Supplementary Material

Ordered mesoporous CoMO$_x$ (M=Al or Zr) mixed oxides for Fischer-Tropsch synthesis

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Supplementary **Table S1**. Catalytic activity and BE of Co 2p of the ordered mesoporous m-CoM catalysts

Supplementary **Figure S1** represents N$_2$ isotherms of the ordered mesoporous fresh m-CoM mixed metal oxides.

Supplementary **Figure S2** represents TEM images of the ordered mesoporous m-CoM mixed metal oxides before FTS reaction; (A) m-Co(0), (B) m-CoAl(25), (C) m-CoZr(12), (D) m-CoZr(25).

Supplementary **Figure S3** represents XRD patterns of the fresh ordered mesoporous m-CoM mixed metal oxides.

Supplementary **Figure S4** represents XPS spectra of Co 2p on the ordered mesoporous m-CoM mixed metal oxides before FTS reaction.

Supplementary **Figure S5** represents the photos of the used FTS catalysts after reaction, which showed a less aggregation of the catalyst particles due to the less wax deposition on the m-CoZr(12) and m-CoZr(25) compared to the conventional Co/SiO$_2$ having an irregular pore structures.

Supplementary **Figure S6** represents XPS spectra of Co 2p on the ordered mesoporous m-CoM mixed metal oxides after FTS reaction.

Supplementary **Figure S7** represents the results of EELS analysis on the used m-CoZr(12) for the mapping of Co, Zr and Al elements.

Supplementary **Figure S8** represents TEM images of the ordered mesoporous m-CoM mixed metal oxides after FTS reaction; (A) m-Co(0), (B) m-CoAl(25), (C) m-CoZr(12), (D) m-CoZr(25).

1. Experimental section

1.1. Synthesis of highly ordered mesoporous KIT-6

The ordered mesoporous KIT-6 was synthesized through hydrothermal synthesis, which is widely known as one of the most powerful techniques for synthesizing ordered mesoporous metal oxides [S1-S5]. For the synthesis of KIT-6, amorphous silicas were deposited on the surfaces of micelles which were formed in an aqueous solution with a structure-directing agent or surfactant. An amphiphilic triblock co-polymer of $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), Aldrich) was used as a structure-directing agent and tetraethylorthosilicate (TEOS, Alfa Aesar) for silicon precursor. For more detail, P123 copolymer was completely dissolved in deionized water and then 37 wt%HCl solution was diluted in deionized water. The dissolved P123 aqueous solution was poured into the diluted HCl solution at once under a vigorous stirring at 35 °C. After sufficient mixing of the above solution, n-butanol was added to the solution and stirred for 1 h followed by adding TEOS. The final solution was aged under a vigorous stirring for 24 h at 35 °C. After further stirring for one day, the mixture solution was transferred to an autoclave and kept for 24 h at 100 °C without stirring. Hydrothermally treated solution was filtered without washing procedure, and the as-prepared white precipitant powder was dried at 100 °C. To extract the P123 copolymer from the dried powder, it was immersed in HCl/ethanol solution about 2 h, and washed with deionized water several times. Rinsed powder was dried again at 100 °C, and it was subsequently calcined in air at 550 °C for 6 h at a heating rate of 1 °C /min.

1.2. Synthesis of the ordered mesoporous CoM mixed metal oxides

The irreducible metal oxides of Al_2O_3 and ZrO_2 incorporated in the mesoporous Co_3O_4 were synthesized by co-impregnation of the metal precursors into the ordered mesopores of the KIT-6 through nanocasting method. The metal precursors of cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) (or zirconium oxy nitrate dehydrate ($ZrO(NO_3)_2 \cdot 2H_2O$)) were previously dissolved in deionized water and they were co-impregnated into the pores of the KIT-6, which was further dried at 100 ^{o}C for 1 h. After the solution of the cobalt and aluminum (or zirconium) precursor was sufficiently impregnated into the mesopores of the KIT-6, it was dried at 80 ^{o}C overnight. The mixed metal precursors impregnated KIT-6 was calcined in a muffle furnace at 550 ^{o}C for 3 h at a heating rate of 1 ^{o}C /min to transform the mixed metal oxides of Co_3O_4-Al_2O_3 (or Co_3O_4-ZrO_2), separately. To remove the hard-template of KIT-6 from the Co_3O_4-Al_2O_3 (or Co_3O_4-ZrO_2) impregnated KIT-6, the sample was rinsed with 2 M NaOH aqueous solution and washed several times with deionized water and acetone. The template-free mixed metal oxides of Co_3O_4-Al_2O_3 (or Co_3O_4-ZrO_2) were dried at room temperature. The molar composition of the metal precursors on the Al_2O_3 and ZrO_2 incorporated Co_3O_4 was varied in the rage of 0.125, 0.25 and 0.375 for the metal molar ratio of Al or Zr to Co, and the mixed oxides were denoted as CoM(x), where x for the metal molar ratio of M (M = Al or Zr) to Co. For comparison, mesoporous Co_3O_4 was also synthesized by the same procedure without using the irreducible metal oxides of Al_2O_3 and ZrO_2. For preparing the final FTS catalysts, the irreducible Al_2O_3 impregnated mesoporous CoM(x) was further synthesized by incipient wetness impregnation with a fixed amount of 5wt%Al_2O_3. For more detail, aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) precursor was dissolved in deionized water and mixed with the dried mesoporous CoM(x) powder to fill the mesopores partially with pillaring material of

