Eskişehir Osmangazi Üniversitesi Müh.Mim.Fak.Dergisi C.XIX, S.2, 2006
Eng&Arch.Fac. Eskişehir Osmangazi University, Vol. .XIX, No:2, 2006

Makalenin Geliş Tarihi : 01.08.2005
Makalenin Kabul Tarihi : 21.11.2005

DEACTIVATION OF AMBERLITE IR-120 USED IN THE ESTERIFICATION OF ACETIC ACID WITH ISOBUTANOL AS A CATALYST

Alime ÇITAK

ABSTRACT: *The resins in their acidic form are often used to catalyze esterification reaction in place of mineral acids. Deactivation of the catalyst, in heterogeneous catalytic reactions are often important to industry. In this study, the deactivation of Amberlite IR-120 in an esterification reaction was investigated.*

Data on the esterification of acetic acid with isobutanol have been obtained from heterogeneously catalyzed reactions using a stirred batch reactor in dioxane. The reaction has been carried out in the presence of the cation-exchange resin in the H^+ form, Amberlite IR-120, at temperature ranging from 318 to 368 K. It was observed that there is a negligible catalyst deactivation in 25 days of usage.

KEYWORDS: *Esterification kinetics; Heterogeneous catalyst; Amberlite IR-120; Deactivation.*

ASETİK ASİT-İZOBÜTANOL ESTERLEŞMESİNDE KATALİZÖR OLARAK AMBERLİTE IR-120 KATALİZÖRÜNÜN DEAKTİVASYONU

ÖZET: *Asidik formdaki reçineler mineral asitler yerine esterleşme tepkimesini katalizlemek için çok sık kullanılırlar. Heterojen katalitik tepkimelerde katalizörün deaktivasyonun endüstriyel önemi oldukça büyüktür. Bu çalışmada, esterleşme tepkimesinde Amberlite IR-120 katalizörünün deaktivasyonu araştırılmıştır.*

Asetik asit ile izobutanolün esterleşmesindeki deneysel veriler dioksanlı ortamda karıştırıcılı kesikli reaktör kullanılarak heterojen katalitik tepkimelerden elde edilmiştir. Tepkime 318-368 K sıcaklık aralığında Amberlite IR-120 H^+ formundaki katyon değiştirici reçine varlığında yapılmıştır. 25 günlük kullanım süresinde katalizörün deaktivasyonunun ihmal edilebileceği gözlenmiştir.

ANAHTAR KELİMELER: *Esterleşme kinetiği; Heterojen katalizör; Amberlite IR-120; Deaktivasyon.*

Eskişehir Osmangazi Üniversitesi, Mühendislik Mimarlık Fakültesi,
Kimya Mühendisliği Bölümü, Batı Meşelik Kampüsü, 26480 ESKİŞEHİR.

I. INTRODUCTION

In esterification reactions, generally, mineral acids, for example fluorhydric, sulfuric, fosforic acids are used as catalyst [1]. However, these acid catalysts are toxic and corrosive and, in addition, are hard to remove from the reaction medium. So, it would be reseanable to replace them by solid catalysts as zeolites, alumina or resins in their acidic form, which can be easily separated from the products compared to that of mineral acids [2-5].

Deactivation of the catalyst, in heterogeneous catalytic reactions are often important to industry. This happens due to fouling, desulfonation, chemical decomposition, sulfonic acid neutralization, etc.[6]. In this study, the deactivation of Amberlite IR-120, in an esterification reaction was investigated.

II. EXPERIMENTAL

II.1. Apparatus

The reactor consisted of a three-necked pyrex flask of 400 ml capacity fitted with a reflux condenser, a sampling device, and a thermometer. The temperature was controlled within ±0.1 K by circulating water from a thermostat into a cylindrical water-jacket of the reactor. The reaction mixture was magnetically stirred at about 600 rpm.

