Electronic supplementary information (ESI)

for

Co-activation of methane and nitrogen to acetonitrile over MoC_x/Al_2O_3 catalysts

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Derivation of the rate equation according to the LHHW formalism of methane conversion to ACN

Plausible reactions of CH_4 and N_2 co-activation to form ACN:

s_1 $N_2 + 2s \leftrightarrow 2N \cdot s$ (eq. 1)

s_2 $2CH_4 + 2s \leftrightarrow 2CH \cdot s + 3H_2$ (eq. 2)

s_3 $2CH \cdot s \leftrightarrow C_2H_2 \cdot s + s$ (eq. 3)

s_4 $2C_2H_2 \cdot s + H_2 \leftrightarrow 2C_2H_3 \cdot s$ (eq. 4)

s_5 $C_2H_3 \cdot s + N \cdot s \leftrightarrow C_2H_3N \cdot s + s$ (eq. 5)

s_6 $C_2H_3N \cdot s \leftrightarrow C_2H_3N + s$ (eq. 6)

The aforementioned reactions can be lumped into four steps

s_1' N_2 adsorption $N_2 + 2s \overset{K_{ad,1}}{\longleftrightarrow} 2N \cdot s$ (eq. 7)

s_2' CH_4 adsorption $2CH_4 + s \overset{K_{ad,2}}{\longleftrightarrow} C_2H_2 \cdot s + 3H_2$ (eq. 8)

s_3' surface reaction $2C_2H_2 \cdot s + 2N \cdot s + H_2 \overset{K_{surf}}{\longleftrightarrow} 2C_2H_3N \cdot s + 2s$ (eq. 9)

s_4' ACN desorption $C_2H_3N \cdot s \overset{K_{de}}{\longleftrightarrow} C_2H_3N + s$ (eq. 10)

Since ACN desorption is rapid, the equilibrium constant (K_{de}) of step *s4'* is assumed to be very large. Thus, the terms containing K_{de} in the denominator are negligibly small.

I. Assuming N_2 adsorption step (s_1') is rate-limiting

The rate of the step of N_2 adsorption should be close to the rate of the overall reaction:

$$r = k_{ad,1} P_{N_2} (1 - \Sigma\theta_i)^2 \quad \text{(eq. 11)}$$

Then, CH_4 adsorptions (eq. 8), surface reaction (eq. 9), and ACN desorption (eq. 10) should attain the equilibrium, thereby yielding:

$$K_{ad,2} = \frac{\theta_{C_2H_2} P_{H_2}^3}{P_{CH_4}^2 (1-\Sigma\theta_i)} \quad \text{(eq. 12)}$$

$$K_{surf} = \frac{\theta_{C_2H_3N}^2 (1-\Sigma\theta_i)^2}{\theta_{C_2H_2}^2 \theta_N^2 P_{H_2}} \quad \text{(eq. 13)}$$

$$K_{de} = \frac{P_{C_2H_3N} (1-\Sigma\theta_i)}{\theta_{C_2H_3N}} \quad \text{(eq. 14)}$$

Rearranging eqs. 12, 13, and 14, the expressions of θ_N, θ_{C2H2}, and θ_{C2H3N} can be obtained.

$$\theta_N = K_{ad,2}^{-1} K_{surf}^{0.5} K_{de}^{-1} P_{H_2}^{3.5} P_{CH_4}^{-2} P_{C_2H_3N} (1 - \Sigma\theta_i) \quad \text{(eq. 15)}$$

$$\theta_{C_2H_2} = K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2} (1 - \Sigma\theta_i) \quad \text{(eq. 16)}$$

$$\theta_{C_2H_3N} = K_{de}^{-1} P_{C_2H_3N} (1 - \Sigma\theta_i) \quad \text{(eq. 17)}$$

Accordingly, the sum of the coverages of adsorbed species can be expressed as:

$$\Sigma\theta_i = \frac{K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2} + K_{ad,2}^{-1} K_3^{0.5} K_{de}^{-1} P_{H_2}^{3.5} P_{CH_4}^{-2} P_{C_2H_3N} + K_{de}^{-1} P_{C_2H_3N}}{1 + K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2} + K_{ad,2}^{-1} K_{surf}^{0.5} K_{de}^{-1} P_{H_2}^{3.5} P_{CH_4}^{-2} P_{C_2H_3N} + K_{de}^{-1} P_{C_2H_3N}} \quad \text{(eq. 18)}$$

Since K_{de} is assumed to be very large, the sum of the coverages of adsorbed species can be simplified as:

$$\Sigma\theta_i = \frac{K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2}}{1 + K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2}} \quad \text{(eq. 19)}$$

By taking eq. 19 into eq. 11, the expression of the overall rate by assuming N_2 adsorption is rate-limiting can be obtained as:

$$r = k_{ad,1} P_{N_2} \left(\frac{1}{1 + K_{ad,2} P_{H_2}^{-3} P_{CH_4}^{2}}\right)^2 \quad \text{(eq. 20)}$$

II. Assuming CH_4 adsorption step (s_2') is rate-limiting

The rate of the step of CH_4 adsorption should be close to the rate of the overall reaction:

$$r = k_{ad,2} P_{CH_4}^{2} (1 - \Sigma\theta_i) \quad \text{(eq. 21)}$$

Then, N_2 adsorptions (eq. 7), surface reaction (eq. 9), and ACN desorption (eq. 10) should attain the equilibrium, thereby yielding:

$$K_{ad,1} = \frac{\theta_N^2}{P_{N_2} (1 - \Sigma\theta_i)^2} \quad \text{(eq. 22)}$$

$$K_{surf} = \frac{\theta_{C_2H_3N}^2 (1 - \Sigma\theta_i)^2}{\theta_{C_2H_2}^2 \theta_N^2 P_{H_2}} \quad \text{(eq. 23)}$$

$$K_{de} = \frac{P_{C_2H_3N} (1 - \Sigma\theta_i)}{\theta_{C_2H_3N}} \quad \text{(eq. 24)}$$

