Supplementary Materials

Highly Efficient RGO-Supported Pd Catalyst for Low Temperature Hydrocarbon Oxidation

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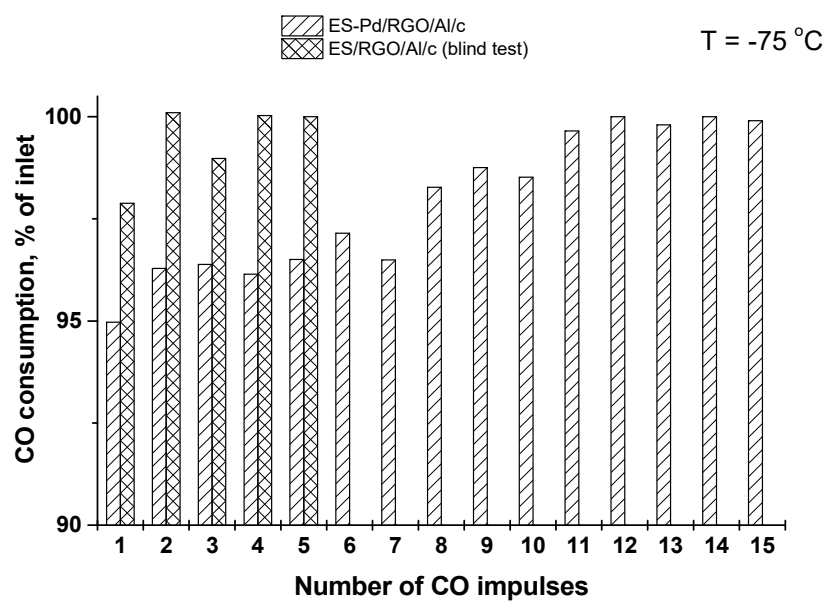* Correspondence: didka@svr.igic.bas.bg

Supplementary Data

Figure S1. CO chemisorption on ES-Pd/RGO/Al/c.

In this supplementary material, an example of the stages of the derivation of the mechanistic models applied in the article for the adsorption of reagents on different types of active centers is presented. Based on the Langmuir isotherm, the reaction rate equation was derived. Adsorption occurs when molecules with a sufficiently high kinetic energy strike free active sites or unoccupied parts of the surface. A process is described as a reaction between a gas-phase molecule and an unoccupied site, s. (A + S → AS). The frequency of collisions is proportional to the partial pressure of the gas, and the probability of adsorption is taken into account in the rate constant k1A. The number of occupied sites is θ, and the number of vacant sites is 1-θ. The total number of sites available for adsorption is included in the rate constant k1A. On this basis, the following equations for adsorption and desorption rates are derived:

$$r_{VOC,ads} = k_{1VOC}P_{VOC}\left(1-\theta_{VOC}\right); \quad r_{VOC,des} = k_{2VOC}\theta_{VOC} \tag{S1}$$

The rates of adsorption and desorption depend exponentially on the temperature (the difference E$_{ads}$ – E$_{des}$ is the heat of adsorption ΔH):

$$k_{1VOC} = ae^{-E_{ads}/RT}; \quad k_{2VOC} = be^{-E_{des}/RT} \tag{S2}$$

The rates of adsorption and desorption are equal in equilibrium conditions:

$$k_{1VOC}P_{VOC}\left(1-\theta_{VOC}\right) = k_{2VOC}\theta_{VOC} \quad\Longrightarrow\quad \theta_{VOC} = \frac{k_{1VOC}P_{VOC}}{k_{2VOC}+k_{1VOC}P_{VOC}} \tag{S3}$$

$$K_{VOC} = \frac{k_{1VOC}}{k_{2VOC}}$$

Substituting for the expression for the fraction of occupied sites (with VOC) is obtained:

$$\theta_{VOC} = \frac{K_{VOC}P_{VOC}}{1+K_{VOC}P_{VOC}} \tag{S4}$$

By extending further to the adsorption of two reactants (VOC and O₂) on the same type of active sites [VOC + S → (VOC)S; O₂ + S → (O₂) S] the following expressions for the fractions of sites occupied by VOC and O₂ can be derived:

$$r_{VOC,ads} = k_{1VOC}P_{VOC}\left(1-\theta\right) = k_{1VOC}P_{VOC}\left(1-\theta_{VOC}-\theta_{Ox}\right); \quad r_{VOC,des} = k_{2VOC}\theta_{VOC} \tag{S5}$$

$$r_{Ox,ads} = k_{1Ox}P_{Ox}\left(1-\theta\right) = k_{1Ox}P_{Ox}\left(1-\theta_{VOC}-\theta_{Ox}\right); \quad r_{Ox,des} = k_{2Ox}\theta_{Ox} \tag{S6}$$

$$\theta_{VOC} = \frac{K_{VOC}P_{VOC}}{1+K_{VOC}P_{VOC}+K_{Ox}P_{Ox}}; \quad \theta_B = \frac{K_{Ox}P_{Ox}}{1+K_{VOC}P_{VOC}+K_{Ox}P_{Ox}} \tag{S7}$$

In the case of bimolecular reaction with adsorption on different sites [VOC + S1 → (VOC)S1; O₂ + S2 → (O₂)S2 ; (VOC)S1 + (O₂)S2 → C] the equation is as follows:

$$r = k\theta_{VOC}\theta_{Ox} = k\frac{K_{VOC}P_{VOC}}{1+K_{VOC}P_{VOC}}\frac{K_{Ox}P_{Ox}}{1+K_{Ox}P_{Ox}} \tag{S8}$$

where k is the reaction rate constant.

