KINETICS OF HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL OVER COPPER CHROMITE CATALYST AND OPTIMUM REGENERATION PROCEDURES

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الخلاصــة :

تبحث هذه الدراسة في ميكانيكية التخميد لَحِـفَّاز النحاس الكرومي والمستخدمة في الهدرجة الانتقائية للفروفرال إلى كحول الفروفريل ، كما وتبحث أيضاً في طرق إعادة هذا الحـفَّاز .

وجدنا أن الجزئيات الكبيرة الناتجة عن التفاعلات الجانبية للفروفرال والمترسبة على أسطح الحوافز تعمل على تعطيل هذه الحفازات . كما وجدنا أن أفضل طريقة لتخميد هذه الحفازات يكون بتجفيفها عند درجة حرارة ١١٠°م لمدة خمسة أيام ، ثم تسخينها عند درجة حرارة ٣٢٥°م لمدة (١٨) ساعة ، ويتبع ذلك إعادة تذويبها بـ (سيكلوهكسانول) لمدة أربع ساعات . أظهرت الحفازات الـمُعالجة بالتبخير كفاءة قدرها ٧٨٪ مقارنة بـ ٧٩ر٥٪ للحفازات الجديدة .

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ABSTRACT

The deactivation mechanism of a copper chromite catalyst, used in selective hydrogenation of furfural to furfuryl alcohol, was investigated and the methods to regenerate it were searched. The catalyst deactivation mechanisms was found to be due to the fouling resin macromolecules, formed by side reactions of furfural on the catalyst surface. The optimum catalyst regeneration was by one drying at 110°C for 5 days, heating at 325°C for 18 hours followed by refluxing in cyclohexanol for 4 hours. The conversion to furfuryl alcohol by the regenerated sample in vapor phase hydrogenation was 78 per cent, compared to 79.5 per cent for the fresh catalyst.

The following rate equation for hydrogenation reaction under investigation was derived from experimental results:

$$\frac{\mathrm{d}X_A}{\mathrm{d}t} = 38.37(1 - X_A)^{3.8}.$$

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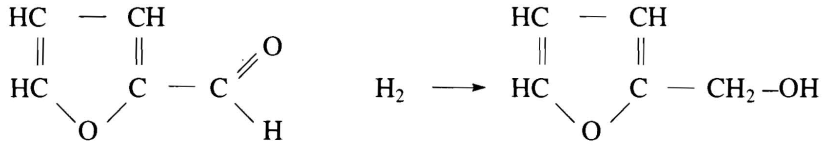
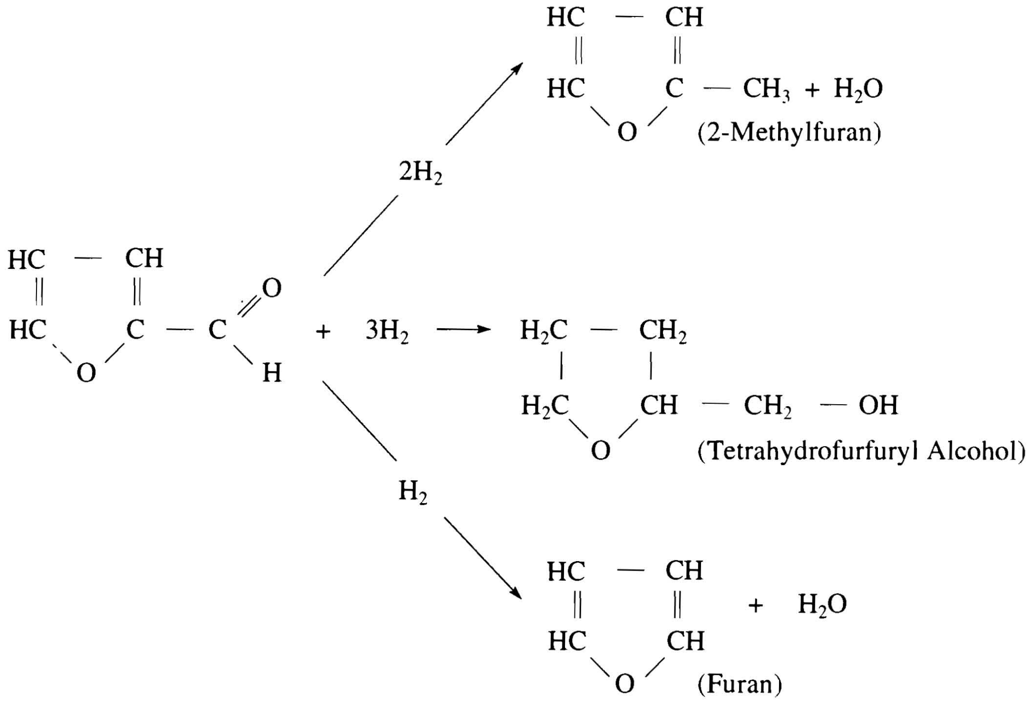
INTRODUCTION

Furfuryl alcohol is produced from furfural* by liquid or vapor phase selective hydrogenation techniques by selective hydrogenation of the aldehyde group as given below [1]:



(Furfural) (Furfuryl Alcohol)

Depending on the reaction conditions, other side reactions may take place with further hydrogen uptake [2]. These would yield tetrahydrofurfuryl alcohol, 2-methylfuran, furan, and so on.



