Electronic Supplementary Information (ESI)

Microwave Catalytic Synthesis of Ammonia from Methane and Nitrogen

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Experimental

(a) Catalyst Preparation

The cobalt doped catalyst containing 5 wt% of cobalt was prepared by incipient wetness technique. Gamma phase aluminum oxide was used as a support for the catalyst synthesis. The aluminum oxide support was supplied by Alfa Aesar. The support was impregnated with the cobalt (II) nitrate hexahydrate aqueous solution and dried in an oven at 110 °C for 12 h. Finally, the dried material was calcined in air at 500 °C for 4 h. For iron promoted cobalt catalyst, the catalyst composition was 0.5 wt% Fe and 4.5 wt% Co. The support was impregnated with the mixture of cobalt (II) nitrate hexahydrate and iron nitrate nonahydrate aqueous solution. The material was dried and calcined in same conditions. The cobalt salt and iron salt were provided by Acros Organics.

(b) Microwave Reactor Setup

The experiments were carried out in a 10.5 mm inner-diameter (ID) quartz tube reactor with Lambda MC1330-200 Variable Frequency Microwave controller under atmospheric pressure and continuous flow condition. The frequency was set as 6250 MHz. One gram of catalyst was loaded for each experiment. Prior to the reaction, the catalyst was reduced in 70 mL/min pure hydrogen at 675 ^{o}C for 4 hours to ensure maximum reduction to Co^0 species. The reduction temperature was selected based on temperature-programmed-reduction (TPR) test, shown in figure S1. During the reaction, the overall gas flow rate was adjusted to 120 mL/min. Diluted methane gas mixture (30 vol% methane balanced with nitrogen) was used to enhance the conversion.

In the case of microwave plasma generation, 100 mL/min of mixture gas was fed into the system accompanying with 20 mL/min of pure argon flow, and a striker was applied to assist plasma formation, This is different from other non-thermal plasma, such as Dielectric barrier discharge (DBD), where high voltage DC power (10,000 volts) is required. For microwave irradiation only case, argon was replaced with nitrogen at the same flow rate. During the reaction, the catalyst was heated to 600 ^{o}C in inert environment before the feed gas was initiated. A solid calcium oxide layer was applied at the outlet stream to remove the potential moisture. For the control experiment conducted in a traditional fixed-bed reactor, the experiment was carried out in a Micromeritics Autochem 2950 analyzer. 0.25 grams of catalyst sample were used and the total flow rate of the feed gas was adjusted to 30 mL/min to maintain the same weight hourly space velocity (WHSV). The outlet gas was monitored by a Pfeiffer Omnistar mass spectrometer and an Agilant 3000A gas chromatography. The temperature of outlet from the reactor was maintained at 120 ^{o}C.

(c) Microwave Reactor Operation

Lambda MC1330-200 Variable Frequency Microwave Reactor is consisted by a power supply, a three-stub applicator, a circulator, a rectangular metallic waveguide and a quartz tube reactor. The microwave is generated by the power supply and the applicator was manually adjust for a minimum reflected power. The closed-structure rectangular waveguide couples the microwave energy and homogeneous planar plasma can be generated.[1] The catalyst was located at the point where the electromagnetic field was maximum. For plasma generation, Argon was introduced as an “igniter” and an

electric striker was applied to assist self-sustained microwave plasma ignition. Microwave irradiation was applied during the whole experiment period and the plasma was sustained during the entire experiment.

(d) Characterization

The TPR analysis of fresh and calcinated catalyst was tested in Micromeritics Autochem 2950 analyzer using 10 vol% of hydrogen in argon. A thermoconductivity (TCD) detector was used to track the signal which reflects the hydrogen concentration change in outlet stream. The catalyst sample was heated to 150 ^{o}C to remove the moisture, after which the temperature was programmed to 1000 ^{o}C at a rate of 2 ^{o}C/min. The result is shown in Figure S2 and the peak information is presented in Table S2. Carbon composition on spent catalysts was analyzed by Raman spectrum of each sample. Raman spectrums were obtained from a Renishaw inVia Raman Spectrometer using laser excitation at wavelength of 523 nm. Thermogravimetric analysis (TGA) under oxygen was applied to quantify the coking amount and it was performed in TA SDT-650 Discovery model instrument. Oxygen concentration was 5 vol% in Helium. A JEOL TEM-2100 transmission electron microscope (TEM) was applied to observe carbon structures of spent catalyst samples under 400,000 times magnification.

(e) Calculation

The productions of all products from this microwave catalytic reaction are evaluated by the amount of moles of products obtained per gram catalyst per second (mol/g/s). The mole number was obtained by ideal gas law. Pressure is atmospheric pressure and the temperature is outlet temperature which was maintained at 150 ^{o}C during all

experiments. Total ammonia production during the experiment was evaluated by integrating production curves showing in Figure 2a.