aluminum. The well-mixed Al-impregnated CoM(x) was dried at 80 °C for 12 h by slowly evaporating the solvent and followed by calcination at 550 °C for 3 h at a heating rate of 1 °C/min. The as-prepared 5wt%Al-impregnated mixed metal oxides were denoted as the m-CoM(x) where x = 12, 25, 38 for a molar percentage of the M (M for Al or Zr) to cobalt metal, and m-Co(0) for 5wt%Al-impregnated mesoporous Co_3O_4 catalyst for the comparison. The mesoporous CoMOx catalysts contain a slightly different amount of cobalt species according to the molar ratio of Co/M. However, these differences seem to be insignificant for activity variation compared to a structural stability of the mesoporous CoMOx. The calculated metallic cobalt in the CoMOx catalysts showed a slightly different concentration, for example, the mesoporous Co_3O_4 contain a metallic cobalt of approximately 73.4%, and 64.3 % for the m-CoZr(12) and 62.3 % for the m-CoZr(25). In the case of the mixed metal oxides of CoMOx, the differences of the metallic cobalt content are below 10% in weight.

1.3. Catalytic activity measurement

Catalytic activity test of the ordered mesoporous m-CoM mixed metal oxides was carried out in a stainless steel fixed bed tubular reactor with an outer diameter of 12.7 mm. Around 0.1 g m-CoM catalyst was loaded to the reactor by mixing with a gamma-Al_2O_3 as a diluent. Prior to the FTS reaction, the m-CoM catalyst was reduced in situ at 400 °C under a flow of 5% H_2/N_2 for 12 h. After the pretreatment, the reactor temperature was cooled down to room temperature and a syngas containing a feed gas composition of $H_2/N_2/CO = 62.84/5.60/31.56$ was continuously introduced into the reactor. Reactor pressure and temperature were slowly raised to the FTS reaction condition sequentially, and the catalytic activity was in-situ measured. The FTS reaction was performed for around 60 h on stream under the following

reaction conditions; T = 240 °C, P = 2.0 MPa, and weight hourly space velocity (WHSV) = 24000 L(mixed gas)/(kg$_{cat}$·h). The product gases from the reactor were analyzed by using an online gas chromatograph (GC, YoungLin Acme 6500) equipped with a HP-PLOT/Q capillary column connected to a flame ionization detector (FID) for the analysis of the vaporized hydrocarbons, and a Carboxen-1000 packed column connected to a thermal conductivity detector (TCD) for the analysis of CO, CO_2, CH_4 and H_2. CO conversion with time on stream and product distribution were calculated from the results of GC analyses based on the carbon balance and the average values of them for 10 h at a steady-state activity are summarized. The reaction rate and turnover frequency (TOF) of the m-CoM catalysts were defined as reacted CO µmoles/(g$_{cat}$·s) and reacted CO molecules/(surface cobalt atom·s), respectively.

1.4. Catalyst characterizations

The specific surface area, average pore diameter and pore volume of the as-prepared (calcined) m-CoM catalysts were analyzed by N_2 adsorption-desorption analysis at -196 °C using an Micromeritics ASAP2020 instrument. These properties was obtained by using Brunauer-Emmett-Teller (BET) model, and the pore size distribution of the m-CoM catalysts was obtained using Barrett-Joyner-Halenda (BJH) model from the desorption isotherm data of the N_2 adsorption-desorption isotherms. The surface area of the metallic cobalt crystallites were measured by H_2 chemisorption method at 100 °C using Micromeritics ASAP2020C instrument. Prior to H_2 chemisorption analysis, the as-prepared m-CoM catalyst with 1.0 g was pretreated in situ at 400 °C for 12 h under a flow of 5 vol% H_2/N_2. To calculate the surface area of the metallic cobalt on the fresh m-CoM catalysts, H/Co stoichiometry ratio of

1.0 is assumed. In addition, the degrees of reduction of the metal cobalt on the m-CoM catalysts were also measured by O_2 titration. The degree of reduction of the pre-reduced m-CoM catalysts was calculated using the equation of [amount of O_2 consumed during O_2 titration (mmol O_2)] / [theoretical amount of O_2 consumption after full reduction of cobalt oxides (mmol O_2) with the assumption of ($3Co + 2O_2 \rightarrow Co_3O_4$)] $\times$ 100, which is based on the concentration of the total cobalt species on the m-CoM catalysts.