(2-Methylfuran)

(Tetrahydrofurfuryl Alcohol)

(Furan)

The use of an adequate selective catalyst, such as "Adkins" type of copper chromium oxide would selectively, catalyze the furfuryl alcohol production [3, 4]. However, this specific "Adkins" type catalyst deactivates very quickly and brings an economical load on the process.

Studies showed that addition of barium, calcium, or magnesium stabilizes the catalyst against reduction and consequent deactivation. This apparently enhances its activity by modifying the relative rates of competitive hydrogenation reactions [5, 6].

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* Furfural is a chemical used as solvent, especially in the extraction of lubricating oils in the petroleum refining industry.

The catalytic hydrogenation of furfural over copper chromite was studied earlier [7] and it was concluded that the source of selectivity is the presence of copper. In a different study by Soviet scientists, the positive effects of additions of various elements, like Cu, Cr, on the activity of a nickel catalyst supported on clay were observed and their use as additive is recommended for the hydrogenation of furfural in water [8].

It was the aim of this work to find an effective procedure for the regeneration of the catalyst used in the industry for catalyzing the hydrogenation of furfural to furfuryl alcohol selectively, along with finding a rate equation.

EXPERIMENTAL

The physical properties of the fresh and industrially used catalysts were examined. During these studies about 100 different regeneration processes were tried, and the catalyst samples whose physical properties resemble the properties of the fresh catalyst were tested for their activity in a vapor phase hydrogenation system.

Used catalyst samples were first dried at 110°C for 5 hours. A 100 gram sample of dried used catalyst was washed with solvents such as nitrobenzene, benzene, cyclohexanol, methanol, diethylene glycol, ethyl alcohol, toluene, acetone, different ethers, *etc*. The sample to washing liquid weight ratio was 1 to 5. The contents were then filtered and the catalyst was dried, followed by refluxing operations. The ratio of refluxing liquid to catalyst was 2.5 to 1.0 by weight and the refluxing time was 4 hours.

To assess the effect of heating, 50 grams of all the initially treated samples were heated just below the limiting value of 350°C, which is the decomposition temperature of copper in catalyst, for overnight time periods in oxidizing atmosphere. The highest yield was obtained from the sample which was dried at 110°C for five days and heated at 320°C for 18 hours and further refluxed in cyclohexanol for 4 hours.

Analysis of the Samples

A mercury porosimeter (Aminco Digital 30 000 psi Mercury Porosimeter) was used to analyze the pore structures of the samples. The standard method based on the physical adsorption of a gas (nitrogen) on solid surface was used for surface area determination.

The catalyst samples were tested for their activity in catalytic hydrogenation of furfural to furfuryl alcohol selectively, in a tubular reactor which had 25 cm length and 10 cm^3 volume. The products were analyzed in a Varian Aerograph Model 940-01 F.I.D. gas chromatograph connected to a recorder. The column used for analysis was a Marlophen-87 type. The schematic representation of the system is given in Figure 1.

DISCUSSION OF RESULTS

The porosity and pore-volume distributions of fresh and used catalysts samples were studied and their penetration and pore-volume distribution curves are shown in Figures 2 and 3, respectively. The data from these experiments are given in Table 1. Further the surface areas of the fresh and used catalyst were found to be 54.01 m^2/g and 68.09 m^2/g respectively. These show that the average micropore size of the used catalyst is smaller than that of the fresh while the average macropore size is larger than the fresh catalyst. Although the total porosity of the used catalyst is larger, the microporosity is smaller but macroporosity is greater than that of the fresh catalyst. These data show that some of the micropores of the fresh catalyst are plugged while some of them become narrower and new macropores are formed on the external surface of the catalyst. This increases the surface area of the catalyst, but at the same time deactivates the catalyst.

These results can be explained by the fouling action of some impurities or products on the catalyst surface which could plug the pores or divide them to smaller pores, thus resulting in low microporosity value and smaller average micropore radius. At the same time the fouling components are deposited on the external surface of the catalyst creating new macropores and hence increasing the surface area of the catalyst.

The physical properties of the samples which resembled the fresh catalyst, were tested for their activity in vapor phase hydrogenation of furfural to furfuryl alcohol. The products obtained from the experiments were analyzed and the yields are given in Table 2.

