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Supplementary Information

Mechanistic Insight into Selective Catalytic Combustion of Acrylonitrile (C_2H_3CN): NCO Formation and its Further Transformation towards N_2

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Microkinetic analysis

Reaction rate constant (*k*) was calculated based on the harmonic transition sate theory (HTST) using the classic equation[23] as formulated in Eq. (1.1).

$$k=\frac{k_BT}{h}\left(\frac{P^\theta}{RT}\right)^{1\text{-n}}exp\left(\frac{-\Delta_rG_m{}^\theta(P^\theta)}{RT}\right) \qquad (1.1),$$

where k_B is Boltzmann constant; $\Delta_rG_m{}^\theta$ (p^θ) 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 $\Delta_rG_m{}^\theta$ (P^θ) = $\Delta_rH_m{}^\theta$ (P^θ) - $T\Delta_rS_m{}^\theta$ (P^θ), where $\Delta_rH_m{}^\theta$ (P^θ) and $\Delta_rS_m{}^\theta$ (P^θ) represent the standard molar activation enthalpy and entropy, respectively.

$$k=\frac{k_BT}{h}\left(\frac{P^\theta}{RT}\right)^{1\text{-n}}exp\left(\frac{\Delta_rS_m{}^\theta(P^\theta)}{R}\right)exp\left(\frac{-\Delta_rH_m{}^\theta(P^\theta)}{RT}\right) \qquad (1.2)$$

Moreover, the activation energy (E_a) can be correlated with the $\Delta_rH_m{}^\theta$ (P^θ) 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.

$$E_a=\Delta_rH_m{}^\theta(P^\theta)+\mathrm{n}_1RT \qquad (1.3)$$

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

$$k=\frac{k_BT}{h}\mathrm{e}^{\mathrm{n}_1}\left(\frac{P^\theta}{RT}\right)^{1\text{-n}}exp\left(\frac{\Delta_rS_m{}^\theta(P^\theta)}{R}\right)exp\left(\frac{-E_a}{RT}\right) \qquad (1.4)$$

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

$$A=\frac{k_BT}{h}\mathrm{e}^{\mathrm{n}_1}\left(\frac{P^\theta}{RT}\right)^{1\text{-n}}exp\left(\frac{\Delta_rS_m{}^\theta(P^\theta)}{R}\right) \qquad (1.5)$$

The activation energy (E_a) can be calculated according to the energy barrier of each reaction step [from the reactant sate (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 $\Delta_rS_m{}^\theta$ (P^θ) was calculated according to Eq. (1.6).

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

$CH_2=CH\text{-}CN_{(ad)} \rightarrow CH=CH_{2(ad)} + CN_{(ad)}$ (Reaction step A1)

$CN_{(ad)} + O_{(ad)} \rightarrow NCO_{(ad)}$ (Reaction step A2)

$CH=CH_{2(ad)} + O_{2(ad)} \rightarrow C_xH_yO_z\ (C_2H_3OH,\ CH_3COOH)_{(ad)}$ (Reaction step A3)

$C_xH_yO_z + O_{2(ad)} \rightarrow CO_{2(g)} + H_2O_{(g)}$ (Reaction step A4)

$CN_{(ad)} + H_2O_{(g)} \rightarrow CONH_{2(ad)} \rightarrow NH_{3(g)}$ (Reaction step B1)

$NH_{3(ad)} + O_{2(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$ (Reaction step B2)

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
		$\angle N\text{-}C_1\text{-}O$	-	111.0	155.0	177.1
		$\angle N\text{-}C_1\text{-}C_2$	180.0	125.9	-	-
		$\angle C_1\text{-}C_2\text{-}C_3$	122.9	121.1	-	-
II	100.9	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
		$\angle NCO$	180.0	177.6	-	-
III	48.7	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
		$\angle N_1C_1O_1$	180.0	174.9	161.6	-
		$\angle N_2C_2O_2$	-	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
		$\angle NCO_2$	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
		$\angle N_1CO_1$	180	137.1	128.7	
		$\angle C_1O_1O_2$	-	132.4	136.6	175.9
VI	31.0	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
		N_2-O_2	1.16	1.14	1.21	1.18
		$\angle N_1CO_1$	180.0	176.1	129.5	-
		$\angle N_1N_2O$	-	-	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-Z_{20} 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]
δ_s(-CH_2)	1416	1406	1414	1446
ν(C_2=C_3)	1615	1631	-	1627
ν(C_1≡N)	2239	2258	2267	-
ν(N=C_1=O)	-	-	2213	2248
ν_s(-CH_2)	3042	3061	3035	3070
ν(-CH)	3078	3072	3077	3109
ν_{as}(-CH_2)	3116	3148	3121	3158

[a] The frequency correction factor is 0.9613