The equilibrium studies were carried out using sealed tubes of 5 ml capacity.

II.2. Materials

Isobutanol of higher than 98.5 % purity (Merck), and acetic acid of 99.8 % purity (Merck) were used as the reactants. The cation-exchange resin in the H^+ form, Amberlite IR-120, was obtained from Rohm and Haas Co. Its physical properties are listed in Table 1. The reaction was realized in the solution of dioxane of 99.0 % purity (Merck). All the aqueous solutions used in the analysis were prepared with distilled water.

Table 1. Physical properties of Amberlite IR-120 cation exchange resin.

Commercial name	Matrix structure	İonic form	pH range, stability	Total exchange capacity a) meq/g (dry) b) meq/ ml (wet)	Moisture retention (H^+ form) %	Crosslinkage (% DVB)	Maximum operating temperature, K	Particle Size range, mm
Amberlite IR-120 (Fluka)	Styrene-DVB	H^+	0-14	a) 4.4 b) 1.9	44-48	8	393	0.45-0.60

II.3. Procedure

In a typical run, dioxane and one reactant were placed in the reactor. A known weight amount of the catalyst was added and the reactor contents well mixed. After a steady value of the desired temperature was attained, the second reactant, at the same temperature, was added and this was taken as zero time for a run. 2 mL of liquid sample was withdrawn from the reactor at regular intervals for analysis.

After reaching seventy percent conversion, reactor contents, apart from the catalyst, were taken out from the reactor. Thereafter, the reactor was refilled with fresh reactants, and the same procedure was repeated four times. Thus, twenty five days elapsed between initial time and end of the final process.

II.4. Analysis

Unconverted acetic acid was determined by standardized 0.1 N NaOH. Water content of the reaction mixture was measured by Karl Fischer titration (784 Model Titrino). Total ester, after saponification process, was determined by back titration of excess base with standard acid.

By these analyses, it was found that the concentration of species are in agreement with the stoichiometry of the reaction. Therefore, the side reactions consider to be eliminated completely.

III. THE DEACTIVATION KINETIC

Catalysts used for a long time may be deactivated as a result of fouling, desulfonation, chemical decomposition, sulfonic acid neutralization, etc. The reaction rate including activity of the catalyst is given by [7];

$$-r_A^{'} = -r_{Ao}^{'}a(t_d) \tag{1}$$

Where, $-r_A^{'}$ is the rate of reaction in the presence of catalyst used for a time t_d and $-r_{Ao}^{'}$ is the rate of reaction in the presence of the fresh catalyst ($t_d = 0$). If the activity of the fresh catalyst is accepted to be unity, $a(t_d = 0)=1$, $a(t_d)$ will be a fraction of the activity. Decreasing of activity with time depends on species of catalyst, purity of feed and mechanism of reaction, etc. [8].

The kinetics of esterification reaction between acetic acid and isobutanol in the presence of Amberlite IR-120 was found to be given by Eley-Rideal mechanism [9].

$$-r_{Ao}^{'} = \frac{k_f(C_A C_B - \frac{C_E C_W}{K_e})}{1 + K_B C_B + K_W C_W} \tag{2}$$

Heterogeneous reaction rate can be related to that of homogeneous reaction by equation, $-r_A = \frac{m}{V}(-r_A^{'})$ [7]. Using this relationship together with Eq. (1) and (2), the following expression can be obtained;

$$-r_A = C_{Ao}\frac{dX_A}{dt} = \frac{k_f \frac{m}{V}(C_A C_B - \frac{C_E C_W}{K_e})}{(1 + K_B C_B + K_W C_W)}a(t_d) \tag{3}$$

Where subscripts A, B, E and W refer to acid, alcohol, ester and water respectively, k_f is forward reaction rate constant, K_e is equilibrium constant of the reaction, K's are adsorption equilibrium constants, m is quantity of dry-resin, and V is the volume of the reaction mixture.

