

Modelling the combined HCHO/SCR reaction on V₂O₅/WO₃/TiO₂ catalyst in lean gas engine exhaust

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Significance and Relevance

The study deals with the kinetic modelling of the combined HCHO and SCR conversion on a $V_2O_5/WO_3/TiO_2$ catalyst in lean gas engine exhaust including the formation and decay of HCN along the catalyst. The modelling of this complex reaction system is novel and is a breakthrough to minimize the secondary emission of HCN formed as a by-product during the reaction of HCHO and NH₃.

Preferred and 2nd choice for the topic: Automotive and stationary emission control / Multiscale modeling and advanced simulation aspects. Preferred presentation: Oral preferred or Short Oral.

Introduction and Motivations

The emission of greenhouse gases (GHG) is worldwide considered with great concern. Lean-burn gas engines can provide a relevant contribution due to their high efficiency and GHG neutrality when using biomethane. In addition to carbon dioxide (CO₂) and water, gas engine combustion also results in the output of NO_x, carbon monoxide (CO) and hydrocarbons such as HCHO. Due to the strict emission limits a catalytic exhaust gas aftertreatment for NO_x and HCHO is mandatory for stationary lean-burn gas engines. As the SCR with NH₃ is deployed to remove NO_x from the exhaust gas of biomethane fueled lean gas engines the competing consumption of NH₃ by HCHO resulting in the formation of the highly toxic HCN has to be considered. Though the commonly used VWT catalyst is capable to remove both HCHO and HCN from the exhaust gas. Thus, a kinetic model has been developed which describes the conversion of NO_x, NH₃ and HCHO as well as the simultaneous formation and decay of HCN.

Materials and Methods

A commercially available cylindrical VWT honeycomb (2.54 cm in diameter and 1 cm in length) with a cell density of 400 cells per square inch (cpsi) and a total V load of 2% is tested in gradient free loop reactor which is suitable to measure the intrinsic chemical kinetics without the influence of mass transfer as confirmed by residence time tests showing a residence time distribution closely to a continuous stirred tank reactor (CSTR). The kinetics of the relevant reactions (see Tab. 1) were tested and determined independently using a flow rate of 600 ml/min (STP) and recycling an inner flow of 50 L/min resulting in a recycle ratio (φ) of 83 except for the NH₃ adsorption and desorption (TPD) and the formation of HCN (plug flow experiments). A kinetic model based on the experimental findings was developed using CSTR balances for the species (Eq. 1) where c denotes the concentration, θ the adsorbed NH₃ species and τ the residence time. The surface balance of the adsorbed NH₃ species is defined by Eq. 2 where Γ represents the surface density which is derived from the NH₃-TPD experiments. The rate equations r_i were described by Arrhenius type expressions (Eq. 3). For the activation energy of the NH₃ desorption a linear dependency on the surface coverage was considered. Furthermore, for the rate approaches of the NH₃ oxidation and the NH₃-SCR the numerical dependencies of the Arrhenius parameters are decoupled using a reference temperature [1] The resulting model was implemented in MATLAB using lsqcurvefit for the parameter estimation and the ode15s function for solving the differential mass balances.

$$\frac{dc_{i}}{dt} = \frac{c_{in,i} - c_{out,i}}{\tau} + \sum v_{j} \cdot r_{j}$$

$$\frac{d\theta}{dt} = \sum v_{j} \cdot r_{j}$$
(1)
(2)

$$\mathbf{ICEC}_{i}$$
$$\mathbf{r}_{i} = \mathbf{A}_{i} \cdot \exp\left(-\frac{\mathbf{E}_{\mathbf{A},i}}{\mathbf{R} \cdot \mathbf{T}}\right) \cdot \prod \mathbf{c}_{j} \cdot \prod \mathbf{\theta}$$

The suggested overall reaction mechanism and the respective kinetic parameters are presented in Table 1. The model includes the formation of HCN and its subsequent conversion by oxidation as well as hydrolysis. The kinetics of the HCN hydrolysis representing the predominate pathway of the HCN decay is described by a Hougen Watson approach (Eq. 4) [2].

