

Effects of Biofuel Blends on Performance of Exhaust Gas Catalyst: Ethanol and Acetaldehyde Reactions

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Jan Stepanek, Petr Koci and Milos Marek
Institute of Chemical Technology, Prague

Teuvo Maunula and Toni Kinnunen
Ecocat Oy

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ABSTRACT

The use of biofuels in internal combustion engines changes the composition of the engine exhaust gas. When burning a biofuel blend, significant amounts of oxygenated hydrocarbons such as alcohols, ethers and aldehydes are present in the exhaust gas. It is known, that these compounds influence catalytic processes in exhaust gas converters. In this work we propose a global kinetic model for ethanol and acetaldehyde oxidation on commonly used Pt, PtPd and Pd-based catalytic oxidation converters of automobile exhaust gases. The mechanism is based on two steps: (i) partial oxidation of ethanol to acetaldehyde, and (ii) complete oxidation of acetaldehyde to CO₂ and H₂O. Kinetic parameters of ethanol and acetaldehyde reactions are evaluated on the basis of laboratory light-off experiments with several catalytic monolith samples (noble metal loading 9-140 g/cft; Pt, Pd, and PtPd; at space velocity 30 000-240 000 h⁻¹).

Net formation of acetaldehyde from ethanol is observed around the light-off temperature. The Pd-based catalysts exhibit slightly higher selectivity to acetaldehyde. At higher temperatures both ethanol and acetaldehyde are almost fully oxidized, however, internal diffusion effects in 50 µm washcoat layer significantly affect the selectivity of ethanol oxidation and acetaldehyde conversions. The calibrated model is then used for simulation of the NEDC (New European Driving Cycle) test driving cycle for different converter configurations (monolith size, noble metal loading). With very low noble metal activity (low loading or aged catalyst) the acetaldehyde conversion is negative, i.e., more acetaldehyde is produced in the converter by partial oxidation of ethanol. For medium to higher activity of noble metals the

net effect of the catalyst is positive - acetaldehyde is oxidized to CO₂ and H₂O.

INTRODUCTION

Nowadays, an increasing part of common automobile fossil fuels is being replaced with substances of biological origin [1]. One of the frequently used biological fuel compounds is ethanol. However, ethanol and other biofuel compounds influence the exhaust gas composition, as illustrated by Labeckas [2]. The use of ethanol-blended fuel in gasoline engines reduced the raw emission levels of CO by about 18 %, non-methane organic gases level by about 27 % and NO_x concentration level by up to 54 %, but production of significant acetaldehyde amounts has been experimentally observed [3,4]. It has been also observed, that in the presence of Rh-containing catalysts, the C-C bond in ethanol was broken and observable amounts of CO were formed [5]. However, using biological fuel for diesel engines increased the NO_x emission level by about 10 % [6]. Furthermore, diesel fuels containing ethanol reduced particulate emissions [7].

In this work we propose a global kinetic model for Pt, PtPd and Pd based oxidation catalysts operated with ethanol-fossil fuel blends under lean conditions. Precious metals (Pt, Rh, Pd) are considered to be very effective in ethanol oxidation [8]. Oxidation of ethanol and acetaldehyde is studied separately and in the mixtures with other hydrocarbons commonly present in the diesel exhaust gas.

CATALYST SAMPLES AND EXPERIMENTAL SETUP

The catalyst samples were prepared by pre-coating metal monolith substrates (foil thickness 50 μm , cell density 400 cpsi) with washcoat based on aluminium oxide, zeolites and metal oxides (mean washcoat layer thickness 50 μm). Pt and/or Pd were added as active metals into the catalysts by conventional impregnation methods. The noble metal loading was varied in the range of 9-137 g/cft (0.3-4.8 g/dm³) for platinum, 10-140 g/cft (0.3-4.9 g/dm³) for platinum-palladium (4:1) and 70-80 g/cft (2.5-2.8 g/dm³) for palladium catalyst. After the calcination at 550 °C, the catalyst samples were hydrothermally aged using 10 % water in air at 700 °C for 20 hours, space velocity SV=4 000 h⁻¹. The purpose was to study the catalytic activity and kinetic parameters in a stable state, correlating roughly to the conditions after mean driving distances. In earlier engine, field and lab tests it was observed that this hydrothermal ageing correlates roughly to the usual state of DOC after 30 000-100 000 km on road (depending on actual application and configuration of the exhaust gas aftertreatment line).