By rearranging eqs. 22, 23, and 24, the expressions of θ_N, θ_{C2H2}, and θ_{C2H3N} can be obtained.

$$\theta_N = K_{ad,1}^{0.5} P_{N_2}^{0.5} (1 - \Sigma\theta_i) \quad \text{(eq. 25)}$$

$$\theta_{C_2H_2} = K_{ad,1}^{-0.5} K_{surf}^{-0.5} K_{de}^{-1} P_{N_2}^{-0.5} P_{H_2}^{0.5} P_{C_2H_3N} (1 - \Sigma\theta_i) \quad \text{(eq. 26)}$$

$$\theta_{C_2H_3N} = K_{de}^{-1} P_{C_2H_3N} (1 - \Sigma\theta_i) \quad \text{(eq. 27)}$$

Accordingly, the sum of the coverages of adsorbed species can be expressed as:

$$\Sigma\theta_i = \frac{K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,1}^{-0.5}K_{surf}^{-0.5}K_{de}^{-1}P_{N_2}^{-0.5}P_{H_2}^{0.5}P_{C_2H_3N}+K_{de}^{-1}P_{C_2H_3N}}{1+K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,1}^{-0.5}K_{surf}^{-0.5}K_{de}^{-1}P_{N_2}^{-0.5}P_{H_2}^{0.5}P_{C_2H_3N}+K_{de}^{-1}P_{C_2H_3N}}$$ (eq. 28)

Since K_{de} is assumed to be very large, the sum of the coverages of adsorbed species can be simplified as:

$$\Sigma\theta_i = \frac{K_{ad,1}^{0.5}P_{N_2}^{0.5}}{1+K_{ad,1}^{0.5}P_{N_2}^{0.5}}$$ (eq. 29)

By taking eq. 29 into eq. 21, the expression of the overall rate by assuming CH_4 adsorption is rate-limiting can be obtained as:

$$r = k_{ad,2}P_{CH_4}^2\frac{1}{1+K_{ad,1}^{0.5}P_{N_2}^{0.5}}$$ (eq. 30)

III. Assuming the surface reaction step (s_3') is rate-limiting

The rate of the step of surface reaction should be close to the rate of the overall reaction:

$$r = k_{surf}\theta_{C_2H_2}^2\theta_N^2P_{H_2}$$ (eq. 31)

Then, N_2 adsorptions (eq. 7), CH_4 adsorption (eq. 8), and ACN desorption (eq. 10) should attain the equilibrium, thereby yielding:

$$K_{ad,1} = \frac{\theta_N^2}{P_{N_2}(1-\Sigma\theta_i)^2}$$ (eq. 32)

$$K_{ad,2} = \frac{\theta_{C_2H_2}P_{H_2}^3}{P_{CH_4}^2(1-\Sigma\theta_i)}$$ (eq. 33)

$$K_{de} = \frac{P_{C_2H_3N}(1-\Sigma\theta_i)}{\theta_{C_2H_3N}}$$ (eq. 34)

By rearranging eqs. 32, 33, and 34, the expressions of θ_N, θ_{C2H2}, and θ_{C2H3N} can be obtained.

$$\theta_N = K_{ad,1}^{0.5}P_{N_2}^{0.5}(1-\Sigma\theta_i)$$ (eq. 35)

$$\theta_{C_2H_2} = K_{ad,2}P_{CH_4}^2P_{H_2}^{-3}(1-\Sigma\theta_i)$$ (eq. 36)

$$\theta_{C_2H_3N} = K_{de}^{-1}P_{C_2H_3N}(1-\Sigma\theta_i)$$ (eq. 37)

Accordingly, the sum of the coverages of adsorbed species can be expressed as:

$$\Sigma\theta_i = \frac{K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,2}P_{CH_4}^2P_{H_2}^{-3}+K_{de}^{-1}P_{C_2H_3N}}{1+K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,2}P_{CH_4}^2P_{H_2}^{-3}+K_{de}^{-1}P_{C_2H_3N}}$$ (eq. 38)

Since K_{de} is assumed to be very large, the sum of the coverages of adsorbed species can be simplified as

$$\Sigma\theta_i = \frac{K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,2}P_{CH_4}^2P_{H_2}^{-3}}{1+K_{ad,1}^{0.5}P_{N_2}^{0.5}+K_{ad,2}P_{CH_4}^2P_{H_2}^{-3}}$$ (eq. 39)

By taking eq. 39 into eq. 31, the expression of the overall rate by assuming the surface reaction is rate-limiting can be obtained as:

$$r_{ACN} = k_{surf} K_{ad,1} K_{ad,2}^{2} P_{H_2}^{-5} P_{CH_4}^{4} P_{N_2} \cdot (1 + K_{ad,1}^{0.5} P_{N_2}^{0.5} + K_{ad,2} P_{CH_4}^{2} P_{H_2}^{-3})^{-4} \quad \text{(eq. 40)}$$