(3)

$$r_{7} = A_{7} \cdot \exp\left(\frac{E_{7}}{R \cdot T}\right) \cdot c(HCN) \cdot \frac{K(H_{2}O) \cdot c_{0}(H_{2}O)}{\left(1 + K(H_{2}O) \cdot c_{0}(H_{2}O)\right)^{2}}$$
(4)

Tab. 1. Chemical equations and the respective Arrhenius/model parameter in the kinetic model.

#	Reaction	Arrhenius/model parameter
1	NH_3 (g) + * $\rightarrow NH_3$ *	A ₁ = 4.7e9 s ⁻¹ ; E ₁ = 0 kJ/mol
2	$NH_3^* \rightarrow NH_3 (g) + *$	$A_2 = 4.9e17 \text{ mol/m}^3/\text{s}; E_2 = 114.4$
		kJ/mol; α_2 = 65.2 kJ/mol
3	$NH_3^* + NO (g) + 0.25 O_2 (g) \rightarrow N_2 (g) + 1.5 H_2O (g)$	$k_3(T_{ref,3}) = 16.3 s^{-1}; E_3 = 79.8 kJ/mol;$
		T _{ref,3} = 473.15 K
4	$NH_3^* + 0.75 O_2 (g) \rightarrow 0.5 N_2 (g) + 1.5 H_2O (g)$	k4(T _{ref,4}) = 33.9 s ⁻¹ ; E4 = 196.8 kJ/mol;
		T _{ref,4} = 773.15 K
5	HCN (g) + 1.25 O ₂ (g) \rightarrow 0.5 H ₂ O (g) + CO ₂ (g) + 0.5 N ₂ (g)	A ₅ = 3.2e5 s ⁻¹ ; E ₅ = 69.9 kJ/mol
6	HCHO (g) + 0.5 O ₂ (g) \rightarrow CO (g) + H ₂ O(g)	A ₆ = 2.3e3 s ⁻¹ ; E ₆ = 21.9 kJ/mol
7	HCN (g) + H ₂ O (g) \rightarrow NH ₃ * + CO (g)	A ₇ = 6.1e10 s ⁻¹ ; E ₇ = 93 kJ/mol; K ₀ =
		1.5e-10 m³/mol; ΔH = -98.8 kJ/mol
8	HCHO (g) + NH ₃ * + 0.5 O ₂ (g) \rightarrow HCN (g) + 2 H ₂ O (g)	A ₈ = 1.7e10 s ⁻¹ ; E ₈ = 72.9 kJ/mol

The kinetic model was used to simulate the combined HCHO/SCR reactions in the loop reactor setup with various inlet fractions of NH_3 , NO_x and HCHO and provides good prediction of the experimental results, particularly with respect to the HCN and CO formation (Fig. 1). Additionally, the model was transferred to 1D to determine an optimal GHSV of 6700 h⁻¹ for a maximal HCN emission of 0.9 ppm.



Figure 1. Experimental and simulated data of the combined HCHO/SCR reaction in the loop reactor. Conditions: $y_0(HCHO) = 200 \text{ ppm}$; $y_0(NO_x) = 500 \text{ ppm}$; $y_0(NH_3) = 600 \text{ ppm}$; $y_0(O_2) = 5\%$; $y_0(H_2O) = 5\%$; N_2 balance; F = 0.6 L/min (STP); GHSV = 7000 h⁻¹ (STP); $\phi = 83$.

References

- 1. J. R. Kittrell, Advances in Chemical Engineering, 1970, 8, 97-183.
- 2. D. Chiche, J.-M. Schweitzer, Appl. Catal. B: Environ., 2017, 205, 189–200.

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