(f) Particle Size Analysis

Metal particle size in reduced (unreacted) catalyst, spent catalysts after 15 minutes of reaction and spent catalysts after 30 minutes of reaction were measured and compared. For each catalyst sample, about 30 metal particles were measured. Linear regression and analysis of variance (ANOVA) test were performed to analyze how plasma, promoter and reaction time affect the agglomeration of metal particles in the catalyst. Individual t-test was utilized to determine if plasma, promoter and/or reaction time significantly affect particle size. The basic assumptions for ANOVA test are: 1: the residual distributions are normal and 2: homogeneity of sample variance. Normal Quantile-Quantile (Q-Q) plot was used to test the assumption of normal distribution of residuals. Brown-Forsythe test was applied to verify the equality of group variances. For the entire experiment set, five treatments are defined and used in data analysis: none (for fresh, reduced Co catalyst), promoter (for fresh, reduced Co-Fe catalyst) microwave (for reactions using Co catalyst and without plasma generation), microwave plasma (for reactions using Co catalyst with plasma generation), and microwave promoter (for reactions using Co-Fe catalyst without plasma generation). The statistical analysis was done by R programming. p value was set to 0.05.

Showing in Figure S9, although a tail could be observed, the residuals overall fit the normal reference line. This indicates that the residuals are reasonably consistent with the assumption of a normal distribution. Brown-Forsythe test result is shown in

Table S3. A p value of 0.06887 (>0.05) represents the variance in particle size is consistent between treatments. Both assumptions are met; hence the conclusion drew from ANOVA, which is described in main article, is valid.

