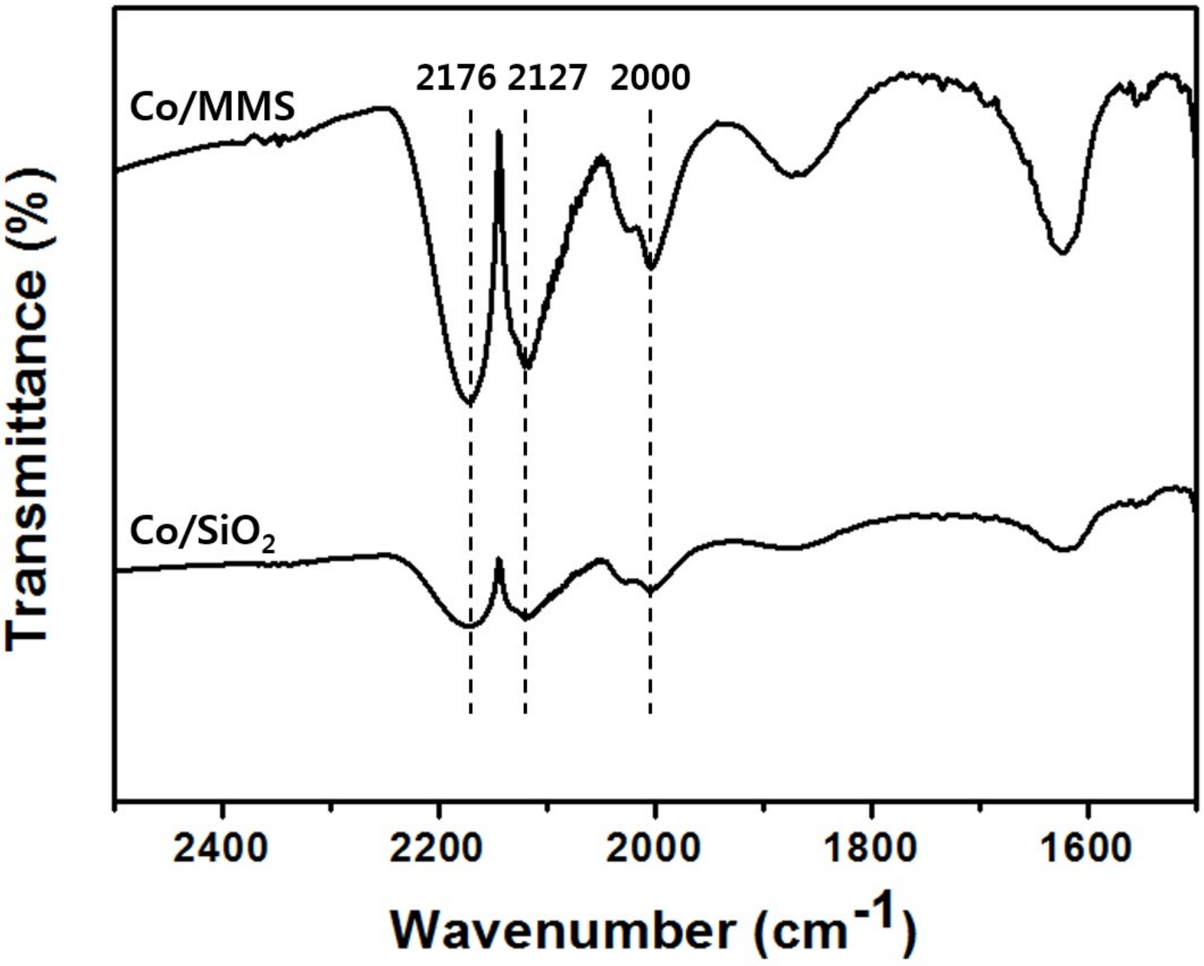

Figure S2. FT-IR spectra of the adsorbed CO molecules on the fresh Co/MMS and Co/SiO_2 catalysts