Laboratory light-off experiments (temperature ramp 10 K/min) were used to evaluate the effects of catalyst formulation (precious group metal type and loading), exhaust gas composition and space velocity (SV) on the conversions in gas mixtures simulating exhaust gases from diesel, diesel-ethanol and ethanol fuelled engines [9]. Gas hourly space velocity was varied from 30 000 to 240 000 h⁻¹. The propene, toluene, decane and ethanol adsorption capacities were measured at 110 °C by step exchange method, where an N₂ flow was changed to an HC/N₂ flow using the same sample size and reactor as in the light-off experiments. Prior to the adsorption, the catalyst has been oxidized at 400 °C to remove adsorbed hydrocarbons and moisture.

Laboratory size catalyst samples (diameter 14 mm, length 74.5 mm) were tested in a steel reactor, where reactants were fed by mass flow controllers (O₂, N₂, CO, CO₂, C₃H₆, NO) or through an evaporator (toluene, decane, water, ethanol, acetaldehyde). The inlet/outlet composition was analyzed by a combination of specific analyzers (IR for CO and CO₂, chemiluminescence for NO_x/NO, and FID for total hydrocarbons, paramagnetic analyzer for oxygen). In addition, the hydrocarbons, ethanol, acetaldehyde and nitrogen oxides were detected separately with an FTIR analyzer (Gaset) connected with a heated line (180 °C).

After evaluation of reaction rate parameters from the above-mentioned experiments, laboratory NEDC simulation was performed to validate the model and to see the effect of transient conditions on oxidation catalyst performance. The NEDC cycle duration is about 1200 seconds, where the first

800 seconds simulate city traffic driving and the end of the cycle simulates highway driving. Temperatures and concentrations of gaseous reactants were varied with fast IR furnace and mass flow meters as a function of time in 80 input steps covering the NEDC conditions according to a light-duty diesel engine.

The transient exhaust conditions were generated in a quartz reactor containing monolith sample with the diameter 14 mm and the length 50 mm. The flow rate was fixed (8350 ml/min, SV 65 000 h⁻¹) during an experiment to avoid the changes in temperature gradients and sampling conditions. The mean feed concentrations in the simulated NEDC were 700 ppm CO, 160 ppm NO, 130 ppm ethanol, 13 % O₂, 5.5 % CO₂, 8 % H₂O, and balance nitrogen. Ethanol inlet concentration was fixed because it was fed by a slow-response evaporator. The outlet gas composition was analyzed by a fast FTIR analyzer (Gaset). More details on the experiments can be found in [9].

MATHEMATICAL MODEL

The simulations of catalytic monolith converter were performed with spatially 2D(1D+1D) model, that extends the standard heterogeneous 1D model by explicit solution of internal diffusion in the catalytic washcoat layer [10,11,12]. The internal diffusion influences catalyst operation namely above the light-off temperature and for higher space velocity. As we will demonstrate in section Results, consideration of the internal diffusion in the studied 50 μm washcoat was necessary to describe correctly the ethanol/acetaldehyde oxidation selectivity.

Both 1D and 2D(1D+1D) models consist of the following balances: mass balances of individual components in the flowing gas (1), (9), in the washcoat pores (2), (10) and on the catalyst surface (3), (11), enthalpy balance of the flowing gas (4), (12) and the enthalpy balance of the solid phase (5), (13).