For the initial reaction rate, with no product present, Eq. (3) can be reduced to;

$$-r_A\Big|_{t=0} = \frac{k_f \frac{m}{V}(C_{Ao} C_{Bo})}{(1 + K_B C_{Bo})}a(t_d) \tag{4}$$

Initial reaction rate was measured in the presence of catalysts at definite age by keeping the other parameters constant. Thus, the coefficient of $a(t_d)$ in Eq. (4) reduced to be a new constant $k^{'}$.

$$-r_A\Big|_{t=0} = k^{'}a(t_d) \tag{5}$$

There fore initial reaction rate in the present of fresh catalyst

($a(t_d)=1$) is to be k'. Thus, t_d versus $\frac{-r_A\big|_{t=0}}{k'} = a(t_d)$ gives a reducing line starting from unity.

IV. RESULTS

Experimental data have been given in Tables (2)-(5). Using these tables, a plot of fractional conversion of A (X_A) against time (t) were also illustrated in Figs. (1)-(4). Using the first values of conversion in these tables, the initial reaction rates were calculated by equation $-r_A\big|_{t=0} = C_{Ao}\frac{X_A}{t}$. The results of these calculation were given in Table (6). The plot of t_d versus $a(t_d)$, obtained from the values in Table (6), was given in Fig. (5). Where, the first initial reaction rate value is to be 0.0672 mol.l^{-1}.h^{-1}.

Table 2. The first deactivation experimental data.

The total deactivation time, hours	The reaction time of the first deactivation, hours	Concentration of Acetic acid, C_A, mol.l^{-1}	Conversion of Acetic acid, X_A
0	0	1.6295	0
2.57	2.57	1.4562	0.1064
5.59	5.59	0.3175	0.1915
22.23	22.23	0.9757	0.4012
26.51	26.51	0.9559	0.4130
30.06	30.06	0.9237	0.4330
45.45	45.45	0.7825	0.5197
53.57	53.57	0.7479	0.5410
71.33	71.33	0.6414	0.6064
121.52	121.52	0.5695	0.6505
193.20	193.20	0.5027	0.6915
196.46	196.46	0.5052	0.6899
213.38	213.38	0.4953	0.6960

Table 3. The second deactivation experimental data.

The total deactivation time, hours	The reaction time of the second deactivation, hours	Concentration of Acetic acid, C_A, mol.l^{-1}	Conversion of Acetic acid, X_A
213.38	0	1.6642	0
215.95	2.57	1.4636	0.1205
218.95	5.57	1.3075	0.2143
235.86	22.48	0.9509	0.4285
240.60	27.22	0.8940	0.4628
243.44	30.06	0.8618	0.4821
259.88	46.50	0.7627	0.5416
266.85	53.47	0.7180	0.5684
284.38	71.00	0.6587	0.6042
335.52	122.14	0.5225	0.6860
363.44	150.06	0.5225	0.6860
381.38	168.00	0.5175	0.6889
405.52	192.14	0.5069	0.6954

Table 4. The third deactivation experimental data.

The total deactivation time, hours	The reaction time of the third deactivation, hours	Concentration of Acetic acid, C_A, mol.l^{-1}	Conversion of Acetic acid, X_A
405.52	0	1.6807	0
408.63	3.11	1.4085	0.1619
411.10	5.58	1.2511	0.2550
428.11	22.59	0.8856	0.4730
432.03	26.51	0.8483	0.4952
435.61	30.09	0.8160	0.5142
450.83	45.31	0.7069	0.5793
459.10	53.58	0.6669	0.6030
478.03	72.51	0.6189	0.6317
528.71	123.19	0.5015	0.7016
573.72	168.20	0.4535	0.7302
597.84	192.32	0.4375	0.7396

Table 5. The fourth deactivation experimental data.

