

Supporting Information

Trapping the Catalyst Working State by Amber-Inspired Hybrid Material and Revealing the Cobalt Nanostructure Evolution in Gas-to- Liquid Processing

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Table S1. Reduction and FTS conditions of the catalysts.

Catalysts	Support	Reduction		FTS	
		Temperature (°C)	Time (h)	Temperature (°C)	Time (h)
Co/OMMT-350-220-8	OMMT	350	3	220	8
Co/OMMT-300-150-8	OMMT	300	3	150	8
Co/OMMT-300-220-8	OMMT	300	3	220	8
Co/OMMT-300-220-16	OMMT	300	3	220	16
Co/MMT-300-220-8	MMT	300	3	220	8

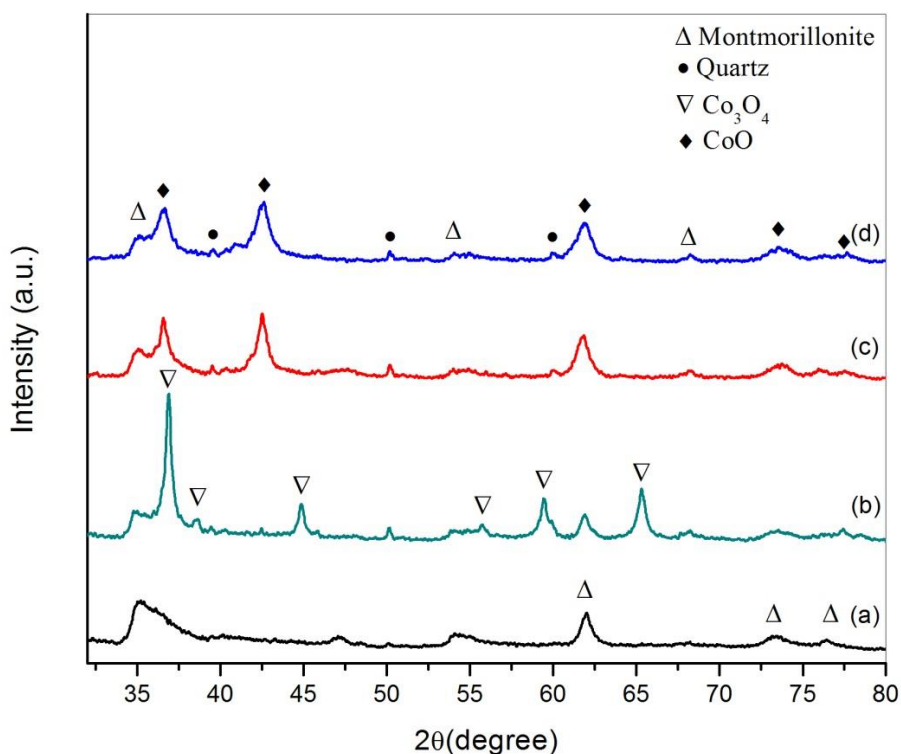


Figure S1. XRD patterns of the support and catalysts: (a) sodium montmorillonite (Na-MMT), (b) the catalyst Co/MMT after calcination, (c) the fresh catalyst Co/MMT after reduction at 300 °C for 3 h in 2.0 MPa, (d) spent Co/MMT-300-220-8.