Equations for the spatially 1D heterogeneous model:

$$\frac{\partial c_k(z, t)}{\partial t} = \frac{-\partial(v \cdot c_k)}{\partial z} + \frac{k_c a}{\varepsilon^g} \cdot c \cdot (y_k^s - y_k), \quad k = 1, \dots, K \quad (1)$$

$$\frac{\partial c_k^s(z, t)}{\partial t} = \frac{k_c a}{\varepsilon^s} (1 - \varepsilon^g) \varphi^s \cdot c \cdot (y_k - y_k^s) + \frac{1}{\varepsilon^s} \sum_{j=1}^J \nu_{k,j} R_j, \quad k = 1, \dots, K \quad (2)$$

$$\frac{\partial \psi_m(z, t)}{\partial t} = \frac{1}{\Psi_m^{\text{cap}}} \sum_{j=1}^J \nu_{m,j}^{\psi} R_j, \quad m = 1, \dots, M \quad (3)$$

$$\rho^g c_p^g \frac{\partial T(z, t)}{\partial t} = -v \frac{\partial T}{\partial z} \rho^g c_p^g + \frac{k_h a}{\varepsilon^g} (T^s - T) \quad (4)$$

$$\rho^s c_p^s \frac{\partial T^s(z, t)}{\partial t} = \lambda^s \frac{\partial^2 T^s}{\partial z^2} + \frac{k_h a}{1 - \varepsilon^g} (T - T^s) - \varphi^s \sum_{j=1}^J \Delta H_{r,j} R_j \quad (5)$$

Boundary conditions for the 1D model:

$$z = 0 : T = T^{\text{in}} \quad (6)$$

$$z = 0 : c_k = c_k^{\text{in}}, k = 1, \dots, K \quad (7)$$

$$z = 0 \wedge z = l : \frac{\partial T^s}{\partial z} = 0 \quad (8)$$

Equations for the spatially 2D(1D+1D) model:

$$\frac{\partial c_k(z, t)}{\partial t} = \frac{-\partial(v \cdot c_k)}{\partial z} + \frac{k_c a}{\varepsilon^g} \cdot c \cdot (y_k^s|_{r=\delta} - y_k), \quad k = 1, \dots, K \quad (9)$$

$$\frac{\partial c_k^s(z, r, t)}{\partial t} = \frac{D_k^{\text{eff}}}{\varepsilon^s} \frac{\partial^2 c_k^s}{\partial r^2} + \frac{1}{\varepsilon^s} \sum_{j=1}^J \nu_{k,j} R_j, \quad k = 1, \dots, K \quad (10)$$

$$\frac{\partial \psi_m(z, r, t)}{\partial t} = \frac{1}{\Psi_m^{\text{cap}}} \sum_{j=1}^J \nu_{m,j}^{\psi} R_j, m = 1, \dots, M \quad (11)$$

$$\rho^g c_p^g \frac{\partial T(z, t)}{\partial t} = -v \frac{\partial T}{\partial z} \rho^g c_p^g + \frac{k_h a}{\varepsilon^g} (T - T^s) \quad (12)$$

$$\rho^s c_p^s \frac{\partial T^s(z, t)}{\partial t} = \lambda^s \frac{\partial^2 T^s}{\partial z^2} + \frac{k_h a}{1 - \varepsilon^g} (T^s - T) - \frac{a}{1 - \varepsilon^g} \sum_{j=1}^J \int_{r=0}^{\delta} \Delta H_{r,j} R_j dr \quad (13)$$

Boundary conditions for the 2D(1D+1D) model:

$$z = 0 : T = T^{\text{in}} \quad (14)$$

$$z = 0 : c_k = c_k^{\text{in}}, k = 1, \dots, K \quad (15)$$

$$z = 0 \wedge z = l : \frac{\partial T^s}{\partial z} = 0 \quad (16)$$

$$r = \delta : D_k^{\text{eff}} \frac{\partial c_k^s}{\partial r} = k_c (c_k - c_k^s), k = 1, \dots, K \quad (17)$$

$$r = \delta : \frac{\partial c_k^s}{\partial r} = 0, k = 1, \dots, K \quad (18)$$

Cf. Definitions/Abbreviations for the explanation of the symbols. The values of spatially distributed mass and heat transfer coefficients along the monolith channel ($k_c(z)$ and $k_h(z)$, respectively) are calculated from the correlations proposed by Ramanathan [13].