Powder X-ray diffraction (XRD) patterns of the calcined m-CoM catalysts were obtained by using a X'Pert PRO Multi-Purpose X-Ray Diffractometer operating at 60 kV and 55 mA with Cu-Kα radiation at a scanning rate of 5°/min. The Co_3O_4 crystallite size on the m-CoM catalysts was calculated using Debye-Scherrer formula using the values of full width at half maximum (FWHM), which were obtained from the most intense diffraction peak of Co_3O_4 at $2\theta = 36.8°$. The particle size of metallic cobalt was also obtained from the Co_3O_4 particle size by using the correlation for a relative molar volume of metallic cobalt with the equation $d(Co^0) = 0.75 \times d(Co_3O_4)$ [S5].

Transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) measurements for the mapping analysis of the Co, Zr and Al elements were carried out to elucidate the surface morphology and the elemental distribution of Co, Zr and Al species on the as-prepared fresh and used m-CoM catalysts using TECNAI G2 instrument operated at an accelerating voltage of 200 kV. In addition, the photos of the used FRS catalysts was included to verify the extent of aggregation of catalyst particles. The used FTS catalysts of the m-CoZr(12) and m-CoZr(25) compared to the conventional Co/SiO_2 having an irregular pore structures showed a less aggregation of the catalyst particles due to the less wax deposition on the catalyst surfaces.

Temperature-programmed reduction (TPR) with H_2 was carried out to verify the reduction behaviors of the as-prepared m-CoM catalysts using a BETCAT instrument equipped with TCD. Prior to the analysis, the sample was pretreated with Ar flow at 350 °C for 2 h to remove adsorbed water and contaminants, and followed by cooling to 50 °C. The reducing gas containing $5\%H_2/Ar$ was introduced to the sample at a flow rate of 30 ml/min with a heating rate of 10 °C/min from 50 to 950 °C. The effluent gas was passed over a molecular sieve trap to remove the water produced from reduction process, and then reduction patterns of the m-CoM catalyst were obtained. In addition, the possible formation of the spinel structured cobalt species such as $CoAl_2O_4$ was also verified by the results of TPR. It has been known that a strong metal support interaction between cobalt oxides and irreducible supporting materials can increase the amount of the strongly absorbed hydrogen [S6], the formation of metal-support complexes such as $CoAl_2O_4$ or $CoZr_2O_4$ species [S7] which subsequently change the electronic state through electron transfer between metal and support [S8]. In addition, the small amount of structural promoter of Al_2O_3 on the mesoporous Co_3O_4 showed a highly stable and a superior activity during FTS reaction from our previous research [S9].

The electronic state, outermost surface composition and binding energy (BE) of Co $2p_{3/2}$, Zr 2p and Al 2p on the fresh mesoporous m-CoM catalysts were determined from X-ray photoelectron spectroscopy (XPS; VG Multilab 2000) analysis with a monochromated Al Kα X-ray source (1486.6 eV) working at high energy from 0.1 to 3.0 KeV in a vacuum level at around 10^{-7} Pa. The obtained BEs was corrected by using the reference BE of C1s (284.6 eV). In addition, the intensity ratio of I_M/I_{Co} (where M = Al or Zr), defined as the integrated area ratio of the Al and Co metal after correction with atomic sensitivity factor was calculated to

elucidate the changes in surface chemical composition before and after FTS reaction.

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[**S9**] C.I. Ahn, H.M. Koo, J.M. Jo, H.S. Roh, J.B. Lee, Y.J. Lee, E.J. Jang and J.W. Bae, *Appl. Catal. B: Environ.*, 2016, **180**, 139-149.