The XRD experiments were conducted for sodium montmorillonite (Na-MMT), catalyst Co/MMT after calcination, catalyst Co/MMT after reduction at 300 °C for 3 h in 2.0 MPa and the spent catalyst Co/MMT-300-220-8, and the results are shown in Figure S1. The diffraction peaks (Figure S1a) appeared at $2\theta = 35.3^\circ$, 54.5° , 62.0° , 73.3° and 76.5° were assigned to the reflections of MMT, which were also clearly visible in the Co/MMT catalysts (Figures S1b-d). The diffraction peaks appeared at $2\theta = 39.6^\circ$ and 50.3° (Figures S1a-d) indicates the presence of a small amount of quartz impurity in the purified Na-MMT and the Co/MMT catalysts. For the calcined catalyst Co/MMT (Figure S1b), the diffraction peaks appeared at $2\theta = 36.9^\circ$, 38.6° , 44.9° , 55.8° , 59.5° and 61.3° are assigned to 311, 222, 400, 422, 511 and 440 reflections of cubic Co_3O_4 (JCPDS card no. 43-1003), respectively. It obviously indicated that cobalt oxides were dispersed on the MMT support only in the form of Co_3O_4 after calcination. For the catalyst Co/MMT after reduction at 300 °C for 3 h in 2.0 MPa (Figure S1c) and the spent catalyst Co/MMT-300-220-8 (Figure S1d), the diffraction peaks appeared at $2\theta = 36.4^\circ$, 42.3° , 61.6° , 73.6° and 77.6° were assigned to 111, 200, 220, 311, 222 reflections of cubic phase CoO (JCPDS card no. 43-1004), respectively. The XRD patterns of catalysts Co/MMT after

reduction and reaction proved that the active metallic cobalt was fully oxidized to CoO without protection thin films.

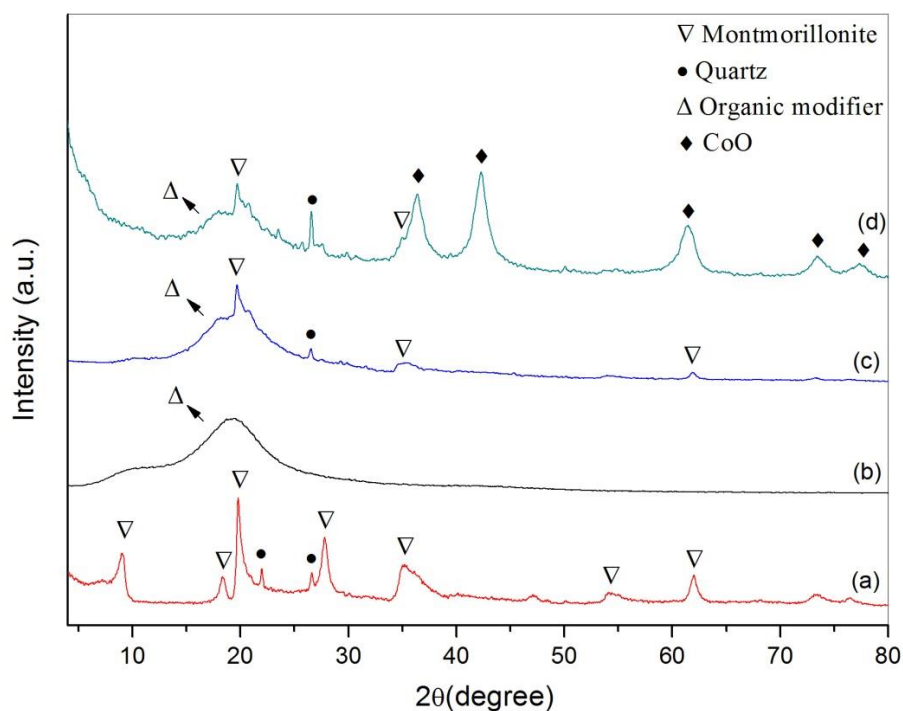


Figure S2. XRD patterns of support and catalysts: (a) Na-MMT, (b) organic modifier polystyryl quaternary ammonium salt, (c) OMMT, (d) catalyst Co/OMMT after calcination.