In the present study, the equation for the adsorption of reactants on different types of active sites (S8) was applied. Taking into account the reactor design equations, it is more convenient the use of concentrations of the reagents, instead the partial pressures. Thus, the rate equation, takes the form given in Table 6:

$$r = \frac{kK_{voc}C_{voc}K_{ox}C_{ox}}{(1+K_{voc}C_{voc}+K_{water\text{-}voc}C_{water})(1+K_{ox}C_{ox}+K_{water\text{-}ox}C_{water})}$$

The steps followed for the final equation in the case of use of Mars–Van Krevelen [1] mechanistic model are given below.

The catalytic oxidation can proceed according to:

$$\text{reduced catalyst (Pd)} + O_2 \xrightarrow{r_{ox}} \text{oxidized catalyst (PdO)} \tag{S9}$$

$$C_6H_5CH_3 + \text{oxidized catalyst (PdO)} \xrightarrow{r_{red}} \text{reduced catalyst (Pd)} + CO_2, \text{ads} + H_2O\text{ads} \tag{S10}$$

$$CO_2, \text{ads} + H_2O\text{ads} \xrightarrow{r_{des}} CO_2, \text{gas} + H_2O\text{gas} \tag{S11}$$

The effect of water vapor (coming from the reaction or/plus added to the gas feed) is included, by taking into account its competition with the oxidized sites as follows:

$$r_{red} = k_{red}P_{voc}\theta_{ox} \tag{S12}$$

$$\theta_{red} = 1 - \theta_{ox} - \theta_{w,ox} \tag{S13}$$

$$r_{ox} = k_{ox}P_{ox}\theta_{red} = k_{ox}P_{ox}(1-\theta_{ox}-\theta_{w,ox}) \tag{S14}$$

$$\gamma = r_{ox}/r_{red} \; ; \; r_{red} = r_{ox}/\gamma \tag{S15}$$

where k_{red} and k_{ox} are the rate constants for the reactions of reduction and oxidation of the catalyst, P_{voc} and are the partial pressures of the toluene and oxygen. The stoichiometric coefficient γ shows the number of oxygen molecules needed for the complete oxidation of one molecule of toluene.

Taking into account that $\gamma = r_{ox}/r_{red}$ at the steady state:

$$k_{ox}P_{ox}(1-\theta_{ox}-\theta_w) = \gamma k_{red}P_{voc}\theta_{ox} \tag{S16}$$

where θ_{ox} and θ_w are the degrees of surface coverage of oxygen and water molecules. With water in the gas, the adsorption – desorption equilibrium is:

$$k_{ads,ox}P_w\theta_{ox} = k_{des,ox}\theta_{w,ox} \tag{S17}$$

$$\theta_{w,ox} = \left(\frac{k_{ads,ox}}{k_{des,ox}}\right)P_w\theta_{ox} = K_{w,ox}P_w\theta_{ox} \tag{S18}$$

where k_{ads}, k_{des} and $K_{w,ox}$ are the rate constants of adsorption and desorption of water molecules and the equilibrium constant, respectively.

The expression for θ_{water} from (S13) is substituted in (S11) and for θ_{ox} and at equilibrium, it can be written:

$$\theta_{ox} = \frac{k_{ox}P_{ox}}{\gamma k_{red}P_{voc} + k_{ox}P_{ox}(1+K_{w,voc}P_w)} \tag{S19}$$

By substituting θ_{ox} in (S10) the rate equation for the toluene oxidation via Mars–van Krevelen mechanism is:

$$r_{red} = \frac{k_{red}P_{voc}k_{ox}P_{ox}}{\gamma k_{red}P_{voc} + k_{ox}P_{ox}\left(1 + K_{w,voc}P_w\right)}$$

(S20)

Similarly, in the case that water molecules compete for reduced sites on the catalytic surface, the rate equation for the process is derived. The inhibitory effect of water vapor (as a product of the reaction or in the reaction gas mixture) is accounted for by modifying the Mars-Van Krevelen model, resulting in two different equations for the reaction rate, depending on the type of active site of the catalyst (reduced or oxidized). Both models contain an additional term in the denominator accounting for water adsorption. With competitive adsorption between water and toluene on both reduced and oxidized centers and slow desorption of the reaction products, the equation takes the form:

$$r_{red} = \frac{k_{ox}P_{ox}k_{red}P_{voc}}{\gamma k_{red}P_{voc}\left(1 + K_{w,red}P_w\right) + k_{ox}P_{ox}\left(1 + K_{w,ox}P_w\right) + \left(k_{ox}k_{red}/k_{des,prod}\right)P_{voc}P_{ox}}$$

(S21)

Using the concentrations of the reagents at working conditions instead of the partial pressures, the final rate equation is obtained (Table 5):

$$r = \frac{k_{red}k_{ox}C_{voc}C_{ox}}{\gamma k_{red}C_{voc}\left(1 + K_{water-voc}.C_{water-voc}\right) + k_{ox}C_{ox}\left(1 + K_{water-ox}.C_{water-ox}\right) + \left(k_{red}k_{ox}/k_{des}\right)C_{voc}C_{ox}}$$

References:

[1] Mars, P.; van Krevelen, D. W. Oxidations carried out by means of vanadium oxide catalysts. *Special Supplement to Chem. Eng. Sci.* 1954, 3, 41–59. https://doi.org/10.1016/S0009-2509(54)80005-4.