**Table S1**. Catalytic activity and BE of Co 2p of the ordered mesoporous m-CoM catalysts

Catalysts	Reaction duration (h)	CO conv.[a] (C-mol%)	Product distribution (C-mol%)		XPS
			C_1 / C_2-C_4 / C_5+	Olefins in C_2-C_4	BE of Co $2p_{3/2}$ (eV) (fresh / used)
m-Co(0)[b]	20	88.2	11.6 / 11.1 / 77.3	11.6	780.5 / 780.3
	40	83.6	9.7 / 11.9 / 78.4	16.5	
m-CoAl(25)	20	95.8	13.4 / 7.5 / 79.1	4.2	780.9 / 782.4
	60	85.9	12.3 / 8.9 / 78.8	25.2	
m-CoZr(12)	20	92.4	17.6 / 10.9 / 71.5	5.2	781.2 / 781.6
	60	96.6	13.4 / 9.7 / 76.9	15.2	
m-CoZr(25)	20	100.0	10.6 / 6.6 / 82.8	3.5	782.5 / 781.8
	60	100.0	9.7 / 7.1 / 83.2	5.0	
m-CoZr(38)	20	5.0	4.4 / 3.3 / 92.3	54.7	780.4 / 782.1
	60	2.4	1.5 / 1.0 / 97.5	58.6	