To clarify the decomposed product of the loaded $\text{Co}(\text{NO}_3)_2$ after calcination, XRD experiments were conducted for the Na-MMT, organic modifier polystyryl quaternary ammonium salt, OMMT and the calcined catalyst Co/OMMT. The results are shown in Figure S2. The diffraction peaks (Figure S2a) appeared at $2\theta = 19.7^\circ$, 27.8° , 35.3° , and 54.5° were assigned to the reflections of MMT, which were also clearly visible in OMMT (Figure S2c) and the catalyst Co/OMMT (Fig. S2d). The diffraction peak at $2\theta = 9.1^\circ$ (Figure S2a) was assigned to 001 reflections of MMT, corresponding to the basal spacing of MMT (d_{001}) of about 0.97 nm. Generally speaking, the d_{001} of OMMT changes with the type of organic modifiers and the length of alkyl chains. In our case, no obvious diffraction peaks occurred in the range of less than 10° (2θ) were observed in OMMT (Figure S2c) and the catalyst Co/OMMT (Figure S2d), which indicates that the organic modifier was intercalated into the interlayer spacing of MMT, and the MMT layers were exfoliated completely in the organic matrix. The diffraction peaks appeared at $2\theta = 20.7^\circ$ and 26.4° (Figures S2a, c, d) indicates the presence of a small amount of quartz impurity in the purified Na-MMT and the OMMT as well as the catalyst Co/OMMT. For the catalyst Co/OMMT (Figure S2d), the diffraction peaks appeared at $2\theta = 36.4^\circ$, 42.3° , 61.6° , 73.6° and 77.6° were assigned to 111, 200, 220, 311, 222 reflections of cubic phase CoO (JCPDS card no. 43-1004), respectively. No peak

related to the Co_3O_4 phase was observed, which obviously indicated that cobalt oxides were dispersed on the OMMT support only in the form of CoO after calcination.¹

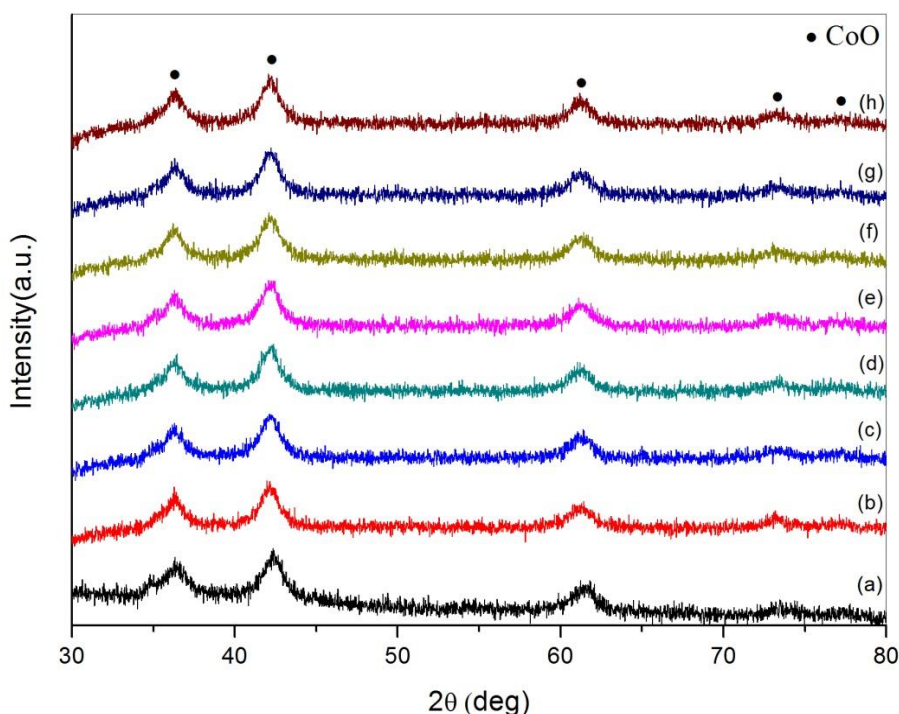


Figure S3. *In situ* XRD patterns of (a) the catalyst Co/OMMT before reduction and the catalyst Co/OMMT treated with H₂/N₂ (10%/90%) mixture at 300 °C for different time in atmospheric pressure: (b) 0.5 h, (c) 1.0 h, (d) 1.5 h, (e) 2.0 h, (f) 2.5 h, (g) 3.0 h, (h) 3.5 h.

