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Kinetics of Oxidation of Tetralin over Supported NiO Catalyst

The liquid-phase oxidation of Tetralin with soluble catalysts has been studied extensively. The work reported so far on insoluble catalysts for the oxidation of Tetralin is mainly that of George (*1*) and Mukherjee and Graydon (*2*). Recently Srivastava and co-workers (*3*, *4*) studied this reaction in the region where inhibition was effective. The kinetics and catalytic behavior of the oxidation of Tetralin over supported nickel oxide have not been discussed in the literature although it is well documented that the activity of a catalyst can be drastically altered by the support used and its method of preparation.

In the present work, the supported nickel oxide on alumina catalyst was prepared by an impregnation technique and its effect on kinetics of the liquid-phase oxidation of Tetralin was studied. The effects of nickel oxide concentration, calcination period, Tetralin concentration, catalyst amount, and temperature on the reaction rate are reported. The experiments were conducted in the temperature range 45 to 85°C at regular intervals of 10°C. In this investigation, we limit ourselves to presenting results using catalysts containing up to 20 wt% NiO on Al_2O_3.

Pure Tetralin was obtained from Koch–Light Laboratories Ltd. It was further purified by vacuum distillation. Monochlorobenzene of Sarabhai Chemicals was used as an inert solvent for varying the concentration of Tetralin. Oxygen was supplied by Indian Oxygen Ltd., Kanpur. Nickel nitrate hexahydrate and aluminum oxide were obtained from "Robert Johnson" and Sarabhai Chemicals, respectively. Tetralin hydroperoxide was prepared by thermal oxidation at 60°C.

The catalysts were prepared by impregnating γ-alumina with nickel nitrate hexahydrate (*5*, *6*). Reference to various samples will be made by giving their compositions as weight percentage of NiO followed by temperature and duration of calcination; hence, NiO-5-450-12 means a sample of NiO supported on γ-alumina having 5% of the active element as NiO calcined at 450°C for 12 hr in air. X-Ray diffraction patterns were obtained using a General Electronics difractometer with copper ($K\alpha$) radiation (*7*).

The symbols RH, ROOH, and ROH are used for hydrocarbons, hydroperoxides, and alcohols, respectively. Catalyst ratio is defined as the weight of the catalyst in grams divided by the volume of the hydrocarbon in milliliters. The oxidation apparatus and operating procedure have been described previously (*8*).

From the earlier experiments (*2*), it was concluded that addition of both the catalyst and hydroperoxide was necessary to initiate the oxidation of Tetralin. This was evident in the present study. A critical ratio of hydroperoxide concentration to catalyst amount of approximately 3 to 4×10^{-4} g·mol/g of catalyst was obtained. Further runs were conducted with this ratio.

Figure 1 shows the rate of oxygen absorp-

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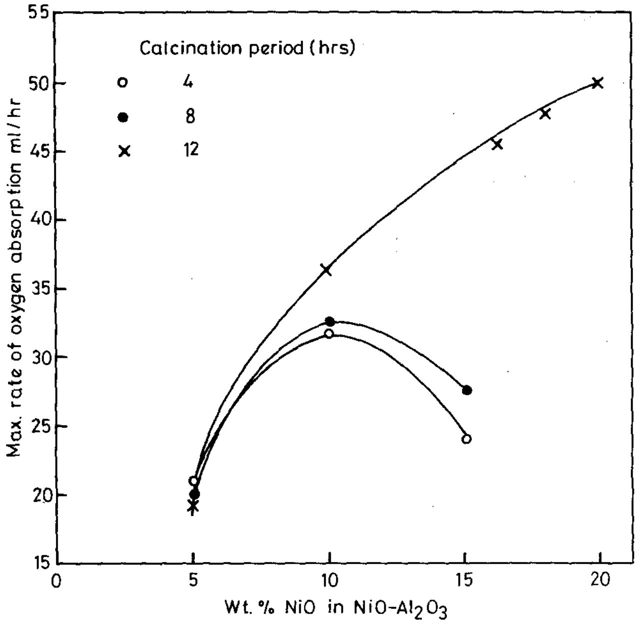

FIG. 1. Rates of oxygen absorption as a function of wt% NiO for Tetralin at 65°C for a catalyst ratio of 0.25 g/ml with different calcination periods. The value for 1 ml of O_2 is 4.46×10^{-5} mole of O_2.

tion as a function of weight percentage NiO for different calcination periods at 450°C. For the cases of 4- and 8-hr calcination, the rates declined after an NiO concentration of 10 wt%; however, for the 12-hr calcination period, the rates continuously increased with increase in concentration of NiO.

