Catalysis Today 27 (1996) 237–242

Catalytic combustion of solvent-containing air on base metal catalysts

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Abstract

The study of the catalytic combustion of solvent containing air on base metal catalysts has shown that not only the desired total oxidation to carbon dioxide and water, but also the production of partially oxidized intermediates takes place.

Keywords: Combustion; Base metal catalysts; Solvent containing air

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1. Introduction

The catalytic combustion is one of the several industrial processes for pollution abatement. The aim is to convert volatile organic compounds (VOC) to carbon dioxide and water. Usual catalysts are noble metals like platinum and palladium or oxides of base metals such as copper manganate and copper chromite [1,2].

As the catalytic combustion is normally applied at low VOC concentrations, the use of multifunctional reactors — coupling regenerative heat transfer with chemical reaction — is preferable. In that case, the precise knowledge of the reaction kinetics is needed [3,4]. We therefore investigated the oxidation kinetics of typical volatile organic compounds (e.g., acetone, isopropyl alcohol and butyl acetate) on copper manganate in detail.

2. Experimental

Either commercially available or self-prepared copper manganate ($CuMn_2O_4$) was used. The powdered oxides (1 g) having BET surfaces between 3 and 100 m^2/g were deposited on an inert carrier (steatite balls, $\varnothing = 3$ mm) to obtain catalysts of the egg shell type.

The kinetic measurements were carried out by monitoring the gas phase composition along the length of a fixed bed of catalyst through distributed local sampling (Fig. 1). The tubular reactor was divided into 7 segments with sampling ports and individual temperature control. Nitrogen was loaded with the solvent in a saturator (S) at constant temperature and mixed with oxygen and additional nitrogen.

The VOC concentration at reactor inlet could be checked through the carbon balance by use of

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SSDI 0920-5861(95)00193-X

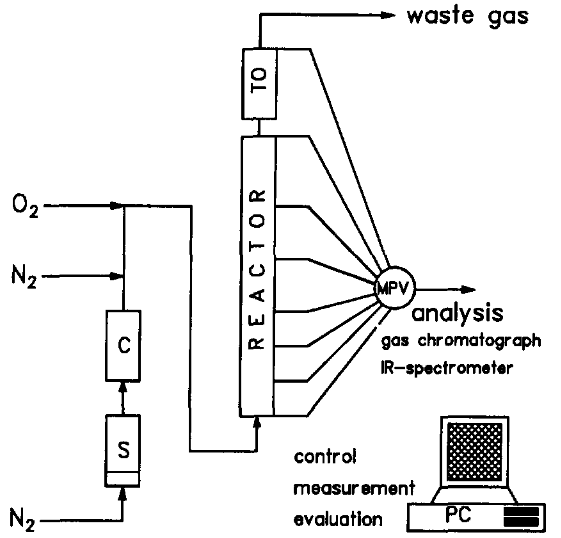


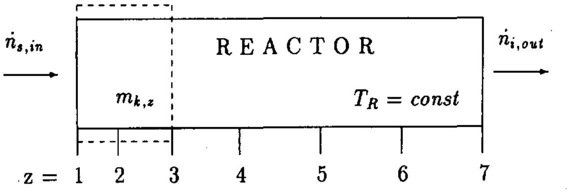
Fig. 1. Experimental set-up: fixed bed reactor with side stream exits.

a 2nd reactor (TO) containing a sufficient quantity of catalyst to oxidize all carbon containing compounds to CO_2 and H_2O. The analytical section consisted of a gas chromatograph with a capillary column and FID detector and of two non-dispersive IR spectrometers for the determination of CO and CO_2. Measurements were made in the temperature range between 200 and 450°C and at VOC concentrations between 0.01 and 0.5% in air. The reactor operation and sampling were automatically controlled by use of a computer.

Blank reactor experiments indicated that the contribution from the homogeneous reaction or from the activity of the reactor walls was not significant below temperatures of 450°C.

3. Evaluation

The measurements were carried out in the open system at steady state. Each quantity can be determined at the location of each of the analytical ports (z) distributed along the catalyst bed.