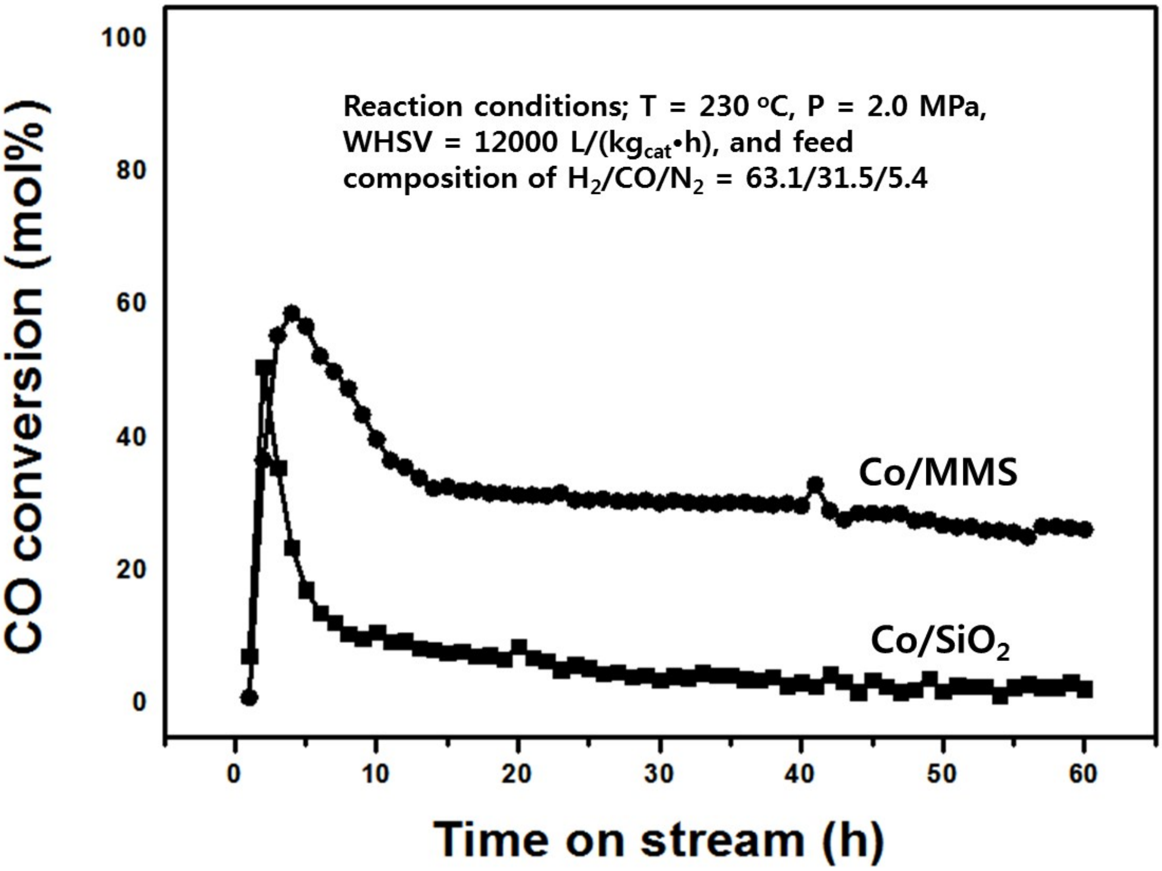

Figure S3. Long-term catalytic stabilities of the Co/MMS and Co/SiO_2 catalysts at the following reaction conditions; T = 230 °C, P = 2.0 MPa, weight hourly space velocity (WHSV) of 12000 L/(kg$_{cat}$•h), and the feed syngas composition of $H_2/CO/N_2$ = 63.1/31.5/5.4 for 60 h, where N_2 was used as an internal standard gas by using 0.2 g catalyst with 2.0 g of inert material of SiC.