[a]FTS reaction was carried out at the following reaction conditions; T = 240 °C, P = 2.0 MPa, WHSV = 24000 L/(kg_{cat}·h), and feed gas molar compositions of $H_2/N_2/CO$ = 62.84/5.60/31.56 for 60 h on stream.
[b]The results of the physicochemical properties and catalytic activity on the m-Co(0) were cited from our previous work [**11**].
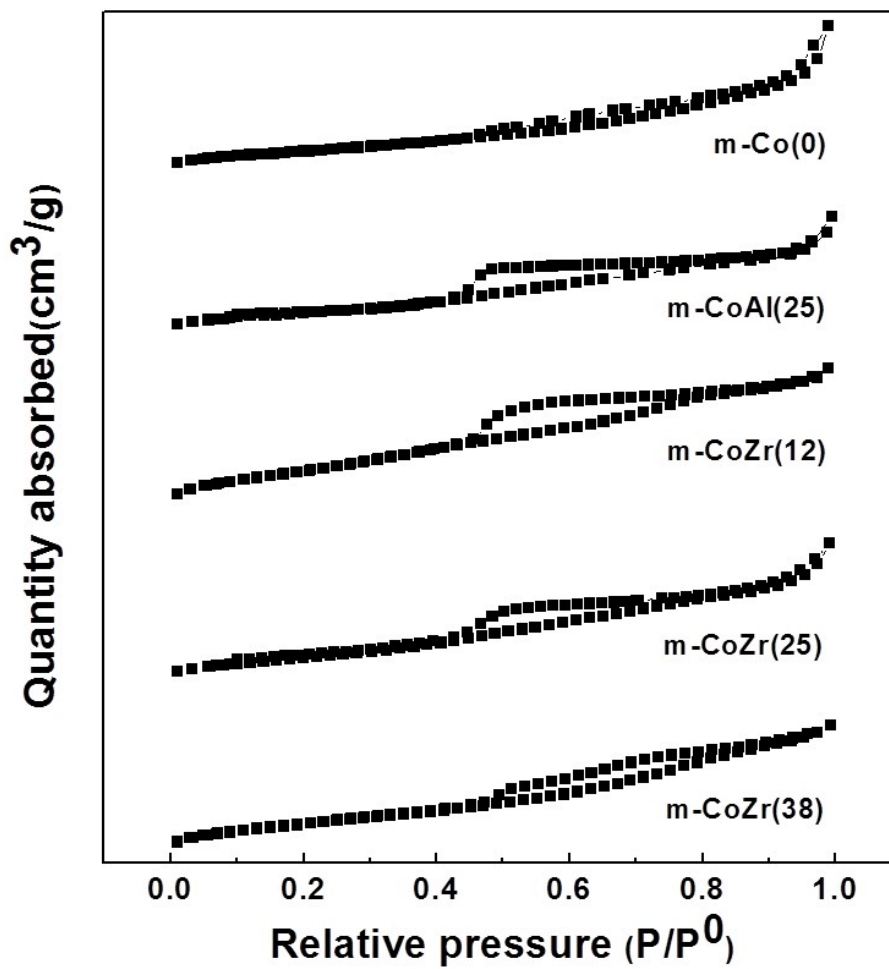
Figure S1. N_2 isotherms of the ordered mesoporous fresh m-CoM mixed metal oxides
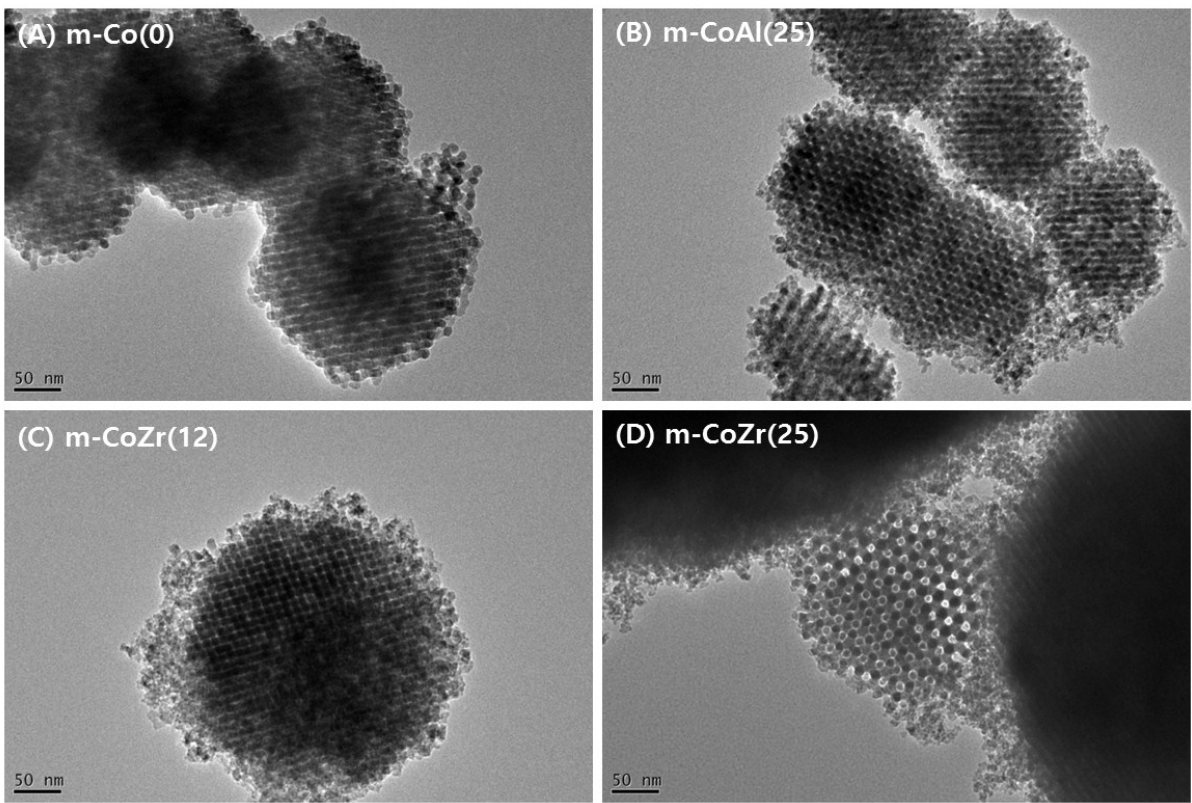
Figure S2. TEM images of the ordered mesoporous m-CoM mixed metal