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Catalyzed Beckmann rearrangement of cyclohexanone oxime in heterogeneous liquid/solid system Part 1: Batch and continuous operation with supported acid catalysts

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Abstract

Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam has been studied in heterogeneous liquid/solid system at room temperature and pressure. In this first part preparation, characterization and reactivity of impregnated strong acids on solid support have been investigated, with particular attention to H_2SO_4/SiO_2 catalysts. The influence of many preparative variables on catalyst's microstructure and reactivity has been studied. Surface characterization suggests a progressive filling of the silica pores as the amount of acid increases without a sensible modification in the silica porosity. Conversion and selectivity in Beckmann rearrangement are directly related to the amount of acid loaded on the solid catalyst as well as to the kind of support. Measurement of kinetic parameters together with the apparent activation energy of few kJ mol^{-1} and the inspection of Carberry and Weeler-Weisz number suggest that diffusion phenomena affect the kinetics. Comparing liquid/liquid and liquid/solid systems, Beckmann rearrangement occurs only with really strong acid and employing aprotic solvent. On the contrary, oxime hydrolysis occurs also with solid or liquid acid catalysts with low protonation ability which generally do not allow the rearrangement under mild conditions. Fast catalyst deactivation has always been observed, suggesting a relation with oxime hydrolysis by which neutralization of the acid phase on catalyst surface occurs.
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1. Introduction

Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, which is a valuable intermediate for the manufacture of fibers, plastics and resins, has been studied for a long time [1–6]. Actually, industrial processes require the use of oleum as homogeneous catalyst that causes several problems like: product separation, hazardous working conditions, corrosion of the reactor and large amount of ammonium sulfate formed as by-product [7]. The environmental regulations and the process safety drive researchers to develop solid acids to replace liquid acid processes.

The first patented example of solid catalyst applied to the gas phase Beckmann rearrangement of cyclohexanone oxime can be found in early 40s [8]. Furthermore, in the past two decades several solid catalysts have been developed to be applied in the Beckmann rearrangement, especially the zeolite ones [9–14]. These studies relate mainly to vapor phase Beckmann rearrangement reaction over solid acid at temperatures higher than 250 °C. Such conditions cause rapid catalyst deactivation due to irreversible adsorption of the reaction products which cause coke or peach formation [11–14]. Different reactor tricks with continuous reactivation of catalysts have been proposed to overcome the problems encountered with fast catalyst poisoning [15]. The vapor/solid system is interesting but needs large capital investment. An alternative to this industrial strategy is the use of solid acid catalysts on the liquid phase process, an improvement particularly attractive in the revamping of existing plants [16,17]. A big improvement on the efficiency and environmental impact

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of liquid phase processes can be obtained by developing solid acid catalysts which need no great modification of the existing plants, since the reaction can proceed at a moderate temperature, and the presence of the solvent may reduce catalyst deactivation [18]. As a matter of fact, the challenge is developing a poisoning resistant catalyst in order to avoid the reactivation step. Only recently a certain number of papers are available on heterogeneous catalyzed liquid phase Beckmann rearrangement, but the reasons of deactivation in liquid/solid processes are not yet entirely explored [18–25].

The acid catalyzed conversion of ketoximes to amides has been widely studied and many mechanistic aspects of the reaction have long been firmly established [2–5,26–29]. Reaction mechanism could be of great relevance to understand the reasons of deactivations in solid acid catalysts since the thermodynamic and the kinetic behavior of each step in homogeneous phase can be compared with the products obtained with the heterogeneous reactions. For instance, oxime and lactam basicity, hydrolysis and ketones condensation are phenomena of paramount importance to understand the whole process [2–5]. Many homogeneous reaction systems are efficient in the Beckmann rearrangement (e.g. $SOCl_2$, PCl_5, sulfamic acid, etc.) and the need of an acid system is, however, the common feature of all reaction media [2–5]. Despite of the large number of systems active in Beckmann rearrangement, oleum is the only one industrially employed in the caprolactam production, mainly because it is cheap, largely available, and the reaction is fast and selective. The particular kinetics behavior of this acid can also be a starting point for investigations on supported solid acid catalysts.

Solid acid catalysts prepared by employing acid supported on oxides are known and used from a long time, for instance, H_3PO_4/SiO_2 is employed in benzene alkylation for cumene production in Hook process [30]. The parallelism between solid impregnated liquid catalysts and the activity of the homogeneous equivalent in liquid phase could be of great importance to link the behavior between homogeneous and heterogeneous systems. Characterization of such catalysts is quite easy since amount and strength of the acid sites can be studied by titrimetric techniques [31]. As a matter of fact, the impregnated acid generates sites whose acidity is of Bronsted or Lewis type in correspondence of the kind of acid employed, as well as the acid strength is strictly related with that of the acid impregnated [32]. Different supports have been used, e.g. alumina, silica titania, zirconia, etc.; in any case strong interaction between acids and surface is reported [33]. In some cases, modifications of support microstructure occur. For instance, zirconia reacts with sulfuric acid giving the corresponding sulfate; during the calcination stage, a reconstruction of the surface oxide occurs due to decomposition of the sulfate species [34]. On the contrary, silica shows no modification of the microstructure after strong acid impregnation (except when hydrofluoric acid is used). The reason of such a behavior is the stability of the Si–O–Si bonds, which is not attacked by strong acid also at high concentration. The interactions of the acids with surface silanols allow stability of the active phase. Furthermore, reactive supports not only give Bronsted sites but also Lewis ones [33,34], the latter, in some cases, are most active for alkane isomerization [35,36]. For instance, chlorided alumina, which is a commercial catalyst for naphtha reforming, has practically only Lewis acid sites, on the contrary sulfated zirconia has Lewis and Bronsted sites and both are effective in the alkylation of isobutane [37].

The complete work on the Beckmann rearrangement of cyclohexanone oxime catalyzed by solid acid will be divided into two parts in order to give a clear explanation of many aspects of the well known but not entirely understood reaction.

In such first paper, activity and selectivity of supported sulfuric acid on different carriers have been investigated as catalysts in the Beckmann rearrangement of cyclohexanone oxime. Moreover, the influence of the operative parameters of catalyst preparations on their reactivity has been given. Comparisons between batch and continuous operations allow a qualitative evaluation of catalyst poisoning.

2. Experimental

2.1. Materials

Purified samples of commercially available Silica Gel (90 μm average particle size (S_{BET}) 364 m^2/g, pore volume 1.14 ml/g, Grace) were obtained by washing the material with aqueous solutions of perchloric acid, then with distilled water. Reagents and solvents (i.e. CF_3SO_3H, indicators, cyclohexane, etc.) were used after purification of the commercially available samples and their purity was checked by the usual methods (melting point, TLC, HPLC, GC and GC–MS). A treatment of the solvents was carried out in a double bed column, filled with H_2SO_4/SiO_2 and SiO_2 to adsorb solvent impurity, which may cause catalyst deactivation. Water content was checked by HPLC analysis [38]. Commercial catalysts: macro-reticular sulfonated styrene divinyl benzene resins Amberlyst 15^{TM} (S_{BET} 36 m^2/g purchased from Aldrich) and Amberlyst 36^{TM} (S_{BET} 30 m^2/g purchased from Aldrich Aldrich, Amberlyst 15 and Amberlyst 36 are a trade mark of Rohm and Haas), Montmorillonite, fuyasite G54 and zeolite HZSM5 (Engelhard).