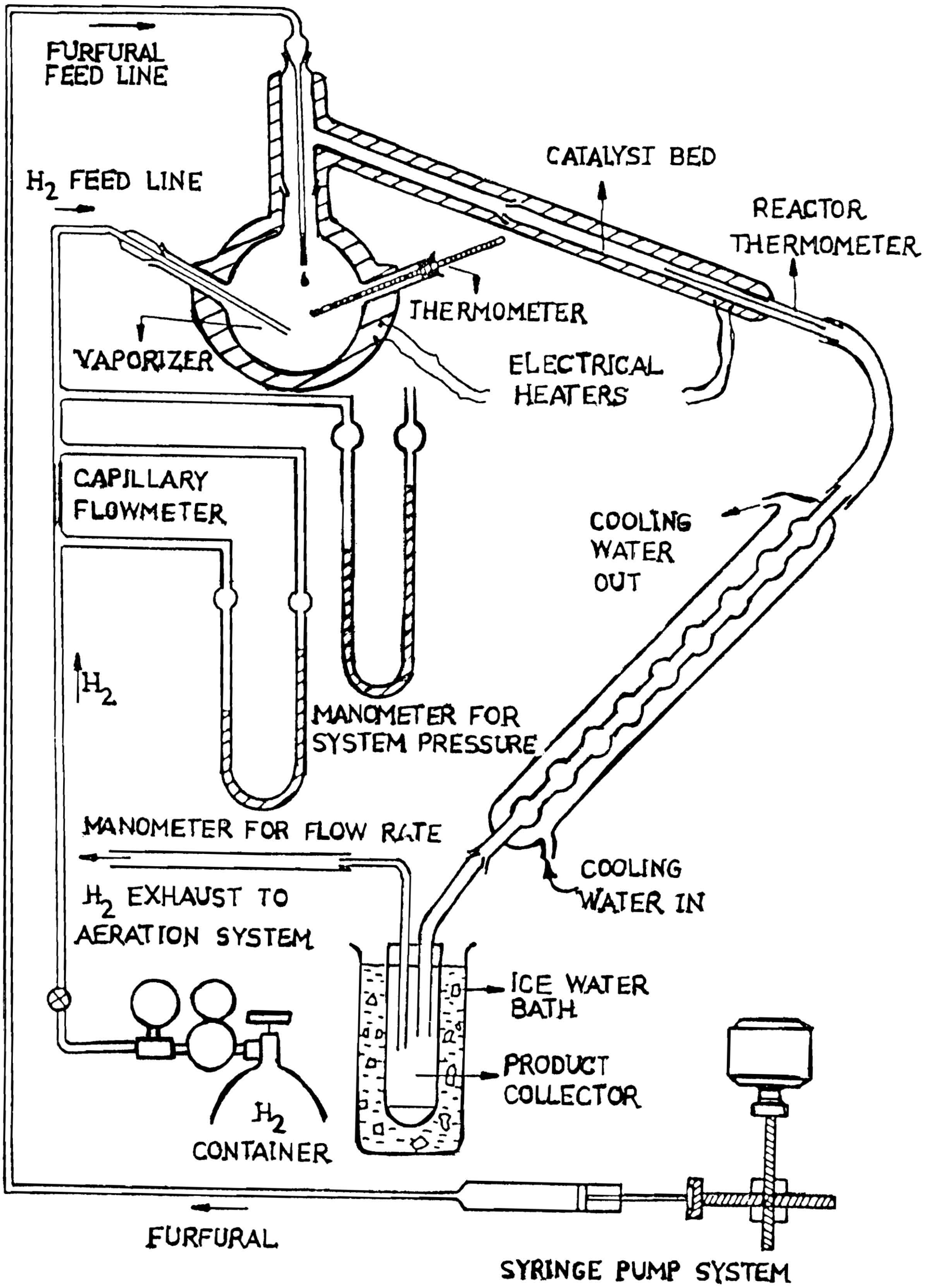

Figure 1. Vapor-phase Hydrogenation Setup.

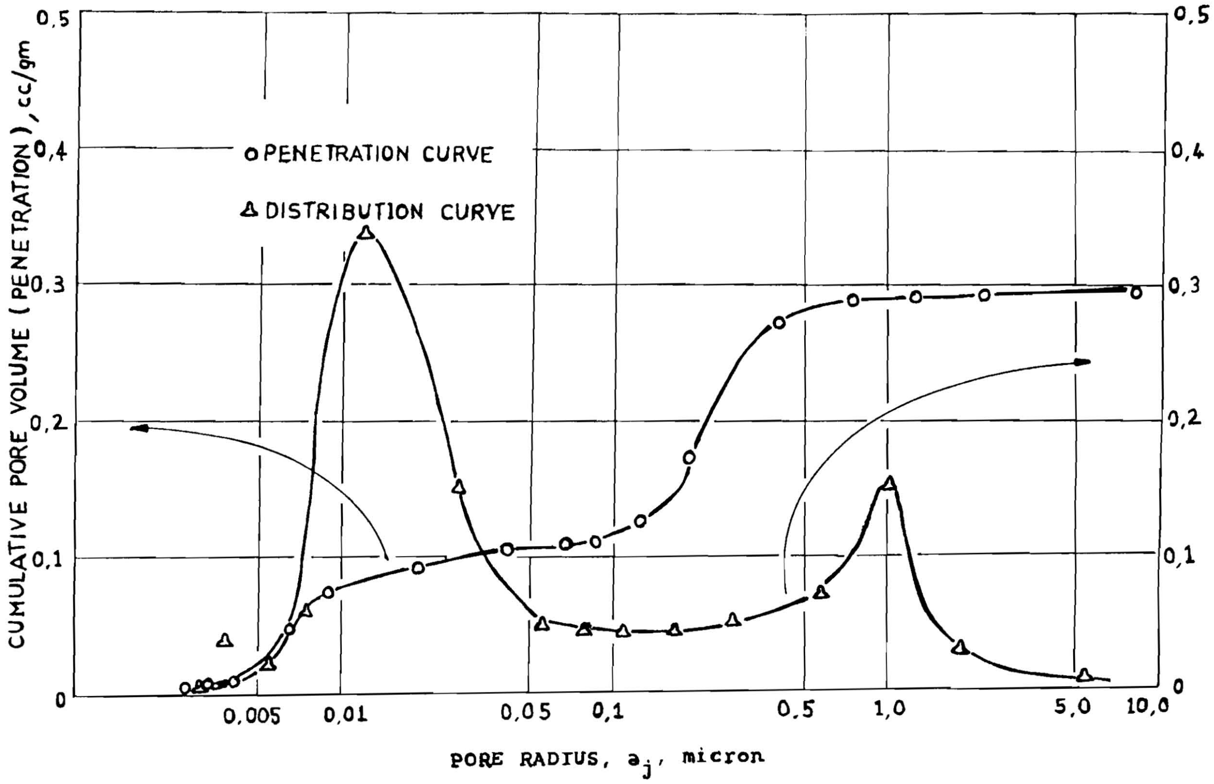

Figure 2. Pore-Volume Distribution of Fresh Catalyst.