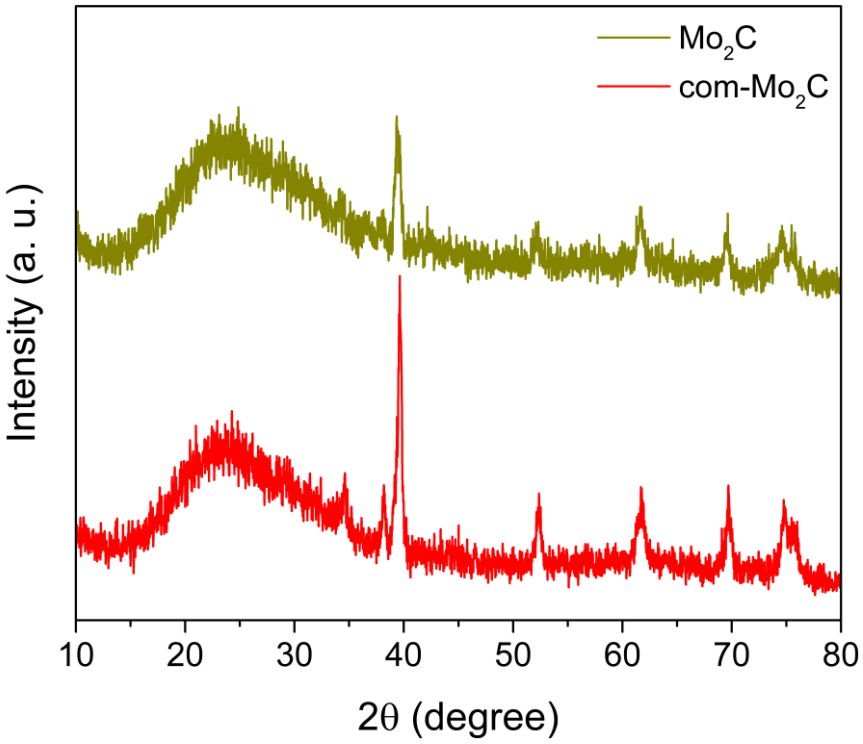

Figure S1. XRD patterns of unsupported Mo_2C and commercial Mo_2C (com-Mo_2C).

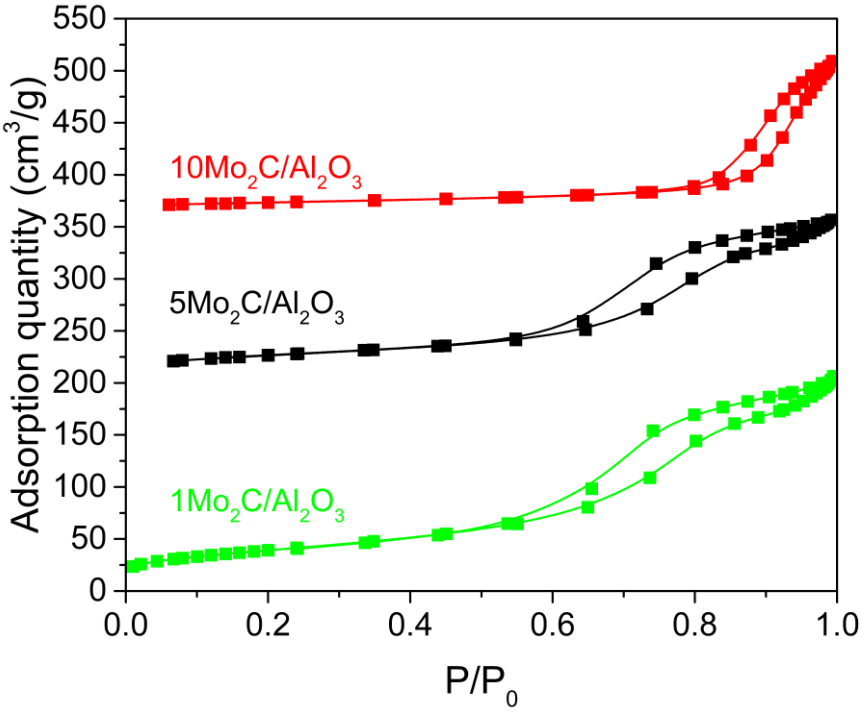

Figure S2. N_2 adsorption-desorption isotherms of Al_2O_3-supported MoC_x catalysts.

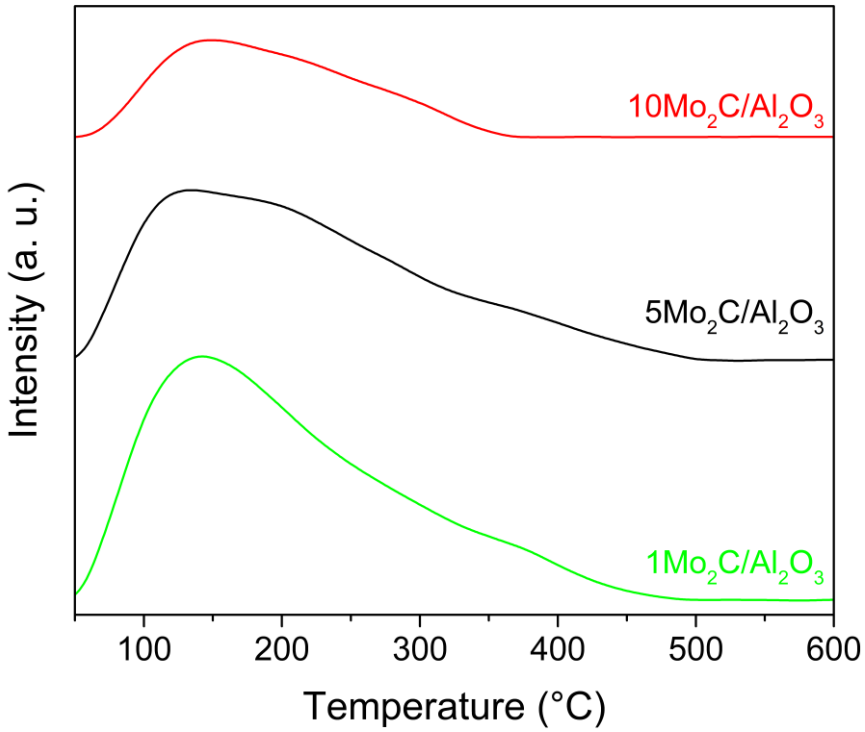

Figure S3. NH_3-TPD profiles of Al_2O_3-supported MoC_x catalysts.

