KINETICS OF HYDROGENATION OF CYCLOHEXENE ON A SULFIDED Ni-W/Al$_2$O$_3$ CATALYST

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Kinetics of hydrogenation of cyclohexene on a sulfided Ni-W/Al$_2$O$_3$ catalyst has been studied with a flow microreactor under normal atmospheric pressure. The reaction rate is found to be zero and first order with respect to cyclohexene and hydrogen partial pressures, respectively, in the temperature range 250-350 °C.

Кинетика гидрирования циклогексена на сульфидном катализаторе Ni — W/Al$_2$O$_3$ исследовалась в проточном микрореакторе при атмосферном давлении. Скорость реакции имеет нулевой и первый порядок по парциальному давлению циклогексена и водорода, соответственно, в интервале температур 250—350 °C.

INTRODUCTION

Hydrogenation of cyclic olefins and aromatic hydrocarbons are industrially important reactions and are efficiently done on sulfided hydroprocessing catalysts like Ni—W/Al$_2$O$_3$ [1, 2]. Although the kinetics and mechanism of hydrogenation of olefins have extensively been studied on metallic catalysts [3], similar studies on sulfided catalysts, especially under normal atmospheric pressure, are scarce. The multifunctional nature of these catalysts leads to difficulties in understanding the mechanism of the hydroprocessing reactions. Recent studies indicate that hydrogenation reactions occur on sites which are different from the HDS or HDN sites [4]. Therefore, this simple reaction was studied in order to throw some light on the mechanism of the hydrogenation reactions.

EXPERIMENTAL

An all-glass flow microreactor system (operable at one atmosphere pressure), connected with a gas chromatograph was used to study the reaction. A six-way sampling valve interfaced with the reactor and the GC column allowed sam-

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pling of the effluent gas and analysis with the help of a 2 m stainless steel column packed with 10% SE-52 on Chromosorb wax. A thermal conductivity detector was used for this purpose.

High purity hydrogen (99.9%), further treated with Pd 'Deoxo' catalyst and zeolite molecular sieve (4A), was passed through two saturators containing pure cyclohexene maintained at appropriate temperature to achieve the desired partial pressure. Nitrogen was used as diluent whenever necessary.

A Harshaw Ni-W/Al_2O_3 catalyst (W: 10%, Ni: 6%, S.A.: 230 m^2g^{-1}) was used for the reaction. Sulfiding of the oxide precursor of the catalyst was done by passing hydrogen saturated at 25 °C with carbon disulfide through the catalyst in the following sequence. The gas mixture was passed for 15 min at 100 °C and then the catalyst was heated up to 400 °C (at 4 °C per min) while still in contact with the sulfiding gas mixture. Sulfiding was continued at 400 °C for 2 h, whereafter the temperature was brought down to the reaction temperature and CS_2/H_2 flow gas stopped. The catalyst was flushed at the reaction temperature by H_2 until no CS_2 could be detected in the effluent gas. At this stage the catalyst was ready to be contacted with the reaction gas mixture.

A fresh catalyst was used for each temperature and the useful data were collected under steady state and in absence of any external and internal diffusion effects. Cyclohexane was the predominant product formed. Traces of methylcyclopentane were detected only at the very high conversion level.

RESULTS AND DISCUSSION

The rates were calculated directly from the equation:

$$r = x/(W/F)$$

where r = rate; x = fractional conversion; W = mass of catalyst; and F = total gas flow. A plot of x vs. (W/F) showed a linear correlation up to a conversion of 20% at all the temperatures studied. For the kinetic experiments, the conversion was kept well within this level in order to be able to apply the ,,differential reactor'' conditions for the treatment of the rate data. The effect of partial pressures of cyclohexene (p_c) and hydrogen (p_H) on the rate is shown in Figs. 1 and 2, respectively, as a function of temperature. The rate was found to be zero and first order with respect to p_c and p_H, respectively.