The color of the catalysts varied from green, grayish green, to black with increases in the weight percentage of the NiO in the catalyst samples as well as with the duration of calcination. The samples of 12-hr calcination were black. X-Ray analysis of the black, gray, and green forms of NiO showed a greater broadening of the diffraction lines of the black form over those of the gray and green forms. The green form is the stoichiometric oxide and the blackening indicates the presence of excess oxygen in the lattice of NiO; this could account for the increase in activity (*9–11*). For the case of 4- and 8-hr calcination, there appeared to be occluded oxides of nitrogen in the impregnated samples thus accounting for the decrease in rate after the concentration of NiO in the catalyst samples reached 10 wt%. The increase in rate in all the samples calcined for 12 hr may be due to the removal of occluded gas by prolonged heating (*12*). Since NiO-20-450-12 gave the maximum rate (Fig. 1), further experiments were performed with this catalyst. The surface areas of the catalysts prepared using a 12-hr calcination period for 5, 10, 15, and 20 wt% NiO were 96, 97.5, 87.6, and 77.9 m^2 g^{-1}, respectively.

Figure 2 compares the rates of oxygen absorption versus catalyst ratio for 20 wt% NiO/Al_2O_3 and pure NiO. The rate with 20 wt% NiO/Al_2O_3 catalyst is higher than that with pure NiO. The rate increased with increased catalyst ratios and for NiO-20-450-12 reached a maximum at 0.28 g/ml. The decrease in rate after the maximum was also observed by Mukherjee and Graydon (*2*), who studied Tetralin oxidation in the presence of MnO_2.

The influence of hydrocarbon concentration on the rate of oxidation was studied with mixtures of Tetralin and monochlorobenzene. A catalyst ratio of 0.10 g/ml. was chosen since in this region of catalyst ratios, the limiting rate of oxidation was not attained. The order with respect to hydrocarbon concentration was 1.0 (Fig. 3). A plot of rate of oxygen consumption versus hydrocarbon concentration at a catalyst ratio, where the limiting oxidation is reached, is also given in Fig. 3. An order of 2.0 was found with respect to hydrocarbon concentration. In order to improve confidence in the reported orders, runs were also made at catalyst ratios near levels at which the kinetic regime was considered unstable. Included in Fig. 3 is a plot of rate against hydrocarbon concentration for a catalyst ratio of 0.2 g/ml. The apparent order of 1.3 possibly results from a transition between these more normal responses. A log-log plot of rate of oxygen absorption versus catalyst ratio is given in Fig. 4. An order of 0.5 was found with respect to the catalyst amount considering all the points at the catalyst ratios below 0.2 g/ml. The apparent activation energy for the overall oxidation, determined from plots of log rate versus $1/T$ for the range 318–358 K, was 11.8 kcal mol^{-1}.

Another important reaction characteristic, that of product distribution, was also obtained. The products were analyzed using a Perkin–Elmer, Model 137 ir spectrophotometer. The distribution as a function of catalyst weight is presented in Table 1. The molar concentrations of alcohol and ketone produced were the same.

