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# TRANSIENT MOLECULAR FLOW THROUGH CAPILLARIES FOR THE STUDY OF CATALYTIC REACTIONS

R. Haul and W. Littmann

Inst. f. Physikalische Chemie und Elektrochemie,
Techn. Univ. Hannover, Fed. Republ. Germany

Abstract: Residence times, adsorption isotherms (-16 to +30°C) and isobars (up to 100°C) of $C_2H_4$ were measured on "clean" and oxygen covered Ag. Freundlich type isotherms on "clean" Ag at coverages between $5 \cdot 10^{11}$ and $2 \cdot 10^{13}$ molecules/$cm^2$ resulted in isosteric heats of adsorption between 76 and 21 kJ/mole. At pressures ($10^{-3}$ to $10^{-1}$ Torr) on a silver wire catalyst the oxidation of $C_2H_4$ leads only to $CO_2$ and $H_2O$. Transient molecular flow curves under reaction conditions were treated by means of computer simulations.

## INTRODUCTION

Residence times of physisorbed molecules and adsorption isotherms of rare gases, isomeric and isotopic hydrocarbons have been previously studied by transient molecular flow through single glass capillaries /1-4/. This technique has now been modified to investigate collision processes with capillary surfaces which are catalytically active. As an example the oxidation of ethylene on silver was chosen. Despite extensive research the mechanism of this industrially important reaction is still controversial. No kinetic studies have as yet been carried out under UHV-conditions.

## EXPERIMENTAL

The column consisted of a glass capillary spiral (2m, 1mm Ø tightly packed with a bundle of 30 oriented silver wires (0,15mm Ø.). From a gas inlet system various gases could be suddenly introduced at constant pressures $p_1$ ($10^{-4}$-$10^{-2}$ Torr). The exit side was evacuated with a turbomolecular pump and the flux of molecules recorded with a quadrupol mass spectrometer. The Ag surface was cleaned after contamination with oxygen by flowing $C_2H_4$ or $H_2$ at 250°C and subsequent evacuation to a basic pressure $<10^{-8}$ Torr.

## ADSORPTION OF ETHYLENE

Typical transient flow curves for $C_2H_4$ on "clean" Ag are shown in fig. 1. From experiments with $N_2$ which is pratically not adsorbed above room temperature Knudsen diffusion coefficients D can be evaluated /1/. As expected a straight line is obtained when D is plotted versus $\sqrt{T}$ (fig.2). From the slope, assuming cylindrical capillaries a mean diameter d of $1.54.10^{-2}$cm results which is equivalent to the actual pore width of the capillary system.

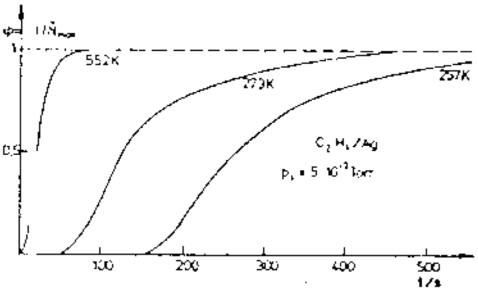

Fig.1. Transient flow curves

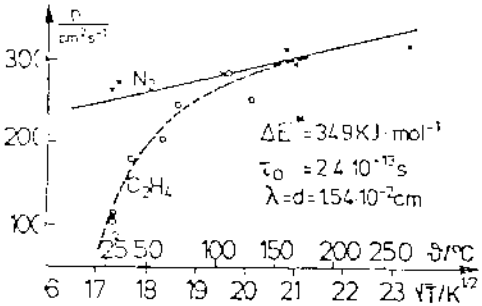

Fig.2. Diffusions coefficients from flow experiments.

Comparison between the results for $N_2$ and the isobaric $C_2H_4$ (fig.2.) clearly demonstrates the adsorption of the olefine on the silver surface. The broken line has been calculated with

$$D_{C_2H_4} = \frac{D_{N_2}}{\left(1 + \frac{\tau}{\lambda/\bar{v}}\right)}$$

where the mean residence time is given by

$$\tau = \tau_o \cdot \exp(E^{*}_{des}/RT)$$

with $E^{*}_{des}$ activation energy for desorption, $\lambda$ mean free path, $\bar{v}$ mean molecular velocity.

From the transient flow curves of $C_2H_4$ residence times were evaluated /1/ resulting in $E^{*} = 35$kJ/mole and $\tau_c = 2.4.10^{-13}$s for surface coverages corresponding to $p_1 = 5.10^{-3}$Torr.

As previously described /1,3/ adsorption isotherms can be obtained from molecular flow experiments. Typical Freundlich type isotherms of $C_2H_4$ for a "clean" silver surface are shown in fig.3. The isotherms indicate a common point of intersection which, however, on theoretical grounds /5/ cannot be directly interpreted as corresponding to the monolayer capacity, as has been suggested /6/.

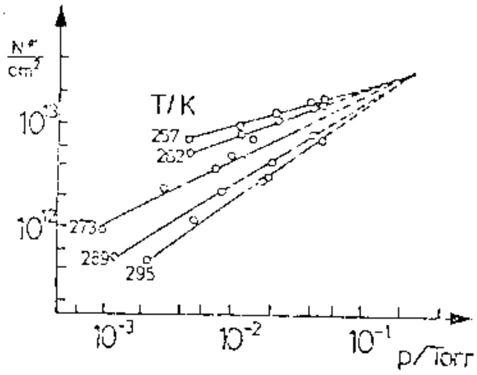

Fig.3. Adsorption isotherms for $C_2H_4$ on "clean" Ag.