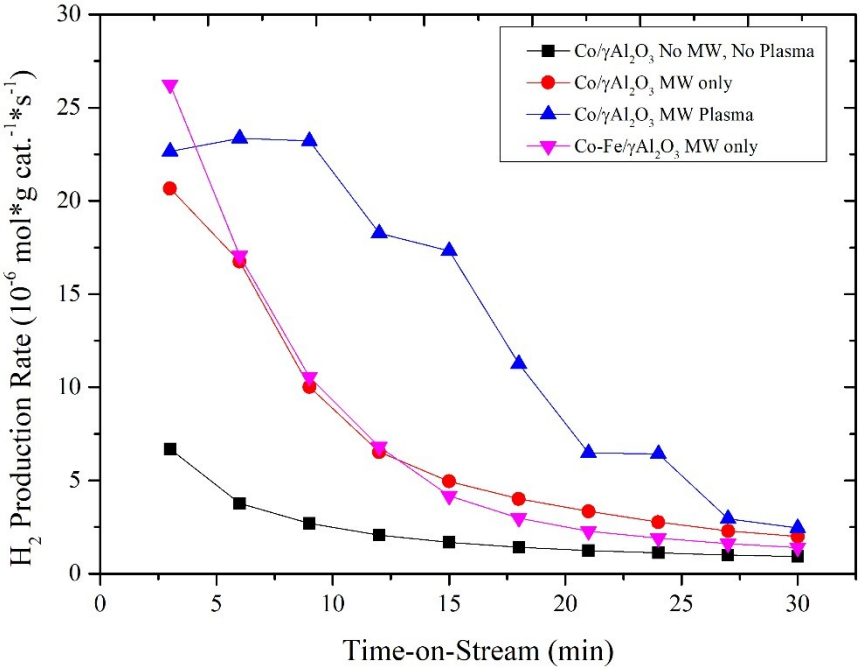


Figure S1: Reaction performance showing by hydrogen production

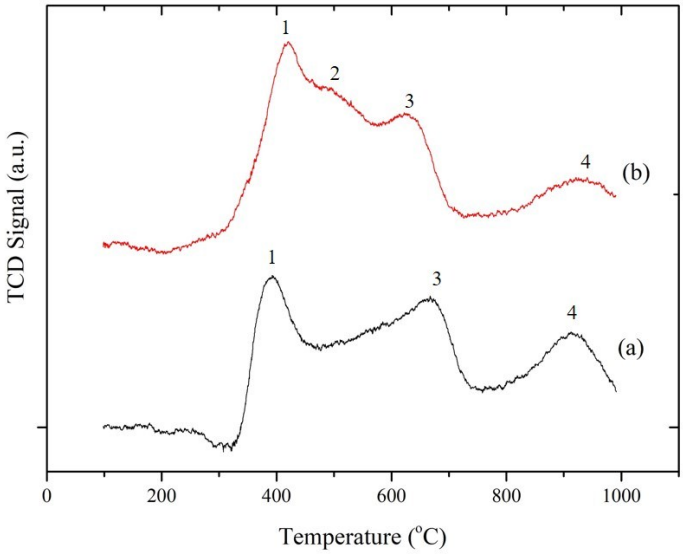
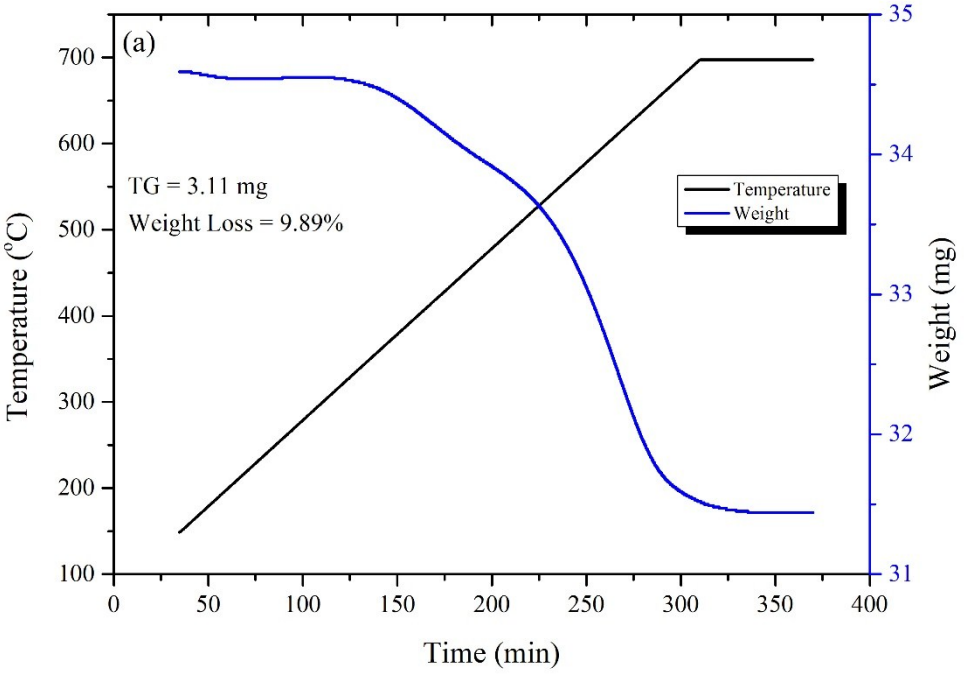
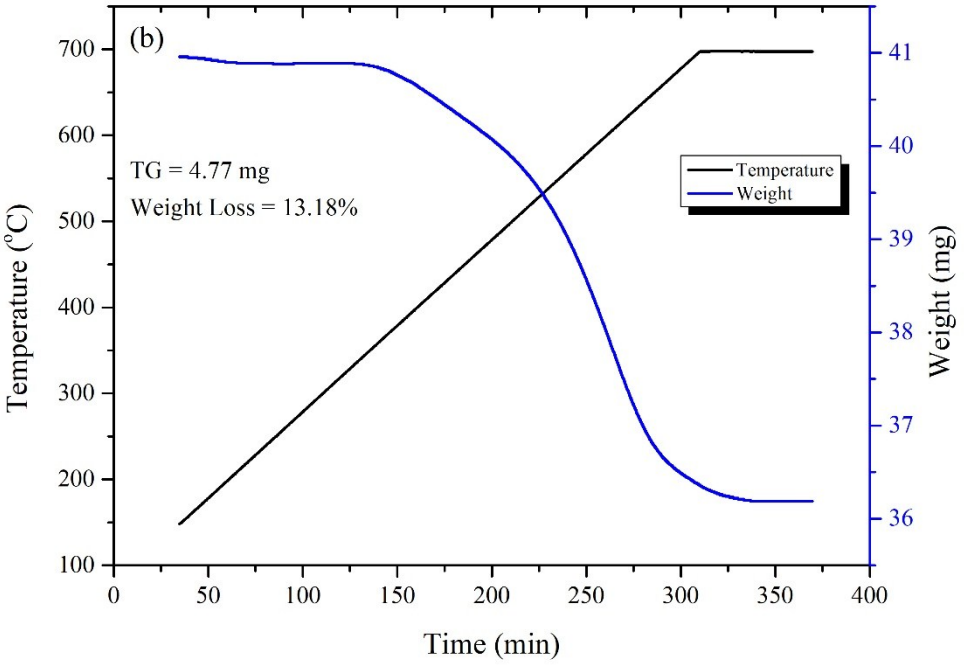


Figure S2: TPR profiles for (a): Co/γAl_2O_3 and (b): Co-Fe/γAl_2O_3.