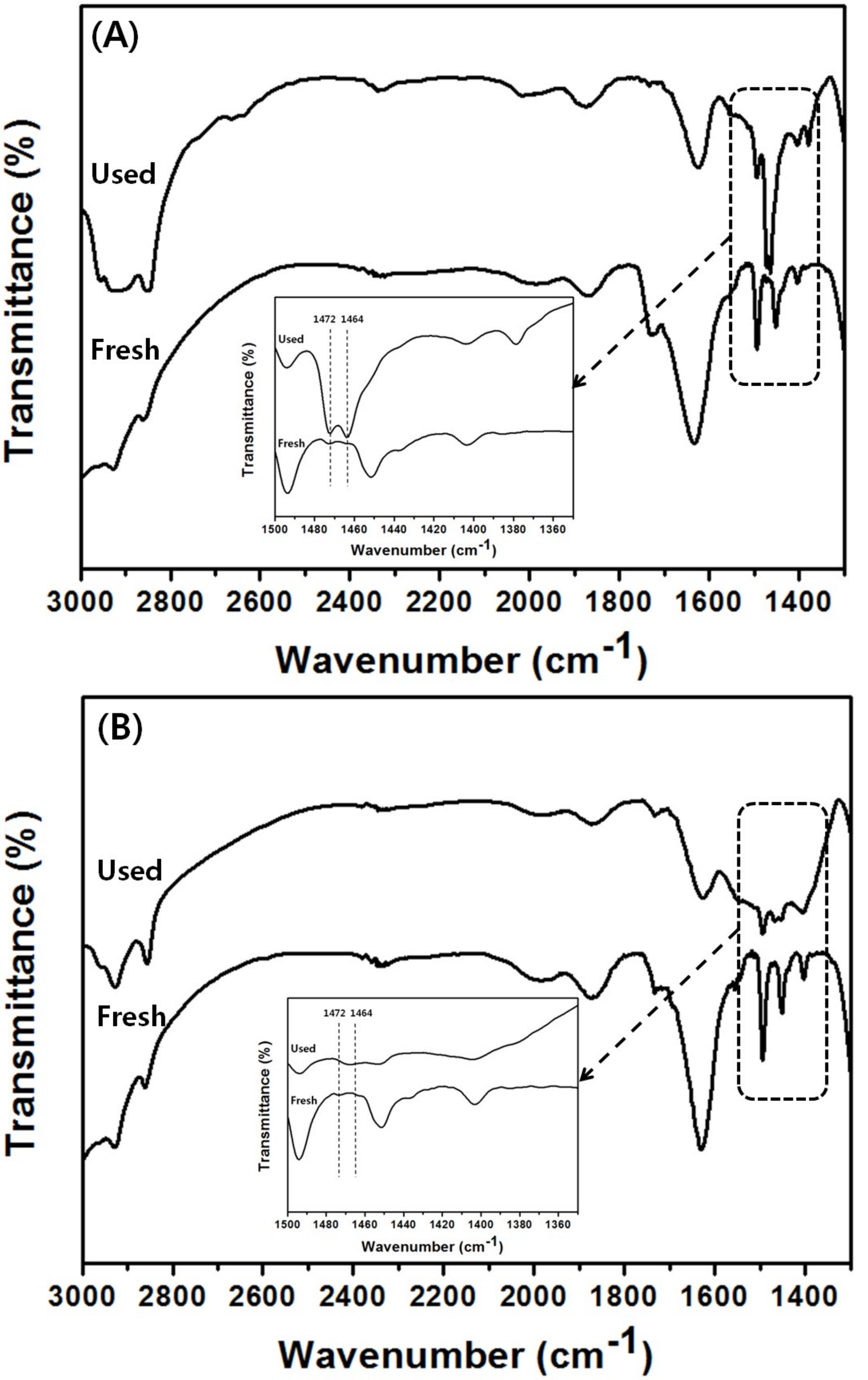

Figure S4. Full range FT-IR spectra of the fresh and used (A) Co/MMS and (B) Co/SiO$_2$ catalysts