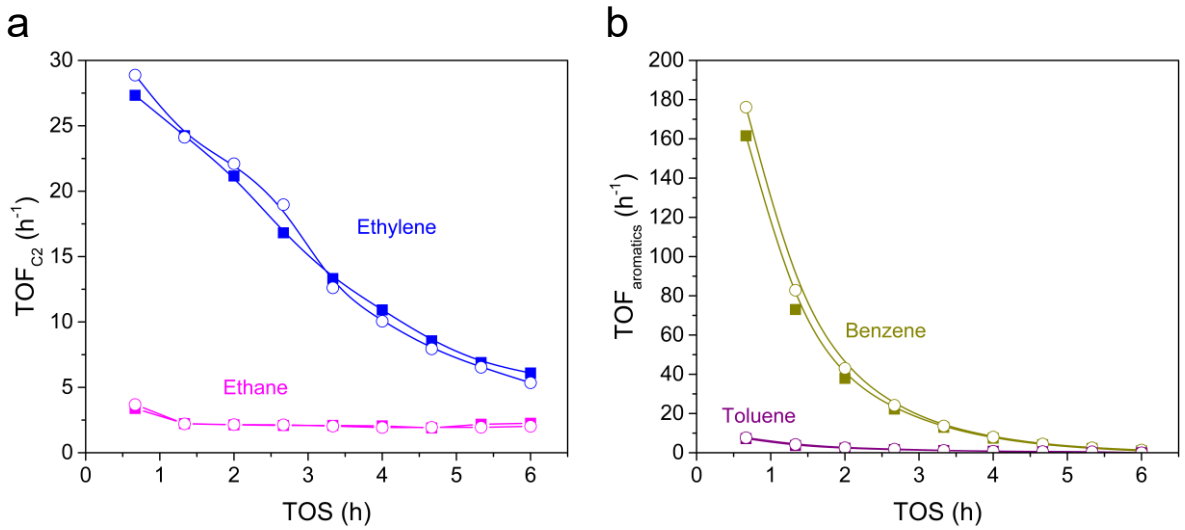

Figure S4. TOS profile of TOFs of (a) C_2 (ethylene, blue; ethane, magenta) and (b) aromatics (benzene, dark yellow; toluene, purple) in N_2 (closed squares) and Ar (opened circles) steams. *Reaction conditions: 0.18 g of 1MoC$_x$/Al$_2$O$_3$, reaction temperature = 750 °C, GHSV = 1500 mL$_{CH4}$/g$_{cat}$/h, feed = 4.5/4.5/1 mL/min of CH$_4$/N$_2$/Ar or 4.5/5.5 mL/min of CH$_4$/Ar.*

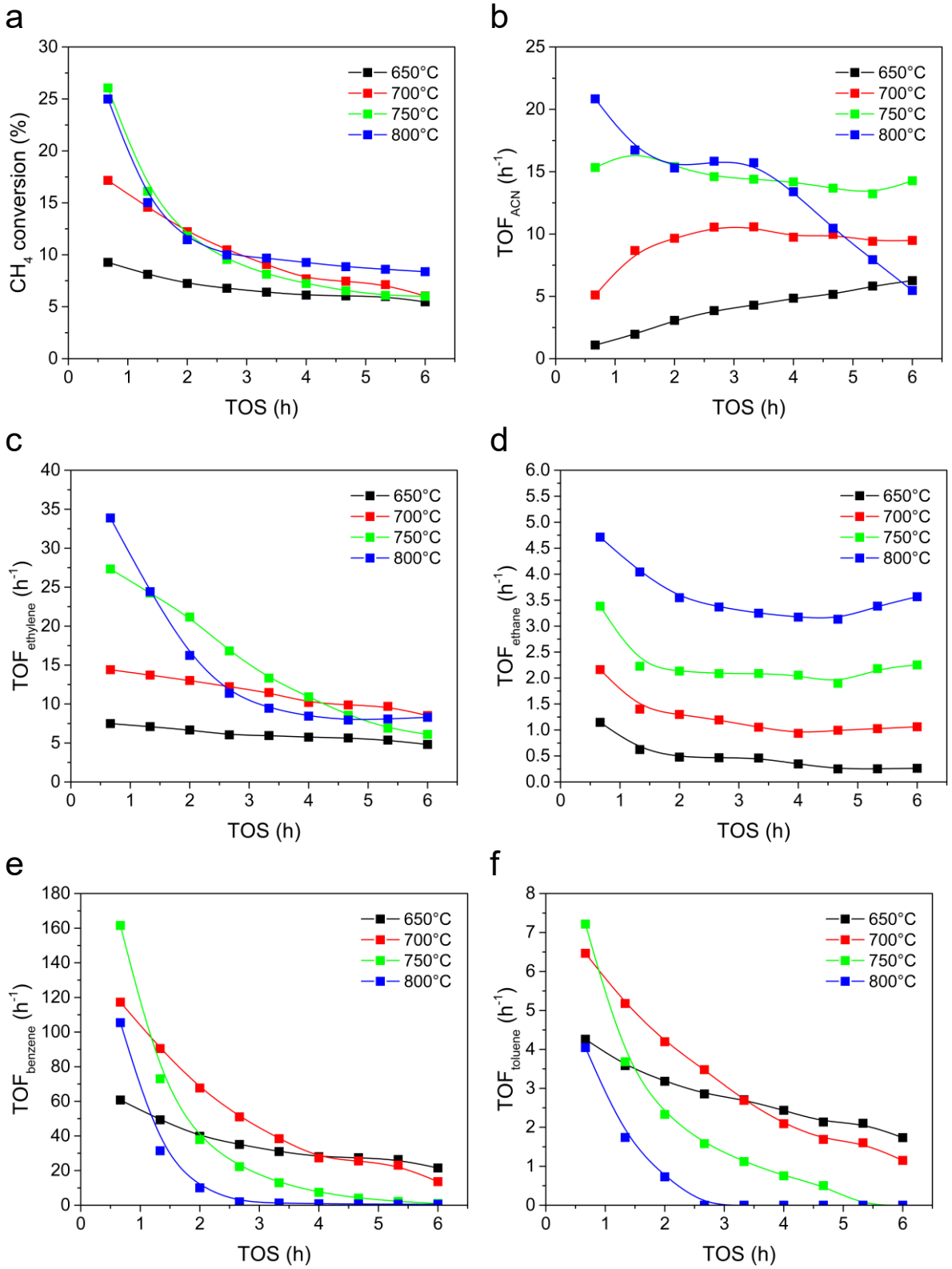

Figure S5. TOS profiles of the temperature effect on (a) CH_4 conversion and TOF profiles of (b) ACN, (c) ethylene, (d) ethane, (e) benzene, and (f) toluene by using $1MoC_x/Al_2O_3$.