(a)
TG = 3.11 mg
Weight Loss = 9.89%
Temperature
Weight
Temperature (°C)
Weight (mg)
Time (min)
100
200
300
400
500
600
700
31
32
33
34
35
0
50
100
150
200
250
300
350
400


(b)
TG = 4.77 mg
Weight Loss = 13.18%
Temperature
Weight
Temperature (°C)
Weight (mg)
Time (min)
100
200
300
400
500
600
700
36
37
38
39
40
41
0
50
100
150
200
250
300
350
400

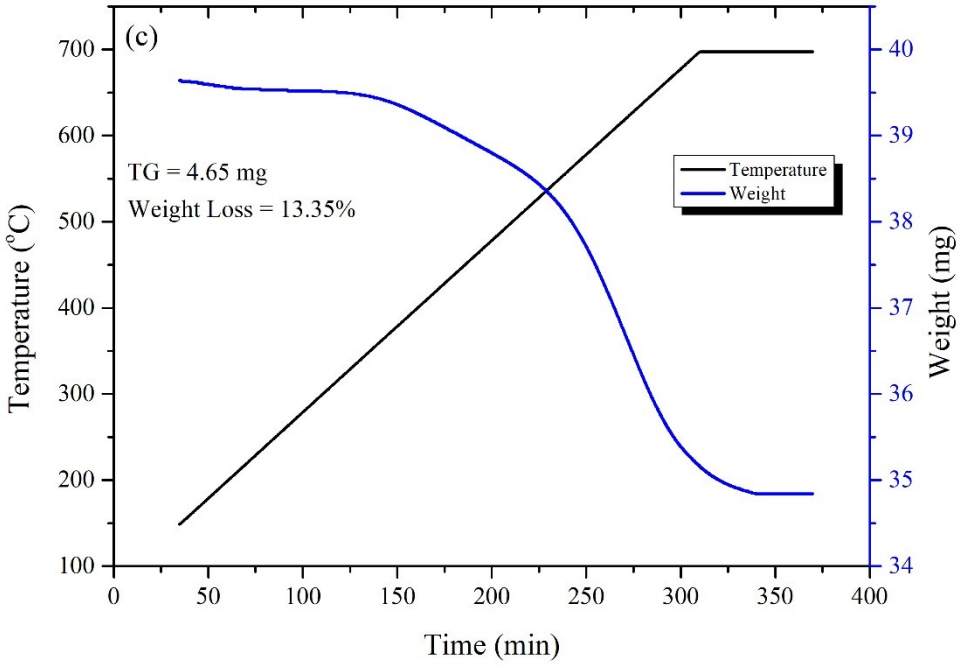


Figure S3: TGA analysis for spent catalyst with coke deposit (a): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave irradiation only) (b): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave plasma); and (c): $Co\text{-}Fe/\gamma Al_2O_3$

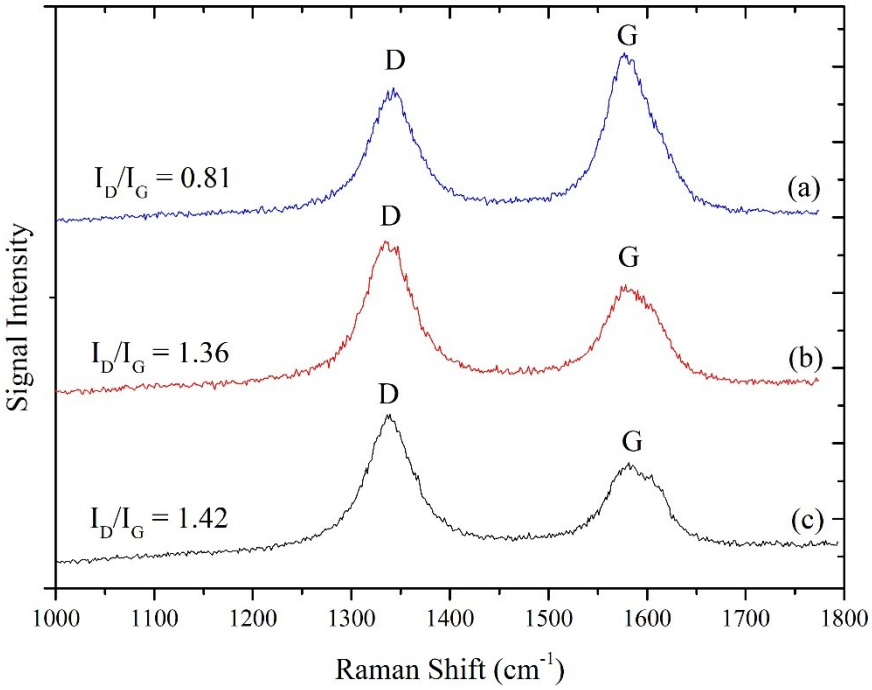


Figure S4: Raman spectrums of spent with coke deposit (a): Co-Fe/γAl_2O_3; (b): Co/γAl_2O_3 (reaction was carried out under microwave plasma); and (c): Co/γAl_2O_3 (reaction was carried out under microwave irradiation only)

