

Supplementary Information

Mechanistic Insight into Selective Catalytic Combustion of Acrylonitrile (C₂H₃CN): NCO Formation and its Further Transformation towards N₂

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Microkinetic analysis

Reaction rate constant (k) was calculated based on the harmonic transition state theory (HTST) using the classic equation²³ as formulated in Eq. (1.1).

$$k = \frac{k_B T}{h} \left(\frac{P^\theta}{RT}\right)^{1-n} \exp\left(\frac{-\Delta_r G_m^\theta(P^\theta)}{RT}\right) \quad (1.1),$$

where k_B is Boltzmann constant; $\Delta_r G_m^\theta(P^\theta)$ stands for the standard molar activation Gibbs energy; n is the coefficient amount of the reactants as well as h , T , and R respectively denote Plank constant, temperature, and gas constant. The Eq. (1.1) can also be formulated as Eq. (1.2) according to the basic thermodynamic formula $\Delta_r G_m^\theta(P^\theta) = \Delta_r H_m^\theta(P^\theta) - T\Delta_r S_m^\theta(P^\theta)$, where $\Delta_r H_m^\theta(P^\theta)$ and $\Delta_r S_m^\theta(P^\theta)$ represent the standard molar activation enthalpy and entropy, respectively.

$$k = \frac{k_B T}{h} \left(\frac{P^\theta}{RT}\right)^{1-n} \exp\left(\frac{\Delta_r S_m^\theta(P^\theta)}{R}\right) \exp\left(\frac{-\Delta_r H_m^\theta(P^\theta)}{RT}\right) \quad (1.2)$$

Moreover, the activation energy (E_a) can be correlated with the $\Delta_r H_m^\theta(P^\theta)$ according to the Eq. (1.3), where n_1 represents the coefficient amount of the gaseous reactants. For the condensed phase reaction the value of n_1 is 1.

$$E_a = \Delta_r H_m^\theta(P^\theta) + n_1 RT \quad (1.3)$$

Finally, we got the final reaction rate constant formulated as Eq. (1.4) by including the Eq. (1.3) into the Eq. (1.2).

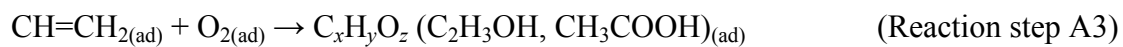
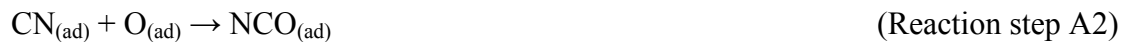
$$k = \frac{k_B T}{h} e^{n_1} \left(\frac{P^\theta}{RT}\right)^{1-n} \exp\left(\frac{\Delta_r S_m^\theta(P^\theta)}{R}\right) \exp\left(\frac{-E_a}{RT}\right) \quad (1.4)$$

Comparing Eq. (1.4) with the Arrhenius equation, the preexponential factor (A) can be calculated as the Eq. (1.5).

$$A = \frac{k_B T}{h} e^{n_1} \left(\frac{P^\theta}{RT}\right)^{1-n} \exp\left(\frac{\Delta_r S_m^\theta(P^\theta)}{R}\right) \quad (1.5)$$

The activation energy (E_a) can be calculated according to the energy barrier of each reaction step [from the reactant state (RS) to the TS] during the DFT energy calculations. The entropy containing three contributions, vibrational, rotational, and translational degrees of freedom, was calculated by the frequency calculations of DFT at 1 atm and 298.15 K. The $\Delta_r S_m^\theta(P^\theta)$ was calculated according to Eq. (1.6).

$$\Delta_r S_m^\theta(P^\theta) = S_{TS}^\theta(P^\theta) - S_{RS}^\theta(P^\theta) \quad (1.6)$$



Scheme S1. Schematic reaction mechanism of AN-SCC over Cu-ZSM-5 derived from in-situ DRIFTS.