The reaction mechanism will now be discussed. Our results have convincingly showed that: (a) The apparent orders of the reaction with respect to catalyst ratio and the hydrocarbon concentration are 0.5 and 1.0, respectively, and (b) there is a critical weight of the catalysts above which the rate of oxidation drops sharply and this limiting rate of oxidation is proportional to the square of hydrocarbon concentration. To explain the kinetics of cyclohexene oxidation, a general mechanism was proposed by Neuberg *et al* (*13*) and used by Srivastava and co-workers (*3*, *4*, *7*) to explain the kinetics of cumene oxidation. Their scheme is adapted below:

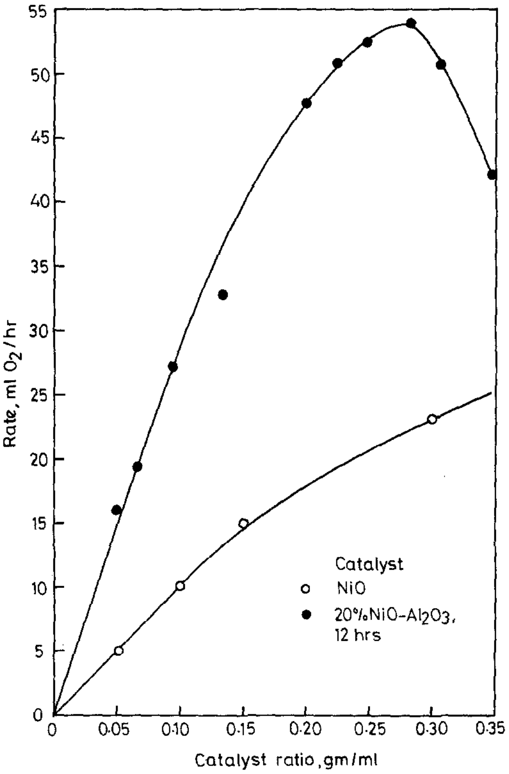

FIG. 2. Rates of oxygen absorption versus catalyst ratio for Tetralin at 65 °C for pure NiO and 20% NiO supported on alumina calcined for 12 hr. The value for 1 ml of O_2 is 4.46×10^{-5} mole of O_2.

Initiation:

$$\mathrm{ROOH+M} \overset{k_1}{\rightleftharpoons} \mathrm{(ROOH\ldots M)}, \quad (1)$$

$$\mathrm{(ROOH\ldots M)} \xrightarrow{k_2} \mathrm{RO^{\cdot}+{}^{\cdot}OH\ldots M}, \quad (2)$$

$$\mathrm{ROOH+OH\ldots M} \xrightarrow{k_3} \mathrm{RO_2^{\cdot}+H_2O+M}, \quad (3)$$

$$\mathrm{RO^{\cdot}+RH} \xrightarrow{k_4} \mathrm{ROH+\dot{R}}. \quad (4)$$

Propagation:

$$\mathrm{\dot{R}+O_2} \xrightarrow{k_5} \mathrm{RO_2^{\cdot}}, \quad (5)$$

$$\mathrm{RO_2^{\cdot}+RH} \xrightarrow{k_6} \mathrm{ROOH+R^{\cdot}}. \quad (6)$$

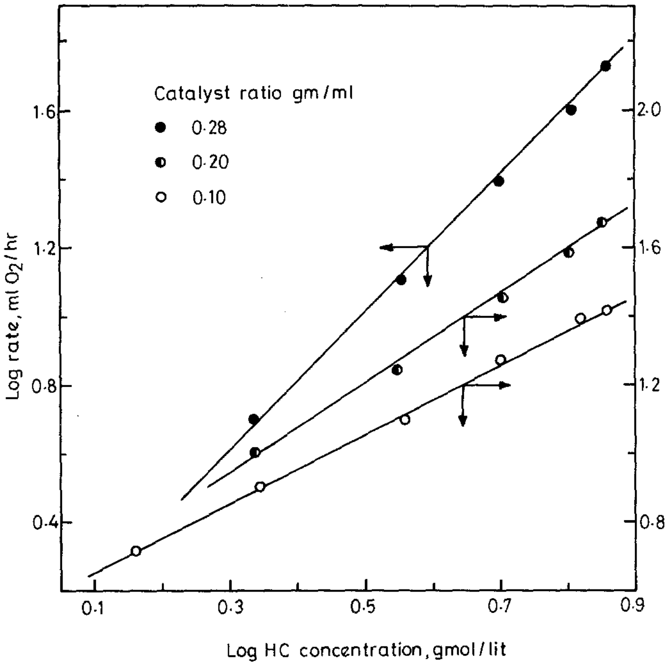

FIG. 3. Rate dependence with respect to Tetralin concentration for 0.10, 0.20, and 0.28 g/ml catalyst ratios at 65°C. The value for 1 ml of O_2 is 4.96×10^{-5} mole of O_2.