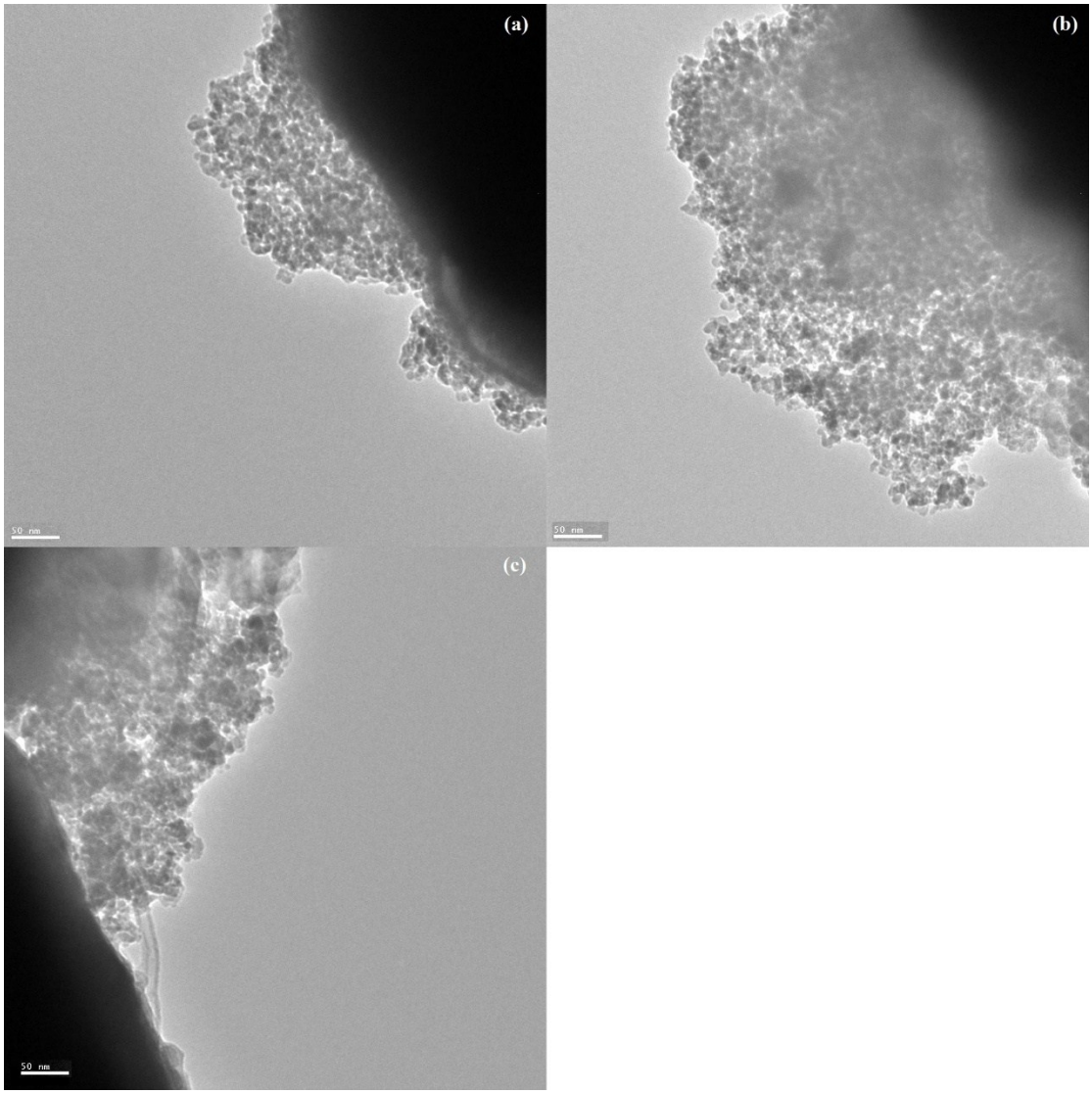


Figure S5: TEM images of spent catalyst with coke deposit after 15 minutes time-on-stream (a): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave irradiation only); (b): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave plasma). (c): $CoFe/\gamma Al_2O_3$ (reaction was carried out under microwave irradiation only)

