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Combustion of volatile organic compounds on a MnCu catalyst: A kinetic study

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ABSTRACT

Catalytic combustion is a well-developed process to eliminate volatile organic compounds (VOCs). Although there is a continuous effort in formulating new catalytic materials, studies devoted to estimate kinetic parameters suitable for design and optimization of catalytic combustors are scarce. A kinetic study of ethanol combustion on an efficient catalyst identified as Mn_9Cu_1 is reported in this contribution. Ethanol is a typical VOC, which is found, for example, in effluents of printing industries. The study aims to develop reaction rate expressions and estimate kinetic parameters. The presence of only one intermediate, namely acetaldehyde, has been detected in significant amounts. Acetaldehyde turns out to react more slowly than ethanol. Experimental data were satisfactorily fitted employing LHHW type kinetic expressions. The estimated activation energy of ethanol oxidation lies in the range of values reported in the literature for similar catalysts.

1. Introduction

Volatile organic compounds (VOCs) emitted from many industrial processes are an important class of air pollutant. Particularly, printing industries often employ two of these VOCs as solvents, namely ethanol and/or ethyl acetate. Therefore, the emissions to the atmosphere should be first treated to reduce the concentration at levels tolerated by current regulations. Catalytic combustion is one of the processes more frequently used to destroy this type of VOCs [1]. Research efforts in this field are oriented towards the developing of new catalytic materials with low manufacturing cost and capable to show high activity at moderate temperatures. An efficient catalyst of Mn and Cu has been formulated by Morales et al. [2]. However, studies devoted to obtain kinetic parameters, as needed for the purpose of design and optimization of catalytic reactors, are scarce. The objective of this contribution is to present a kinetic study of ethanol combustion on a Mn/Cu catalyst, which was performed with the aim of formulating plausible reaction rate expressions and estimating the corresponding kinetic parameters.

2. Experimental

The catalyst employed, Mn_9Cu_1, was prepared by a co-precipitation method from $Cu(NO_3)_2{\cdot}4H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ aqueous solutions, as described by Morales et al. [2]. The weight ratio between Mn and Cu was 9:1. Further information regarding the preparation and physical characterization of the catalyst can be found in Morales et al. [2] and Pramparo [3].

The experimental runs for the kinetic study were carried out in a quartz tubular fixed bed reactor operated at atmospheric pressure. A milled sample of the catalyst was used (particle size: 500–841 μm), diluted with glass pellets of the same size. The reactor diameter was 10 mm. A thermocouple, housed inside a sheath, was set just at the top of the catalyst sample. The reactor was placed inside an oven to operate at the desired temperature.

The reactive mixture was composed of helium, oxygen and ethanol. The molar fraction of oxygen was kept at 21% to simulate the air concentration. A fixed flow rate was employed: 100 ml/min at 25 °C and 1 atm. Ethanol was the only VOC present in the feed. It was supplied through a system of ethanol-filled columns immersed in thermostatic baths. Ethanol feed concentration ranged from 2360 to 3980 ppm. Samples of the mixture, before and after contacting the catalyst sample, were analyzed by gas chromatography.

Two levels of catalyst mass were used, 100 and 200 mg. The catalyst density was 2750 kg/m^3; therefore, the volumetric GHSV were 82,500 and 165,000 h^{-1}.

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At each set of experimental conditions (total flow rate, ethanol feed concentration and catalyst mass), temperature was increased steadily from 80 to 250 °C, with the purpose of achieving a complete VOCs conversion. At the lowest temperature, conversion of ethanol was negligible.

Exploratory runs performed adding CO_2 and H_2O in the feed (at concentration levels equivalent to those produced for complete ethanol oxidation) confirmed that the final reaction products do not show any effect on the kinetic behaviour of the catalytic reactions.

Further information regarding the experimental system and protocol can be found in [3].

3. System modeling

Overall trends were first analyzed to establish the reaction-path scheme and reaction rate dependence on the reactant concentrations.

Fig. 1 shows the results of two runs on the same catalyst sample using two levels of ethanol concentration in the feed. There is a significant amount of acetaldehyde produced in both runs. Acetaldehyde behaves as the most refractory species to eliminate. The difference in acetaldehyde mole fraction is due to the different ethanol concentration in the feed. Formation of acetaldehyde has been reported in several studies with different kinds of catalysts [4–7]. Although carbon monoxide has also been detected [4], in this study neither acetic acid nor carbon monoxide has been found. These findings suggest that the main reaction path on the tested catalyst can be described as consecutive reactions; ethanol first produces acetaldehyde and this intermediate is finally oxidized to CO_2 and H_2O products.

