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Oxidative Dehydrogenation of Ethylbenzene Over Nickel–Tungsten Mixed Oxides

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The production of styrene by oxidative dehydrogenation of ethylbenzene with molecular oxygen has been studied over nickel and tungsten mixed oxides supported on alumina. Both the total content and mole ratio of the oxides were varied.

Experiments have been carried out to study the influence of reaction temperature, contact time and partial pressure of the reactants on yields and selectivities. Major oxidation products obtained include styrene and the carbon oxides, while benzaldehyde, benzene and benzoic acid are only minor products of the reaction.

The experimental data strongly suggest that the reaction proceeds through a series of consecutive oxidation steps, each intermediate adsorbed species being able either to desorb to the gas phase or react further on the surface of the catalyst. Overall reaction rates appear to follow a classic Langmuir kinetic law, in which the reaction takes place between hydrocarbon and oxygen adsorbed species on different sites of the catalyst surface.

1. INTRODUCTION

The oxidative dehydrogenation of paraffins, monoolefins and alkylbenzenes has attracted considerable attention during the last 10 or 15 yr and, consequently, a number of publications have appeared both in the patent and periodical literature. A well-documented general review on this subject has been published by Skarchenko (*1*).

Most of the work on ethylbenzene has been devoted to the selection of suitable catalysts and appropriate reaction conditions for improved styrene yields and selectivities. The more attractive catalysts appear to be mixtures of bismuth and cobalt oxides with molybdenum (*2–5*), although comparable results have also been attained on oxides of other transition and groups IV B and V B metals, such as vanadium and antimony (*6*), tungsten with nickel, bismuth, cobalt or manganese (*7*), chromium and niobium (*8*). Reaction conditions usually employed include atmospheric pressure and temperatures between 400 and 600°C.

Two other articles dealing with the oxidative dehydrogenation of ethylbenzene have also recently been published (*9, 10*). Not much information, however, is available about the kinetics and mechanism of the reaction compared with that of butenes. This, therefore, is the reason for the present investigation.

2. EXPERIMENTAL SECTION

Apparatus and Procedure

All experiments were conducted in a conventional, electrically heated, fixed-bed glass tubular reactor.

The temperature in the catalyst bed was measured with a chromel–alumel thermocouple located in a coaxial thermowell. Temperature control was achieved by introducing nitrogen with the reaction mixture and diluting the catalyst with inert silicon carbide (SiC/cat. = 2 vol/vol).

Reaction products were condensed at

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0°C and analyzed by gas chromatography. After removal of the water, the liquid condensate was analyzed in a column of 5 wt% silicone oil UC-W98 on Chromosorb W (30–100 mesh) at 120°C, and the gases were analyzed at 40°C in two columns, one of active charcoal for CO and another of Porapak Q for CO_2.

Catalyst Preparation

Catalysts were prepared by impregnation without any excess solution using ammonium tungstate Prolabo (CP), nickel nitrate Riedel de Haen (cp, max 0.01% cobalt) and α-alumina (Saht-99) from Carborundum Co. as support. This α-Al_2O_3 was previously calcined for 5 hr at 600°C. (Pore volume $0.17 \equiv cm^3/g$ and surface area 3.2 m^2/g for pores 37.5 to 75,000 Å, as determined by mercury porosimetry.) After impregnation the catalysts were dried at 120°C, and then calcined in air at 550°C for 3 hr. Average particle size was about 3 mm.

Reactants used in this work were high purity nitrogen (N_2) and oxygen (O_2) from Sociedad Española de Oxígeno (>99.9%), and pure grade ethylbenzene (PhEt) from Fluka (>99% by gc) with small amounts of toluene as the major impurity. They were not further purified before use.

RESULTS AND INTERPRETATION

Influence of the Amount of Active Phase

A series of catalysts with constant W/Ni atomic ratio of 1:1.6 was prepared, in which the total metal content ranged from 0.4 to 13.9 g/100 g of support.

Experimental reaction data obtained at 460°C, with 10 g of catalyst, contact time $W/F = 20$ g sec/cm^3 and feed composition 10% O_2, 10% PhEt and 80% N_2 by volume, are summarized in Fig. 1. (Total volumetric flow referred throughout this article to STP conditions.)

Ethylbenzene conversion and yields to styrene (Sty) increase rapidly with the amount of active phase for concentrations up to about 5 g of (W + Ni)/100 g of support, and then start to level off. This is characteristic of such supported catalysts, the conversion being a function of the content and degree of dispersion of the active components.