2.2. Catalysts preparation

Samples of catalysts were prepared by wet impregnation (W.I.) using aqueous and non-aqueous acid solutions. Many supports were employed using the same procedure of impregnation. For instance, a weighted amounts of purified silica gel was mixed with a known amount of an aqueous acid solution of appropriate concentration (5–30%). After stirring for desired time (from 5 min to 3 days), the supernatant solution was removed by filtration and the wet catalyst was dried for 72 h at 378 K in a stream of nitrogen, then stored in a dry apparatus. Some samples, after the first treatment, were processed at different temperature (403–573 K) under nitrogen.

In the case of adsorption from organic solvent (O.A.), weighted amounts of purified silica gel was mixed with a known amount of the acid mixtures (i.e. $CH_2Cl_2 + CH_3NO_2 +$ acid). The solvents were removed under stirring at room temperature for 3 h and at 378 K for 18 h under nitrogen flow, and then stored in a dry apparatus.

In the case of the sample H_2SO_4/Fe_2O_3, the catalyst was obtained from $FeCl_3$ by precipitation with ammonium hydroxide; the precipitate was washed with plenty of water to remove ammonium chloride and finally impregnated with sulfuric acid by wet impregnation (P.W.I.).

A sample of H_2SO_4/ZrO_2 has been obtained by a sol–gel technique (S.G.) employing an ethanol solution of zirconium isopropoxide and adding an aqueous solution of sulfuric acid while stirring. The resulting gel was left to stand for 72 h then dried under nitrogen flow at 383 K for 72 h.

Some catalysts were prepared by gas phase adsorption (G.A.) of SO_3 on SiO_2 or ZrO_2 at room temperature for 1 h. SO_3 was obtained by bubbling nitrogen into oleum at 20% of SO_3. In order to ensure homogeneous impregnation, SO_3 was injected from the bottom of the column and the flow (c.a. 3.6 $dm^3\ h^{-1}$) was regulated in order to obtain a mixed bubbling bed.

2.3. Catalysts characterization

The acid percentage composition in the solids after impregnation was determined by potentiometric titration against standard solutions of NaOH and checked before use. It avoids the uncertainties due to hygroscopicity of the catalysts.

The surface layer of the solid acid samples has been characterized by XPS measurements using pyridine chemisorption [31] and investigation of the N1s XPS band. A single peak at 401.4 eV was found in all cases, highlighting only the presence of rather strong Bronsted acid sites.

Additional measurements related to protonating ability of the catalysts in the protonation of a weak base were performed in a thin UV cell (0.1 cm) filled with the solid acid, the solvent and the indicator [31]. The protonating ability of the catalysts was checked by using nitroanilines with different basicity [31].

BET surface area (SA), pore size distribution (BJH model) and total pore volume (relative pressure of $p/p_0 = 0.98$) of the catalysts have been determined by nitrogen adsorption and desorption at 94 K using an automatic adsorption unit (*Micromeritics* ASAP 2010C) (Fig. 1).

2.4. Reactions in batch

The kinetic runs were performed in a well-stirred glass reactor thermostated by circulation bath in the range of 253–363 K, containing weighed samples of solvent, reagents and catalyst at atmospheric pressure. In order to minimize catalyst deactivation by air moisture, all the operations were carried out in a glove box. Small amounts of the solution were drawn at different times and the samples were analyzed by GC and GC–MS using an HP5 capillary column (300 μm i.d. 30 m long, 95% methyl, 5% phenyl silicone phase), the samples were also checked by HPLC using a Perkin-Elmer apparatus and a Lichrospher 100 (RP-18, 5 μm) column.

2.5. Reactions in plug flow reactor (PFR)

Reactions were carried out in a thermostated down flow packed bed reactor. Pressure was maintained constant by a mercury regulator (10–50 mmHg) and temperature by a circulation bath. In order to avoid bypassing and ensure reproducibility, catalyst was packed by vibration until no reduction of volume was observed, followed a treatment under N_2 flow (1.8 $dm^3\ h^{-1}$) for 1 h at 363 K. The system was now thermostated at the reaction temperature, loaded with solvent and regulated the pressure (typically 20 mmHg) in order to obtain the selected flow. The resulting solution was recovered in calibrated flask and analyzed by GC, GC–MS and HPLC under the same experimental conditions of the reactions carried out in batch (Fig. 2).

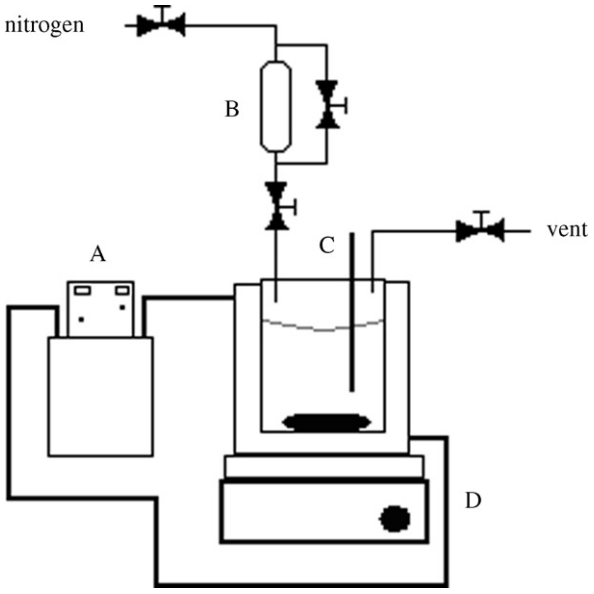


Fig. 1. Batch reactor: A, thermostat; B, reagent reservoir; C, thermometer; D, magnetic stirrer driver.