The total deactivation time, hours	The reaction time of the fourth deactivation, hours	Concentration of Acetic acid, C_{A}, mol.l^{-1}	Conversion of Acetic acid, X_A
597.84	0	1.7020	0
601.09	3.25	1.4219	0.1645
603.40	5.56	1.2850	0.2445
620.41	22.57	0.9177	0.4608
624.3	26.46	0.8670	0.4906
627.03	29.19	0.8456	0.5031
643.87	46.03	0.7229	0.5752
651.37	53.53	0.6882	0.5956
669.03	71.19	0.6295	0.6300
719.85	122.01	0.5360	0.6849
743.03	145.19	0.5015	0.7053
788.95	191.11	0.4720	0.7225
797.05	199.21	0.4720	0.7225
835.44	237.60	0.4588	0.7304

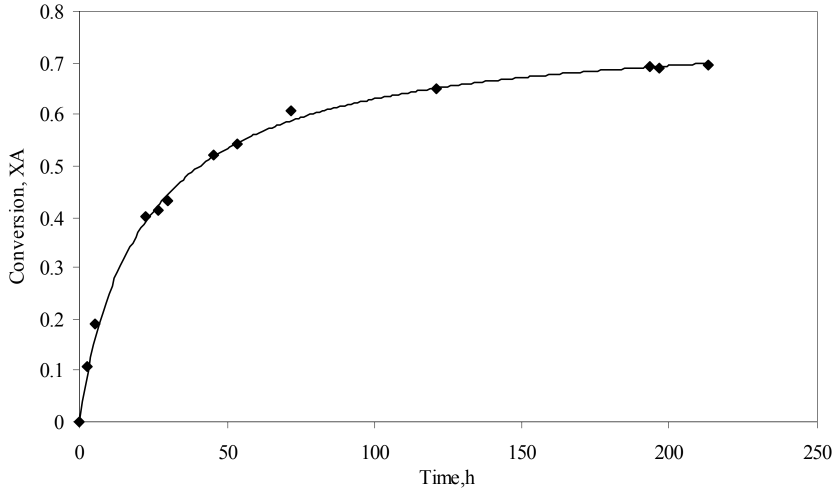

Figure 1. Conversion as a function of time for first deactivation.

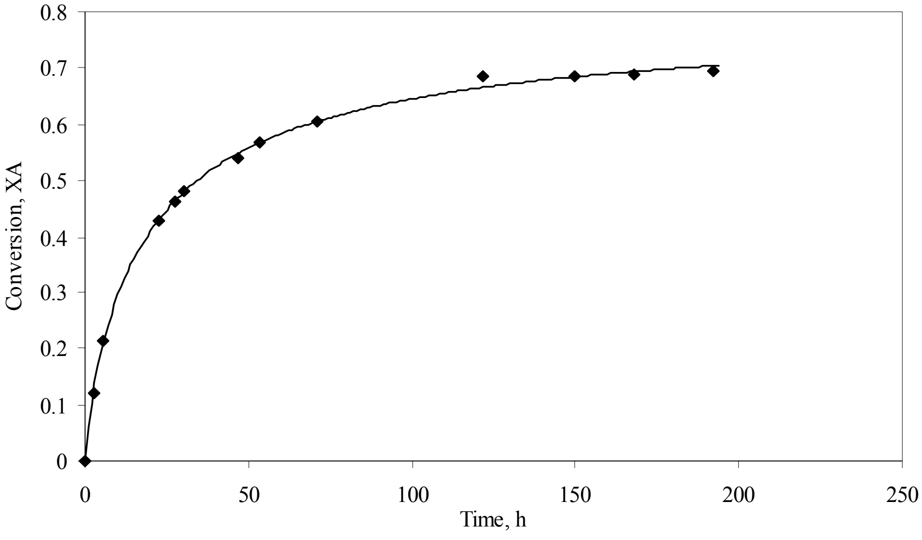

Figure 2. Conversion as a function of time for second deactivation.