The sets of partial differential equations were solved by semi-implicit finite differences method, with equidistant spatial discretization, quasi-linearization of reaction rates R_j , and adaptive time-step control. Analytical expressions for the derivatives of reaction rates have been used to further decrease the computational demands. If not explicitly specified, all the simulations have been calculated using the more detailed spatially 2D(1D+1D) model.

Table 1 shows the considered DOC reactions and global rate laws R_j . The rate, inhibition, and selectivity coefficients (k_j , K_j^{inh} and K_j^{sel} , respectively) are calculated in dependence on temperature from the following equations:

$$k_j = k_{0,j} \cdot e^{\frac{-E_{a,j}}{R \cdot T^s}} \quad (19)$$

$$K_j^{\text{inh}} = K_{0,j}^{\text{inh}} \cdot e^{\frac{E_j^{\text{inh}}}{T^s}} \quad (20)$$

$$K_j^{\text{sel}} = K_{0,j}^{\text{sel}} \cdot e^{\frac{E_j^{\text{sel}}}{T^s}} \quad (21)$$

The original DOC model developed earlier [12] involved CO oxidation, HC (propene, decane and toluene) adsorption & oxidation, and HC-SCR of nitrogen oxides (reactions 1-12 in Table 1). In this work we extend the model by the studied

Table 1. DOC model reactions and respective reaction rates. The reactions 1-12 are taken after [12], the ethanol and acetaldehyde reactions 13-16 are newly considered.