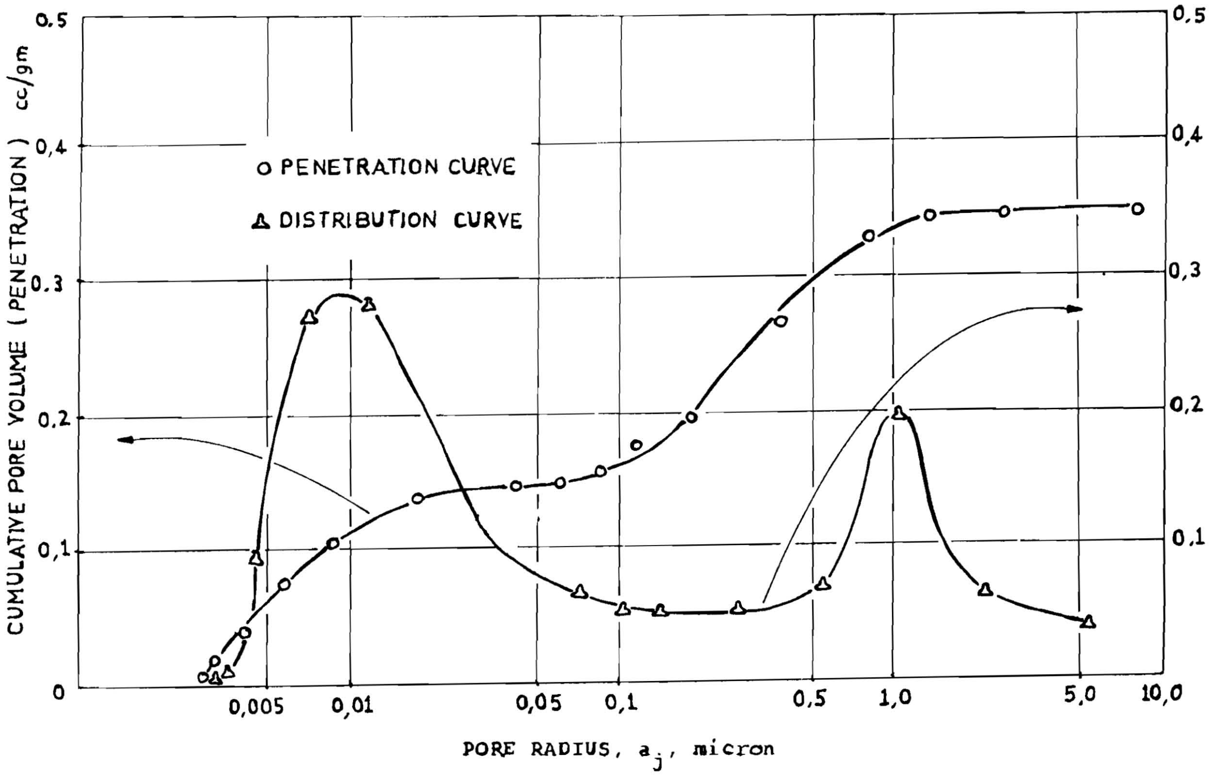

Figure 3. Pore-Volume Distribution of Untreated Used Catalyst.

It was observed that the most active regenerated catalyst is the sample dried at 100°C for five days and heated at 325°C for 18 hours, without solvent wash. On the other hand, catalyst samples washed with solvents and heated for the same period of time gave less yield. This proves the fouling type of deactivation process to be effective and that solvents sometimes fix the fouling component on the catalyst surface doing a reverse action and this makes the regeneration process more difficult. Since the copper in the catalyst structure can be affected above 350°C, higher temperatures cannot be applied to the catalyst.

The effect of cyclohexanol refluxing on activity can be seen from the yield increase of the fresh catalyst itself. The same procedure when applied to the catalyst gives a good yield just below the value reached with the most effectively regenerated catalyst.

Comparing Figures 4 and 5 with the pore-volume distributions of the untreated fresh and untreated used catalyst samples, it can be deduced that cyclohexanol activates the samples by removing the condensation-like adsorbed species from the catalyst surface. The effect of diethylene glycol reflux is very much like the effect of cyclohexanol reflux, because the two chemicals have similar physical and chemical properties.

Table 1. Porosimetric Results for Untreated Virgin and Used Catalysts.

Catalyst	Fresh	Used
Apparent density gm/cc	2.0213	1.8395
Micro porosity	0.4038	0.3862
Macro porosity	0.1905	0.2398
Total porosity	0.5943	0.6260
Average micropore radius (micron)	0.0290	0.0250
Average macropore radius (micron)	0.9600	1.5890
Surface area m^2/g	54.01	68.09

Table 2. Furfuryl Alcohol Yields for Successful Catalyst Samples.