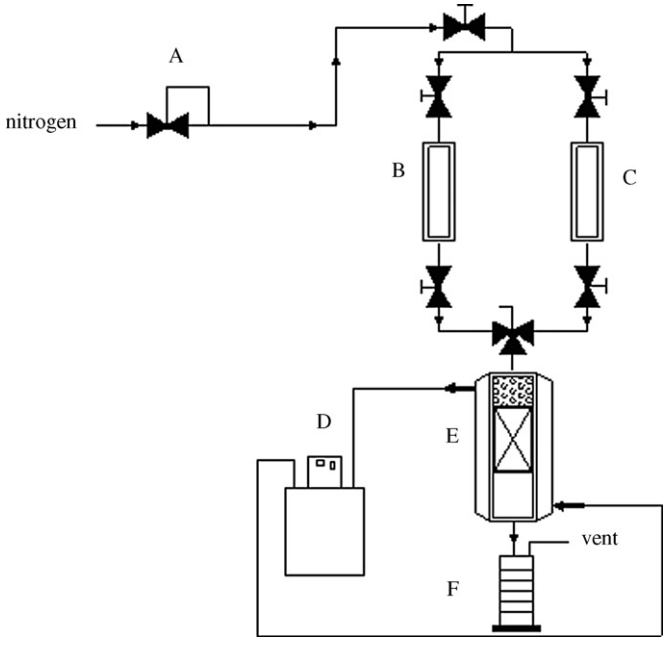


Fig. 2. PFR reactor: A, pressure regulator; B, solvent reservoir; C, reagent reservoir; D, thermostat; E, packed bed reactor; F, calibrated flask.

Table 1
H_2SO_4/SiO_2 catalysts preparation and characterization

Catalyst	H_2SO_4 [wt%]	Time of impregnation [min]	Time of desiccation at 383 K [min]	Temperature of treatment [K]	Time of calcinations [min]	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]
1SSi10	10	5	4320	110	4320	3.1	/
2SSi10	10	60	4320	110	4320	3.0	290
3SSi10	10	180	4320	110	4320	3.1	/
4SSi10	10	1180	4320	110	4320	2.9	298
1SSi20	20	60	4320	110	4320	5.2	215
2SSi20	20	60	4320	130	120	5.3	/
3SSi20	20	60	4320	150	120	5.4	/
4SSi20	20	60	4320	180	120	5.3	214
1SSi25	25	60	4320	120	4320	6.3	170
1SSi30	30	60	4320	110	4320	9.0	114
2SSi30	30	60	4320	130	120	8.9	112
3SSi30	30	60	4320	150	120	8.9	109
4SSi30	30	60	4320	180	120	9.0	101
5SSi30	30	60	120	150	120	9.2	105
1SSi35	35	60	120	/	/	10.1	/
1SSi40	40	60	4320	/	/	11.8	/
SO_3Si	/	60	/	G.A. of SO_3 at 298 K		1.5	/
SO_3SSi20	20	60	4320	G.A. of SO_3 at 298 K		4.5	/

3. Results and discussion

3.1. H_2SO_4/SiO_2 catalysts characterization: acidity, surface area and catalyst model

The amount of acid was measured by titration with NaOH and the results are reported in Table 1 together with surface area measurements.

A first analysis of data suggests that impregnation time is not important to determine the total amount of acid incorporated into the silica pores. Analogously, temperature, time of exsiccation and calcination do not influence the amount of acid sites on the catalyst. Only the concentration of the acid employed in the impregnation determines the amount of H^+ on silica surface as well as the surface area of the catalyst. As expected, Fig. 3 clearly shows that H^+ concentration on the surface of the catalysts increases almost linearly with acid concentration despite

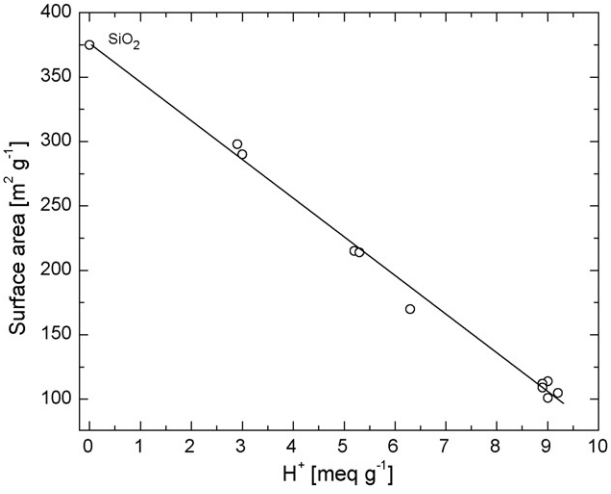


Fig. 4. Behavior of the surface area at different H_2SO_4 loading.

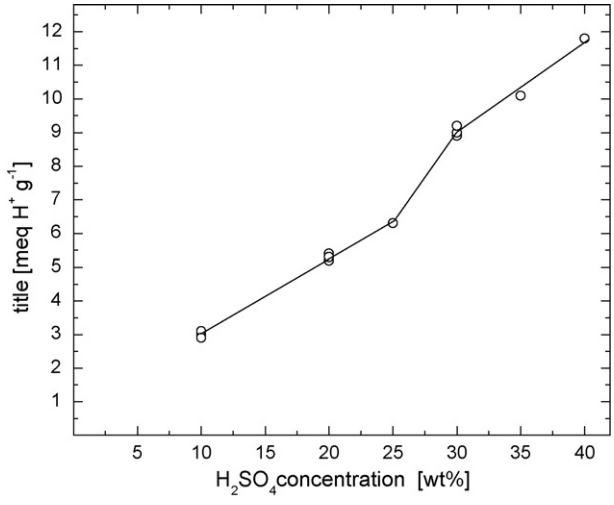


Fig. 3. Influence of H_2SO_4 concentration on the amount of H^+ on SiO_2.

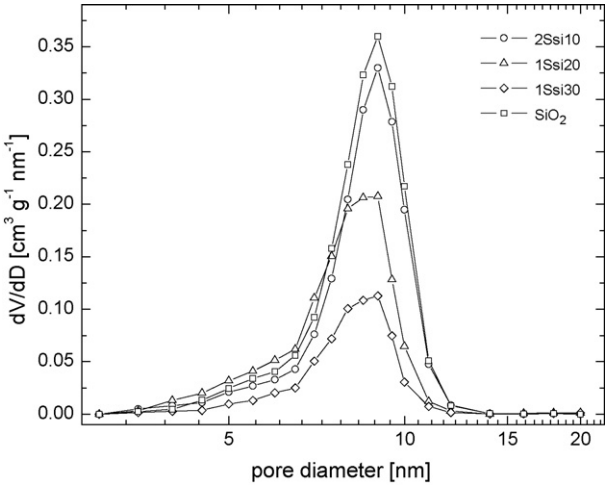


Fig. 5. Pore size distribution of H_2SO_4/SiO_2 catalysts.

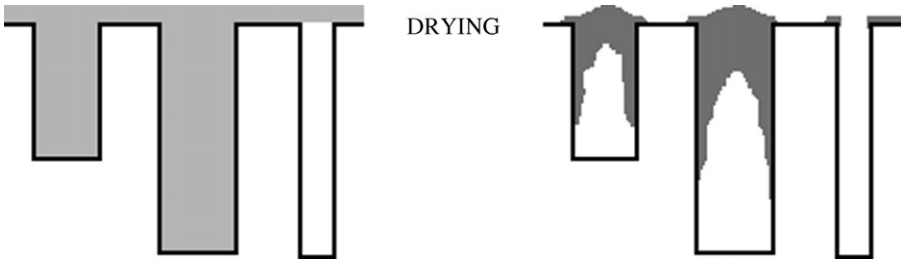


Fig. 6. Catalyst model: scheme of the pores filled with sulfuric acid.

of the different methods of preparation. Only at concentration higher than 25 wt% a deviation is observed.