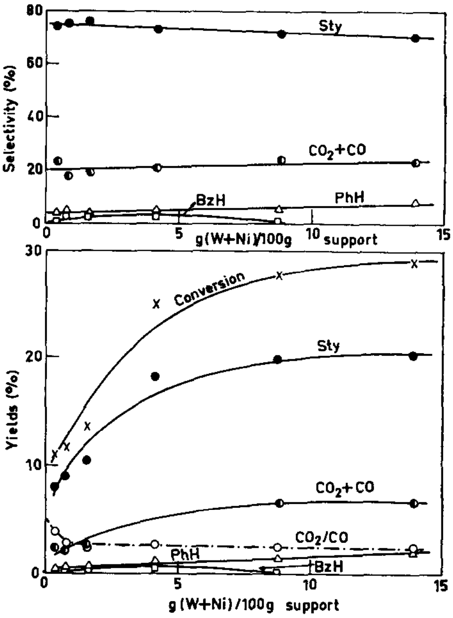


FIG. 1. Oxidation of ethylbenzene. Influence of Ni, W oxide content on yields and selectivities.

Selectivity to styrene slightly decreases from about 76 to 70%.

Influence of the Atomic Ratio W/Ni

Experiments have also been carried out on a series of catalysts with constant amount of active phase (0.048 at. g (W + Ni)/100 g Al_2O_3) and different W/Ni atomic ratios from 0 to ∞ (i.e., W/(W + Ni) between 0 and 100%). Reaction conditions were the same as indicated above.

Run data (Fig. 2) indicate that somewhat better results are obtained with W/Ni ratios of 2 to 4. Similar values have been reported in the literature for other catalysts on this type of reaction. Thus, in the oxidative dehydrogenation of butenes to butadiene over cobalt–molybdenum oxides, optimum Mo/Co ratios of 2 to 5 were found (*11*), and on bismuth-molybdenum Mo/Bi values of 2 to 4 mentioned (*1*). Boutry *et al.* (*12*), in particular, pointed out the

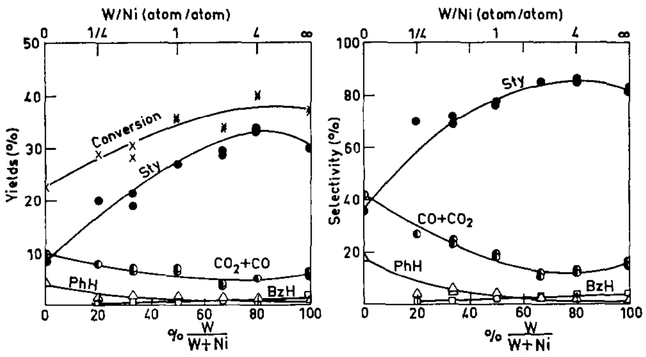


FIG. 2. Influence of atomic ratio W/Ni on yields and selectivities.

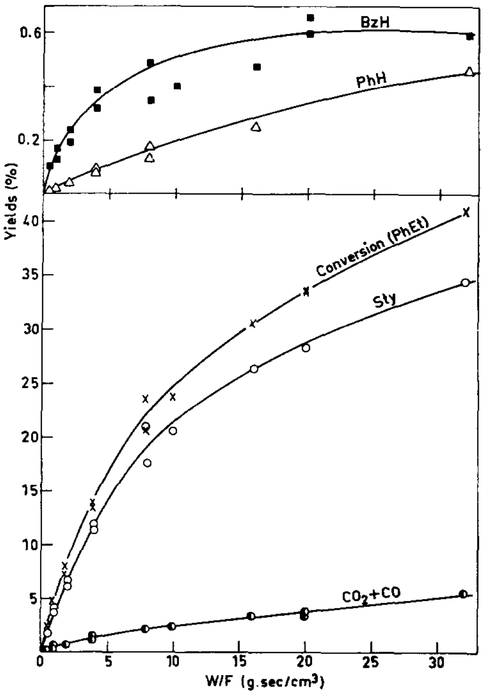


FIG. 3. Oxidation of ethylbenzene at 460°C. Yields vs contact time.

formation of cobalt molybdite during the course of the reaction by reduction of their cobalt–molybdenum catalysts.

We have studied the above series of tungsten–nickel catalysts before use, by magnetic susceptibility and X-ray diffraction analysis (*13*), and detected the presence of WO_3 and $NiWO_4$. However, no simple relationship was found between catalytic activity and the amount of the above two species as detected by X-ray and magnetic susceptibility.

Reaction Mechanism

To establish the reaction mechanism we have studied the oxidation of ethylbenzene, styrene and benzaldehyde as a function of contact time on a catalyst sample containing 0.048 g at. of (W + Ni)/100 g of alumina and atomic ratio W/Ni = 2 (pore volume 0.16 cm^3/g and surface area 2.4 m^2/g for pores 37.5 to 75,000 Å, by mercury porosimetry).