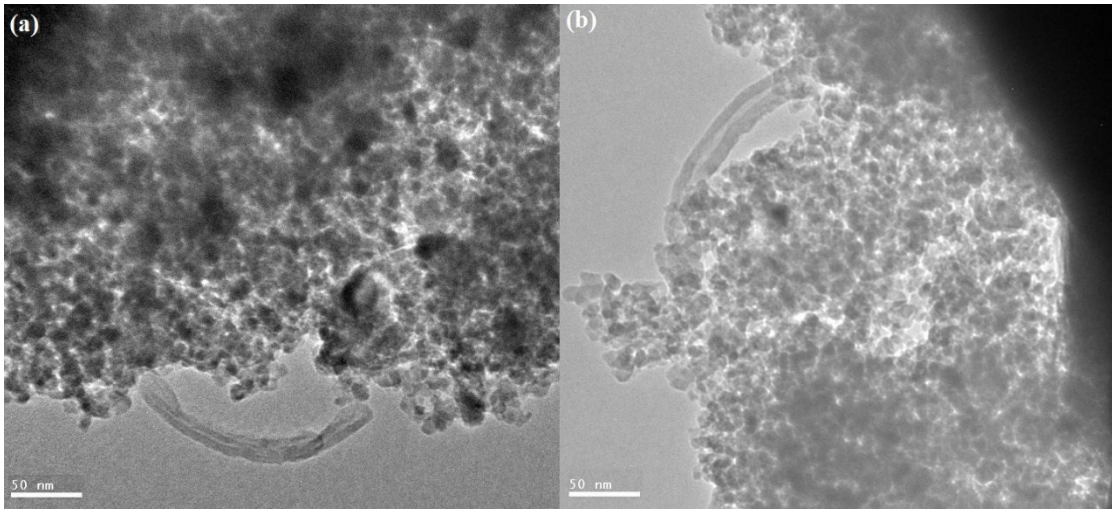


Figure S6: TEM images of spent catalyst after 30 minutes time-on-stream with coke deposit (a): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave irradiation only); (b): $Co/\gamma Al_2O_3$ (reaction was carried out under microwave plasma).

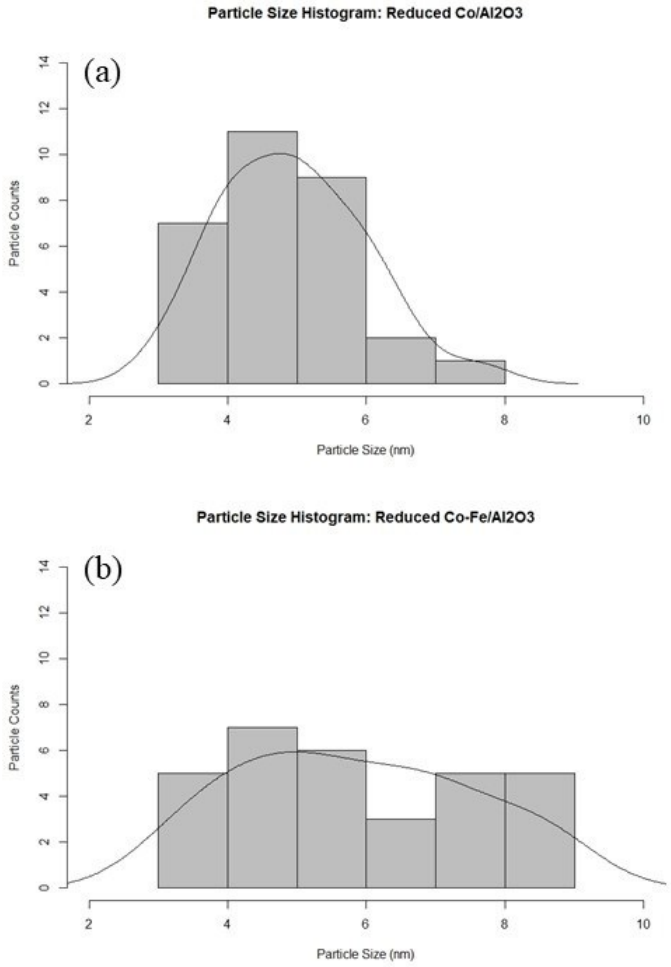


Figure S7: Particle size histograms of reduced, unreacted (a): Co/γAl_2O_3 and (b): Co-Fe/Al_2O_3