Adsorption iosbars (fig.4.) show a decrease of the amount adsorbed up to about 50°C with a subsequent slight increase of $N_{ads}$ for the "clean" silver. $N_{ads}$ is comparatively smaller on the oxygen covered surface.

Isosteric heats of adsorption depend logarithmically on surface coverage and range between 76 and 21 kJ/mole at $5.10^{11}$ and $1.10^{13}$ molecules/cm$^2$ based on the geometric surface. These heats of adsorption indicate strong surface heterogeneity and are comparable with the scanty data in the literature of about 38 kJ/mole /7,8/.

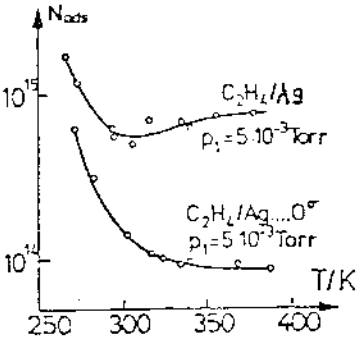

Fig.4. Adsorption isobars

The present results indicate an interaction of $C_2H_4$ with clean and oxygen covered Ag which could be interpreted as essentially physisorption at the lower temperatures with indications for weak chemisorption as the temperature is raised. It is generally agreed that at temperatures of the catalytic oxidation, usually 250°C, $C_2H_4$ is not adsorbed on clean Ag. In the presence of oxygen either a chemisorption complex ($C_2H_4OO$-Ag) is postulated /9/ or more recently /10/ on the basis of IR findings it is assumed that $C_2H_4$ is chemisorbed on partially charged $Ag^{\delta+}$ formed by adjacent oxygen chemisorption.

## OXIDATION OF ETHALENE

Two sets of catalytic flow experiments were carried out under the following reproducible conditions: (i) after cleaning the Ag by treatment with $O_2/H_2$ and subsequent evacuation a mixture of $C_2H_4$ and $C_2$ was fed to the column. (ii) after covering the Ag surface with oxygen by means of a steady $O_2$ flow a stream of $C_2H_4$ was added. Transient flow curves of such two typical experiments are shown in fig. 5 and 6.

At temperatures between 100 and 300°C, pressures between $10^{-3}$ and $10^{-1}$ Torr and $C_2H_4/O_2$ ratios of 1:10 to 10:1 only $CO_2$ and $H_2O$ were found as reaction products; no traces of ethylene oxide were detectable. This is in agreement with both antagonistic reaction mechanisms which are presently discussed. In one case /9,11,12/, i.e. epoxide formation via chemisorbed molecular $O_2^-$, the concentration of this species as compared to adsorbed $O^-$ can be expected to be neglibibly small at the low pressures used in the molecular flow experiments. In the other case /10/ the formation and mutual reaction of surface complexes

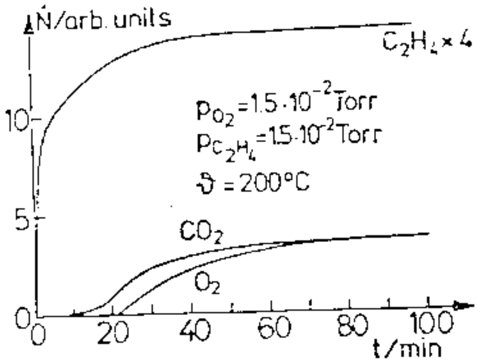

Fig.5. Ethylene oxidation: $C_2H_4$-$O_2$ mixture/Ag

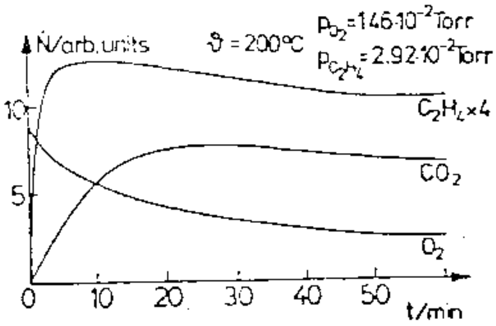

Fig.6. Ethylene oxidation: $C_2H_4$/oxygen covered Ag

($Ag^{\sigma+}C_2H_4$, $Ag^+O^-$) leading to $CO_2$ and $H_2O$ would be prefered at low pressures to the reaction of $Ag^+O^-$ with $C_2H_4$ from the gas phase leading to $C_2H_4O$.

The process of transient molecular flow has been treated by Gottwald and Roth/13/ using computer simulation techniques. This method has now been extended to include chemical reactions /14/.

As an example the experiments of fig. 5 and 6 were succesfully simulated on the basis of the following processes:

1) transport of reaction components characterizied by transport coefficients
2) dissociative chemisorption
$$O_2^g \xrightarrow{k_1} 2O^\sigma$$
3) Eley-Rideal mechanism
$$C_2H_4^g + 2O^\sigma \xrightarrow{k_2} [C_2H_4OO]^\sigma$$
4) immobilization of oxygen by bulk diffusion and/or surface oxide formation.
$$O^\sigma \xrightarrow{k_3} O_{immob}$$
5) combustion reaction
$$[C_2H_4OO]^\sigma + 2O_2^g \xrightarrow{k_4} 2CO_2^g + 2H_2O^g$$

Of course, other and additional elementary steps can be considered. Experiments at various pressures, $C_2H_4/O_2$ ratios, temperatures and catalyst treatments are in progress. The described method enables a study of the kinetics of catalytic reactions under well defined geometric and clean surface conditions. The flow experiments can be extended to higher pressures and then be compared with transient gaschromatographic studies with commercial catalysts /11/.

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