No.	Reaction/adsorption/desorption step	Rate law
1	$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	$R_1 = A_{\text{NM}} k_1 y_{\text{CO}} y_{\text{O}_2} \frac{1}{G_1}$
2	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$R_2 = A_{\text{NM}} k_2 y_{\text{H}_2} y_{\text{O}_2} \frac{1}{G_1}$
3	$\text{C}_3\text{H}_6 + \frac{9}{2} \text{O}_2 \rightarrow 3 \text{CO}_2 + 3 \text{H}_2\text{O}$	$R_3 = k_3 y_{\text{C}_3\text{H}_6} y_{\text{O}_2} \frac{1}{G_1}$
4	$\text{C}_{10}\text{H}_{22} + \frac{31}{2} \text{O}_2 \rightarrow 10 \text{CO}_2 + 11 \text{H}_2\text{O}$	$R_4 = A_{\text{NM}} k_4 y_{\text{C}_{10}\text{H}_{22}} y_{\text{O}_2} \cdot \frac{1}{(1+K_{4,\text{C}_{10}\text{H}_{22}}^{\text{inh}} y_{\text{C}_{10}\text{H}_{22}})} \cdot \frac{1}{(1+K_{4,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
5	$\text{C}_6\text{H}_5\text{CH}_3 + 9 \text{O}_2 \rightarrow 7 \text{CO}_2 + 4 \text{H}_2\text{O}$	$R_5 = A_{\text{NM}} k_5 y_{\text{C}_6\text{H}_5\text{CH}_3} y_{\text{O}_2} \cdot \frac{1}{(1+K_{5,\text{C}_6\text{H}_5\text{CH}_3}^{\text{inh}} y_{\text{C}_6\text{H}_5\text{CH}_3})} \cdot \frac{1}{(1+K_{5,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
6	$\text{C}_3\text{H}_6 + 2 \text{NO} + \frac{7}{2} \text{O}_2 \rightarrow \text{N}_2 + 3 \text{CO}_2 + 3 \text{H}_2\text{O}$	$R_6 = R_3 K_{6,\text{NO}}^{\text{sel}} y_{\text{NO}} \cdot \frac{1}{(1+K_{6,\text{O}_2}^{\text{inh}} y_{\text{O}_2})(1+K_{6,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
7	$\text{C}_{10}\text{H}_{22} + 2 \text{NO} + \frac{19}{2} \text{O}_2 \rightarrow \text{N}_2 + 10 \text{CO}_2 + 11 \text{H}_2\text{O}$	$R_7 = R_4 K_{7,\text{NO}}^{\text{sel}} y_{\text{NO}} \cdot \frac{1}{(1+K_{7,\text{O}_2}^{\text{inh}} y_{\text{O}_2})(1+K_{7,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
8	$\text{C}_6\text{H}_5\text{CH}_3 + 2 \text{NO} + 8 \text{O}_2 \rightarrow \text{N}_2 + 7 \text{CO}_2 + 4 \text{H}_2\text{O}$	$R_8 = R_5 K_{8,\text{NO}}^{\text{sel}} y_{\text{NO}} \cdot \frac{1}{(1+K_{8,\text{O}_2}^{\text{inh}} y_{\text{O}_2})(1+K_{8,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
9	$\text{NO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}_2$	$R_9 = A_{\text{NM}} k_9 \left(y_{\text{NO}} y_{\text{O}_2}^{0.5} - \frac{y_{\text{NO}_2}}{K_{9,\text{eq}}} \right) \frac{1}{G_2}$
10	$\text{C}_{10}\text{H}_{22} + \text{Zeol} \rightleftharpoons \text{C}_{10}\text{H}_{22} \cdot \text{Zeol}$	$R_{10} = \Psi_{\text{cap},\text{C}_{10}\text{H}_{22}} \cdot \left(k_{10}^{\text{ads}} y_{\text{C}_{10}\text{H}_{22}} (1 - \psi_{\text{C}_{10}\text{H}_{22}}) - k_{10}^{\text{des}} \psi_{\text{C}_{10}\text{H}_{22}} \right)$
11	$\text{C}_6\text{H}_5\text{CH}_3 + \text{Zeol} \rightleftharpoons \text{C}_6\text{H}_5\text{CH}_3 \cdot \text{Zeol}$	$R_{11} = \Psi_{\text{cap},\text{C}_6\text{H}_5\text{CH}_3} \cdot \left(k_{11}^{\text{ads}} y_{\text{C}_6\text{H}_5\text{CH}_3} (1 - \psi_{\text{C}_6\text{H}_5\text{CH}_3}) - k_{11}^{\text{des}} \psi_{\text{C}_6\text{H}_5\text{CH}_3} \right)$
12	$\text{NO}_2 + \frac{1}{2} \text{O}_2 + \text{Alu} \rightleftharpoons \text{NO}_3 \cdot \text{Alu}$	$R_{12} = \Psi_{\text{cap},\text{NO}_x} \left(k_{12}^{\text{ads}} y_{\text{NO}_2} \cdot (1 - \psi_{\text{NO}_2}) - k_{12}^{\text{des}} \psi_{\text{NO}_2} \right)$
13	$\text{C}_2\text{H}_5\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$	$R_{13} = A_{\text{NM}} k_{13} y_{\text{C}_2\text{H}_5\text{OH}} y_{\text{O}_2} \cdot \frac{1}{(1+K_{13,\text{C}_2\text{H}_5\text{OH}}^{\text{inh}} y_{\text{C}_2\text{H}_5\text{OH}})} \cdot \frac{1}{(1+K_{13,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
14	$2\text{NO} + \text{C}_2\text{H}_5\text{OH} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$	$R_{14} = R_{13} \cdot K_{14,\text{NO}}^{\text{sel}} y_{\text{NO}} \cdot \frac{1}{(1+K_{14,\text{O}_2}^{\text{inh}} y_{\text{O}_2})(1+K_{14,\text{NO}}^{\text{inh}} y_{\text{NO}})}$
15	$\text{C}_2\text{H}_5\text{OH} + \text{Zeol} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} \cdot \text{Zeol}$	$R_{15} = \Psi_{\text{cap},\text{C}_2\text{H}_5\text{OH}} \cdot \left(k_{15}^{\text{ads}} y_{\text{C}_2\text{H}_5\text{OH}} (1 - \psi_{\text{C}_2\text{H}_5\text{OH}}) - k_{15}^{\text{des}} \psi_{\text{C}_2\text{H}_5\text{OH}} \right)$
16	$\text{CH}_3\text{CHO} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$	$R_{16} = A_{\text{NM}} k_{16} y_{\text{CH}_3\text{CHO}} y_{\text{O}_2} \cdot \frac{1}{(1+K_{16,\text{CH}_3\text{CHO}}^{\text{inh}} y_{\text{CH}_3\text{CHO}})} \cdot \frac{1}{(1+K_{13,\text{NO}}^{\text{inh}} y_{\text{NO}})}$

Table 2. Physical parameters of the examined monolith catalysts.