The linear trend of Fig. 4 suggests that as acid loading increases, catalyst pores are progressively filled; then surface area decreases. Fig. 5 reports the pore size distribution of silica and of three catalysts with different acid loadings. It is noteworthy that there are no particular variations on the pore size distribution and only a small decrease of the larger pore fraction is observed. Leaching away the acid phase from the catalyst by extracting with water gives a SiO_2 with the same features of the starting material (same surface area and pore size distribution). Such a behavior is in agreement with previous results suggesting that silica microstructure modification does not occur even at prolonged time of impregnation and/or desiccation [39].

On the basis of the previous results an illustrative representation of H_2SO_4/SiO_2 catalysts can be attempted (see Fig. 6). After impregnation, H_2SO_4 solution fills all the wettable pores, during drying stage H_2SO_4 moves to the pore mouth pushed by water evaporation and by the air entrapped into the catalyst pore forming little bubble of liquid H_2SO_4 which gradually reaches the equilibrium concentration 96–98 wt% [39]. Then, on the surface there are bubbles of liquid H_2SO_4 at 96–98 wt% and free silanols. Such a hypothesis is also supported by spectroscopic evidences reported in previous papers where the characteristic Raman band of sulfuric acid and of isolated silanols has been recognized [40]. At low acid loading (<0.5 meq g^{-1}) catalysts show behavior similar to that of diluted sulfuric acid (40–50 wt%) as proven by thermodynamic measurements of indicator [31,41,42]. On the contrary, at high acid loadings the behavior is similar to that of sulfuric acid at 96–98 wt% in liquid phase [31,41,42].

Thermodynamic measurements related to protonating ability of weak bases were carried out on solid catalysts with the following indicator 3-methyl-2,4,6-trinitroaniline, 3-bromo-2,4,6-trinitroaniline and 2,4,6-trinitroaniline. These compounds are very weak bases and their half protonation in aqueous solutions of sulfuric acid is occurring at 85.5, 92.8, 96.4 wt% H_2SO_4, respectively [31,41,42], with an order 3Me > 3Br > H different from that expected according to the relationship between basic strength and substituent effects.

The results in solids show an analogous trend since the protonation can be easily observed for 3-methyl-TNA but not for the unsubstituted TNA, the behavior of 3-Br-TNA is between them. It appears to be a complication of the liquid and solid systems with sulfuric acid, indeed, the expected protonation order 3Me > H > 3Br was found in concentrated aqueous CF_3SO_3H [40]. Surface nitronium ions, detected by Raman spectroscopy on H_2SO_4/SiO_2 catalysts furnish corroborating evidence for the reliability of the model [40].

3.2. Characterization of other catalysts: acidity, surface area

In Table 2 the main features of some catalysts prepared starting from different supports or acids are reported, the comparison of microstructure and acidity does not allow any consideration since different method support and acid was employed. It is noteworthy that higher acid content and surface area are achieved with H_2SO_4/SiO_2 catalysts (see Table 1), however the use of dif-

Table 2
preparation and characterization of catalysts other than H_2SO_4/SiO_2

Catalyst	Support		Acid	Concentration [wt%]	Method	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]
	Type	Surface area [m^2 g^{-1}]					
PSi10	SiO_2	376	H_3PO_4	10	W.I.	2.5	/
PSi12/17	SiO_2	376	H_2SO_4/H_3PO_4	12/17	W.I.	4.2	/
PMoSi	SiO_2	376	HPMo	0.25	W.I.	1.4	
PWSi	SiO_2	376	HPW	10	W.I.	/	/
TFSi	SiO_2	376	CF_3SO_3H	7.5	O.A.	3.3	130
NSSi	SiO_2	376	$(NH_4)_2SO_4/H_2SO_4$	10	W.I.	1.5	/
SZr	ZrO_2	10	H_2SO_4	10	S.G.	0.16	/
SO_3Zr	ZrO_2	10	SO_3	/	G.A.	0.6	/
SFe	Fe_2O_3	/	/	10	P.W.I.	/	/
1SBa	$BaSO_4$	2	H_2SO_4	30	W.I.	0.4	/

W.I.: wet impregnation; O.A.: adsorption from organic solvents; P.W.I.: precipitation followed by wet impregnation; S.G.: sol–gel; G.A.: direct SO_3 adsorption.

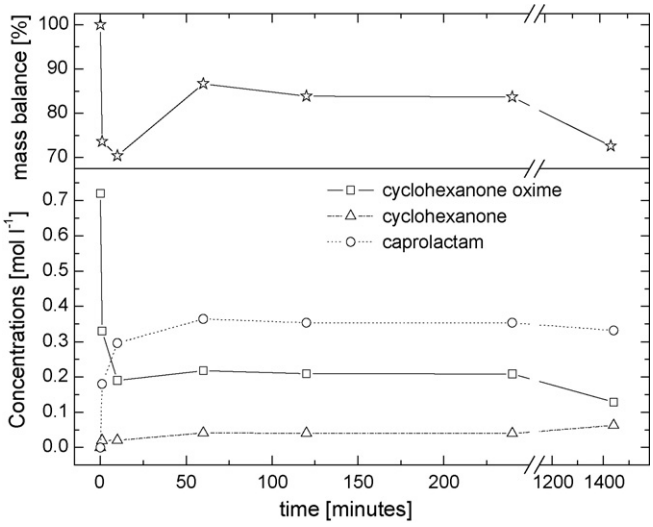


Fig. 7. Kinetic trend of H_2SO_4/SiO_2 catalyst. Run conditions: *T*, 298 K; reaction volume, 10 ml; catalyst 1SSi25, 500 mg; cyclohexanone oxime concentration, 0.72 mol dm^{-3}.

ferent supports and acids allow to test if the interactions between them provide sites with different reactivity.

3.3. Kinetics of Beckmann rearrangements over H_2SO_4/SiO_2 catalysts

A typical kinetic profile of the reaction over H_2SO_4/SiO_2 is reported in Fig. 7. Formation of caprolactam occurs almost immediately and practically at the final conversion. Temperature has little influence on the reaction rate, as a matter of fact similar behavior has been observed between 253 and 333 K then the values of the apparent activation energy is as low as 2–4 kJ mol^{-1}. Such a behavior suggests that diffusion phenomena affect the overall kinetics in agreement with the results obtained by the inspections of Carberry ($Ca = 0.37$) and Weeler-Weisz ($\eta\phi^2 = 2.1$) numbers (see Appendix A) [43]. About 15% of the starting material disappear from solution and remains irreversibly adsorbed into the catalyst. Leaching the acid phase with water and extracting with methylene chloride, it appears that cyclohexanone and cyclohexanone oxime are the larger part of the adsorbed products together with other products of condensation and hydrolysis (e.g. hydroxylamine). Starting from these evidences the performances of the catalysts in terms of conversion and selectivity have been compared after 60 min of reaction since a longer time of reaction does not give higher yield to CPL but only the formation of cyclohexanone increases slightly.