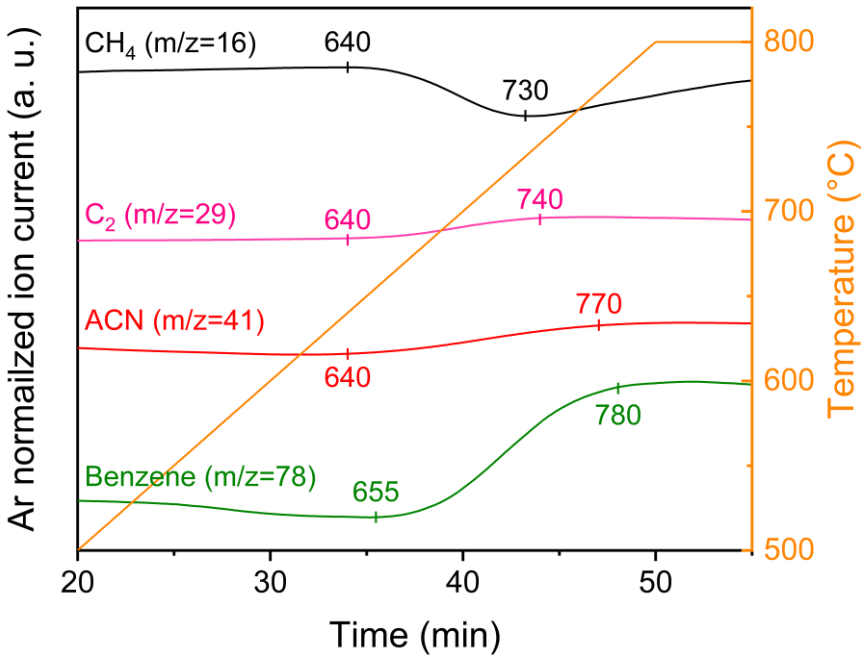

Figure S6. CH_4-TPSR profile of $1MoC_x/Al_2O_3$. *Reaction conditions: 0.18 g of $1MoC_x/Al_2O_3$, 300-800 °C (10 °C/min), 4.5 + 4.5 + 1 mL/min of CH_4 + N_2 + Ar.*