In situ XRD experiments were used to investigate the stabilizing and protecting effects of the organic modifier for the active nanoparticles in the catalyst. Figure S3 shows the *in situ* XRD patterns of the Co/OMMT catalyst sample reduced with H₂/N₂ (10%/90%) mixture at 300 °C for different time. In all cases, only the diffraction peaks of cubic phase CoO ($2\theta = 36.4^\circ, 42.3^\circ, 61.6^\circ, 73.6^\circ$ and 77.6°) were observed, and no specific pattern of metallic cobalt could be found even after reduction with H₂/N₂ (10%/90%) mixture at 300 °C for 3.5 h. It can be seen that the crystallinity and the intensity of CoO were retained almost unaltered throughout the entire periods of time in this reduction condition. In other words, no metallic cobalt species of amorphous or disordered could be found after the reduction process. Just like the organic-coated CoO was protected from contacting with NO₂ to avoid further oxidation to Co₃O₄ in calcination procedure, the hydrogen reductant also was prevented by the organic thin films from approaching to the embedded CoO. Consequently, no any reduction occurred in such circumstances.

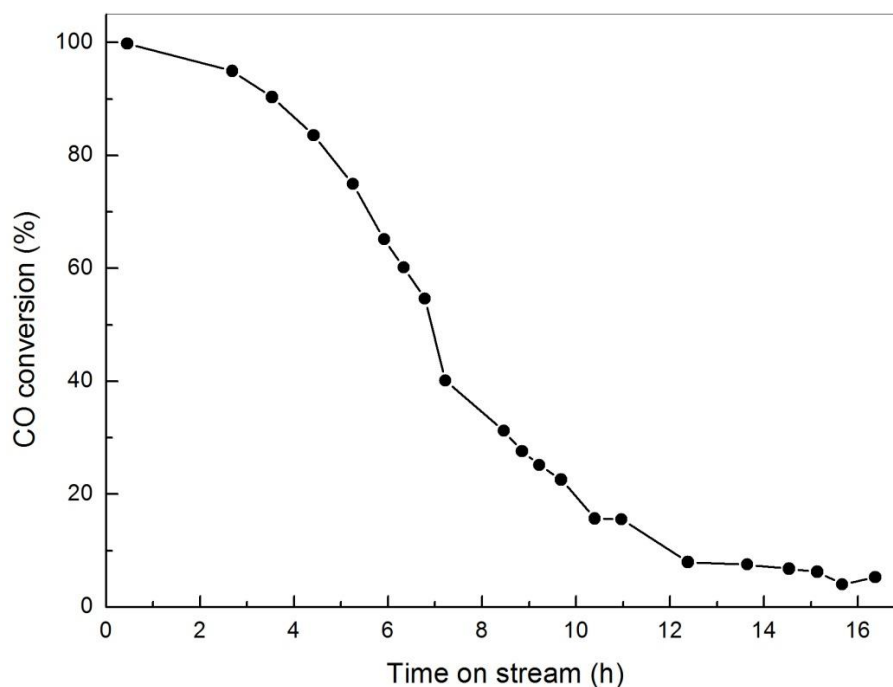


Figure S4. CO conversion as a function of time on stream for the catalyst Co/OMMT. The calcined catalyst Co/OMMT was reduced with H₂ at 300 °C for 3 h in 2.0 Mpa, and then fed with the synthesis gas for FTS (pressure = 2 MPa, temperature = 220 °C, GHSV = 500 h⁻¹, H₂/CO = 2.0).

Figure S4 presented the CO conversion as a function of time on stream for the catalyst Co/OMMT. As can be seen in Figure S4, drastic deactivation of catalyst Co/OMMT was observed during the initial reaction stages (the time on stream <16 h).