Table S1 Energy barrier of each reaction route (unit of kcal mol⁻¹) and optimized geometrical parameters of models utilized in the DFT mechanism simulations (distances in Å, angles in °)

Route	Energy Barrier/ kcal mol ⁻¹	Structures	Gas phase	1 ^a	2 ^b	3 ^c
I	17.0	Cu-N	-	1.97	1.81	1.82
		Cu-O	-	2.11	3.93	-
		C ₁ -N	1.16	1.35	1.24	1.22
		C ₁ -O	-	1.29	1.20	1.18
		C ₁ -C ₂	1.43	1.46	2.14	3.17
		C ₂ -C ₃	1.34	1.34	1.31	1.31
		∠N-C ₁ -O	-	111.0	155.0	177.1
		∠N-C ₁ -C ₂	180.0	125.9	-	-
II	100.9	∠C ₁ -C ₂ -C ₃	122.9	121.1	-	-
		Cu-N	-	1.82	1.90	1.90
		N-C	1.23	1.21	2.16	-
		C-O	1.19	1.18	1.14	1.14
III	48.7	∠NCO	180.0	177.6	-	-
		Cu-N ₁	-	1.97	1.87	-
		N ₁ -N ₂	-	1.40	1.29	1.10
		N ₁ -C ₁	1.23	1.25	1.25	-
		C ₁ -O ₁	1.19	1.16	1.17	1.14
		N ₂ -C ₂	-	1.24	1.92	-
		C ₂ -O ₂	-	1.17	1.14	1.14
		∠N ₁ C ₁ O ₁	180.0	174.9	161.6	-
∠N ₂ C ₂ O ₂	-	169.8	126.9	-		
IV	7.8	Cu-O ₁	-	1.88	2.78	-
		O ₁ -N	-	1.38	1.21	1.15
		N-C	1.23	1.25	1.55	-
		C-O ₂	1.19	1.17	1.16	1.14
		∠NCO ₂	180	167.3	134.9	-
V	0.8	Cu-N ₁	-	2.02	2.01	-
		N ₁ -N ₂	-	1.30	1.23	1.11
		N ₁ -C	1.23	1.49	1.61	-
		C-O ₁	1.19	1.17	1.17	1.16

		N ₂ -O ₂	1.16	1.47	1.74	
		C-O ₂	-	1.40	1.32	1.18
		∠N ₁ CO ₁	180	137.1	128.7	
		∠C ₁ O ₁ O ₂	-	132.4	136.6	175.9
		Cu-N ₁	-	1.91	-	1.91
		N ₁ -C	1.23	1.22	1.65	-
		C-O ₁	1.19	1.18	1.15	1.14
		N ₁ -N ₂	-	2.11	1.24	1.13
VI	31.0	N ₂ -O ₂	1.16	1.14	1.21	1.18
		∠N ₁ CO ₁	180.0	176.1	129.5	-
		∠N ₁ N ₂ O	-	-	131.8	179.8

^a Adsorption state (AS)

^b Transition state (TS)

^c Product

Table S2 The calculated vibration frequencies of free and adsorbed acrylonitrile on 20T-O-Cu-Z₂₀ with respect of the literature report and the DRIFTS result.

Vibration mode	IR frequency of gaseous AN ²⁶	Calculated IR frequency of gaseous AN	DRIFTS result of adsorbed AN	Calculated result of adsorbed AN ^a
$\delta_s(-CH_2)$	1416	1406	1414	1446
$\nu(C_2=C_3)$	1615	1631	-	1627
$\nu(C_1\equiv N)$	2239	2258	2267	-
$\nu(N=C_1=O)$	-	-	2213	2248
$\nu_s(-CH_2)$	3042	3061	3035	3070
$\nu(-CH)$	3078	3072	3077	3109
$\nu_{as}(-CH_2)$	3116	3148	3121	3158

^aThe frequency correction factor is 0.9613