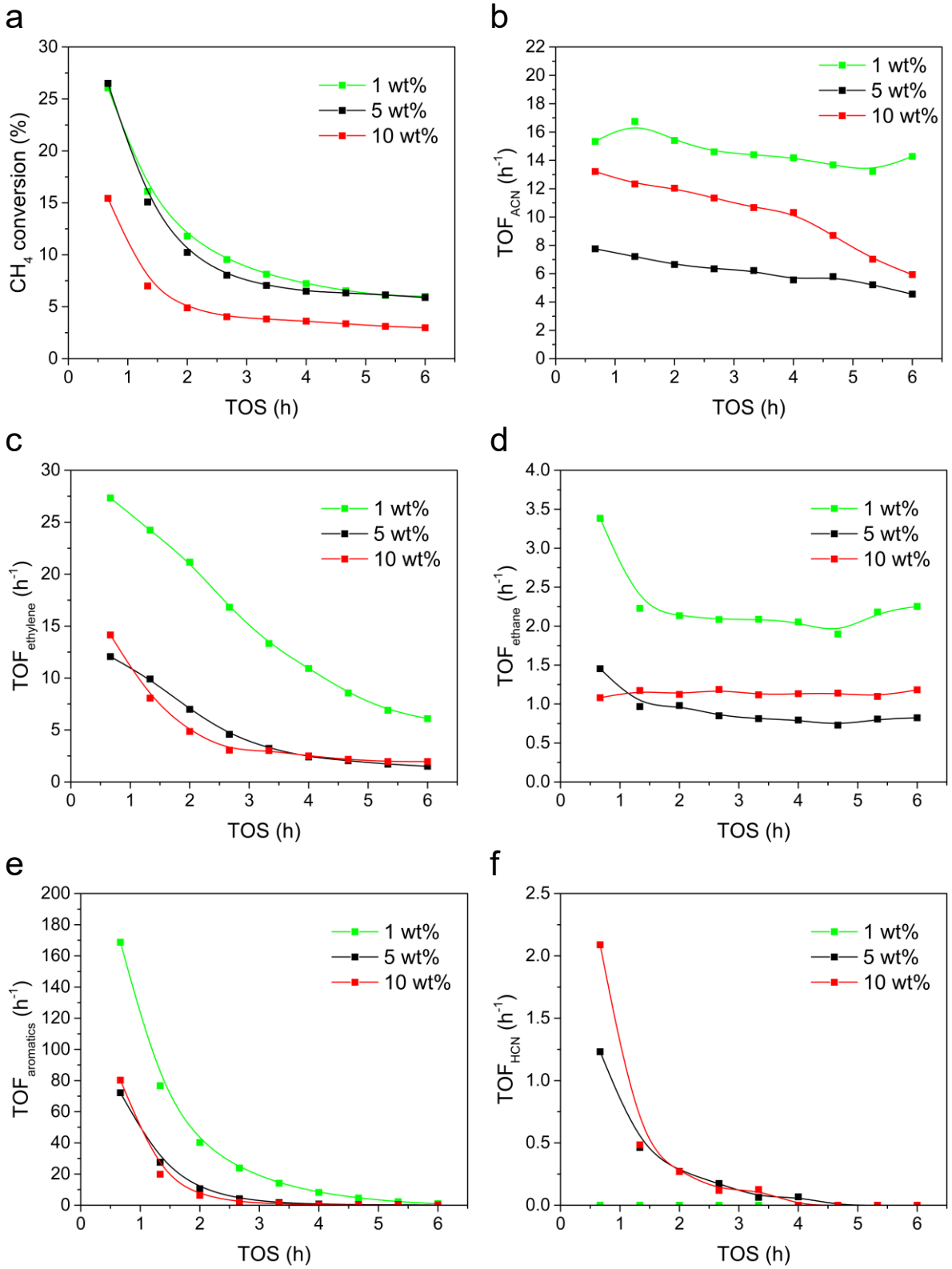

Figure S7. TOS profiles of the effect of Mo loading on (a) CH_4 conversion and TOFs of (b) ACN, (c) ethylene, (d) ethane, (e) aromatics, and (f) HCN.

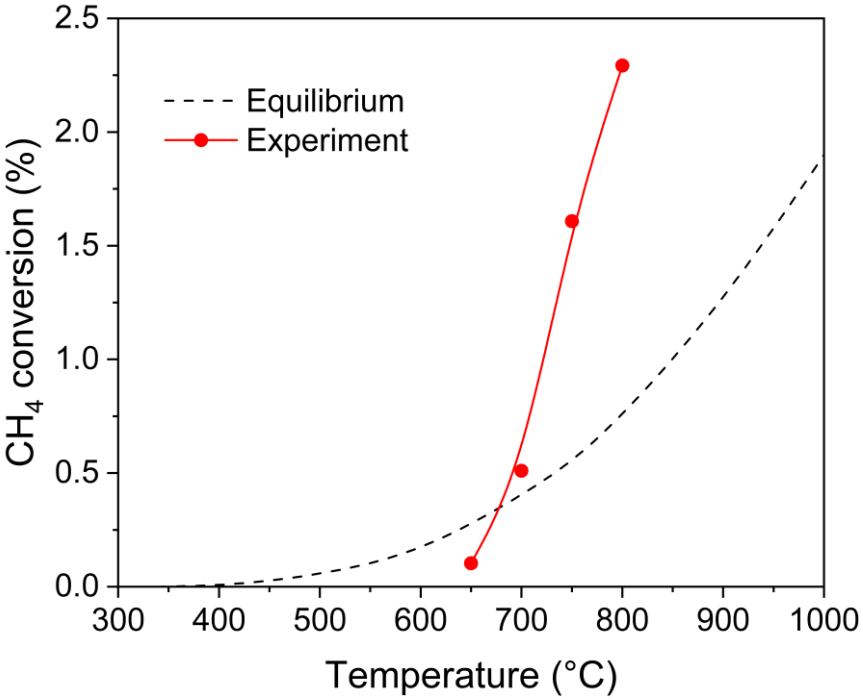

Figure S8. Methane conversion as a function of temperature.