Of significance is the fact that the straight lines in Fig. 2 do not pass through the origin when the rate is extrapolated to zero partial pressure of hydrogen. This will be discussed later. From all the facts noted above, the following rate equation is proposed for the process:

$$r = k_0 + k_1 p_c^0 p_H^1,$$

where k_0 and k_1 are constants for a particular temperature. Since $p_c = 1$, the final form of the rate equation becomes:
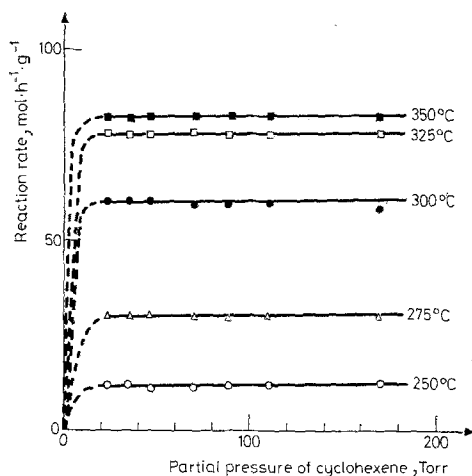
$$r = k_0 + k_1 p_H^1,$$

Fig. 1. Rate of hydrogenation of cyclohexene as a function of p_c at various temperatures. $p_H = 590.0$ Torr, total $p = 760.0$ Torr, $W = 0.2$ g, $F = 80.0$ ml/min
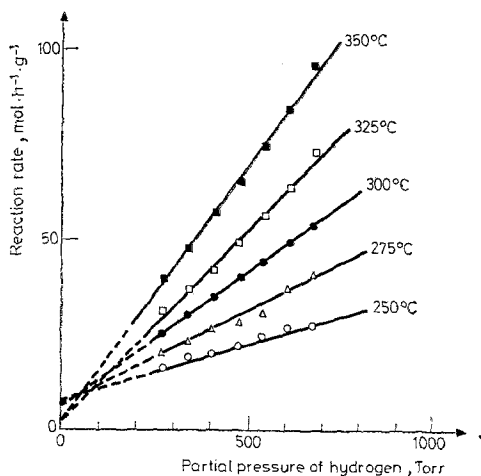

Fig. 2. Rate of hydrogenation of cyclohexene as a function of p_H at various temperatures. $p_c = 84.0$ Torr, total $p = 760.0$ Torr, $W = 0.2$ g, $F = 80.0$ ml/min

The constant k_0 is indicative of some ,,residual'' activity of the catalyst even in the absence of hydrogen in the reaction gas mixture. This was verified to be true by passing a mixture of cyclohexene and nitrogen (instead of hydrogen) over a freshly sulfided catalyst when some hydrogenation was noted.

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The apparent energy of activation of the process was found to be 35.5 kJ/mol. In contrast to our findings, a first order rate with respect to p_c and a much higher energy of activation were reported by Voorhoeve and Stuiver [5]. However, they performed the reaction under high pressure (48 atm) and always in the presence of CS_2 which did strongly adsorb on the catalyst surface. However, low energies of activation comparable to what we found, have widely been reported for the hydrogenation of olefins on metallic catalysts [3].

Recent MES and EXAFS studies [6] on sulfided catalysts have revealed that small one-dimensional crystallites (10—20 Å) of WS_2 remain in highly dispersed condition on alumina surface. The coordinatively unsaturated sites (W^{3+} ions) on the edges of these crystallites are identified as the active sites for hydrogenation of cyclohexene [5]. Wright et al. [7] have reported that on WS_2 catalysts, hydrogen adsorbs dissociatively on the exposed sulfide ions. They also speculated that part of hydrogen adsorbs on the exposed W^{3+} ions and then migrates to the remote S ions by some 'spillover' mechanism. Based on these observations, we are tempted to believe that strongly adsorbed cyclohexene (as indicated by the zero order dependence of rate on p_c) reacts with dissociatively adsorbed hydrogen which remain as SH groups on the catalyst surface. The low energy of activation, then, might suggest that the rate is probably controlled by some kind of surface migration or spillover of hydrogen akin to the type envisaged by Wright et al. [7].

The 'residual' activity, as indicated by the positive values of k_0, can be rationalized by the fact that the surface of a freshly sulfided catalyst remains filled with SH groups which are formed during the sulfiding step. These SH groups, as indicated earlier, take part in the reaction.

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