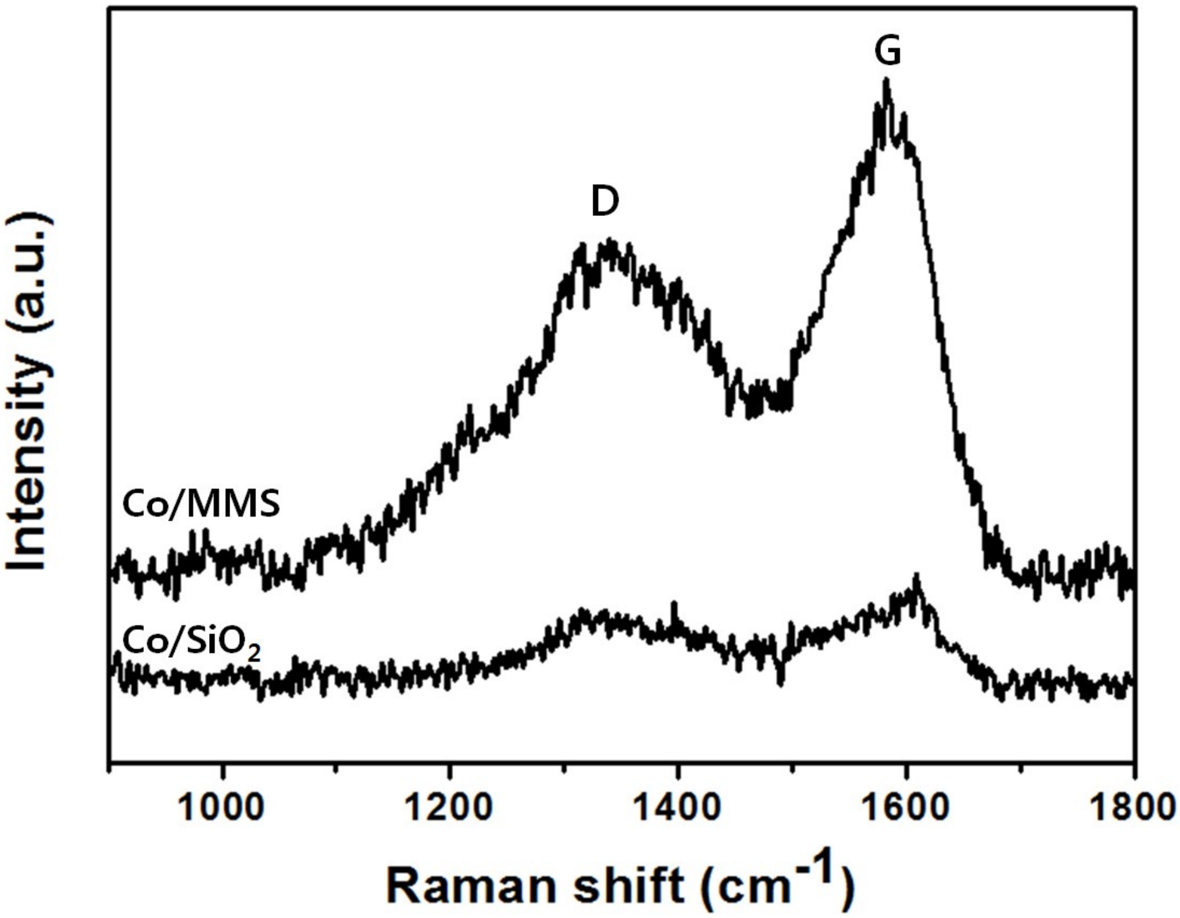

Figure S5. Raman spectra of the used Co/MMS and Co/SiO_2 catalysts

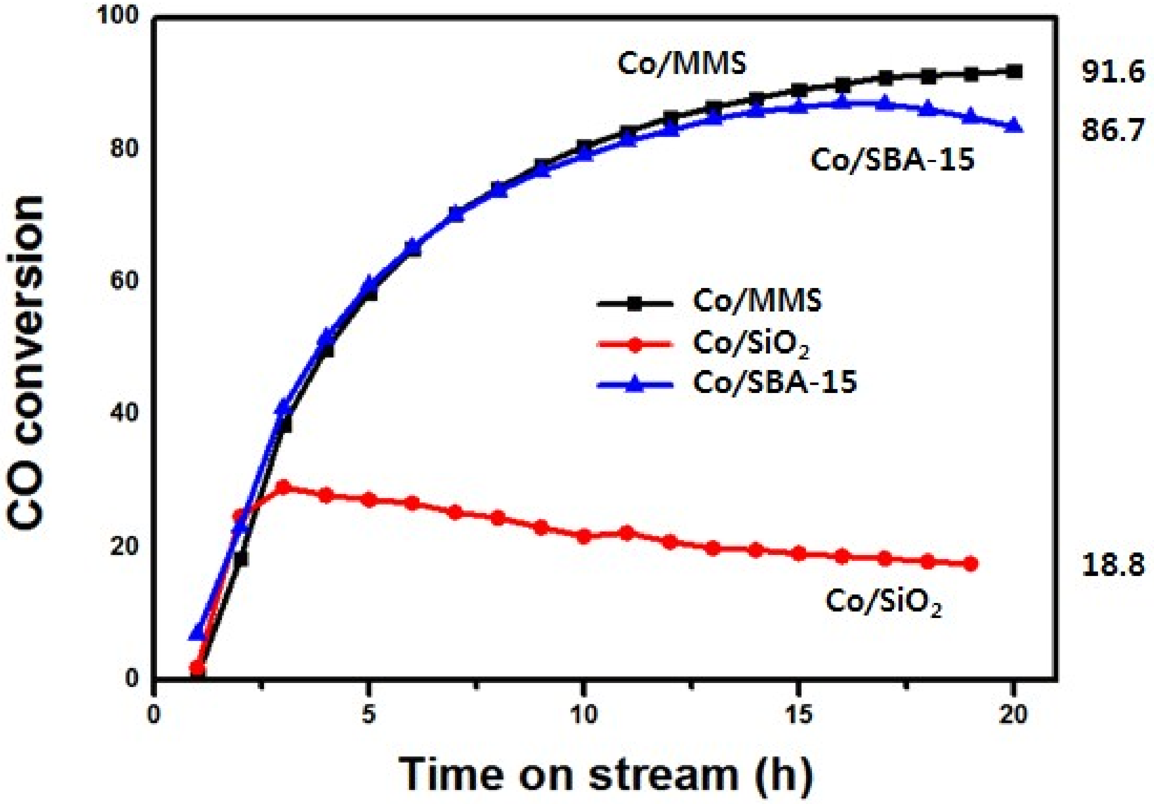

Figure S6. Catalytic activity on the Co/MMS, Co/SiO$_2$ and Co/SBA-15 catalysts for 20 h on stream at the reaction conditions of T = 230 ^{o}C, WHSV = 4000 L/(kg$_{cat}$•h), P = 2.0 MPa, and H$_2$/CO = 2.0 by using 0.2 g catalyst with SiC inert material of 2.0 g.

Table S1. Summary of the respective TPR and FT-IR of adsorbed CO molecules calculated from the results of **Figure 2** and **Figure S2**

Notation	TPR (relative peak area (%) and its ratio of P(I)/P(II))			Adsorbed CO FT-IR at different oxidation states of cobalt	
	< 300°C (P(I))	> 300°C (P(II))	Ratio of P(I)/P(II)[a]	Area at 2020 ($ICo^{\delta+}$) and 2000 (ICo^0) cm^{-1}	Ratio of ($ICo^{\delta+}$)/(ICo^0)[b]
Co/MMS	36.3	63.7	0.571	11.5 / 89.5	0.128
Co/SiO_2	20.3	79.7	0.255	8.8 / 38.3	0.230

[a] The ratio of P(I)/P(II) represents the ratio of the integrated peak area assigned for a low temperature reduction peak below 300 °C (P(I)) to the peak assigned for a high temperature reduction peak above 300 °C (P(II)).