Termination:

$$R\dot{O}_2 + R\dot{O}_2 \xrightarrow{k_7} \text{inactive products} + O_2, \quad (7)$$

$$R\dot{O}_2 + M \overset{k_8}{\rightleftharpoons} (R\dot{O}_2 \ldots M), \quad (8)$$

$$R\dot{O}_2 + (R\dot{O}_2 \ldots M) \xrightarrow{k_9} \text{inactive products}. \quad (9)$$

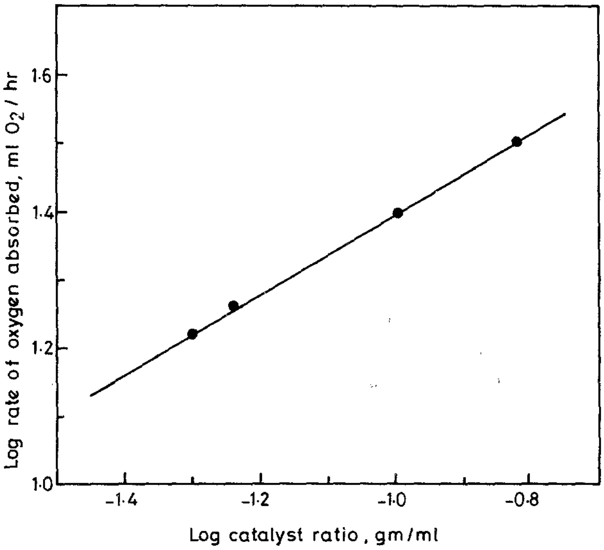

FIG. 4. Rate dependence with respect to catalyst ratio at 65°C.

TABLE 1

Distribution of Products of Tetralin Oxidation[a]

Catalyst (g)	Product distribution (mole % total oxidized product)		
	Hydro-peroxide	Tetralyl alcohol	Tetralone
1.00	87	7.4	5.6
2.50	80	8.2	11.8
5.00	57.6	21.2	21.2
10.00	44.4	26.0	29.6
15.00	13.3	45.5	41.2

[a] Temperature, 65°C; duration of run, 30 min; volume of Tetralin, 50 ml.

If the termination rate of peroxy radicals on the catalyst surface (Eqs. (8) and (9)) is negligible compared with the biradical termination rate (Eq. (7)), then the rate of oxidation will be given by

$$-\frac{d[O_2]}{dt} = k_6\left(\frac{R_i}{2k_7}\right)^{\frac{1}{2}}[RH]. \qquad (10)$$

It may be assumed that R_i is proportional to the amount of catalyst. The experimental orders agree well with the derived rate expression.

If it is assumed that at the limiting rate of oxidation the rate of formation of hydroperoxide through Reaction (6) becomes equal to the rate of decomposition, then the limiting rate of oxidation is given as

$$-\frac{d[O_2]}{dt} = \frac{\alpha k_6^2[RH]^2}{2k_7 + k_8k_9[M]}, \qquad (11)$$

where α is the fraction of hydroperoxide yielding free radicals. This derivation is similar to one proposed by Neuberg *et al.* (*13*). The reaction order of this expression is consistent with the experimental results of the present work. Therefore, it can be concluded that the catalytic activity of supported NiO is mainly due to its capability of decomposing hydroperoxide in the chain initiating radicals. The similarity in the kinetic behavior of cyclohexene and Tetralin may be due to formation of resonance-stabilized radical species ($\dot{R}$) in each of these cases.

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K. M. Prasad
R. Athappan
R. D. Srivastava[1]

Department of Chemical Engineering
Indian Institute of Technology
Kanpur-208016, India

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[1] Author to whom correspondence should be sent.