The results are quantified by use of the following definitions: ϵ_i is the number of carbon atoms in the molecule i (e.g., $\epsilon_{\text{acetone}} = 3$). The conversion is defined as the difference between the molar flow rate of solvent at the inlet ($z = 1$) and the flow rate at port z divided by the inlet flow rate.

$$X_{s,z} = \frac{\dot{n}_{s,\text{in}} - \dot{n}_{s,z}}{\dot{n}_{s,\text{in}}} \qquad (1)$$

The selectivity ${}^{R}S_{i,z}$ of the species i at port z is defined as the amount of component i formed divided by the amount of solvent reacted.

$${}^{R}S_{i,z} = \frac{\epsilon_i \dot{n}_{i,z}}{\epsilon_s (\dot{n}_{s,\text{in}} - \dot{n}_{s,z})} \qquad (2)$$

y_i denotes the distribution of the total carbon in the different species i and is related to the inlet carbon flow. y_i is identical to the yield of species i:

$$y_{i,z} = \frac{\epsilon_i \dot{n}_{i,z}}{\epsilon_s \dot{n}_{s,\text{in}}} \qquad (3)$$

The modified residence time is related to the mass $m_{k,z}$ of the catalytically active compound:

$$t_{v,z} = \frac{m_{k,z}}{\dot{V}} \sim \frac{1}{\text{GHSV}} \qquad (4)$$

4. Results and discussion

In all cases partially oxidized intermediates could be observed. The on line identification of the different organic species was verified by analyzing the product mixture off line after collecting in a cold trap. Additionally a gas chromatograph coupled with a mass spectrometer (GC/MS) was used. Experimentally observed intermediates are listed in Table 1 for the case of butyl acetate oxidation.

Up to 1% of the carbon at inlet could appear in the form of acetaldehyde. The yield of intermediates is similar for the three solvents investigated. Therefore, only the results of the oxidation of ace-

Table 1
Identified products for the case of butyl acetate oxidation on copper manganate

Compound	GC (experimental set up)		GC-MS
	on line	off line (content of cold trap)	
Acetaldehyde	●	●	●
Acetic acid	●	●	
Acetone	●	●	●
Acrolein		●	●
Butyl acetate	●	●	●
i-Butyl acetate	●	●	●
Butanol	●	●	●
Crotonaldehyde	●	●	●
Furan		●	●

tone on copper manganate will be discussed exemplarily in the following.

Typical results of the kinetic investigation are shown in Fig. 2 where the carbon fractions y_i contained in the different species are plotted against the residence time for the oxidation of acetone on copper manganate. One can observe the consumption of acetone and it is clearly shown that the main part of the carbon content of the solvent is found in the deep oxidation product CO_2. However, it is equally indicated that intermediate products are formed during the reaction. The concentration of intermediates passes through a maximum before declining.

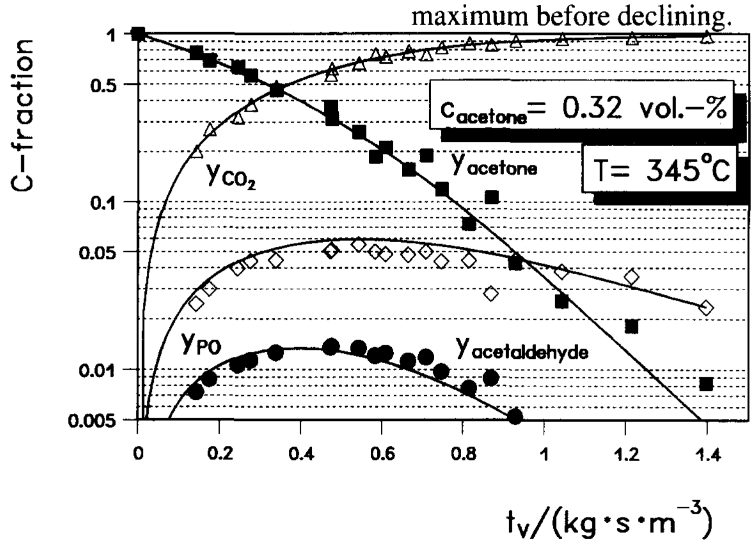


Fig. 2. Carbon fraction of acetone, CO_2, acetaldehyde and PO intermediates plotted against the residence time.