oxides before FTS reaction; (A) m-Co(0), (B) m-CoAl(25), (C) m-CoZr(12), (D) m-CoZr(25)
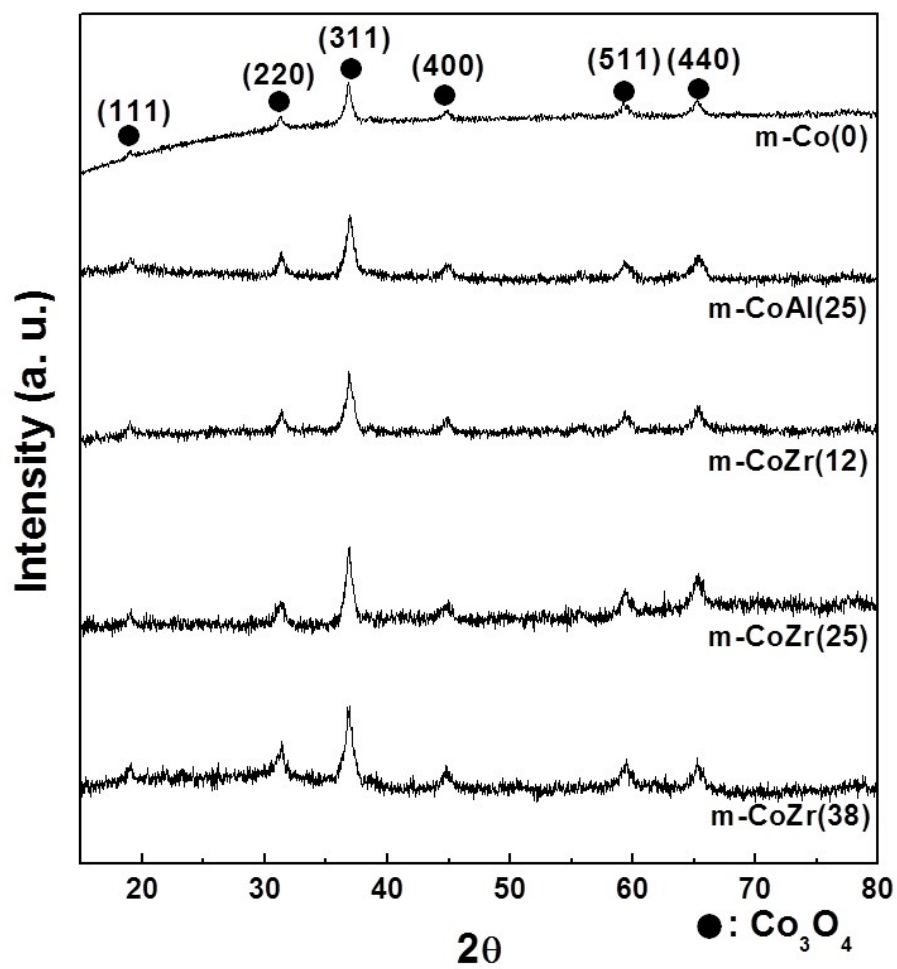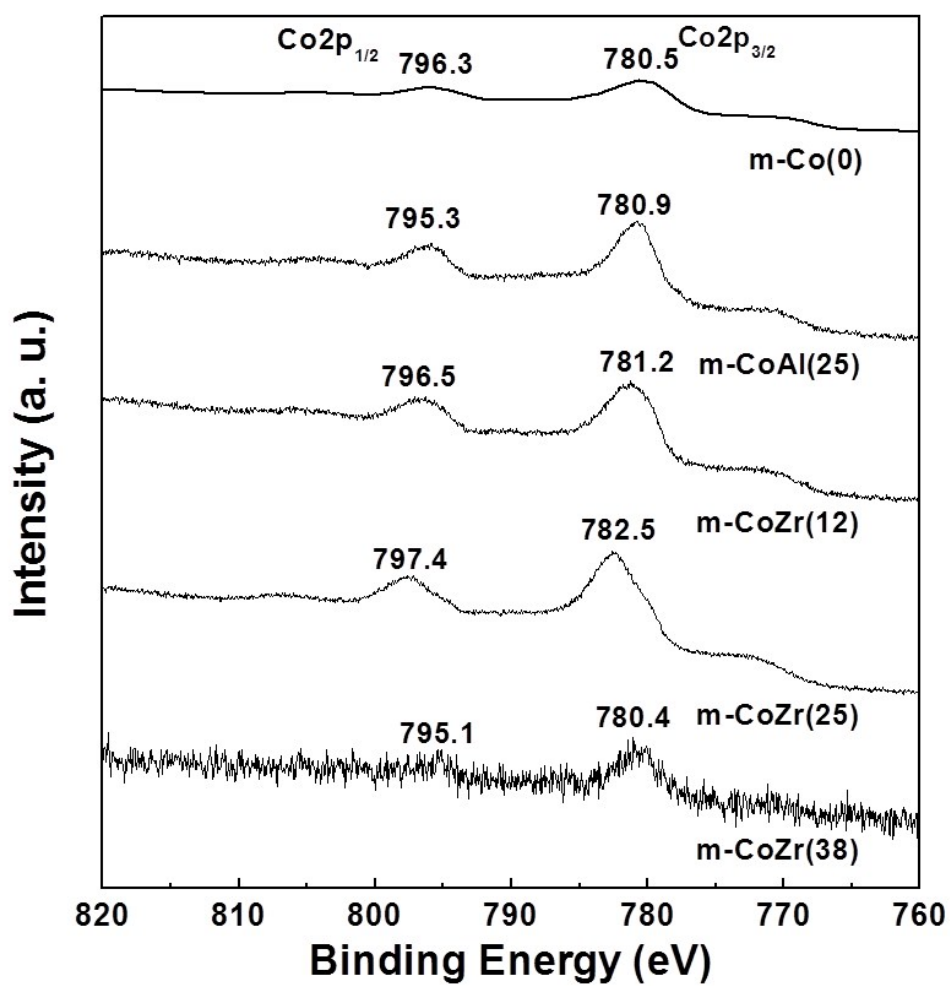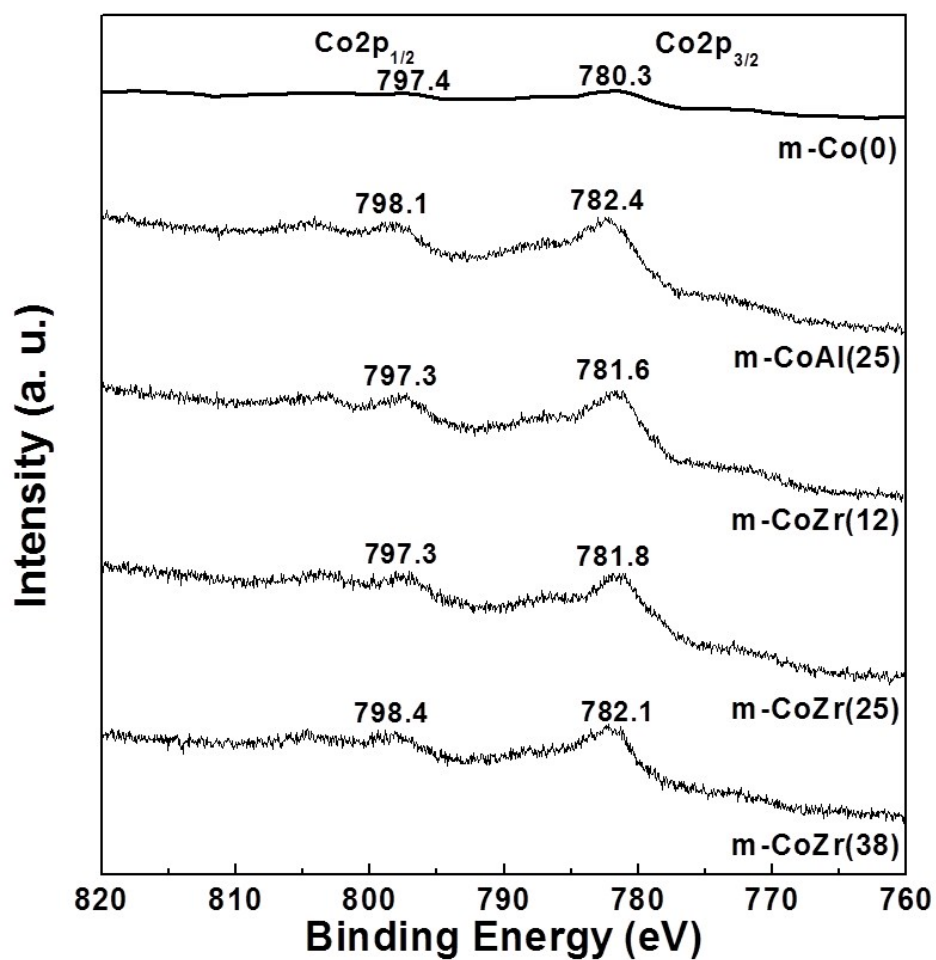
Figure S3. XRD patterns of the fresh ordered mesoporous m-CoM mixed metal oxides