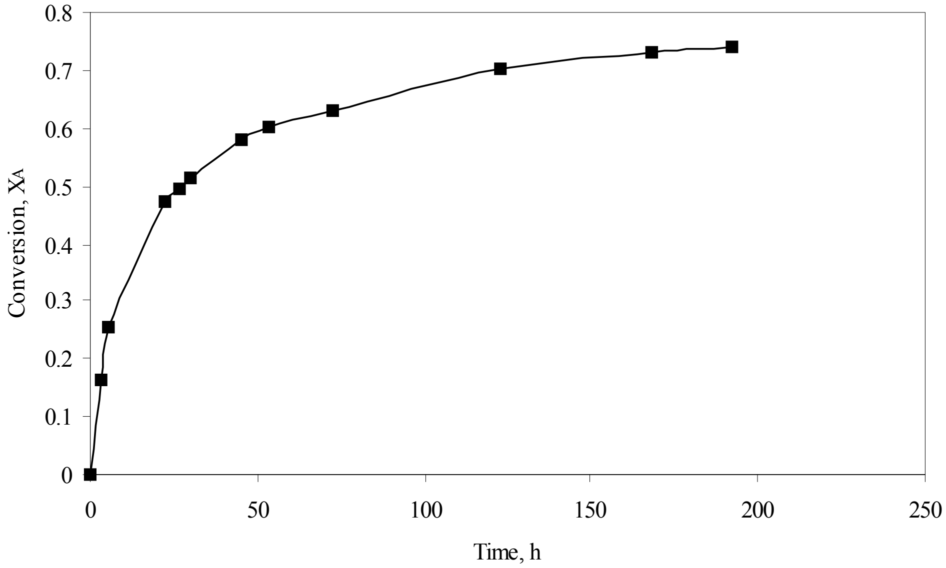

Figure 3. Conversion as a function of time for third deactivation.

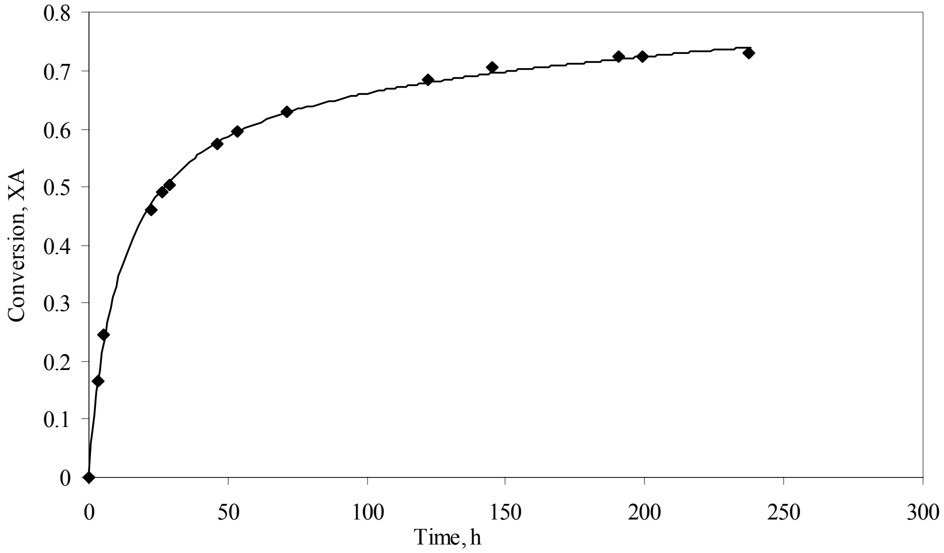

Figure 4. Conversion as a function of time for fourth deactivation.

Table 6. The initial reaction rate for the different deactivation durations.