[b] The ratio of I($Co^{\delta+}$)/(ICo^0) was calculated using the relative integrated peak area of the adsorbed CO molecules on the partially oxidized $Co^{\delta+}$ (assigned to $ICo^{\delta+}$ for a shoulder peak at the wavenumber of ~2020 cm^{-1}) divided by the peak area on the metallic Co^0 (assigned to ICo^0 for the main peak at 2000 cm^{-1}).

Table S2. Results of in-situ regeneration of the Co/MMS and Co/SiO_2 by introducing liquid octane[a]

Notation	Octane feeding	CO conversion (C-mol%)	CO conversion to CO_2 (C-mol%)	Product distribution (C-mol%)			Olefin selectivity[b] (C-mol%)
				CH_4	C_2-C_4	C_5+	
Co/MMS	-	63.7	1.7	9.9	5.7	81.0	12.1
	1st	48.1	1.3	9.6	1.6	87.4	36.0
	2nd	44.6	1.2	10.2	1.6	87.1	36.5
Co/SiO_2	-	15.0	0.1	12.0	23.8	64.0	36.3
	1st	31.0	0.0	6.7	9.2	84.2	31.3

[a] The results of catalytic reaction were summarized using the maximum conversion of CO after in-situ regeneration by introducing liquid octane with a flow rate of 1.65 ml/min for 20 minutes at the reaction conditions of T = 230 °C, WHSV = 4000 L/(kg_{cat}•h), P = 2.0 MPa, and H_2/CO = 2.0 with 0.1 g Co/MMS and 0.2 g Co/SiO_2 without using inert material of SiC, respectively. The CO conversions with time on stream were displayed in **Figure 6**.

[b] The olefin selectivity (C-mol%) was obtained in the C_2-C_4 light hydrocarbons.