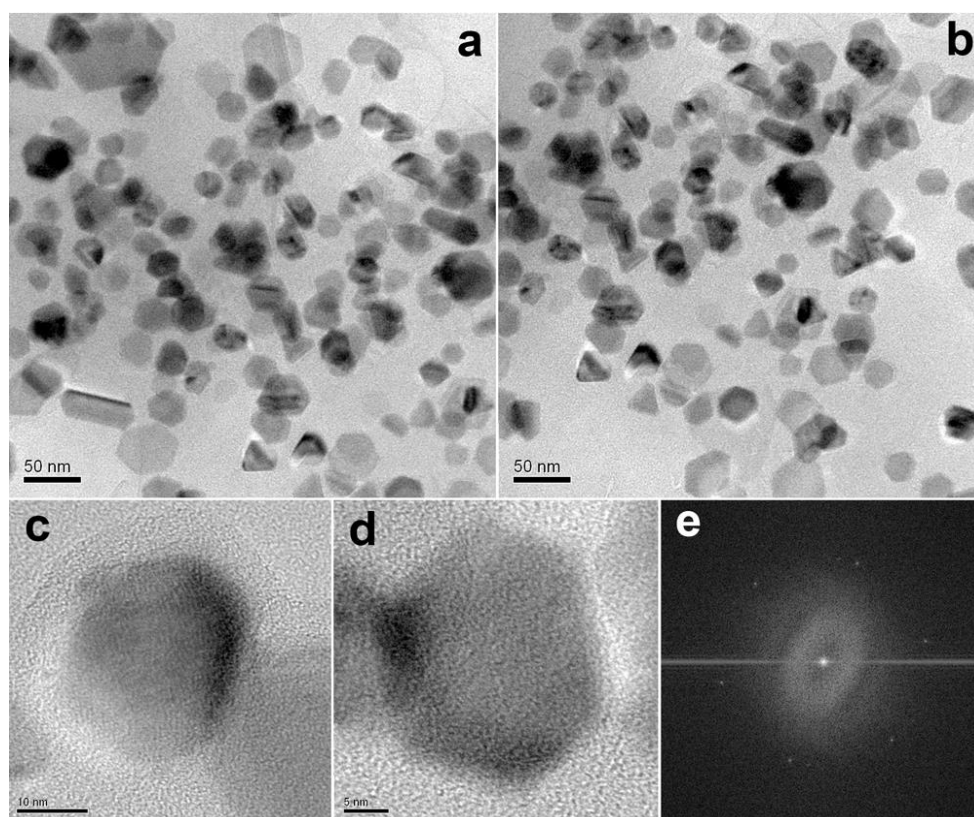


Figure S5. Representative TEM images (a, b) and HRTEM images (c, d) of the spent catalyst Co/OMMT after FTS (reduction at 350 °C for 3 h in 2.0 MPa, then FTS at 220 °C for 8 h in 2.0 MPa). e) The corresponding fast Fourier transform (FFT) pattern of d.

The representative TEM image of Co/OMMT-350-8 catalyst after F-T catalytic reaction was showed in Figures S5a-b. The results indicate that the cobalt nanoparticle growth was more severe in 350 °C. The Co/carbon core-shell structure was also confirmed by the HRTEM images (Figures S5b-c), which clearly showed that the nanoparticles was encapsulated in amorphous carbon shell. The FFT pattern shows hexagonal closed packed (hcp) self-assembly of d.

