Catalytic combustion of waste gases

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Editors:

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POLITECNICO DI TORINO

Friday, July 3

AFTERNOON

14.45 - 15.05.
21. A. Pekeditz, D. W. Kraemer, J. Chabot, H. I. De
    Lasa, Western Ontario: "Novel Riser Simulator
    Reactor: Concept and Applications for Kinetic
    Studies"
15.05 - 15.25.
22. G. Toscano, Naples: "Deactivation Kinetics of
    Enzymatic Proteins"
15.25 - 15.45.
23. C. Pagella, Genova: "Biotechnological Hydrogen
    Sulphide Gas Treatment with Thiobacillus Ferroxidans"
15.45 - 16.05.
24. T. Nietsch, Berlin: "Measurement and Calculation of
    the Equilibrium Isothermal Curve in Metal Hydrides"
16.05 - 16.20. BREAK

16.20 - 16.40.
25. K. Sundmacher, Clausthal-Zellerfeld: "Catalytic
    Distillation in a Fixed Bed Reaction Column for
    Producing the Antiknock Enhancer MTBE"
16.40 - 17.00.
26. A. Gianetto, M. Farag, J. M. Arandes, H. D. Lasa,
    Western Ontario: "Novel Cracking Catalyst with Metal
    Traps for Production of Benign Gasoline"
17.00 - 17.20.
27. A. Barresi, Turin: "Catalytic Combustion of Waste
    Gases"
17.20 - 17.40.
28. G. Cao, A. Servida, M. Pisu, M. Morbidelli, Cagliari:
    "Experimental Analysis and Modeling of p-Xylene
    Liquid Phase Catalytic Oxidation"
17.40 - 18.00.
29. A. Pintar, Ljubljana: "Catalytic Liquid-Phase
    Oxidation of Toxic Organics in Aqueous Solutions"

After Dinner Talk: G. Astarita, "Miscellaneous Thoughts
        on PhD Programs in Chemical Engineering"

CATALYTIC COMBUSTION OF WASTE GASES

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Introduction

Deep catalytic oxidation of V.O.C.s (Volatile Organic Compounds) is widely employed for treatment of waste gases and is competitive with other air pollution control technologies especially when the concentration of the organic compounds in the waste stream is very low [1].

In spite of the wide diffusion of this type of equipment, fundamental aspects has received scarce attention in scientific literature, even if their knowledge would make possible to optimize or better predict the performances of the afterburners.

The work carried out at Politecnico di Torino has been focused on the investigation of the deep oxidation kinetics of pure compounds and mixtures over platinum based catalysts. The correlations for mass transfer in monolithic supports available from literature have also been compared and tested with experimental results in reactive conditions.

In cooperation with Yale University the role of the catalyst in the catalytically stabilized thermal (CST) combustor has also been investigated. This innovative technology is very promising for the treatment of waste gases containing chlorinated hydrocarbons, as it allows to get the high destruction efficiency of the thermal combustors at a lower temperature, reducing the required residence time and the risk of PIC emissions [2].

Deep oxidation kinetics of pure compounds and mixtures

Very few informations concerning the deep oxidation kinetics of the V.O.C.s are available in literature. In addition "mixture effects" have been observed in many cases, when mixtures of pollutants are oxidized. Mutual inhibitions may occur, reducing dramatically the destruction efficiency of some compounds or causing the ignition temperature of the reactor to increase [3, 4].

These effects can be relevant, but they may be predicted and estimated only if the true reaction mechanism of the single components is known. On the other hand it must be pointed out that the method of competitive reactions is very powerful in the investigation of oxidation kinetics, allowing discrimination between different mechanisms leading to similar rate equations.

Fig. 1. Hydrocarbon reaction rate in air, at atmospheric pressure. $\square$, benzene; $\blacktriangle$, toluene; O, ethylbenzene; $\bullet$, ethenylbenzene.

The deep oxidation of benzene, toluene, ethylbenzene, ethenylbenzene (styrene) and ethanol, and their binary mixtures, over a platinum based monolithic catalyst (VOC catalyst, supplied by Engelhard Corp.) has been investigated. The experiments have been carried out in a differential tubular reactor; only very low concentrations of organic compounds (< 2000 ppmV) have been studied [5].