Catalyst Sample	% Yield
Untreated used catalyst	2
Untreated fresh catalyst	40
Fresh catalyst refluxed in cyclohexanol 4 hours	57
Used catalyst dried at 110°C for 5 days and heated at 3250°C for 18 hours.	33
Used catalyst refluxed in cyclohexanol for 4 hours	21
Used catalyst refluxed in diethylene glycol for 4 hours	21
Used catalyst washed with water at 40°C, dried, and heated at 325°C for 26 hours	12
Used catalyst washed with 0.5 N NaOH solution and heated at 300°C for 22 hours	10
Used catalyst washed with toluene and heated at 300°C for 18 hours.	10

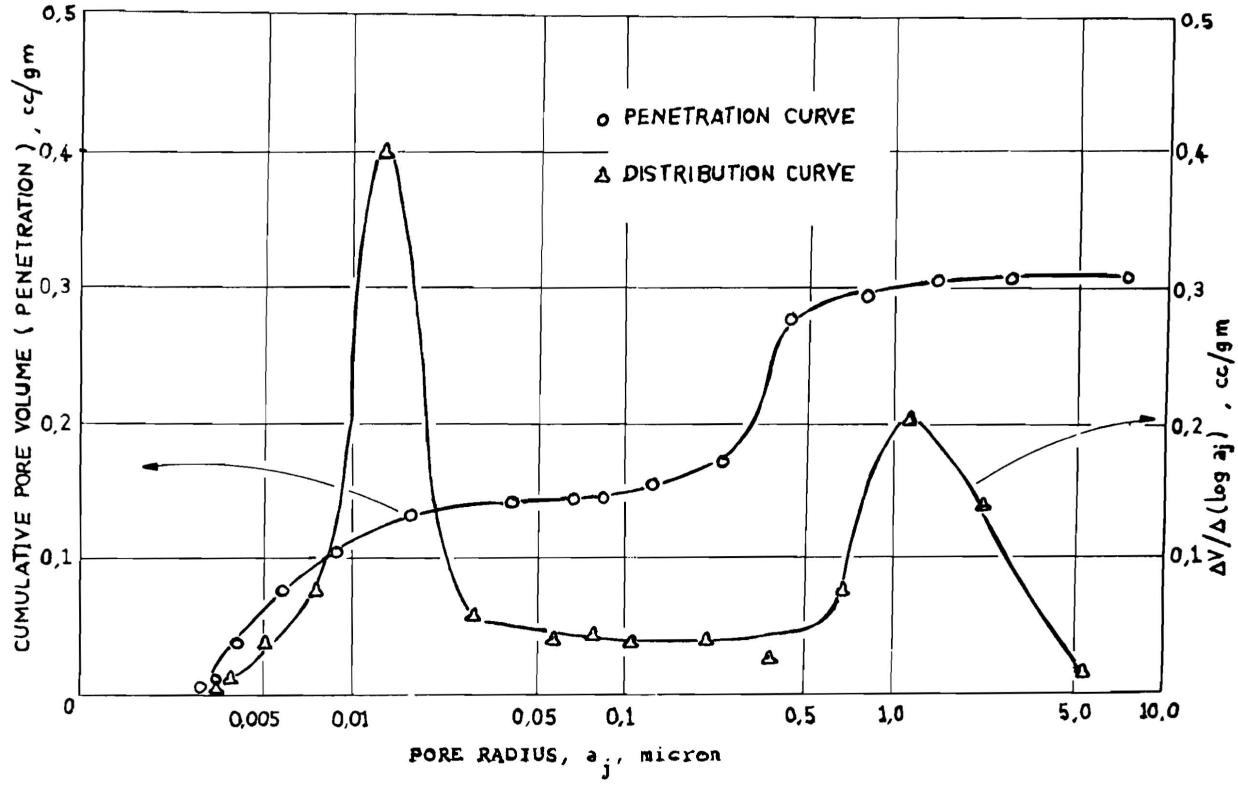

Figure 4. Pore-Volume Distribution of Fresh Catalyst Refluxed in Cyclohexanol for Four hours.