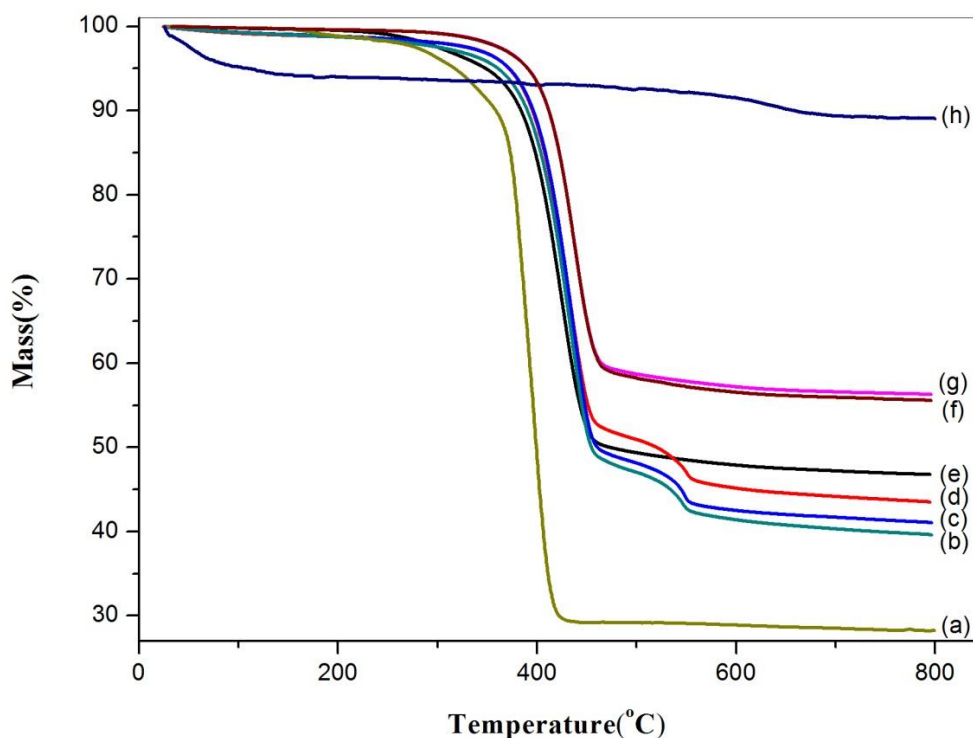


Figure S6. TGA curves of the support and catalyst samples: (a) OMMT, (b) catalyst Co/OMMT after calcination, (c) spent Co/OMMT-300-220-8, (d) spent Co/OMMT-300-220-16, (e) the fresh catalyst Co/OMMT after H₂ reduction at 300 °C for 3 h in 2.0 MPa, (f) the fresh catalyst Co/OMMT after H₂ reduction at 350 °C for 3 h in 2.0 MPa, (g) spent Co/OMMT-350-220-8, (h) Na-MMT.

To clarify if the OMMT support decomposed after reduction procedure and catalytic reaction, TGA experiments of the fresh catalyst Co/OMMT samples after H₂ reduction and the spent catalysts were performed. The MMT (Figure S6h) exhibited mass losses by 6% at 20–200°C and 3.8% at 600–800°C due to the thermal evolution of moisture and interlayer water, and structural OH groups, respectively.² The OMMT (Figure S6a) demonstrated mass losses by 1.1 and 70.6% in the temperature range of 20–200 and 200–800°C, respectively, corresponding to thermal evolution of moisture, and decomposition of organic modifier and removal of structural OH of the clay, respectively.³ The TGA plot of the catalyst Co/OMMT after calcination (Figure S6b) presents two evident weight losses by 49.5 and 9.6% in the temperature range at about 200–460 and 460–800°C, which were ascribed to the thermal decomposition of organic modifier and the reduction of CoO to metallic cobalt, respectively. It should be mentioned that if weight losses of the catalysts after reduction or reaction are far less than 49.5%, the catalyst support OMMT would be decomposed. One noticeable mass loss by 49.0% in the temperature range at about 200–460 °C exhibited in the TGA curve of the

fresh catalyst Co/OMMT samples after H₂ reduction at 300 °C (Figure S6e) was assigned to the decomposition of organic modifier, indicating that the organic modifier almost did not decompose during reduction at 300 °C. And no obvious mass losses were found in 460–800°C, which is well consistent with the XRD results (only metallic cobalt phases were obtained after reduction). The TGA curve of the Co/OMMT-300-220-8 (Figure S6c) exhibited mass losses by 48.9 and 9.0% in the temperature range at about 200–460 and 460–800°C, which was similar to the thermal behavior of the catalyst after calcination (Figure S6b), indicating that the organic modifier almost did not decompose after the catalytic reaction for 8 h. The TGA curves of the Co/OMMT-300-220-16 (Figure S6d) exhibited mass losses by 46.4 and 9.0% in the temperature range at about 200–460 and 460–800°C, indicating that the organic modifier only decomposed slightly after the catalytic reaction for 16 h. By comparing Figure S6e with Figures S6f and 6g, it can be seen that only 39.2 and 39.1% mass losses in 200–460°C were observed for the fresh catalyst Co/OMMT samples after H₂ reduction at 350 °C (Figure S6f) and Co/OMMT-350-220-8 (Figure S6g), respectively. The lower mass losses were ascribed to the partial decomposition of organic modifier to amorphous carbon with the reduction temperature increasing from 300°C to 350°C.