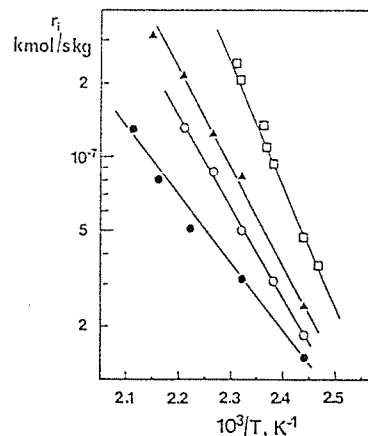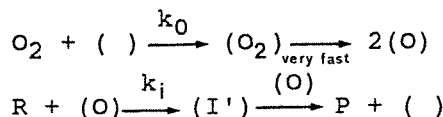The reaction rates of the aromatic hydrocarbons are compared in fig. 1.

The redox mechanism (first proposed by Mars and van Krevelen [6] and modified by Downie [7]) is usually adopted for aromatic hydrocarbon oxidation. According to this mechanism, the hydrocarbons react from gas phase with the adsorbed oxygen; a steady state is established in which the rate of removal of oxygen by chemical reaction equals the rate of adsorption:

$r_i \cdot 10^8$ kmol/s kg

Fig. 2. Ethylbenzene reaction rate versus hydrocarbon partial pressure (a) and oxygen partial pressure (b).
$\triangle$, 410 K; $\bullet$, 420 K; O, 430 K; $\blacktriangle$, 441 K; $\square$, 452 K; $\blacksquare$, 462 K.

$$O_2 + (\ ) \xrightarrow{k_0} (O_2) \xrightarrow[\text{very fast}]{} 2(O)$$

$$R + (O) \xrightarrow{k_i} (I') \xrightarrow{(O)} P + (\ )$$

$$r_i = \frac{k_0\, k_i\, p_{O_2}\, p_R}{k_0\, p_{O_2} + \nu\, k_i\, p_R} \qquad (1)$$

The experimental results show that, for all the hydrocarbons tested, the reaction rate is independent of the aromatic partial pressure in a wide concentration range. The kinetics is first order in respect of oxygen for benzene oxidation, but an apparent fractional order in respect of oxygen is exhibited by the other compounds (see fig. 2).

Benzene oxidation may be well described by the previous model; in fact, if $k_0 p_{O_2} \ll \nu k_i p_R$, the reaction rate reduces to $r_i = k_0 p_{O_2}/\nu$ (where ν is the oxygen stoichiometric coefficient). But the same reaction rate is not suitable to interpret the behaviour of the other aromatics: in the range of zeroth order reaction in respect of hydrocarbon, the reaction rates should be proportional to the oxygen partial pressure and the value of k_0 (the oxygen adsorption kinetic constant) should be independent of the hydrocarbon considered (cf. fig. 1).

It is interesting to analyze the behaviour of the binary mixtures: if competition for adsorbed oxygen took place, the species with higher reaction rate would inhibit the others. But an opposite trend has been observed; the inhibition effect on the other compounds decreases in the order (cf. fig. 3):
  ethenylbenzene > ethylbenzene > toluene > benzene

The reduction in reaction rate caused by ethenylbenzene is dramatic, and concentration dependent (see fig. 4). Benzene on the contrary does not influence the conversion of toluene and ethenylbenzene significantly, and only a weak effect is observed on ethenylbenzene.

This experimental behaviour cannot be satisfactorily described if the same reaction mechanism is adopted for all the aromatics and if only one kind of active sites is assumed for all the intermediates [8]. On the other hand, the experimental results suggest that the hydrocarbons adsorb on the catalyst, and that ethenylbenzene adsorption is very strong, probably as a consequence of the alchenic chain in its structure.

Thus a new mechanism is proposed; a steady state condition is assumed for oxygen adsorption, while almost equilibrium adsorption (on different sites) is assumed for the hydrocarbon:
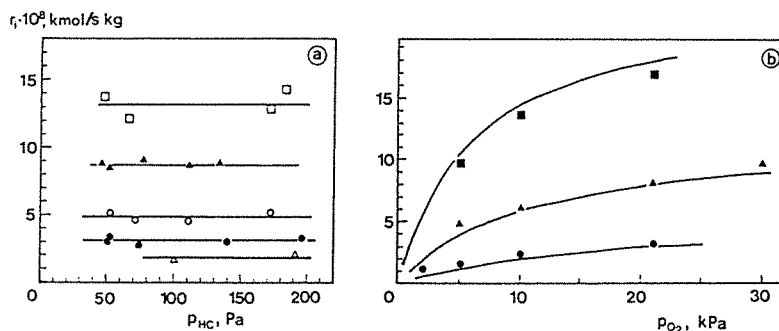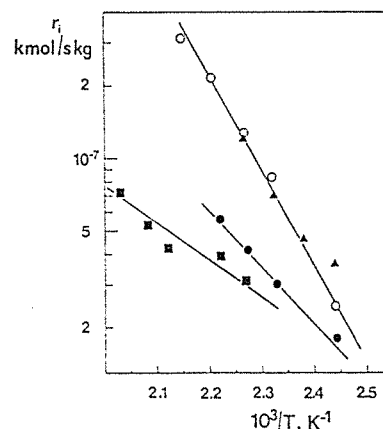