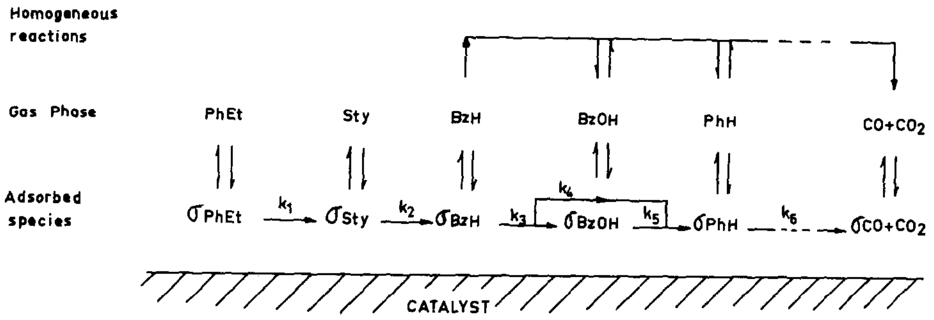
The experiments were done at 460°C, atmospheric pressure (about 710 mm Hg) and feed composition 10% O_2, 10% PhEt and 80% N_2. Results are shown in Figs. 3, 4 and 5a and b) and Table 1.

Styrene and CO + CO_2 are major products from ethylbenzene (Fig. 3), while benzaldehyde (BzH) and benzene (PhH) are only present in small quantities. All appear to be initial products of the reaction (Fig. 4). Benzoic acid (BzOH) was also detected in the liquid condensate.

Styrene is more refractory than ethylbenzene towards oxidation (Fig. 5), while benzaldehyde is fairly easy to oxidize and gives mainly CO + CO_2, benzoic acid and benzene (Table 1).

A separate experiment with benzaldehyde in the absence of oxygen showed that benzene is produced not only through benzoic acid, but partly by decarbonylation of benzaldehyde.

On the basis of this evidence we propose the following reaction scheme



(PhEt = ethylbenzene, Sty = styrene, BzH = benzaldehyde, BzOH = benzoic acid, PhH = benzene) which represents a type of mechanism as postulated by De Boer and Van der Borg (*14*), where each intermediate adsorbed species can either desorb to the gas phase as a product, or further react on the catalyst surface. In other words, every product can be produced directly from ethylbenzene through a series of consecutive oxidation steps on the surface of the catalyst, thus explaining their simultaneous appearance at the beginning of the reaction.

The homogeneous oxidations of benzaldehyde, benzoic acid and benzene have also been included, in agreement with our experimental evidence in the absence of any catalyst. They are of less importance, however, as compared with the catalyzed reactions.

The fact that styrene and CO + CO_2 are the major products, even at fairly high conversions, suggests that k_2 is much smaller than all other rate constants indicated in the above mechanism. We have made no attempts to complete the set of reactions in between benzene and the final oxidation products CO and CO_2.

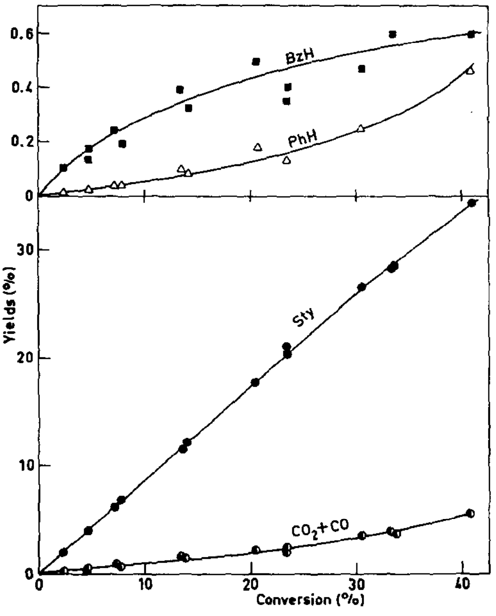


FIG. 4. Oxidation of ethylbenzene at 460°C. Curves of yields vs conversion.

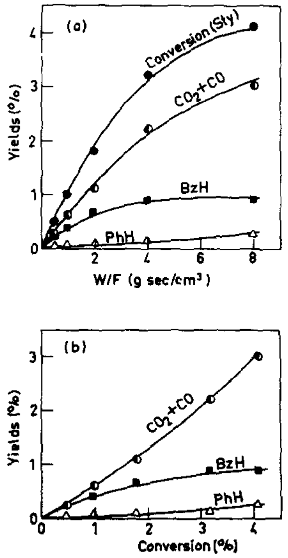


FIG. 5. Oxidation of styrene at 460°C: (a) Yields vs contact time; (b) yields vs conversion.

TABLE 1
OXIDATION OF BENZALDEHYDE (BzH) ON W AND Ni MIXED OXIDES[a]

W (g)	F (cm^3/min)	Yields (mole%) PhH	BzOH	$CO + CO_2$	CO_2/CO (mole/mole)
2	240	0.6	4.4	1.7	1.1
10	60	2.2	6.8	6.8	1.2

[a] Temp, 460°C; feed: 10% O_2; 10% BzH, 80% N_2.