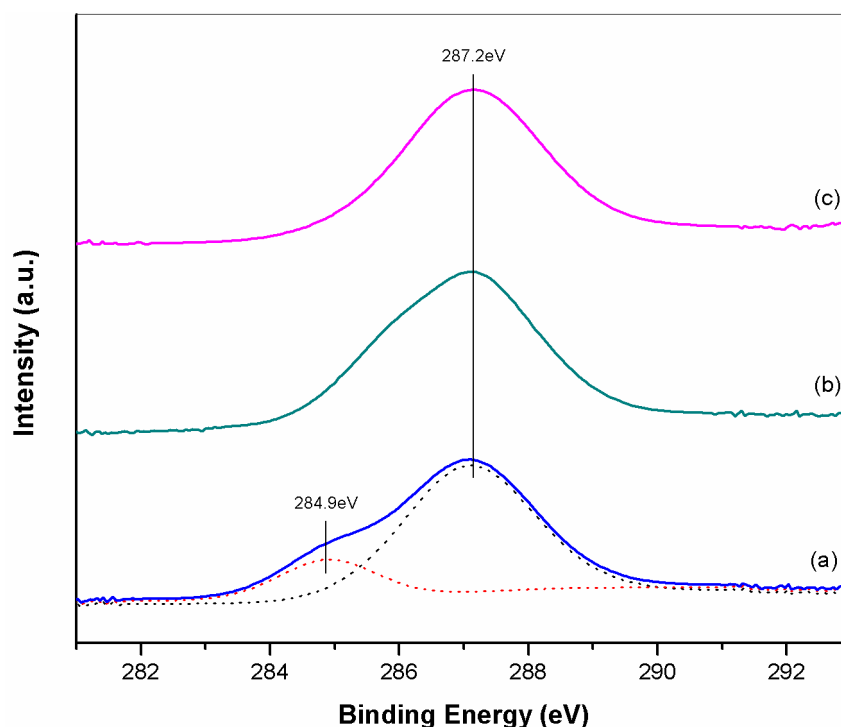


Figure S7. XPS spectra for carbon in catalyst samples: (a) spent Co/OMMT-350-220-8, (b) spent Co/OMMT-300-220-8, (c) Co/OMMT after calcination.

It was shown that the C 1s XPS spectra of Co/OMMT after calcination (Figure S7c) was very similar with that of spent Co/OMMT-300-220-8 catalyst (Figure S7b). The peak at around 287.2 eV in the two samples was assigned to the carbon in organic modifier. By comparing Figure S7a with Figures S7b and 7c, it can be seen that the FWHM (full width at half maximum) of peak at 287.2 eV decreased obviously for the spent Co/OMMT-350-220-8 catalyst (Figure S7a). This decrease was ascribed to the partial decomposition of organic modifier while the reduction temperature increasing to 350°C. For the spent Co/OMMT-350-220-8 catalyst, the new emerging peak (284.9eV) indicated the formation of amorphous carbon, which was well consistent with the previously reported experimental results that the C 1s peak energy value of amorphous carbon lies at about 285eV.^{4,5} From the above results, it can be concluded that amorphous carbon formed after H₂ reduction at 350 °C for 3 h, which was in good agreement with the XRD result and the TGA curve.