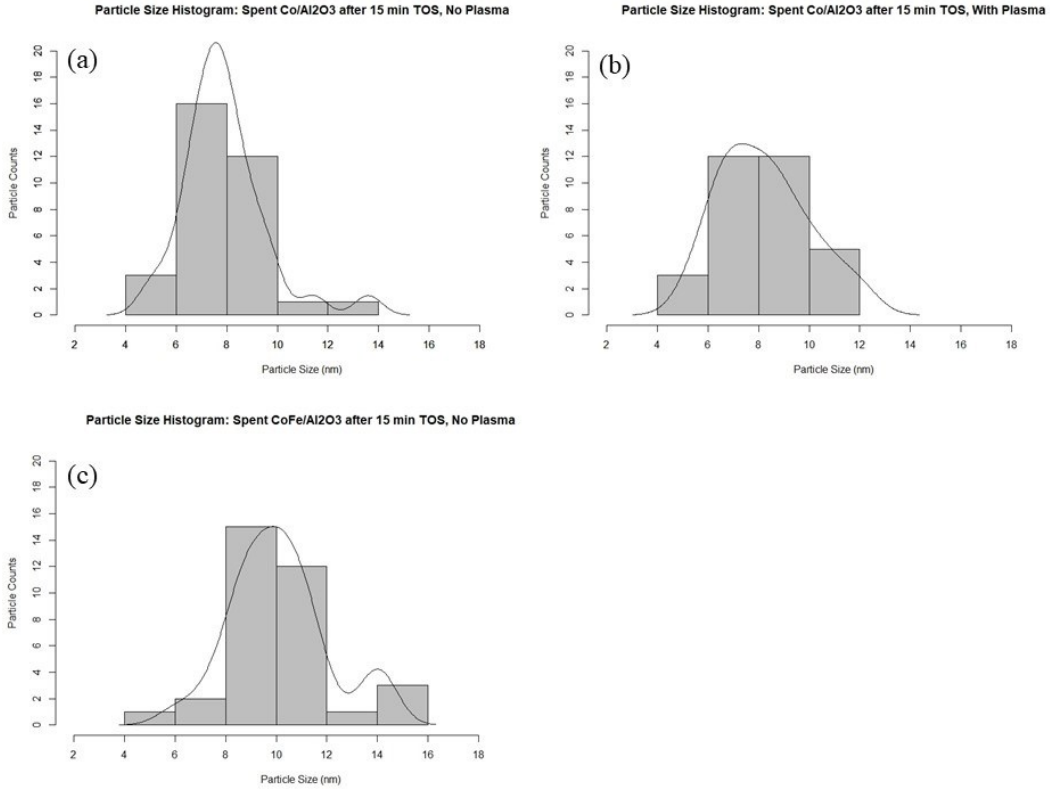


Figure S8: Particle size histograms of spent catalyst after 15 minutes time-on-stream: (a): Co/γAl_2O_3, microwave only; (b): Co/γAl_2O_3, microwave plasma; and (c): Co-Fe/Al_2O_3, microwave only.

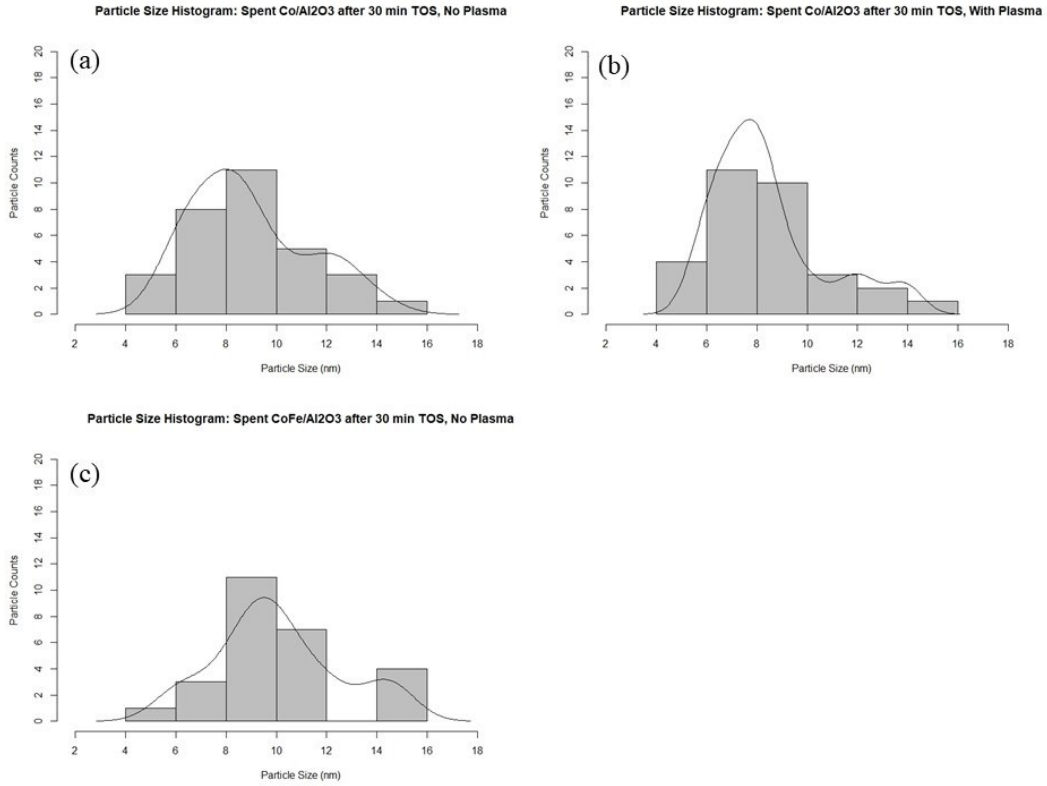


Figure S9: Particle size histograms of spent catalyst after 15 minutes time-on-stream: (a): Co/γAl_2O_3, microwave only; (b): Co/γAl_2O_3, microwave plasma; and (c): Co-Fe/Al_2O_3, microwave only.