Wall thickness	δ^{wall}	50 μm
Mean washcoat thickness	δ^{washcoat}	51 μm
Equivalent inner channel diameter	d_h	0.99 mm (400 cpsi) ^a / 1.18 mm (300 cpsi) ^b
Total washcoat porosity	ε^s	0.7
Fraction of open frontal area in monolith	ε^g	0.741 (400 cpsi) ^a / 0.770 (300 cpsi) ^b
Effective density of the solid ^c	ρ^s	3183 $\text{kg} \cdot \text{m}^{-3}$
Effective heat capacity of the solid ^c	c_p^s	788 $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
Specific surface area	a	3490 $\text{m}^2 \cdot \text{m}^{-3}$ (400 cpsi) ^a / 2980 $\text{m}^2 \cdot \text{m}^{-3}$ (300 cpsi) ^b

^a Pt-only monolith ^b Pd-containing monoliths ^c solid = washcoat + substrate

ethanol and acetaldehyde oxidation reactions, namely: ethanol partial oxidation (i.e. acetaldehyde formation; reaction 13 in Table 1), selective catalytic reduction of NO_x by ethanol (reaction 14 in Table 1), ethanol adsorption/desorption (reaction 15 in Table 1), and acetaldehyde oxidation (reaction 16 in Table 1). Physical parameters of the examined catalytic monolith samples are summarized in Table 2.

<tables 1, 2 here>

RESULTS

At first, kinetic parameters of ethanol and acetaldehyde reactions had to be evaluated from lab experiments. Simplex optimization method was used to minimize the weighted sum of squares of differences between simulation and experimental results.

Measured light-off curves were used for this purpose. Each simulation and experiment was realized as a 10 K/min temperature ramp, examining the light-off behavior of ethanol and/or acetaldehyde in dependence on catalyst noble metal loading and space velocity.

Table 4. Kinetic parameters of the ethanol and acetaldehyde oxidation reactions, depending on the used noble metal. Reaction numbers refer to Table 1.

Catalyst type	Reaction No. (<i>j</i>)	pre-exponential factor	exponential factor
Pt	13	$k_{0,13} = 4 \times 10^{17}$	$E_{a,13} = 55 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$
	16	$k_{0,16} = 2 \times 10^{16}$	$E_{a,16} = 45 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$
PtPd	13	$k_{0,13} = 1 \times 10^{18}$	$E_{a,13} = 55 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$
	16	$k_{0,16} = 2 \times 10^{16}$	$E_{a,16} = 45 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$
Pd	13	$k_{0,13} = 4 \times 10^{18}$	$E_{a,13} = 55 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$
	16	$k_{0,16} = 8 \times 10^{16}$	$E_{a,16} = 45 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$

Table 5. Kinetic parameters common for Pt, PtPd and Pd catalysts: Ethanol adsorption, desorption, and inhibition constants. Reaction numbers refer to Table 1.