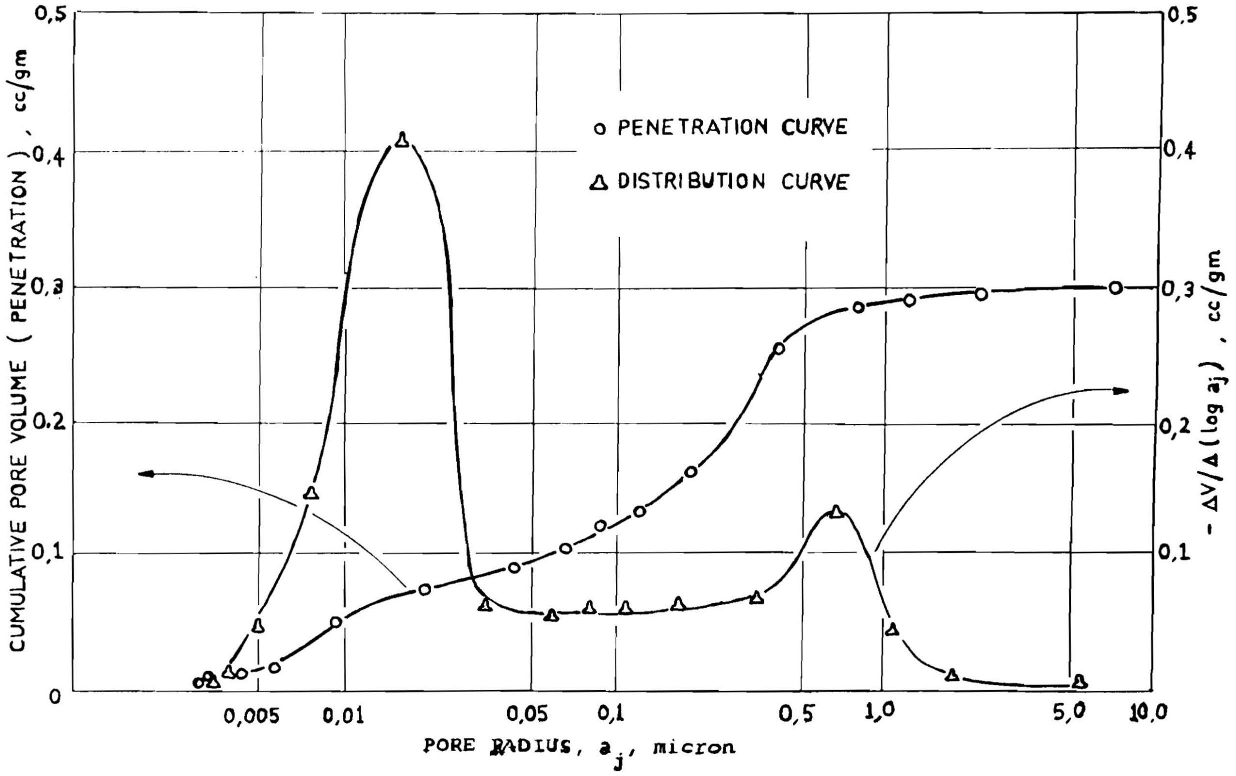

Figure 5. Pore-Volume Distribution of Used Catalyst Refluxed in Cyclohexanol Four Hours.

Kinetic Studies with the Most Active Regenerated Catalyst

For this purpose, fresh catalyst, fresh catalyst refluxed in cyclohexanol, and double treated (first dried at 110°C for five days, then heated at 325°C for 18 hours and refluxed in cyclohexanol for four hours) used catalyst samples were tested for their effectiveness in vapor-phase hydrogenation. The results given in Table 3 show that double treated used catalyst is very effectively regenerated and can be used alone for kinetic studies.

Table 3. Comparative Studies of Conversions.

Catalyst Type	% Conversion	% Yield
Untreated fresh catalyst	54.5	40
Fresh catalyst refluxed in cyclohexanol	79.5	57
Double treated used catalyst	78.0	21

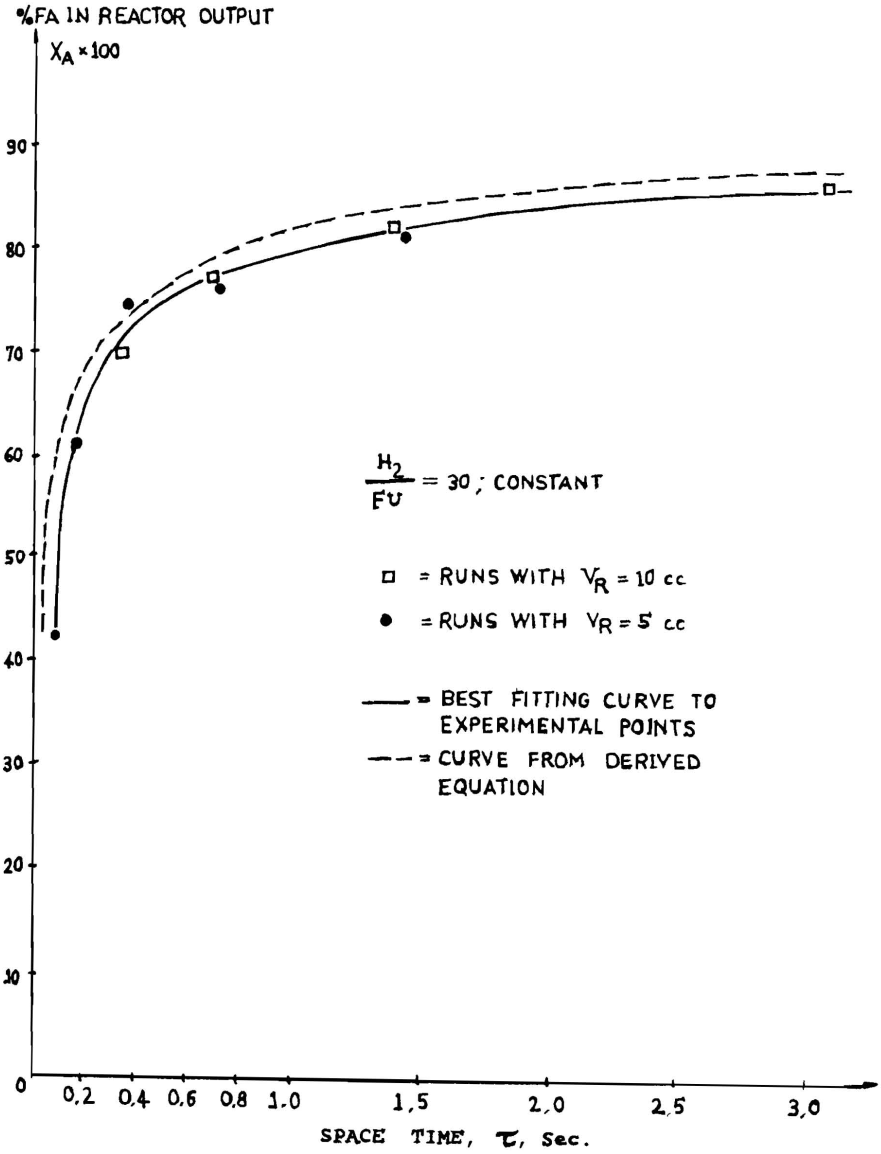

Figure 6. Conversion versus Space Time.