3.4. Reactivity of the H_2SO_4/SiO_2 catalysts

The activity and the selectivity of the catalysts are reported in Table 3. The main features of this catalysts are:

(i) the conversion of the oxime is directly related with the amount of acid impregnated on silica;
(ii) both CPL and cyclohexanone yield increase as the acid loading on the catalysts increases;
(iii) selectivity to CPL raises as acid load increases;
(iv) turnover numbers remain practically constant after few minutes of reaction (TON = [moles of cyclohexanone oxime reacted]/[equivalents H^+]) suggesting fast catalyst deactivation.

An explanation can be found taking into account the studies of the Beckmann rearrangement of oximes in homogeneous solution of strong acid [5,26–28]. It has been pointed out that hydrolysis and rearrangement occur at low and high acidity, respectively [5,26–28]. Then, these evidences suggest that two

Table 3
Activity and selectivity of H_2SO_4/SiO_2

Catalyst	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]	Conversion[a] [%]	TON	Caprolactam		Cyclohexanone	
					Selectivity [%]	Yield [%]	Selectivity [%]	Yield
1SSi10	3.1	/	33	2.1	72	24	8.5	2.8
2SSi10	3.0	290	30	2.0	73	22	8.3	2.5
3SSi10	3.1	/	34	2.2	72	24	7.1	2.4
4SSi10	2.9	298	28	1.9	72	20	7.1	2.0
1SSi20	5.2	215	52	2.0	73	38	16	8
2SSi20	5.3	/	53	2.0	74	39	16	8.6
3SSi20	5.4	/	50	1.9	72	36	17	8.6
4SSi20	5.3	214	52	2.0	71	37	15	8.6
1SSi25	6.3	170	57	1.8	77	44	9	5
1SSi30	9.0	114	73	1.6	79	58	13	9.5
2SSi30	8.9	112	76	1.7	76	58	15	10
3SSi30	8.9	109	73	1.6	77	56	14	9.9
4SSi30	9.0	101	73	1.6	79	58	14	10.1
5SSi30	9.2	105	74	1.6	78	58	14	10
1SSi35	10.1	/	84	1.7	80	67	13	10
SO_3Si	1.5	/	2.4	0.3	71	1.7	21	0.5
SO_3SSi20	5.2	/	40	1.5	85	34	2.7	1

Run conditions: oxime concentration, 0.5 mol dm^{-3}; catalyst load, 500 mg; solvent, 1,2-dichloroethane; reaction volume, 20 ml; temperature, 298 K; time of reaction, 1 h.

[a] Conversion is considered what is disappeared from the solution.

kinds of acid sites may exist on catalyst surface, the ones at high acidity are responsible for the rearrangement and those at low acidity catalyze oxime hydrolysis. Simple explanations about the nature of the sites are not possible since catalysts are biphasic, then surface equilibria between H_2SO_4 and silanols may give a large variety of sites with different acid strength. Moreover, catalyst surface undergoes continuous reconstruction due to the intrinsic high mobility of the liquid acid phase. As a matter of fact, higher selectivity to CPL has been obtained with SO_3SSi20 catalyst, which is treated with SO_3 suggesting that the treatment decreases the concentration of low acidity sites. From a mechanistic point of view, the cause of hydrolysis in anhydrous solvent is not clear since concentration of water in solvent is maintained in the range of 10^{-3} mol dm^{-3}, measured by HPLC analysis [38], but extensive hydrolysis has ever observed.

In Fig. 8, the influence of cyclohexanone oxime concentration on conversion and yield of caprolactam are reported. The decrease in conversion and yield after 1 h of reaction with the increase in cyclohexanone oxime concentration are almost parallel. Moreover, the TON remains practically unaffected by increasing oxime concentration. Such a behavior suggests that catalyst can achieve about 1.5 cycles in spite of the increase in the cyclohexanone oxime concentration.

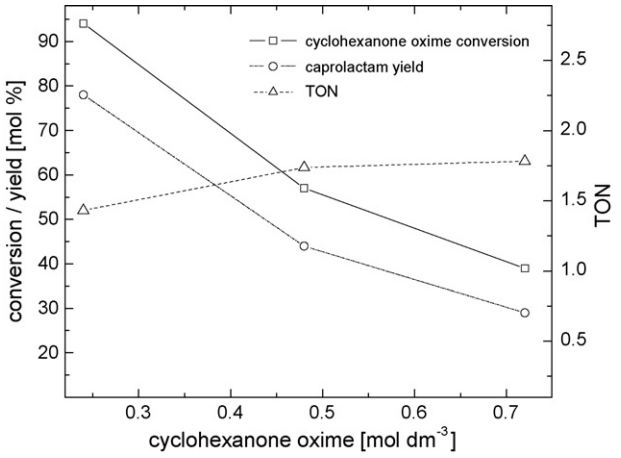


Fig. 8. Influence of cyclohexanone oxime concentration on conversion and caprolactam yield after 1 h of reaction. Run conditions: *T*, 298 K; reaction volume, 20 ml; solvent, 1,2 dichloroethane; catalyst 1SSi25, 500 mg; cyclohexanone oxime concentration, 0.24–0.72 mol dm^{-3}.

3.5. Reactivity of the catalysts other than H_2SO_4/SiO_2

In Table 4, activity and selectivity of the catalysts other than H_2SO_4/SiO_2 are reported. It is noteworthy that the catalysts PSSi12/17 and TFS1, having 4.4 and 3.3 meq g^{-1} of H^+, respectively, give comparable yield in ε-caprolactam with the H_2SO_4/SiO_2 catalysts (see Table 3). In particular, catalyst prepared by mixing sulfuric and phosphoric acid gives the best results. In these cases, however, not only the amount of acid sites play an important role for catalyst activity and selectivity but also the nature of the site, in fact, ZrO_2 adsorbed with SO_3, which has low H^+ content, shows low conversion but high selectivity to ε-caprolactam. On the contrary, STi and SZr give