In order to discard a possible route for the direct oxidation of ethanol to CO_2, as has been reported for certain catalysts [4], the following ratio is also plotted in Fig. 1:

$$\zeta_{CO_2} = \frac{y_{CO_2}}{y_{CO_2}^{max}} \tag{1}$$

where $y_{CO_2}^{max}$ is the maximum CO_2 mole fraction that can be obtained.

It is evident that in both runs ζ_{CO_2} remains at very low values, even for ethanol conversions larger than 50% and it starts increasing approximately when acetaldehyde concentration reaches its maximum value. These results strongly suggest that for the present catalyst the direct oxidization from ethanol to CO_2 is irrelevant. Therefore the following scheme for the oxidation of ethanol can be considered:

$$C_2H_6O + (1/2)O_2 \rightarrow C_2H_4O + H_2O \tag{2}$$

$$C_2H_4O + (5/2)O_2 \rightarrow 2CO_2 + 2H_2O \tag{3}$$

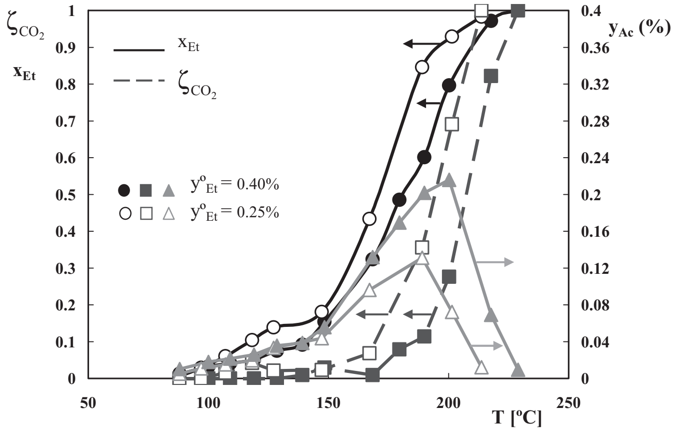

Fig. 1. Variation of ethanol conversion x_{Et}, acetaldehyde mole fraction y_{Ac}, and CO_2 production ratio ζ_{CO_2} (Eq. (1)) with temperature, for two levels of ethanol mole fraction in the feed.

A second aspect that has been inferred from the qualitative analysis is the reaction rate dependency on reactants concentrations. In Fig. 1, the ethanol conversion curve is displaced towards higher temperatures as its feed concentration is increased. In other words, for the same mass of catalyst sample and the same working temperature, the conversion is smaller as the feed concentration is higher. This behaviour cannot be adequately represented by employing a power-law kinetic model with an order one in ethanol. Inhibition terms, either of ethanol or acetaldehyde, or both substances, should be explicitly included to represent this behaviour. Thus, recalling that CO_2 and water showed no kinetic effects, LHHW expressions were proposed for reactions (2) and (3):

$$r_1 = \frac{k_{ref_1} \exp[-(E_1/R)((1/T) - (1/T_{ref}))]C_{Et}}{1 + Kc_{Et}C_{Et} + Kc_{Ac}C_{Ac}} \tag{4}$$

$$r_2 = \frac{k_{ref_2} \exp[-(E_2/R)((1/T) - (1/T_{ref}))]Kc_{Ac}C_{Ac}}{1 + Kc_{Et}C_{Et} + Kc_{Ac}C_{Ac}} \tag{5}$$

where a reference temperature T_{ref} has been introduced to re-parameterize the kinetic coefficient expressions (for regression purposes), and C_{Et} and C_{Ac} are the molar concentrations of ethanol and acetaldehyde inside the catalyst particle.

Expressions (4) and (5) are intended to describe the intrinsic reaction rate, so in order to fit the experimental data, it is necessary to take into account possible inter and intra-particle transport resistances. Employing the criteria suggested in literature [3], it was verified that mass and energy inter-particle gradients were negligible and that the particles behave isothermally. However, the influence of the intra-particle mass transfer resistance could not be disregarded. To this end, the mass conservation balances inside the particles, assuming spherical geometry as well as constant values for the effective diffusion coefficients, were considered:

$$D_{ef,Et}\left[\frac{1}{z^2}\frac{d}{dz}\left(z^2\frac{dC_{Et}}{dz}\right)\right] = r_1 \tag{6a}$$

$$D_{ef,Ac}\left[\frac{1}{z^2}\frac{d}{dz}\left(z^2\frac{dC_{Ac}}{dz}\right)\right] = r_2 - r_1 \tag{6b}$$

where $D_{ef,Et}$ and $D_{ef,Ac}$ are the effective diffusivities of ethanol and acetaldehyde.