r_i kmol/skg

Fig. 3. Toluene reaction rate as single compound (O) and in binary mixture with benzene ($\blacktriangle$), ethylbenzene ($\bullet$), ethenylbenzene ($\blacksquare$). About 500 ppmV of each hydrocarbon in air at atmospheric pressure.
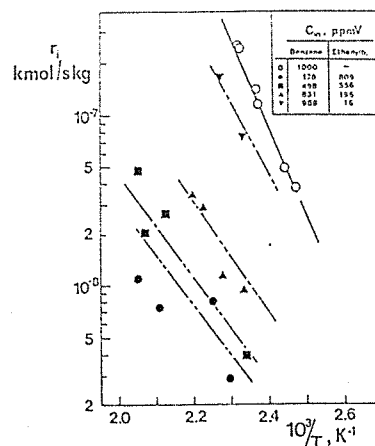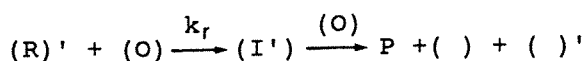

r_i kmol/skg
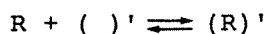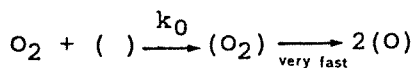
Fig. 4. Benzene reaction rate in mixture with ethenylbenzene (in air at atmospheric pressure).

$$O_2 + (\ ) \xrightarrow{k_0} (O_2) \xrightarrow[\text{very fast}]{} 2(O)$$

$$R + (\ )' \rightleftharpoons (R)'$$

$$(R)' + (O) \xrightarrow{k_r} (I') \xrightarrow{(O)} P + (\ ) + (\ )'$$

$$r_i = \frac{k_0\ k_r\ p_{O_2}\ \vartheta_R}{k_0\ p_{O_2} + \nu\ k_r\ \vartheta_R} \qquad (2)$$

If the hydrocarbon coverage on the catalyst sites, ϑ_R, is close to unity, the conversion rate becomes independent of the hydrocarbon partial pressure, while the apparent reaction order in respect of oxygen is one if $\nu k_r \gg k_0 p_{O_2}$, and decreases if the surface reaction kinetic constant, k_r, decreases.

When mixtures are oxidized, the inhibition effects are due to competition between the hydrocarbons for the adsorption sites.

Inhibition effects in ethanol-aromatic mixtures have been investigated, too. The complete oxidation of ethanol is difficult to achieve, because variable amounts of acetaldehyde always form; in addition the reaction mechanism over Pt has not been identified completely. Experiments at different contact time [9] have evidenced that at low temperature only two parallel oxidation reactions occur, leading respectively to aldehyde and CO_2, but at higher temperature a series-parallel scheme takes place

$$CH_3CH_2OH \longrightarrow CH_3CHO$$
$$\searrow CO_2 \nearrow$$
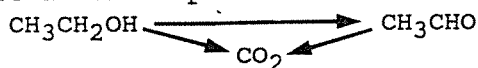
In fig. 5 the contribution of the parallel reaction to ethanol conversion, ζ, is shown. Significant mixture effects have been observed (fig. 6) both on reaction rate and on selectivity [10].

Fig. 5. Ethanol oxidation: contribution of the parallel reaction in the series-parallel scheme.

Fig. 6.(a) Ethanol-benzene (C_{in}=1020-190 ppmV in air) and (b) ethanol-ethenylbenzene (C_{in}=1007-199 ppmV) mixture conversion vs gas preheating temperature (v_s=134,000 h^{-1}). ■, ethanol total ; ●, to CO_2; O, to CH_3CHO conversion. △, benzene; ▲, ethenylbenzene conversion. Pure ethanol (1000 ppmV) total conversion (——) and conversion to aldehyde (---) are shown for comparison.