Table 4
Activity and selectivity of the catalysts other than H_2SO_4/SiO_2

Catalyst	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]	Conversion[a] [%]	TON	Caprolactam		Cyclohexanone	
					Selectivity [%]	Yield [%]	Selectivity [%]	Yield [%]
PSi10	0.84	/	24[b]	5.7	/	/	96	23
PSi10	0.84	/	5.5	1.3	/	/	90	5
PSSi12/17	4.2	/	48	2.3	81	39	9	5
PMoSi[c]	1.5	/	61[b]	8.1	/	/	95	58
PMoSi[c]	1.5	/	7	0.9	/	/	95	6.7
PWSi[c]	/	/	/	/	/	/	/	/
TFSi	3.3	130	34	2.1	76	24	18	6
NSSi	1.5		14	1.9	57	8.0	29	4.0
STi	0.78	/	7.2	1.8	/	/	96	6.8
SZr	0.16	/	5.1	6.4	/	/	96	4.8
SO_3Zr	0.6	/	5.5	1.8	92	5	4	0.2
SFe	/	/	0.3	/	/	/	100	0.3
1SBa	0.4	/	/	/	/	/	/	/
Commercial catalysts								
Amberlyst 15	4.6	36	0.5[b]	0.08	/	/	100	0.5
Amberlyst 15	4.6	36	6.9[b,d]	0.3	29	2.0	71	4.9
Amberlyst 36	5.9	30	7.2[b,d]	0.2	28	2	72	5.2
Hβ	/	589	1		/	/	100	1
HY	/	620	2		/	/	100	2
SiO_2	/	364	/[b]	/	/	/	/	/

Run conditions: oxime concentration, 0.5 mol dm^{-3}; catalyst load, 500 mg; solvent, 1,2-dichloroethane; reaction volume, 20 ml; temperature, 298 K; time of reaction, 1 h.

[a] Conversion is considered what is disappeared from the solution.

[b] $T = 323$ K.

[c] PMo: phosphomolibdic acid, PW: phosphotunstic acid.

[d] Conversion after 20 h.

[e] HZSM5, Montmorillonite, Fuyasite G54, Nafion SAC13 do not react.

only cyclohexanone and 1SBa is completely inactive. Furthermore, in the presence of sulfonated styrene divinyl benzene resins (Amberlyst 15 and 36 having 4.6 and 5.9 meq g^{-1} of H^+, respectively) at room temperature, the reaction practically does not proceed and at 323 K after 20 h only 2% in ε-caprolactam yield with 7% of conversion is obtained. These results confirm that the reaction is strongly influenced by the nature of the acid site, but in the latter case the comparison with the reactivity of the oximes in solution of aqueous sulfonic acids can be of aid to explain such behavior since sulfonic resins are structurally similar to these acids. As a matter of fact, the measured kinetic constants of the Beckmann rearrangement of ketoximes in aqueous sulfonic acids are one order of magnitude lower than those observed in H_2SO_4 solutions, in the same acidity range [28]. These results may explain the low activity and selectivity in the Beckmann rearrangement of cyclohexanone oxime of the sulfonic resins compared to H_2SO_4/SiO_2 catalysts.

3.6. Influence of the solvent on activity and selectivity

Polarity of the solvent influences reaction kinetics provided that charge transition states are involved. In acid catalyzed reaction, carbocation are generally formed from a first fast protonation process [29,44]. In aqueous solution oxime nitrogen is easily protonated in diluted acid (pH ≈ 3), in such a condition however, only hydrolysis to the corresponding ketone occurs [5]. On increasing acidity, rate of hydrolysis decreases and practically stops over 75 wt% of H_2SO_4, while the rate of rearrangement become measurable and increases until 98–100 wt% [5,26,28]. Such behaviors cannot be simply ascribed to a different protonation ability of concentrated *versus* diluted sulfuric acid, but also to "an active solvent participation as catalyst" as already suggested by Nguyen who derives such thesis from computational methods [45]. Moreover, formation of the oxime O-sulfonated at high acidity which is proposed from a long time [3,4,26] cannot explain the great differences observed with other sulfonic acid. For instance, the kinetics measured in CF_3SO_3H at 98 wt%, which has a higher protonating ability than H_2SO_4 at the same concentration, are 10^3 times slower than those measured in sulfuric acid at the same concentration [28]. The special features of H_2SO_4 with respect to other sulfonic acid are likely due to the diprotic nature, which allows a faster proton exchange between N and O [28]. For these reasons, solvent should have an important role also with heterogeneous catalysts, since charge

Table 5
Influence of the solvent on activity and selectivity

Catalyst	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]	Conversion[a] [%]	TON	Caprolactam		Cyclohexanone	
					Selectivity [%]	Yield [%]	Selectivity [%]	Yield [%]
Nitromethane ε = 35.9								
2SSi10	3.1	290	37	2.4	71	24	27	9
1SSi25	6.3	170	74	2.3	78	58	14	10
2SSi30	8.9	112	90	2.0	85	77	10	8
PSi10	2.5	/	5	0.4	76	3.8	20	1
Nitrobenzene ε = 34.8								
2SSi30	8.9	112	80		75	60	15	12
1,2-Dichloroethane ε = 10.4								
2SSi10	3.0	290	30	2.0	73	25	8.3	2.5
1SSi25	6.3	170	57	1.8	77	46	9	5
2SSi30	8.9	112	76	1.7	76	58	15	10
PSi10	0.84	/	5.2	1.2	/	/	96	5
Dichloromethane ε = 8.9								
2SSi10	3.1	290	18	1.2	64	12	11	2
1SSi25	6.3	170	36	1.1	68	25	17	6
2SSi30	8.9	112	49	1.1	70	34	15	8
1,1,1-Trichloroethane ε = 7.5								
2SSi10	3.1	290	5	0.3	35	1.8	60	3.0
1SSi25	6.3	170	14	0.4	64	7	36	4
1SSi25	6.3	170	10 at 273 K	0.3	65	6.5	35	3.5
1SSi25	6.3	170	10 at 253 K	0.3	64	6.4	36	3.6
2SSi30	8.9	112	43	1.0	76	32	24	10
PMoSi	1.4	/	60 at 323 K	8.6	/	/	96	58
Cyclohexene ε = 18.3								
2SSi30	8.9	112	/[b]	/	/	/	/	/
Cyclohexane ε = 2.2								
2SSi30	8.9	112	/[c]	/	/	/	/	/

Run conditions: oxime concentration, 0.5 mol dm^{-3}; catalyst load, 500 mg; reaction volume, 20 ml; temperature, 298 K; time of reaction, 1 h.
[a]Conversion is considered what is disappeared from the solution.
[b]Solvent polymerizes forming peach.
[c]Multiphase reaction due to the low solubility of the oxime; the slurry does not react.

transition states are involved on catalyst surface and different solvents may actively participate to reactions path. Furthermore, in liquid phase heterogeneous reactions, the solvent significantly affects adsorption/desorption equilibria thus selectivity, yield and catalyst deactivation are also influenced as already observed by other authors [23–25].