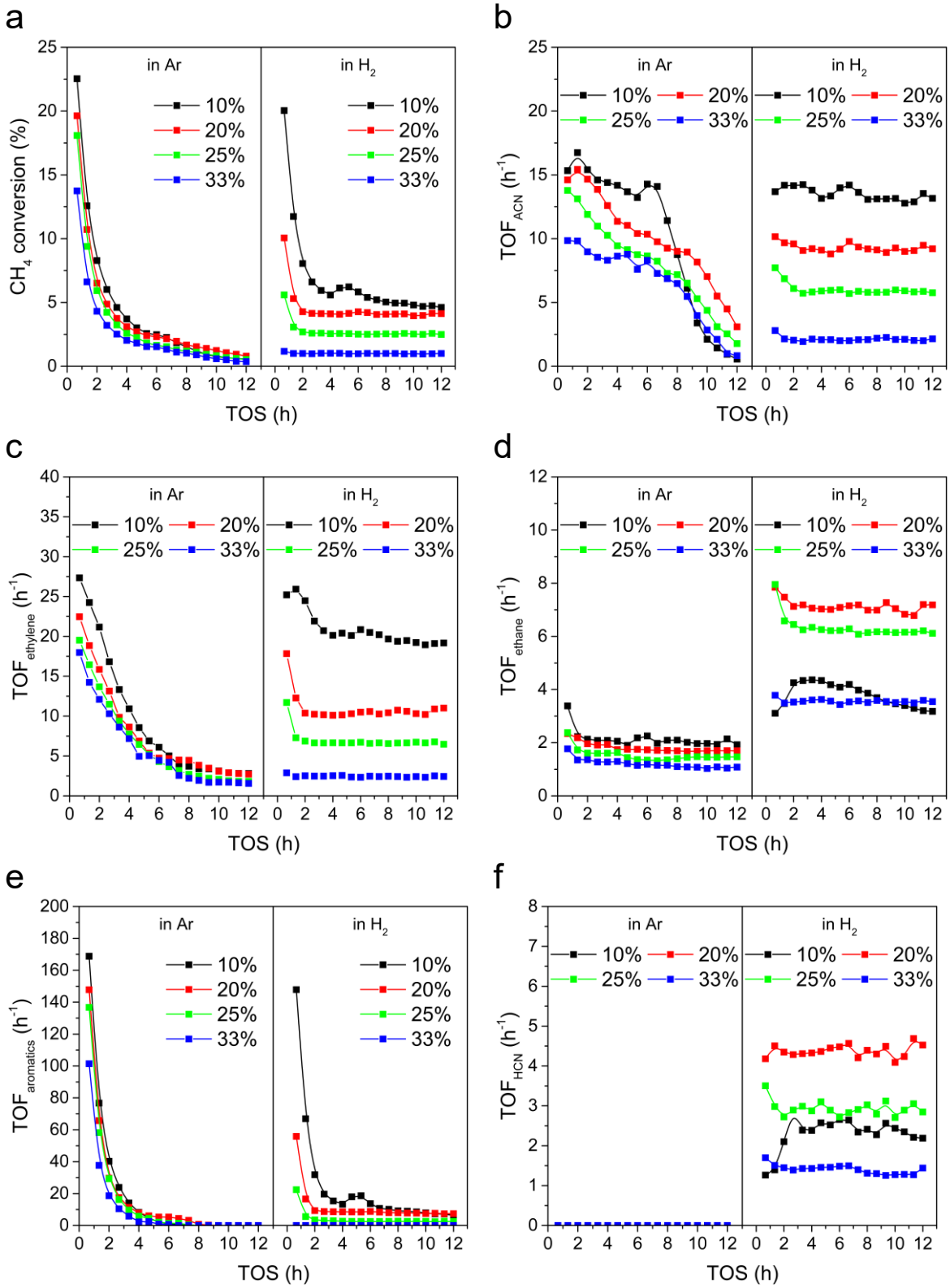

Figure S9. TOS profiles of the dilution and H_2 concentration effect on (a) CH_4 conversion and TOFs of (b) ACN, (c) ethylene, (d) ethane, (e) aromatics, and (f) HCN by using $1MoC_x/Al_2O_3$.

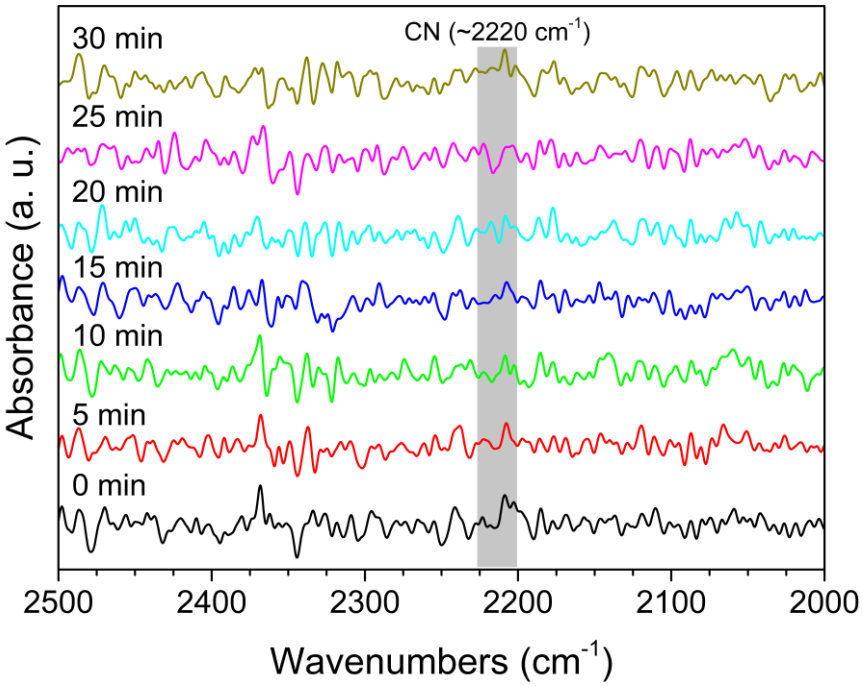

Figure S10. DRIFTS spectra during N_2 purging at 750 °C by using $1MoC_x/Al_2O_3$ catalyst. The background was collected at 750 °C. Each spectrum was collected using 128 scans.