Boundary conditions read:

$$z = 0: \quad dC_{Et}/dz = dC_{Ac}/dz = 0 \tag{6c}$$

$$z = R: \quad C_{Et} = C_{Et}^b, \quad C_{Ac} = C_{Ac}^b \tag{6d}$$

The experimental system has been analyzed by Mariani et al. [8] in order to verify if temperature was uniform inside the catalyst bed. The conclusion was that temperature was indeed uniform, except for the experiments with the highest concentration of ethanol in the feed and at the highest operating temperature, for which the temperature reading had to be slightly corrected to obtain a better estimation of the average within the bed.

As regards the variation of composition along the bed, the plug flow hypothesis could be used safely:

$$\frac{q_v dC_{Et}^b}{dm_{cat}} = \frac{-r_{obs,1}}{\rho_{cat}} \tag{7a}$$

$$\frac{q_v dC_{Ac}^b}{dm_{cat}} = \frac{-(r_{obs,2} - r_{obs,1})}{\rho_{cat}} \tag{7b}$$

Initial conditions were

$$m_{cat} = 0: \quad C_{Et}^b = C_{Et}^{b,0}, \quad C_{Ac}^b = 0 \tag{7c}$$

where C_{Et}^b and C_{Ac}^b are the molar concentrations of ethanol and acetaldehyde in the reaction stream, ρ_{cat} is the catalyst density and q_v is the volumetric flow rate.

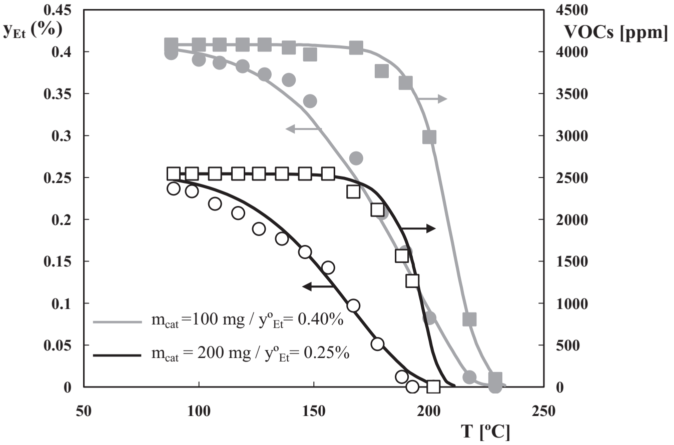

Fig. 2. Comparison between the experimental and model results for two sets of catalyst mass/ethanol mole fraction in the feed.

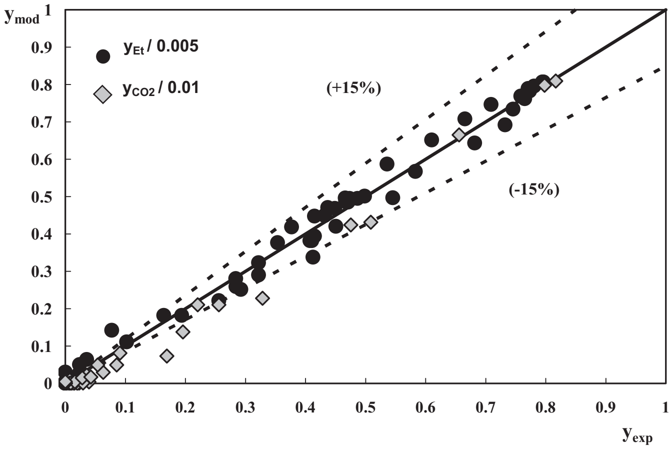

Fig. 3. Parity plot between experimental and model results.

4. Regression of experimental data

To solve the reaction–diffusion equations (Eq. (6)), the algorithm described in [9] was employed. The code DDSAC in the GREGPACK [10], was employed to solve the ODE problem defined by Eq. (7).

The regression analysis was performed using the code GREG in the nonlinear multi-response Bayesian mode [10]. Optimal values of the kinetic parameters were obtained by comparing predicted and experimental mole fractions at the reactor output. The reference temperature used in Eqs. (4) and (5) was $T_{ref} = 448.16$ K. Adsorption constant Kc_j were assumed to be constant in the range of temperature studied.

5. Results and discussion

Table 1 shows the optimum parameter values as well as their confidence intervals. It can be seen that parameters could be tightly adjusted with an uncertainty range less than 20%.

The adsorption equilibrium constant of ethanol could not be properly adjusted due to the very low values arising in the regression analysis. Therefore, $Kc_{Et} = 0$ was adopted.