Effect of Space Times

Conversion values obtained for different space times are plotted in Figure 6. The conversion increases rapidly for space time values up to 0.5 second, after which it slows down going toward an asymptotic value.

The reactor was homogeneously heated, and the catalyst was carefully sieved and filled in it, so no channeling was observed and results were not deviating. Under these conditions the assumed rate equation for plug flow is as follows:

$$C^{o}_{Fu}\frac{dX_A}{dt} = kC^{o\,b}_{Fu}(1 - X_A)^b\left(C^{o}_{H_2} - C^{o}_{Fu}X_A\right)^a$$

$$C^{o}_{Fu}\frac{dX_A}{dt} = kC^{o\,b}_{Fu}(1 - X_A)^b\left(C^{o\,a}_{H_2}(1 - MX_A)\right)^a$$ where $M = 1/30$ for these set of experiments.

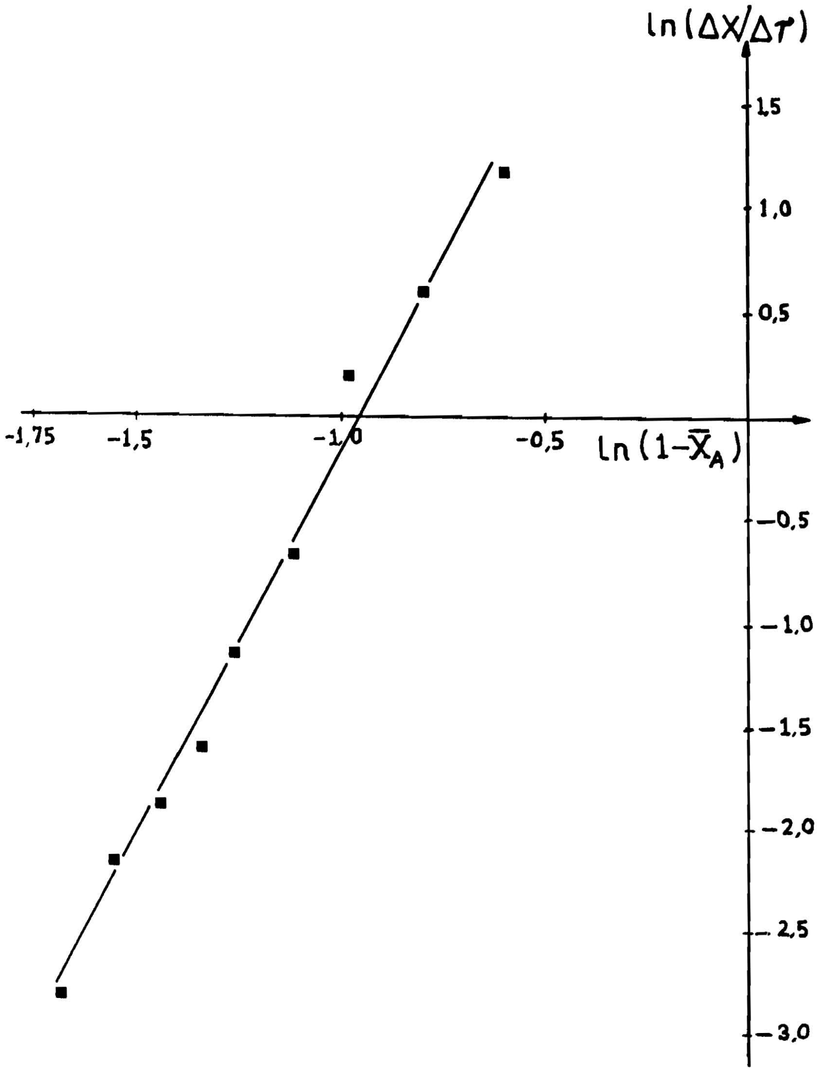

Figure 7. ln $(1 - \bar{X}_A)$ Versus ln $(\Delta X/\Delta\tau)$.

Since the value of M is small, the term $(1-MX_A)^a$ can be assumed to be very close to "one" and can also be neglected. Then:

$C_{Fu}\dfrac{dX_A}{dt} = kC_{Fu}^{o\;b}\, C_{H_2}^{o\;a}(1 - X_A)^b$. This can further be rearranged as:

$\dfrac{dX_A}{dt} = C'(1 - X_A)^b$ where $C' = kC_{Fu}^{o\;(b-1)}C_{H_2}^{o\;a}$. Taking the logarithms of both sides of this equation,

$$\ln\frac{dX_A}{dt} = \ln C' + b\ln(1 - X_A).$$

This equation can be considered as a straight line and when ln $(\Delta X_A/\Delta t)$ is plotted against ln $(1-X_A)$, the straight line given in Figure 7 is obtained proving our original assumption with the following slope and intercept values: ln $C' = 3.647$ and $b = 3.8$. Furthermore rate equation becomes:

$$\frac{dX_A}{dt} = 38.37(1 - X_A)^{3.8}.$$

Upon integration: $(1-X_A)^{-2.8} = 107.44\,t$ can be obtained.