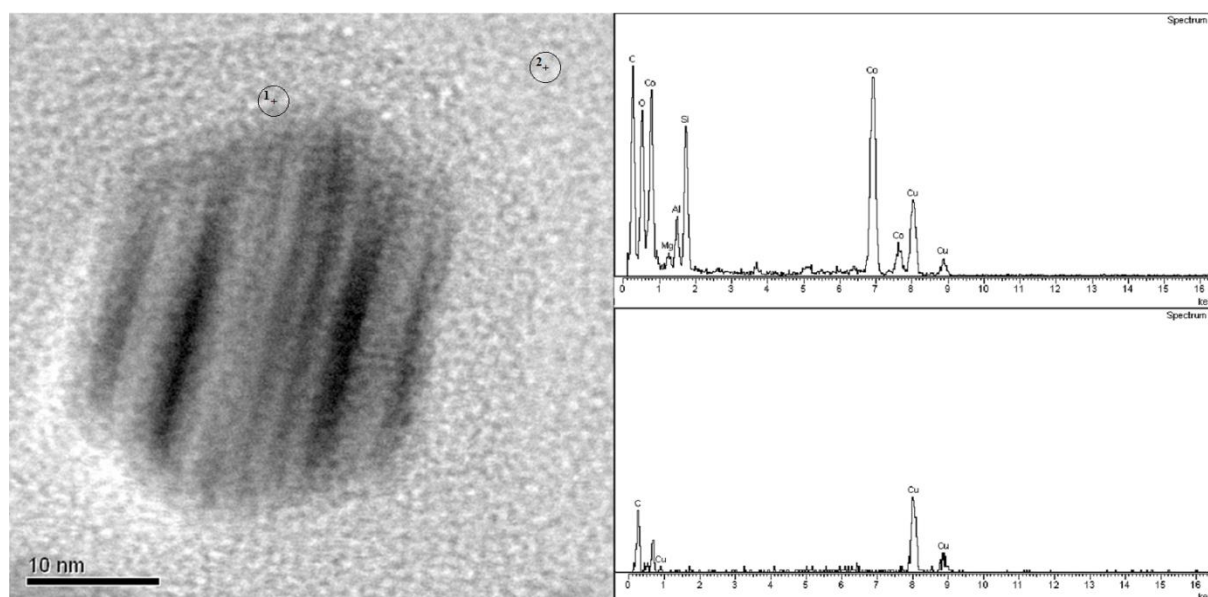


Figure S8. HRTEM image (Left) of the spent catalyst Co/OMMT after FTS (reduced at 350 °C for 3 h in 2.0 MPa, then FTS at 220 °C for 8 h in 2.0 MPa) and the EDS spectra (Right) of the thick coating region (1) and carbon support films on copper grids region (2).

Energy Dispersive X-Ray Spectrometry (EDS) analyses corresponding to Figure 8e was shown in Figure S8. The Co, Si, Al, Mg and O elements were detected in the selected thick coating region (region 1), suggesting the existence of Co particles and montmorillonite support. The Cu and C elements in the selected region 1 were assigned to the mixture of copper grids, thick coating and carbon support films on copper grids. The Cu and C elements detected in the selected carbon support films on copper grids region (region 2) were composed of pure carbon support films and copper grids. By comparing relative intensity of C element in the selected region 1 and 2, the thick coating was confirmed as carbon.

In addition, the electronic diffraction measurement of TEM image of Figure 8e showed no specific diffraction pattern of crystalline carbon, indicating that the thick carbon coating was an amorphous phase. Previous studies on thermal annealing of thin amorphous carbon films have shown that significant structural changes occur around 400 °C followed by completed graphitization at 600-800 °C.^{6,7} So the temperature in here (350 °C) is not high enough for graphitic carbon formation.

Table S2. Chemical composition of the samples

Catalyst	Chemical composition				
	Organic modifier (%)			Co (%)	Montmorillonite (%) ^a
	C (%)	H (%)	N (%)		
Co/OMMT (calcined catalyst)	50.73	4.56	0.55	17.72	26.44
Co/OMMT-300-220-8	48.15	4.32	0.51	19.80	27.22
Co/OMMT-300-220-16	45.68	4.08	0.49	19.76	29.99
Co/OMMT-350-220-8	29.78	3.99	0.19	28.98	37.06

a: The data were calculated on the basis of the experimental results of C, H, N and Co, and the oxygen combined with cobalt was included in the content of montmorillonite.

Table S2 listed the chemical composition of the samples before (the calcined catalyst) and after (the other three samples) FTS. By comparing the Co/OMMT with Co/OMMT-350-220-8, it can be seen that organic modifier decomposed obviously at 350 °C. Nevertheless, only slight decomposition of the organic modifier were observed for Co/OMMT-300-220-8 and Co/OMMT-300-220-16, which was in good agreement with the TGA results (Figure S6).

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