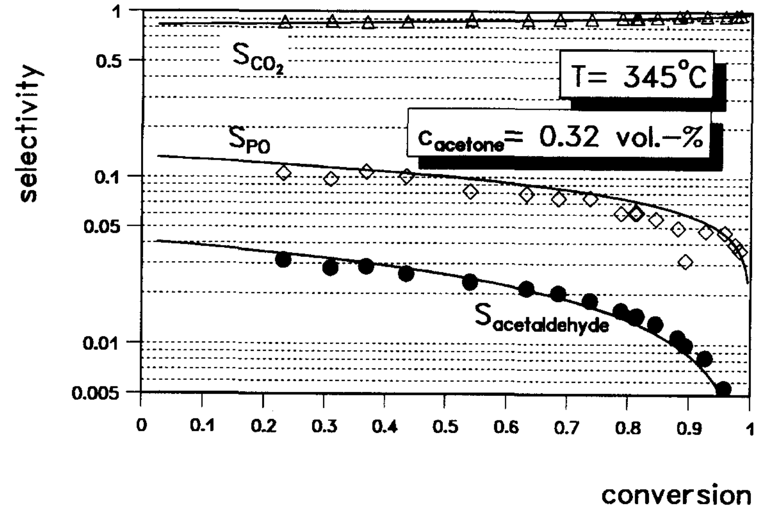


Fig. 3. Selectivity of CO_2, acetaldehyde and PO intermediates plotted against the conversion of acetone.

Fig. 3 illustrates the selectivities to CO_2, acetaldehyde and the partially oxidized (PO) products as a function of the conversion of acetone. The values for the selectivities to CO_2 are significantly higher than those to the intermediates. The combustion of the different solvents on copper manganate can be described by a simplified parallel-consecutive reaction network in all three cases. As acetaldehyde was the main partially oxidized product, it has been treated separately. All other intermediates including CO were lumped together to a pseudo-species PO product. Fig. 4 shows the network of coupled parallel and consecutive reactions, in the case of acetone oxidation.

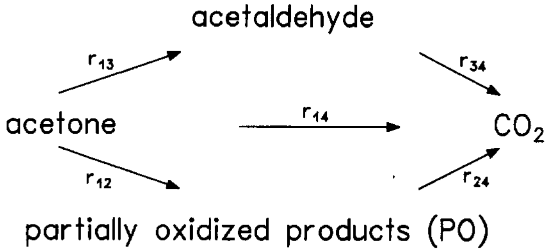


Fig. 4. Reaction network for the oxidation of acetone on copper manganate.

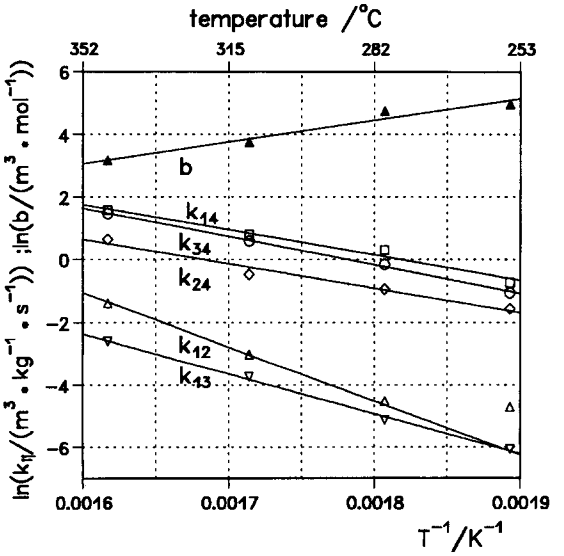


Fig. 5. Arrhenius type relationship for the oxidation of acetone on copper manganate.

Four different species are considered: acetone, acetaldehyde, the product of deep oxidation CO_2 and the lumped species PO products. They are linked by three parallel and two consecutive reactions. Five reaction rates interfering in four coupled differential equations are therefore considered.

$$\frac{\mathrm{d}c_i}{\mathrm{d}\left(\frac{m_{\mathrm{catalyst}}}{\dot{V}}\right)}=\frac{\mathrm{d}c_i}{\mathrm{d}t_V}=\sum_{ij}\upsilon_{i,ij}r_{ij} \qquad (5)$$

In the domain of high conversions of acetone the rate equations can be expressed as:

$$r_{12}=k_{12}c_1 \qquad (6)$$

$$r_{13}=k_{13}c_1 \qquad (7)$$

$$r_{14}=\frac{k_{14}c_1}{1+bc_1} \qquad (8)$$

$$r_{24}=\frac{k_{24}c_2}{1+bc_1} \qquad (9)$$

$$r_{34}=\frac{k_{34}c_3}{1+bc_1} \qquad (10)$$

The oxidation of acetone to CO_2 (r_{14}) was the main reaction. This description holds within the whole temperature range studied. The lines drawn in Fig. 2, Fig. 3 and Fig. 6 are calculated after curve fitting. The agreement of experimental data and model calculations is quite satisfactory (±15%).