Catalyst type	Reaction No. (<i>j</i>)	Pre-exponential factor	Exponential factor
Pt, PtPd, Pd	14	$K_{0,14}^{\text{sel}} = 1000$	$E_{14}^{\text{sel}} = 0 \text{ K}$
	15	$k_{0,15}^{\text{ads}} = 5$	$E_{a,15}^{\text{ads}} = 0 \text{ J} \cdot \text{mol}^{-1}$
	15	$K_{0,15}^{\text{des}} = 5000$	$E_{15}^{\text{des}} = -33\,260 \text{ J} \cdot \text{mol}^{-1}$
	13, 14	$K_{0,\text{C}_2\text{H}_5\text{OH}}^{\text{inh}} = 4.3 \times 10^7$	$E_{\text{C}_2\text{H}_5\text{OH}}^{\text{inh}} = 1000 \text{ K}$
	13, 14, 16	$K_{0,\text{NO}}^{\text{inh}} = 9 \times 10^4$	$E_{\text{NO}}^{\text{inh}} = 600 \text{ K}$
	14	$K_{0,\text{O}_2}^{\text{inh}} = 1 \times 10^{12}$	$E_{\text{O}_2}^{\text{inh}} = -13.2 \text{ K}$
	14	$K_{0,\text{NO}}^{\text{inh}} = 1 \times 10^4$	$E_{\text{NO}}^{\text{inh}} = 50 \times 10^3 \text{ K}$
	16	$K_{0,\text{CH}_3\text{CHO}}^{\text{inh}} = 8 \times 10^7$	$E_{\text{CH}_3\text{CHO}}^{\text{inh}} = 1000 \times 10^3 \text{ K}$

Table 3. Compositions of inlet gas mixtures.

Compound	"Acetaldehyde" mixture	"Ethanol" mixture	"Diesel" mixture	"Diesel-Ethanol" mixture
CO	1500 ppm	1500 ppm	1500 ppm	1500 ppm
O ₂	14 %	14 %	14 %	14 %
H ₂ O	6 %	6 %	6 %	6 %
CO ₂	6 %	6 %	6 %	6 %
NO	200 ppm	200 ppm	200 ppm	200 ppm
C ₂ H ₅ OH	-	248 ppm	-	124 ppm
CH ₃ CHO	248 ppm	-	-	-
C ₃ H ₆	-	-	80 ppm	80 ppm
C ₁₀ H ₂₂	-	-	15 ppm	15 ppm
Toluene	-	-	15 ppm	15 ppm

The tested noble metal loadings were 9, 42, 71 and 137 g/cft (Pt), 70 and 80 g/cft (Pd), and 10, 30, 50, 70 and 140 g/cft (PtPd 4:1). The effects of inlet gas composition were also examined - cf. Table 3.

The ethanol and acetaldehyde kinetic parameters evaluated from experimental data are summarized in Tables 4 and 5. Parameters that proved to be catalyst-type specific (ethanol and acetaldehyde oxidation rate constants) are listed in Table 4. The other parameters (such as ethanol adsorption, desorption and some inhibition constants) were found to be catalyst-type independent and are given in Table 5.

The net acetaldehyde production is determined by the ratio between reactions R_{13} (ethanol partial oxidation) and R_{16} (acetaldehyde total oxidation), cf. Table 1. It can be seen in Table 4 that the Pd-containing catalyst exhibits higher ethanol oxidation rates, but the acetaldehyde oxidation is not

accelerated proportionally. This results in higher selectivity of ethanol oxidation to acetaldehyde.

<tables 4, 5 here>

Note that the reaction rates are related to the catalytic washcoat volume. The rate laws include a factor of noble metals activity A_{NM} that is directly proportional to the concentration of active catalytic sites in the washcoat, i.e. to the product of noble metal concentration c_{NM} and dispersion. The noble metal concentration in the washcoat c_{NM} (mol/m³ washcoat) can be calculated from the commonly used parameter - noble metal loading (L_{NM} , g/m³ monolith; 1 m³ = 35.3147 cft):

$$c_{\text{NM}} = \frac{L_{\text{NM}}}{M_{\text{NM}} \cdot \varepsilon^g \cdot \varphi^s} \quad (22)$$

Here ε^g denotes fraction of open frontal area (i.e., monolith macro-porosity), M_{NM} is molar weight of actually impregnated noble metal, and φ^s is volumetric fraction of washcoat layer in solid phase (solid phase = washcoat + inert substrate).

The equation (22) can be understood as a recalculation of the overall noble metal loading expressed in NM mass per entire monolith volume (including void space and inert substrate) to actual moles of active sites per active washcoat layer itself. This is essential for correct interpretation of various catalyst