Fig. 2 shows the variation of ethanol mole fraction with temperature for two sets of catalyst mass/ethanol mole fraction in the feed. A satisfactory agreement between model predictions and experimental data can be appreciated. Experimental and predicted total VOC ppm (ethanol plus acetaldehyde) are also presented in Fig. 2, in which a very well defined plateau can be observed up to high ethanol conversions. This feature can be attributed to the very low combustion rate of acetaldehyde below 190 °C. As temperature raises beyond this level, acetaldehyde conversion increases dramatically due to the high activation energy of reaction (3) (see Table 1).

Along with the regression of experimental data it was verified a strong influence of intraparticle mass transfer. For the highest temperatures (*i.e.* 217–229 °C) the effectiveness factor for ethanol combustion varies between 0.013 and 0.220 along the reactor. This variation is due to the change in acetaldehyde concentration, which appears as an inhibition term in the kinetic expression.

Table 1
Optimal values of kinetic parameters and confidence intervals.

Parameter	Units	Optimal value and confidence interval
k_{ref_1}	s^{-1}	$(1.81 \pm 0.30) \times 10^3$
k_{ref_2}	$mol\ s^{-1}\ m^{-3}$	$(1.81 \pm 0.26) \times 10^{-1}$
E_1	$J\ mol^{-1}$	$(1.10 \pm 0.04) \times 10^5$
E_2	$J\ mol^{-1}$	$(1.69 \pm 0.09) \times 10^5$
Kc_{Ac}	$m^3\ mol^{-1}$	$(6.75 \pm 1.26) \times 10^2$

Fig. 3 shows the parity plot between experimental and calculated ethanol and CO_2 mole fraction (values are normalized aiming to use only one parity plot). For ethanol a very good agreement can be appreciated, with an average error of 8.9% for a 47-run set. For acetaldehyde mole fraction, the average error is relatively higher (21.3%), a fact that can be explained recalling that for low ethanol conversion acetaldehyde concentration is very low and experimental errors can be more significant (Fig. 1).

Literature information about kinetics parameters for ethanol combustion is generally scarce. However, some values on activation energy are reported, so they can be taken as a reference, despite the fact that other types of catalysts were employed.

Idriss and Seebauer [11], for low ethanol conversion to mostly acetaldehyde, reported a wide range of activation energies (50–130 kJ mol^{-1}) because they employed many different metal oxides as active catalytic materials. In the present contribution, the ethanol to acetaldehyde activation energy (reaction (1)) was 110 kJ mol^{-1}.

Delimaris and Ioannides [6,7] studied ethanol oxidation on catalysts containing Mn/Ce and Cu/Ce in several ratios. Different intermediate products were identified, as acetaldehyde and ethyl-acetate, in amounts depending on the specific catalyst. The authors reported activation energies based on CO_2 production rate in the ranges 85–122 kJ mol^{-1} (for Mn/Ce catalysts [6]) and 101–135 kJ mol^{-1} (for Cu/Ce catalysts [7]). As the consecutive reactions were not discriminated in their analysis, a direct comparison with the value of activation energy of any of the two reactions considered in the present contribution cannot be performed without some level of uncertainty.

Finally, it is interesting to mention that Oyama et al. [12] found an activation energy of 89 kJ mol^{-1} for ethanol oxidation on Mn catalysts.

6. Conclusions

Catalytic combustion of ethanol on a Mn_9Cu_1 catalyst in a fixed-bed laboratory reactor has been studied. The ethanol oxidation produces acetaldehyde, which is further oxidized to the final products, carbon dioxide and water. Direct combustion from ethanol to carbon dioxide was not detected. Thus, a system of two consecutive reactions can be proposed. It was also checked that the final reaction products have no influence on both reaction rates.

Experimental data were fitted using LHHW rate expressions for both reactions: the ethanol oxidation to acetaldehyde as well as the acetaldehyde total combustion. The activation energies and the specific reaction rate constants of both reactions and the adsorption equilibrium constant of acetaldehyde were satisfactorily adjusted. On the contrary, the adsorption equilibrium constant of ethanol could not be properly adjusted due to the very low values arising in the regression analysis. Thus, it was assumed as being nil in the inhibition term.

The activation energy obtained for the ethanol oxidation to acetaldehyde is within the values reported in the literature for other catalysts based on several metal oxides, including CuO and MnO_2. In the case of acetaldehyde oxidation to carbon dioxide, no experimental data were found.

Acetaldehyde was more difficult to eliminate than ethanol; therefore, higher operation temperatures are required to its complete abatement. Nonetheless, the temperature level (around 220 °C) necessary to carry out this operation on the Mn_9Cu_1 catalyst is considered relatively low.

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