Modeling of the monolithic combustor

Monolithic supports are widely used because they reduce pressure drop dramatically. The flow in the channels of the monolith is laminar, and therefore the heat transfer coefficients may be calculated by solving the associated Graetz problem. Solutions are available in literature for different geometries and boundary conditions. The mass transfer coefficients are usually obtained by analogy, but there are few experimental data. Nusselt and Sherwood numbers strongly depend on the boundary conditions selected, but there is not always complete correspondence between boundary conditions for heat and mass transfer.

In fig. 7 experimental data are compared with the predictions of a one-dimensional model, using different correlations from literature for Nu and Sh; a short monolith has been used, in order to make the entrance effects relevant [11, 12]. Large discrepancies are observed; it must be noted that Hawthorn's and Votruba's correlations give averaged transfer coefficients, and of course a better agreement between model and experiments is obtained if local coefficients are employed.
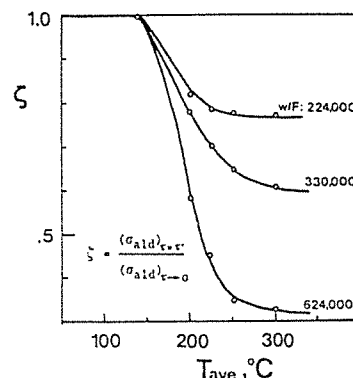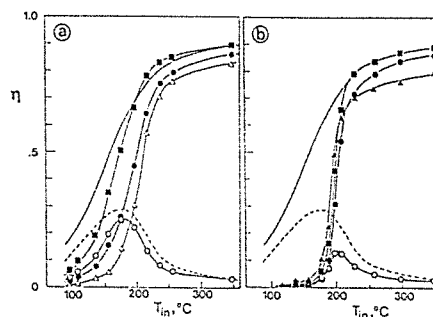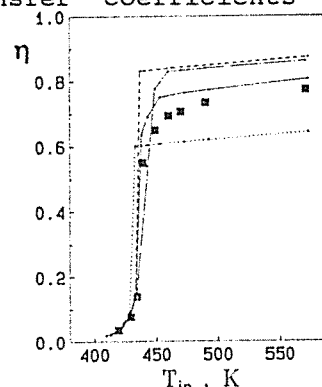
Fig. 7. Benzene conversion (C_{in}=1000 ppmV; v_s=134,000 h^{-1}). Comparison of experimental results (■) and model predictions using the mass transfer coefficient proposed by Hawthorn [13] (---), Votruba [14] (···) and Asako [15] [local (——) and average (—.—).

The catalytically stabilized thermal combustor

In the CST combustor the catalytic reaction keeps the surface of the monolith hot, increasing the stability of the burner, but may also interact with the homogeneous reactions. In order to investigate this aspect, CH_4 and CH_3Cl combustion have been studied in an externally heated, isothermal flow tube reactor of alumina, either non catalytic or coated by Pt or manganese oxide catalyst [5].

In CH_3Cl combustion both catalysts allowed a 150 K reduction in the temperature required for total destruction of the reactant (η >99.99%), while this temperature does not change significantly for CH_4; great changes in selectivity are observed at lower temperatures in both cases.

Fig. 8. Comparison of CH_3Cl conversion in non catalytic and in catalytically stabilized thermal combustor. C_{in}=5000 ppmV in air.

The experimental results indicate that the catalyst, in addition to thermal effects, depletes the reactant concentration close to the wall, hindering propagation of gas ignition to the bulk, but it can also act as a radical source, enhancing homogeneous oxidation reactions [16, 17]. As the chlorine reduces the rate of combustion by scavenging the hydrogen radicals, the generation of free radicals from the surface has a dramatic role in CH_3Cl combustion.
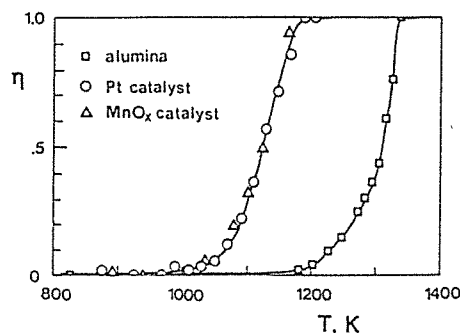
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