In Table 5 the influence of the solvent on activity and selectivity is reported. Nitromethane and nitrobenzene are highly effective as solvent in the rearrangement, but an extensive leaching of the acid phase has been observed. As a matter of fact, the titration with NaOH of the water employed in the extraction of the organic phase indicates that a large part of the acid of the catalyst pass to the solvent. Sulfuric acid has a low solubility in chlorinated compounds, thus, using these solvent, the problem of the leaching of the acid phase from the catalystit is avoided. For instance, 1,2-dichloroethane results the more effective respect to other chlorinated solvent, such as dichloromethane and 1,1,1-trichloroethane. The reason of these results is not completely clear, but they are in agreement with the rearrangement of benzophenone oxime picryl ether in CCl_4 in the presence of co-solvent at increasing polarity [4]. It is likely, however that the higher polarity of 1,2-dichloroethane favors desorption of the products from catalyst surface (see Table 5) giving higher conversion and selectivity compared with other chlorinated solvent.

In order to understand whether reaction takes place homogenously (into the solvent), or heterogeneously at the interface of the systems, the biphasic liquid/liquid system (the mineral acid and the cyclohexanone oxime solution in aprotic solvents) has been studied. The comparison between heterogeneous liquid/liquid (see Table 6) and liquid/solid (see Table 5) reactions suggests the following considerations:

(i) liquid/solid systems give higher conversion;
(ii) conversion increases as dielectric constant in liquid/solid system increases, while in liquid/liquid system decreases;
(iii) in both systems there is a lack on the mass balance due to cyclohexanone oxime adsorption into the acid phase, such a phenomenon is more evident in liquid/liquid system with low polarity solvent (e.g. see Table 6 experiments in 1,1,1 trichloroethane);
(iv) upon dilution of the acid phase with water both in liquid and solid only cyclohexanone oxime and cyclohexanone has been detected.

Liquid/solid systems give higher conversion suggesting that the dispersion of the acid phase on the support plays an important role on the activity of the system. As well known, in homogeneous aqueous liquid phase at high acid concentration cyclohexanone is not formed [5], as well as, in P_2O_5 1,2-dichloroethane as solvent. On the contrary hydrolysis of the oxime has always been observed in heterogeneous liquid/liquid and liquid/solid systems. The reason of such behavior is not clear but a simple explanation could be found considering the formation of a N protonated oxime at the interfaces thus allowing the nucleophilic attack of the water to the carbonium ion of the protonated oxime (see Scheme 1). As a matter of fact, small amounts of water are always present into the organic solvent; such traces promote oxime hydrolysis which, in turn, causes hydroxylamine formation and consequently catalyst deactiva-

Table 6
activity and selectivity in heterogeneous liquid/liquid systems

Acid	Conversion[a] [%]	TON	Caprolactam		Cyclohexanone	
			Selectivity [%]	Yield [%]	Selectivity [%]	Yield [%]
Nitromethane $\varepsilon = 35.9$						
H_2SO_4 [96 wt%]	25	1.1	80	20	13	3.2
CH_3SO_3H[b]	9	0.37	44	4.1	23	2.1
H_3PO_4[c] [80 wt%]	25	1.2	5.2	1.3	40	10
1,2-Dichloroethane $\varepsilon = 10.4$						
H_2SO_4 [96 wt%]	26	1.1	65	17	27	7
CH_3SO_3H	6	0.24	25	1.5	42	2.5
H_3PO_4[c] [80 wt%]	23	1.1	2.2	0.5	22	5
$HClO_4$ [69 wt %]	43	2.7	35	15	4.7	2
P_2O_5	95	/	37	35	0	0
$SOCl_2$[b]	52	/	24	12	2	1
Dichloromethane $\varepsilon = 8.9$						
H_2SO_4 [96 wt%]	45	1.9	53	24	7	3
CH_3SO_3H	28	1.1	43	12	3.6	1
H_3PO_4[c] [80 wt%]	23	1.1	3.6	1	7.2	2
1,1,1-Trichloroethane $\varepsilon = 7.5$						
H_2SO_4 [96 wt%]	59	2.5	53	14	3.3	2
CH_3SO_3H	27	1.1	33	9	11	3
H_3PO_4[c] [80 wt%]	18	0.90	28	5	11	2

Run conditions: oxime concentration, 0.5 mol dm^{-3}; acid, 120 mg; reaction volume, 10 ml; temperature, 298 K; time of reaction, 1 h.
[a] Conversion must be considered what is disappeared from the solution comprised the part adsorbed into the catalyst.
[b] Homogeneous reaction.
[c] Extensive formation of unidentified solid.

Table 7
Conversion yield and selectivity of the reaction carried out in PFR

Catalyst	Title H^+ [meq g^{-1}]	Surface area [m^2 g^{-1}]	WHSV [h^{-1}]	Conversion[a] [%]	Caprolactam		Cyclohexanone	
					Selectivity[a] [%]	Yield[a] [%]	Selectivity[a] [%]	Yield[a] [%]
1SSi20	5.2	215	220	76	90	70	8	6
1SSi25	6.3	170	240	80	80	64	20	16
2SSi30	8.9	112	230	90	94	85	5.5	5

[a] Conversion selectivity and yield after 600 s of time of stream.

tion. In homogeneous aqueous phase at high acid concentration, the oxime protonation coincides with the formation of a complex between the protonated oxime and the anion of the acid. The nature of this complex is not completely clarified, even though, some authors propose a sulfonic acid ester, which may protect the molecule from the nucleophile attack of water [3–5,26].

A similar explanation can be proposed for the reaction carried out in the presence of P_2O_5; moreover, it is also a strong dehydrating agent, which may stop oxime hydrolysis. Recently, such complexes have been proposed to favor the 1-2 shift of the proton by an active solvent participation as catalyst which gives fast rearrangement to nitrilium ion intermediate and finally to caprolactam (see Scheme 1) [45]. Nitrilium ion has been observed has stable carbocation starting from hindered aril methyl oxime in concentrated mineral acid [28].

Fitting all the above evidences together, it can be suggested that the reaction takes place mainly at the liquid/solid or liquid/liquid interface.

3.7. Reaction carried out in a plug flow reactor: catalysts poisoning

PFR, under stationary conditions, gives constant products distribution with time, when catalyst deactivation occurs conversion decreases with time [46]. Fig. 9 shows a typical trend of products distribution *versus* time obtained from H_2SO_4/SiO_2 catalysts employing a PFR. It clearly appears that fast catalyst deactivation occurs, in agreement with the experiments carried out in batch reactor (Table 7). Moreover, in accord with the previous results, by increasing acid content of the catalyst the conversion measured at the same WHSV increases too. The solvent eluted from the reactor shows only small amount of free acidity but at the end of reaction catalyst is practically without acidity. Such a behavior, observed also in batch reactor, can be due to irreversible poisoning of the catalyst due to cyclohexanone oxime hydrolysis which forms hydroxylamine which, in turns, reacts with surface acid giving the corresponding salt. A further cause of catalyst deactivation is the formation of condensation products of cyclohexanone, which cause peach formation on catalyst surface. Such a phenomenon can be easily observed by the change of color of the catalyst turning from white to brown.