Kinetics Based on Initial Rates

Low conversion experiments were carried out at different partial pressures of the reactants on the same catalyst sample, in order to derive a rate equation for the overall oxidation of ethylbenzene. Reaction conditions were 460°C, approximately 710 mm Hg total working pressure, and contact time $W/F = 1$ g sec/cm^3. Under these conditions a blank experiment using inert SiC gave less than 1% conversion.

Experimental rates are plotted in Figs. 6 and 7 versus partial pressure of each reactant. From these values the following rate equation was obtained

$$r = k\,\frac{aP_E}{1 + aP_E} \times \frac{bP_O}{1 + bP_O}, \qquad (1)$$

where $k = 4.3 \times 10^{-3}$ mole hr^{-1} g^{-1}, $a = 1.8$ atm^{-1} and $b = 39$ atm^{-1}, when the reaction rate (r) is given in moles per hour per gram and the partial pressures of ethylbenzene (P_E) and oxygen (P_O) in atmospheres.

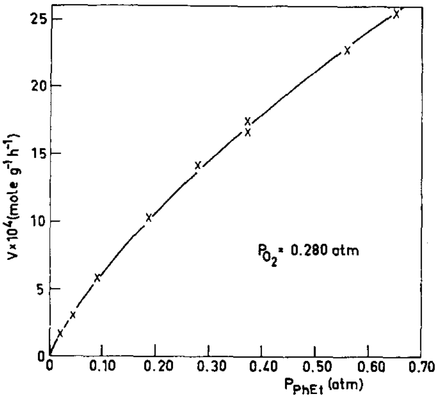


FIG. 6. Rate of reaction as a function of hydrocarbon partial pressure.

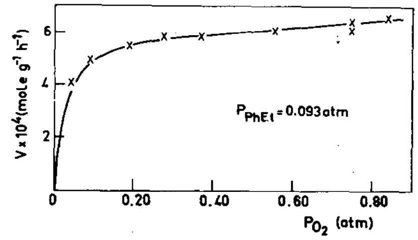


FIG. 7. Rate of reaction vs oxygen partial pressure.

This equation corresponds to a classic Langmuir kinetic law in which reaction takes place between adsorbed species of hydrocarbon and undissociated oxygen on different sites of the catalyst surface. Dissociation of oxygen prior to chemical reaction, however, cannot be ruled out on the basis of our results, although the corresponding equation did not reproduce the experimental data as well as Eq. (1).

We have examined the validity of Eq. (1) and found that it fits the integral reactor data of Fig. 3, up to about 20% conversion. Beyond this conversion level, experimental values fall below the calculated curve (Fig. 8), indicating that the products of the reaction already exert a considerable inhibiting effect on the overall rate, most likely by competitive adsorption.

Reaction Temperature and Activation Energy

Lastly, Fig. 9 shows the effect of reaction temperature on yields and selectivities in the range of 430 to 505°C.

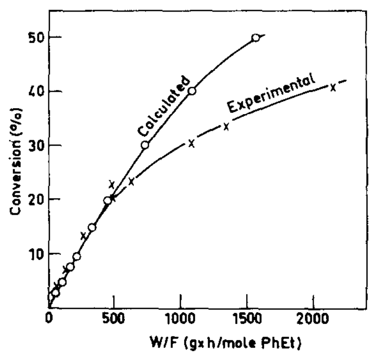


FIG. 8. Comparison between *calculated* and *experimental* values of ethylbenzene conversion, at 460°C.

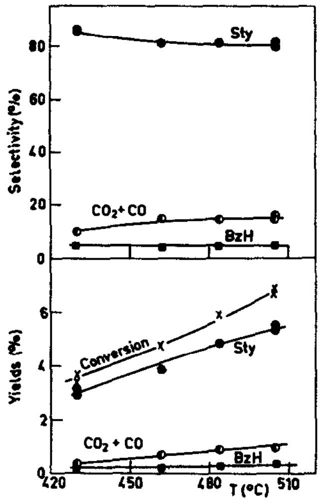


FIG. 9. Oxidation of ethylbenzene at different temperatures (W/F = 1 g sec/cm^3; 30% O_2, 10% PhEt, 60% N_2).

Using the conversion values also given in Fig. 9, an overall activation energy of 10.0 ± 1.2 kcal/mole has been obtained for this oxidation reaction on our tungsten-nickel catalyst. The activation energy is rather low. However, there was no increase in the rate of reaction when the average particle size of the catalyst was reduced; in view of this, and also the low surface and porosity, we do not consider that the low activation energy indicates a diffusion-limited reaction. It should be recalled that it is an apparent activation energy, lower than the true activation energy by at least the magnitude of the heat of adsorption of ethylbenzene.

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