Figure S4. XPS spectra of Co 2p on the ordered mesoporous m-CoM mixed metal oxides before FTS reaction
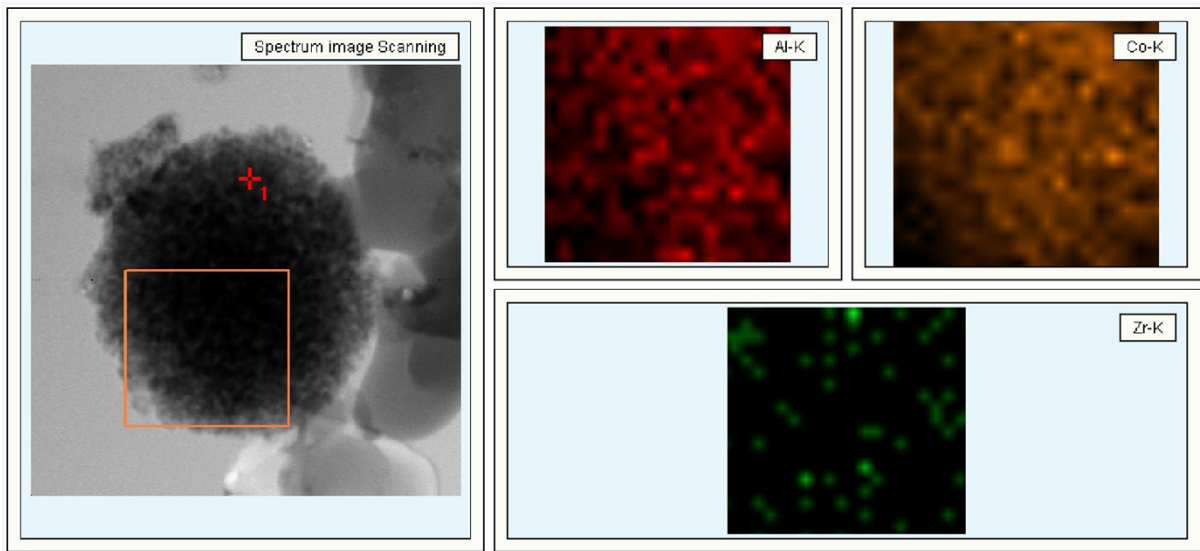
Figure S5. Photos of the used FTS catalysts after reaction, which showed a less aggregation of the catalyst particles due to the less wax deposition on the m-CoZr(12) and m-CoZr(25) compared to the conventional Co/SiO$_2$ having an irregular pore structures
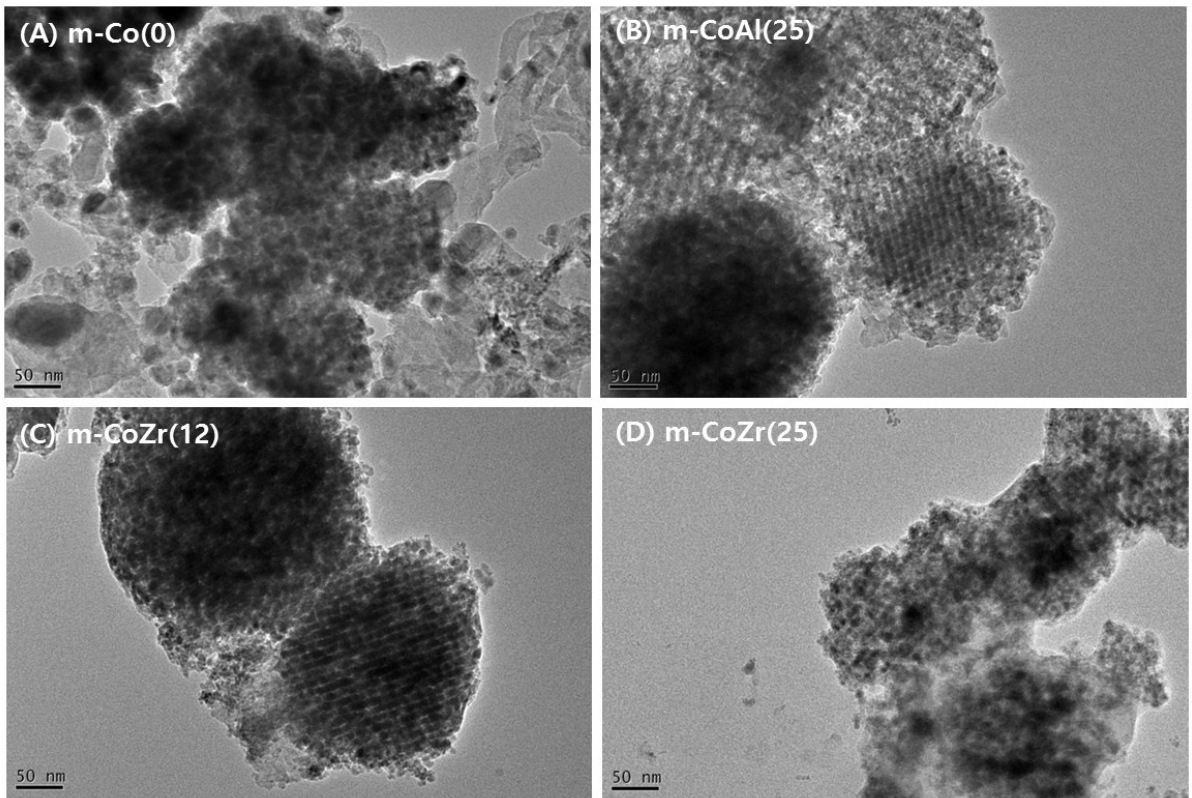
Figure S6. XPS spectra of Co 2p on the ordered mesoporous m-CoM mixed metal oxides after FTS reaction

Figure S7. Results of EELS analysis on the used m-CoZr(12) for the mapping of Co, Zr and Al elements

Figure S8. TEM images of the ordered mesoporous m-CoM mixed metal oxides after FTS reaction; (A) m-Co(0), (B) m-CoAl(25), (C) m-CoZr(12), (D) m-CoZr(25)