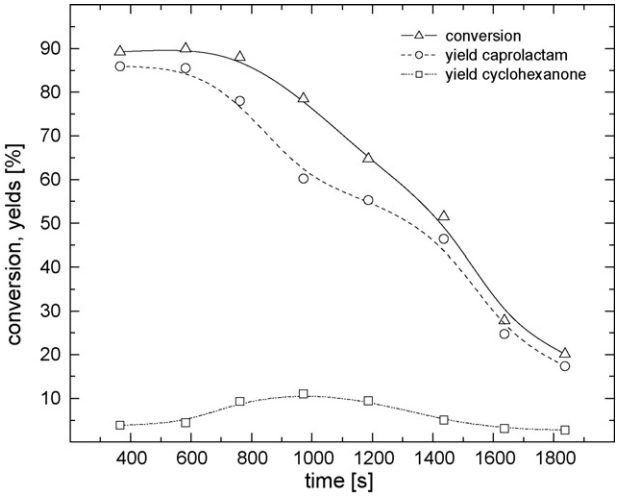
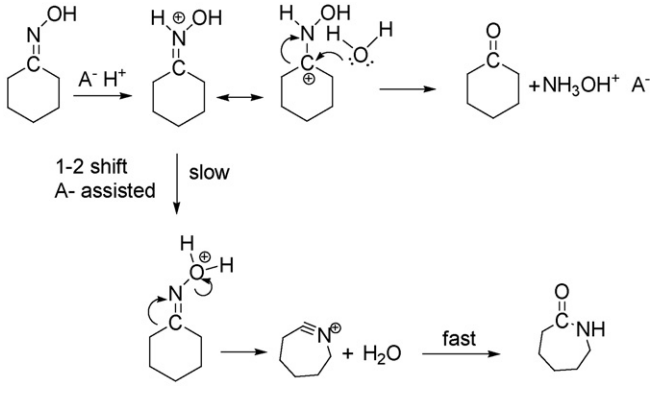


Fig. 9. Products distribution *vs.* time in PFR obtained with 2SSi30. Run conditions: oxime concentration, 0.1 mol dm^{-3}; catalyst 2SSi30, 500 mg; solvent 1,2 dichloroethane; WHSV, 230 h^{-1}; temperature, 298 K.



Scheme 1. Reaction steps for acid catalyzed hydration and Beckmann rearrangement of cyclohexanone oxime.

The reaction profile of the experiments carried out in PFR reactor show catalyst deactivation occurs practically from the beginning of the reaction, as already observed in batch reactions. However, such experiments give an idea of the fastness of the poisoning. Deactivation of the catalysts will be extensively treated in another paper.

4. Conclusions

This first part deals essentially with different aspect of supported liquid acid materials as catalyst in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam at room temperature and pressure in liquid/solid system.

The main features of the catalysts studied are the following:

(i) type and amount of acid influence the yield to caprolactam;

(ii) solvent polarity influences conversion, selectivity and yield to caprolactam;
(iii) the reaction take place at the liquid/solid interface;
(iv) differently of what found for homogeneous reaction in strong acid, hydrolysis of the oxime occurs in any case, with no differences between high and low acidity;
(v) fast catalyst deactivation is observed.

As a matter of fact, the ease of the reaction and high activity of the catalysts are the most promising features of this system. The major problems are oxime hydrolysis and catalyst deactivation, which could be the two aspects of the same problem. On the basis of the above results, in the next part of the study synthesis and characterization of new catalytic systems, will be discussed.

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Appendix A. Evaluation of the rate-determining step

In order to estimate the importance of the diffusion (external liquid/solid and internal) resistance an inspection of the number of Carberry (Ca) and of the Weeler-Weisz group ($\eta\phi^2$) is taken into consideration. The Carberry number is defined as follows [42]:

$$Ca = \frac{r_0}{k_{ls} C_{ox} \frac{6w}{d_p \rho_p}} = \frac{r_0}{r_{ls}}$$

A value of the Carberry number less than 0.05 indicates that the rate of diffusion of a reagent at the liquid/solid interface does not affect the reaction kinetics [42]. Mass transfer coefficient (k_{ls}) has been estimated by Brian and Hales correlation [42]:

$$Sh = 2 + 1.1 Pe^{1/3}$$

The Weeler-Weisz group can be written as follow:

$$\eta\phi^2 = \left(\frac{r_0}{V}\right) \frac{{d_p}^2}{C_{ox} 4 D_{eff}}$$

When $\eta\phi^2$ is less than 1, the kinetics of reaction is practically not influenced by the diffusion of the reagent into the pores of the catalyst [42], whilst values of $\eta\phi^2$ significantly higher than 1 indicate a strong influence of the diffusion of the reagent into the catalyst pores (Table A1).

Table A1
Experimental conditions and physico-chemical data used in the mass transfer calculations

Symbol	Quantity	Values	Dimensions
T	Temperature	298	K
V	Reaction volume	1.6×10^{-5}	m^{-3}
C_{ox}	Cyclohexanone oxime concentration	720	mole m^{-3}
w	Catalyst weight	5×10^{-4}	kg
ρ_s	Solvent density	1.253	kg m^{-3}
ρ_p	Particle density	0.97	kg m^{-3}
d_p	Average particles diameter	10^{-4}	m
μ	Solvent viscosity	8.2×10^{-4}	kg m^{-1} s^{-1}
g	Gravity acceleration	9.8	m s^{-2}
D	Diffusivity	3.2×10^{-9}	$m^2 s^{-1}$
$D_{eff} = \frac{D\theta}{\tau}$	Effective diffusivity	4.6×10^{-10}	$m^2 s^{-1}$
$A_{ls} = \frac{6w}{d_p \rho_p}$	Liquid/solid interfacial area	0.031	m^2
$v = \frac{g d_p (\rho_s - \rho_p)}{18\mu}$	Particle velocity	0.002	m s^{-1}
k_{ls}	Calculated mass transfer coefficient	1.4×10^{-4}	m s^{-1}
$-r_{ls} = k_{ls} A_{ls} C_{ox}$	Calculated liquid/solid mass transfer rate	3.0×10^{-3}	mole s^{-1}
$-r_{obs} = \Delta C_{ox} V \Delta t^{-1}$	Observed initial rate	1.1×10^{-3}	mole $s-^{1}$
$Sh = k_{ls} d_p / 6w$	Sherwood number	4.27548	Dimensionless
τ	Tortuosity factor	4	Dimensionless
θ	Void fraction	0.58	Dimensionless
$Pe = d_p v / D$	Peclet number	58.7187	Dimensionless
Ca	Carberry number	0.37	Dimensionless
$\eta\phi^2$	Weeler-Weisz group	2.1	Dimensionless

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