Table 2

Frequency factors and activation energies for the oxidation of acetone on copper mananate

Reaction *ij*	Frequency factor $k_{0,ij}/(\mathrm{m^3\,kg^{-1}\,s^{-1}})$	Activation energy $E_{A,ij}/(\mathrm{kJ\,mol^{-1}})$
12	8.7×10^{10}	137
13	8.2×10^{7}	107
14	2.0×10^{6}	66
24	4.0×10^{5}	64
34	8.8×10^{6}	75
Factor	Frequency factor $b_0/(\mathrm{m^3\,mol^{-1}})$	Activation energy $E_{A,b}/(\mathrm{kJ\,mol^{-1}})$
b	3.3×10^{-4}	−58

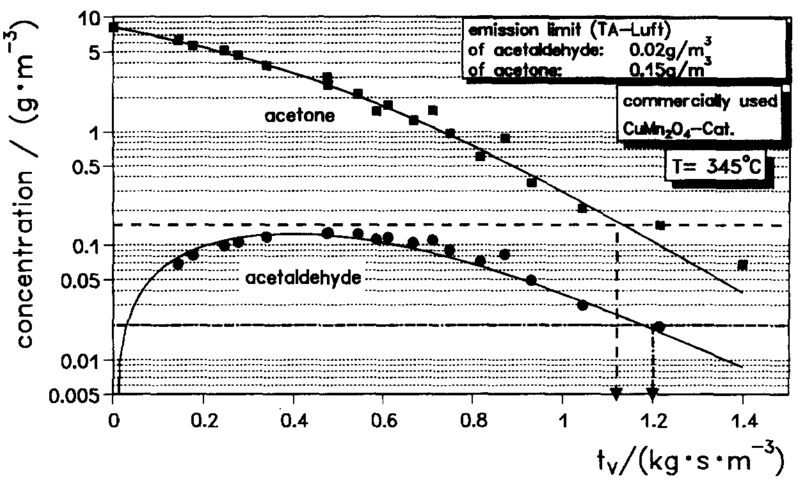


Fig. 6. Mass concentrations of butyl acetate and acetaldehyde plotted against the residence time.

The temperature dependence of the rate constants was also determined. A plot of the natural logarithm of the rate constants versus the reciprocal temperature (Fig. 5) indicates that the Arrhenius' rule (11,12) is followed for all values. Table 2 summarizes the values for the frequency factors and the activation energies. The parameters were obtained from linear regression.

$$\ln k_{ij} = \ln k_{ij0} - \frac{E_{A,ij}}{RT} \tag{11}$$

$$\ln b = \ln b_0 - \frac{E_{A,b}}{RT} \tag{12}$$

Thus the evolution of the reacting system can be quantitatively described. Using the kinetic data a reactor can be designed in a way, that the outlet concentrations of both solvent and intermediates are less than the legal limit.

In Fig. 6 the mass concentrations of acetone and acetaldehyde are plotted against the modified residence time. A decrease of the acetone concentration and a broad maximum of the concentration of acetaldehyde can be observed.

The legal emission limit in the Federal Republic of Germany is much higher for solvents, 0.15 g m^{-3}, than the value for acetaldehyde, 0.02 g m^{-3}. This leads to the somewhat surprising result that the emission limit of the primary solvent is already attained (1.13 kg s m^{-3}) when the content of the secondary by-product acetaldehyde is still too high. A higher residence time (here $t_v = 1.20$ kg s m^{-3}) is needed to eliminate all organic compounds. This typical behavior was found for most of the experiments.

5. Summary

The study of solvent oxidation (example: acetone) on copper manganate catalysts has shown, that the formation of partially oxidized intermediates takes place. Acetaldehyde and carbon monoxide are the major reaction products of acetone oxidation. For most of the experiments the emission limit of the primary solvent is already attained when the content of the secondary by-product is still too high. Both intermediates and CO_2 were produced simultaneously on the copper manganate catalyst. A complete description of the reaction pathways of solvent oxidation on copper manganate is given by a combined series-parallel mechanism and simple rate equations. The rate constants are calculated after curve fitting, Arrhenius' rule is followed for all rate constants. Using the kinetic data optimal reactor dimensions for the case of solvent oxidation can be determined.

Acknowledgements

This work was financially supported by the P.E.F. (Projekt Europäisches Forschungszentrum für Massnahmen zur Luftreinhaltung).

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