Very good fit of the curve from the previous equation was obtained with the experimental values and this proved that the rate equation model is very appropriate and the C' term, accepted to be constant, is constant in fact.

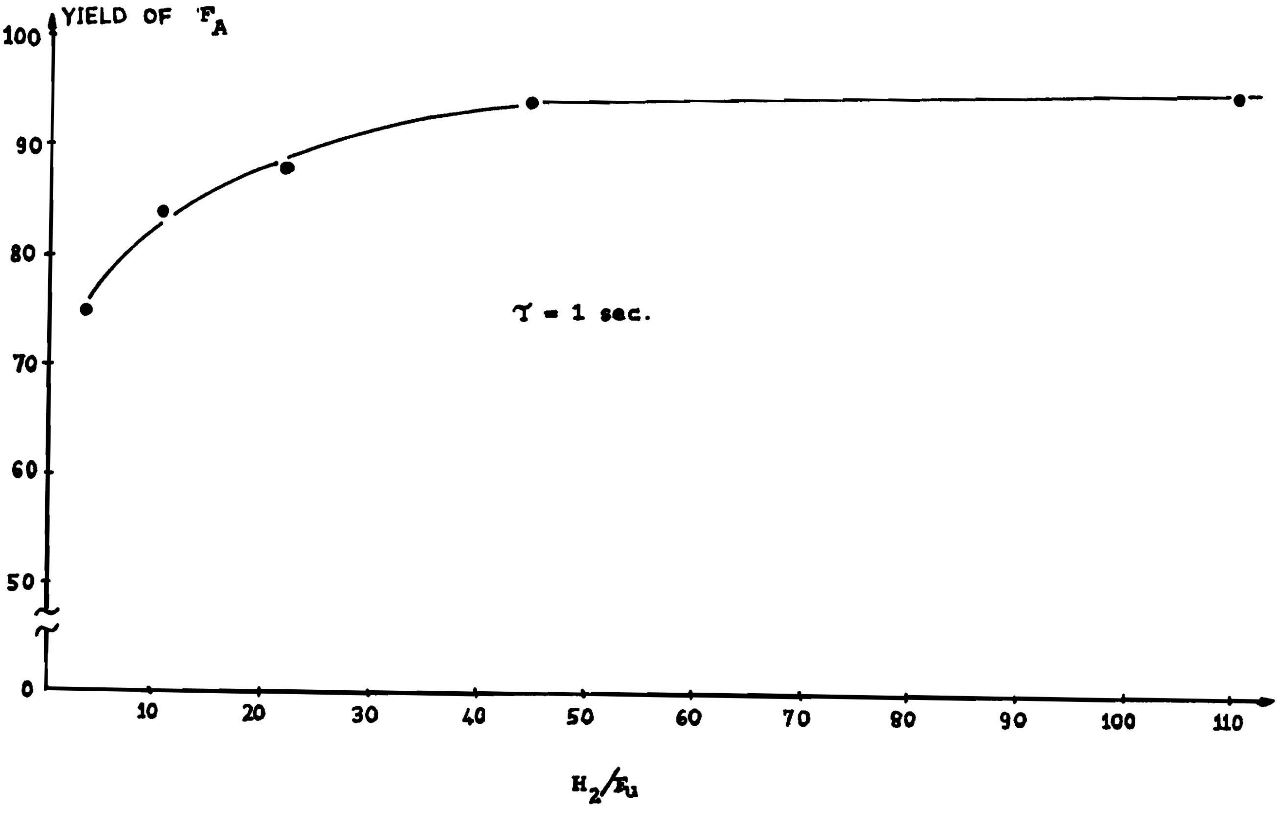

Figure 8. Effect of Hydrogen to Furfural Mole Ratio on Conversion.

Effect of Hydrogen-to-Furfural Mole Ratio

In this set of experiments space time was kept constant at a value of 1 second by fixing the total volumetric flow rate at 10 cm^3/s. for the reactor. The hydrogen to furfural mole ratio was varied by changing their initial concentrations. The resulting curve from this set of experiments is given in Figure 8.

Theoretically the curve should be decreasing as hydrogen to furfural ratio increases. This can be explained by deactivation of the catalyst by forming furan resins from the action of heat on catalyst surface and by capillary condensation of furfural within the micropores of the catalyst at high furfural concentrations, since furfural is a very highly polymerizing chemical.

When the hydrogen to furfural ratio is high, partial pressure of furfural is lower and capillary condensation is smaller. Also when hydrogen is very excess, the polymerization reaction slows down with respect to the hydrogenation reaction. As a result of these two facts the activity of the catalyst is higher for high hydrogen to furfural ratios resulting in a higher conversion of furfural to furfuryl alcohol.

CONCLUSION

The deactivation mechanism of the catalyst was found to be mainly the fouling resin macromolecules formed by side reactions of furfural on the catalyst surface. From the regeneration studies, the most successful one involved drying at 110°C for 5 days, then heating at 325°C for 18 hours and refluxing in cyclohexanol for 4 hours. The conversion to furfuryl alcohol by the regenerated catalyst in the vapor phase was 78 per cent, compared to 79.5 per cent for fresh catalyst.

The following rate equation for the hydrogenation reaction was derived from experimental results.

$$\frac{dX_A}{dt} = 38.37(1 - X_A)^{3.8}.$$

It was also observed that conversion increases up to an asymptotic value as the hydrogen to furfural mole ratio increases.

ACKNOWLEDGEMENT

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REPORTS AND REVIEWS