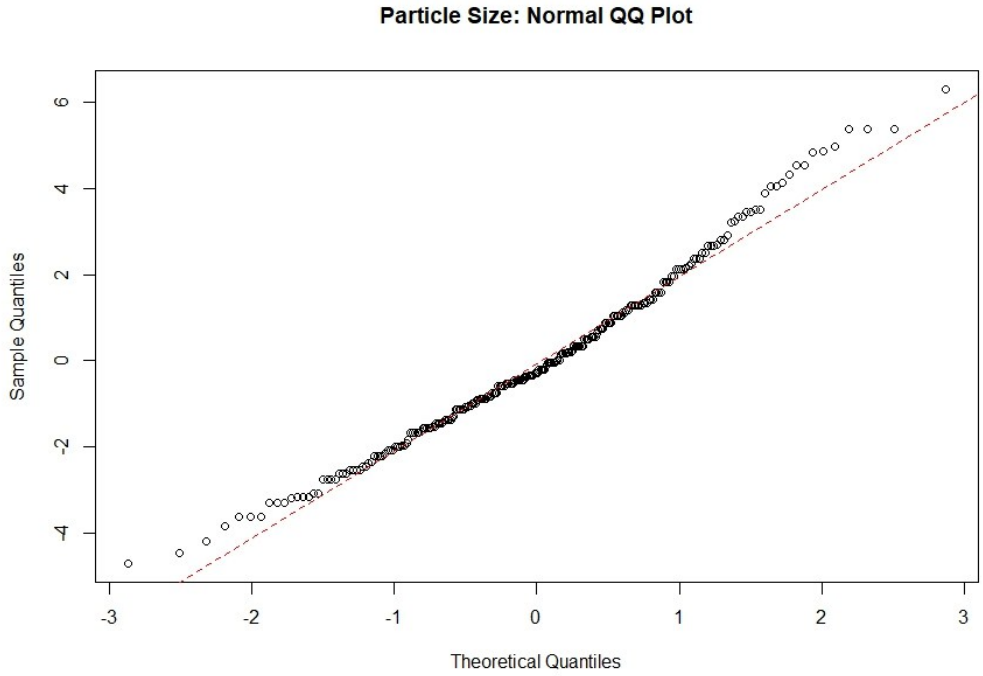


Figure S10: Normal Quantile-Quantile plot for all measured particles

Table S1: Catalyst performance summary

Catalyst	Reaction Condition	Maximum NH_3 Production Rate (10^{-8} mol/g/s)	Total NH_3 Production for 30 minutes (10^{-8} mol)	Maximum Methane Conversion
Co/γ-Al_2O_3	Traditional Heating	1.7	3.0	19.7%
Co/γ-Al_2O_3	Microwave Irradiation Only	40.8	157.3	73.8%
Co/γ-Al_2O_3	Microwave Irradiation and Microwave Plasma	39.9	383.1	80.7%
Co-Fe/γ-Al_2O_3	Microwave Irradiation Only	53.9	441.5	80.6%

Table S2: Peak identification of TPR profiles

Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)*
$Co/\gamma Al_2O_3$	392.5	N/A	667.5	924.1
$Co\text{-}Fe/\gamma Al_2O_3$	419.0	486.0	622.9	914.8

* T_4 stands for the reduction of small metal particles and metal oxide which strongly adhere to the support surface.[2] Hence, Co^0 and Fe^0 will be obtained when reducing temperature reaches at least 667.5 °C.

Table S3: Brown-Forsythe test of homogeneity

Degrees of Freedom	F value	p value
4	2.2067	0.06887
243		

Table S4: Regression analysis predicting metal particle size from existence of plasma, existence of iron promoter and reaction time

	Estimate	Standard Error	t value	p value
Intercept	5.41247	0.28208	19.188	$< 2\times10^{-16}$
Plasma*	0.12800	0.35054	0.365	0.715
Promoter**	1.46777	0.30696	4.782	3.01×10^{-6}
Reaction Time	0.12440	0.01204	10.336	$< 2\times10^{-16}$

*: Plasma = 1 when the plasma was generated during the reaction.

**: Promoter = 1 when Co-Fe catalyst was testing in reaction.

Reference:

(1) Conrads, H.; Schmidt, M. Plasma generation and plasma sources. *Plasma Sources Sci. Technol.,* 2000, 9.

(2) Ali, S.; Zabidi, N. A. M.; Subbarao, D. Correlation between Fischer-Tropsch catalytic activity and composition of catalysts. *Chem. Cent. J.*, 2011, 5 (68).