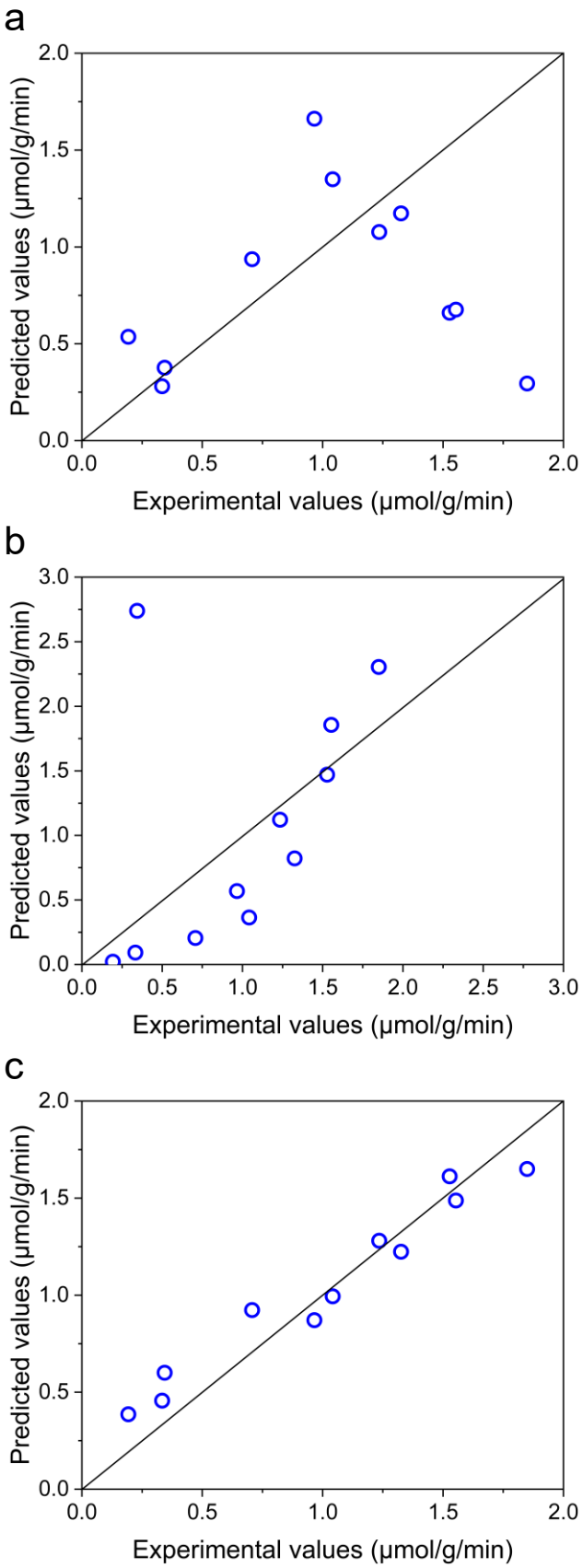

Figure S11. The parity plot of the reaction rate by assuming (a) N_2 adsorption, (b) CH_4 adsorption, and (c) surface reaction is rate-limiting in methane and N_2 conversion to ACN.

Table S1. Equilibrium constant and relative compositions of methane, N_2, ACN, and H_2 as the function of temperature in the conversion of methane to ACN.[a]

Temperature	**K_{eq}**	**Composition (mol)**			
(°C)		**CH_4**	**N_2**	**CH_3CN**	**H_2**
300	3.14×10^{-17}	2.000	0.500	0.000	0.000
400	3.73×10^{-14}	2.000	0.500	0.000	0.000
500	6.25×10^{-12}	1.999	0.500	0.001	0.001
600	2.89×10^{-10}	1.997	0.499	0.002	0.004
700	5.48×10^{-9}	1.992	0.498	0.004	0.010
750	**1.86×10^{-8}**	**1.989**	**0.497**	**0.006**	**0.014**
800	5.48×10^{-8}	1.985	0.496	0.008	0.019
900	3.40×10^{-7}	1.975	0.494	0.013	0.032
1000	1.46×10^{-6}	1.962	0.490	0.019	0.048

Table S2. Percentage of Mo and C species at the surface of MoC_x catalysts.

Catalyst	Mo 3d				C 1s				C/Mo ratio[a]
	Mo^{6+}	Mo^{4+}	Mo^{3+}	Mo^{2+}	C−Mo	C−C	C−O	C=O	
Mo_2C	89.9	0	2.7	7.4	22.7	65.5	5.4	6.4	0.20
$1MoC_x/Al_2O_3$	47.5	15.6	8.8	28.1	32.3	41.8	25.7	0.2	1.04
spent $1MoC_x/Al_2O_3$ (6-h, Ar)	82.8	5.7	3.5	8.0	0	76.8	16.2	7.1	5.66
spent $1MoC_x/Al_2O_3$ (6-h, H_2)	77.0	12.2	2.2	8.6	0	75.9	18.7	5.4	5.56
spent $1MoC_x/Al_2O_3$ (12-h, Ar)	86.7	10.4	0.8	2.1	0	86.5	9.3	4.2	11.23
spent $1MoC_x/Al_2O_3$ (12-h, H_2)	80.2	10.7	2.2	6.9	0	78.7	21.3	0	6.78

[a] Obtained by survey spectra.

Table S3. CO and N_2 uptakes over Al_2O_3-supported MoC_x catalysts.

Catalyst	**CO uptake (μmol/g)**	**N_2 uptake (μmol/g)**	**CO/N_2 ratio**
$1MoC_x/Al_2O_3$	15.2	14.9	1.02
$5MoC_x/Al_2O_3$	17.3	16.0	1.08
$10MoC_x/Al_2O_3$	21.7	21.5	1.01

Table S4. Catalytic data of CH_4 and N_2 conversion to ACN by using $1MoC_x/Al_2O_3$ at 650 °C.

Entry	Feed composition (mL/min)			CH_4 conversion (%)	Components concentration (μmol/mL)			Reaction rate (μmol/g/min)
	CH_4	N_2	Ar		CH_4	N_2[a]	H_2[b]	
1	0.8	8.3	1	4.1	0.95	10.89	0.17	0.03
2	1.5	7.5	1	2.4	1.93	9.90	0.27	0.06
3	2.3	6.8	1	2.7	2.89	8.91	0.47	0.13
4	3.0	6.0	1	2.6	3.86	7.92	0.65	0.19
5	3.8	5.3	1	2.5	4.83	6.93	0.87	0.17
6	4.5	4.5	1	2.4	5.80	5.94	0.90	0.24
7	5.3	3.8	1	2.2	6.78	4.95	1.04	0.22
8	6.0	3.0	1	2.1	7.75	3.96	1.03	0.27
9	6.8	2.3	1	2.1	8.72	2.97	1.25	0.28
10	7.5	1.5	1	2.0	9.70	1.98	1.16	0.33
11	8.3	0.8	1	2.7	10.60	0.99	2.19	0.06

[a] N_2 concentration was estimated using the mass balance of N atom as $C_{N2,\ outlet} = C_{N2,\ inlet} - C_{ACN}$.

[b] H_2 concentration was estimated using the mass balance of H atom as $C_{H2,\ outlet} = 0.5*(4*C_{CH4,\ inlet} - 3*C_{ACN} - 4*C_{C2H4} - 6*C_{C2H6} - 6*C_{C6H6})$.

Table S5. Kinetic parameters obtained from the nonlinear regression of the derived rate expressions (eqs. 20, 30, and 40, respectively, of the ESI).

Rate-limiting step	k_1	K_1	k_2	K_2	k_3
N_2 adsorption	4.8×10^{-1}	-	-	1.2×10^{-2}	-
CH_4 adsorption	-	-6.0×10^{-1}	2.4×10^{-2}	-	-
Surface reaction	-	2.0	-	3.7×10^{-2}	54.7