The total deactivation time, t_d, hours	Reaction time, t, hours	C_{Ao}, mol.l^{-1}	X_A	$-r_A\|_{t=0}$, mol.l^{-1}.hours^{-1}	Fraction of the activity, a(t_d)=$\frac{-r_A\|_{t=0}}{k'}$
2.57	2.57	1.63	0.106	0.0672	1.00
216	2.57	1.66	0.120	0.0775	1.15
409	3.11	1.68	0.16	0.0864	1.28
601	3.25	1.70	0.16	0.0836	1.24

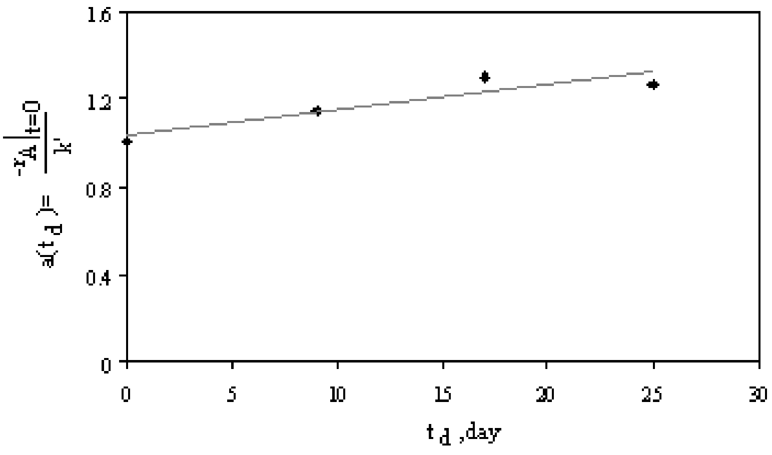

Figure 5. The time variation of the catalyst activity.

As seen in Fig. (5), no sign of deactivation of Amberlite IR-120 resin, used to catalyze the esterification reaction between acetic acid and isobutanol, was observed in 25 days. It implies that this catalyst can be used for a reseanable long time without noticeable deactivation.

REFERENCES

[1] P. Dupont, J.C. Védrine, E. Paumard, G. Hecquet, F. Lefebvre, "Heteropolyacids supported on activated carbon as catalysts for the esterification of acrylic acid by butanol", Applied Catalysis A:General, Vol.129, pp. 217-227, 1995.

[2] Y. Seo, W.H. Hong, "Kinetics of Esterification of Lactic Acid with Methanol in the Presence of Cation Exchange Resin Using a Pseudo-Homegeneous Model", Journal of Chemical Engineering of Japan, Vol.33, No.1, pp.128-133, 2000.

[3] J.I. Choi, W. H. Hong, H. N. Chang, "Reaction Kinetics of Lactic Acid with Methanol Catalyzed by Acid Resins", International Journal of Chemical Kinetics, Vol.28, pp. 37-41, 1996.

[4] S. Dassy, H. Wiame, F.C. Thyrion, "Kinetics of the Liquid Phase Synthesis and Hydrolysis of Butyl Lactate Catalysed by Cation Exchange Resin", J. Chem. Tech. Biotechnol., Vol.59, pp. 149-156, 1994.

[5] C.L. Levesque, A.M. Craig, “Kinetics of an Esterification with Cation-Exchange Resin Catalyst”, Industrial and Engineering Chemistry, Vol.40, No.1, pp. 96-99, 1948.

[6] A. Chakrabarti, M. M. Sharma, “Cationic Ion Exchange Resins as Catalyst”, Reactive Polymers, Vol. 20, pp. 1-45, 1993.

[7] H. S. Fogler, “Elements of Chemical Reaction Engineering”, Prentice-Hall International Inc., 1992.

[8] O. Levenspiel, “Chemical Reaction Engineering”, Second edition, John Wiley&Sons, New York, 1972.

[9] M.R. Altiokka, A. Çıtak, “Kinetics study of esterification of acetic acid with isobutanol in the presence of amberlite catalyst”, Applied Catalysis A:General, Vol.239, pp.141-148, 2003.