



# A New Sustainable Multistep Catalytic Process from Benzene to Caprolactam: Amination, Hydroxylation and Beckmann Rearrangement Promoted and Catalyzed by Trifluoroacetic Acid

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Received: 1 August 2022 / Accepted: 17 October 2022

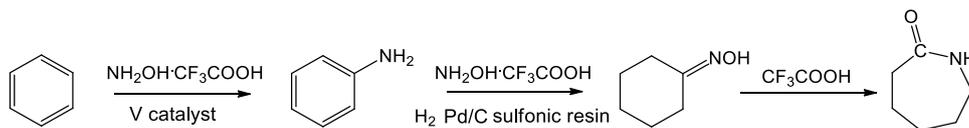
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## Abstract

Here we report some results on a 3 steps benzene caprolactam process via amination, aniline Hydroxylation and Beckmann rearrangement. The amination proceeds with hydroxylamine trifluoroacetate, with 97% of conversion and selectivity of 90%, catalyzed by V compounds. We achieve 98% of conversion and 95% of selectivity in the hydroxylation of aniline in the presence of hydroxylamine trifluoroacetate, sulfonic resin and Pd/C. While in the absence of the resin, hydrogenation of hydroxylamine trifluoroacetate occurs readily to the ammonium salt. The reaction occurs likely by the exchanged hydroxylamine and the aniline reduction intermediate. The use of hydroxylamine trifluoroacetate, instead of the chloride, favors the sustainability of the process by avoiding the ammonium chloride formation. The absence of salt except those derived from the trifluoroacetic acid allows a complete reuse of the trifluoroacetic acid and the only byproduct is ammonium nitrate obtained by resin regeneration. Beckmann rearrangement of the so produced cyclohexanone oxime occurs easily after diethyl ether evaporation and additions of a solution trifluoroacetic acid acetonitrile in high yield and selectivity.

## Graphical Abstract

New three steps caprolactam process via benzene amination and aniline hydrogenation.



New three steps caprolactam process *via* benzene amination and aniline hydrogenation.

**Keywords** Amination · Metal catalysts · Hydroxylamine trifluoroacetate · Hydroxylation · Pd/C · Trifluoroacetic acid · Sulfonic resins

## 1 Introduction

Caprolactam processes are all centered on the Beckmann rearrangement of the cyclohexanone oxime, even the photinitrosation of cyclohexane commercialized by Toray passes through the Beckman rearrangement of a nitrosyl intermediate, which is in equilibrium with the cyclohexanone

oxime [1]. In all processes considered, there is coproduction of salts, and only in the last decade are operative salt free processes in the Far East, employing a step of cyclohexanone amoximation and a second one of a gas phase Beckmann rearrangement [2, 3]. These processes, which are licensed by Eni-Sumitomo and China Petrochemical Co. appear to be highly sustainable, but they have had a development of new plants only in China [4]. On the contrary, Sumitomo very recently announce its exit from caprolactam business [5].

Despite the development of these new processes, several companies such as BASF, China Petroleum & Chemical Co., Honeywell International, UBE Industries, employ

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stoichiometric processes, where ammonium sulfate is quantitatively the main product [1]. An interesting process is the HPO Fibrant (ex DSM), which has actually 25% of the market, this highly optimized liquid phase route allow the lower coproduction of phosphate and sulfate salts, but at the expense of complex recycling of both organic and inorganic stream [6]. The Global Caprolactam Market size was USD 13.7 Billion in 2020 and expected to reach USD 14.7 Billion in 2022, despite of Sars-cov 19 pandemic scenario started in 2020, a production growth rate of 4–5% is forecasted until 2030 [7]. It appears that a complete change of the traditional plants based on liquid phase reactions seems to be not justified in Europe and in the USA since the caprolactam demand in the western region does not growth as in the Far East [1, 8–10]. Anyway, after all these considerations, the revamping of existing plant in Europe and USA could be a more sustainable route, with respect to the construction of new ones.

Hydrogenation of phenol is a classical route for the synthesis of cyclohexanone, which is the starting material for the production of the cyclohexanone oxime [1]. The phenol hydrogenation, is a cleaner way to the cyclohexanone oxime synthesis, however the phenol produced by the Hock process derive from a multistep with quite low overall yield from benzene. Furthermore, the demand of phenol and the coproduction of acetone, whose market value is not comparable with that of phenol, are bottlenecks for a caprolactam production based on this synthetic path [11, 12]. Starting from such a point of view, the use of nitrobenzene as starting material for cyclohexanone oxime production looks like competitive compared to both phenol hydrogenation and cyclohexane oxidation. In fact, nitration of benzene gives nitrobenzene in one-step only. The reaction is selective and obtained in high yield. Furthermore, it could be easily carried out both in continuous and batch operations [13]. For

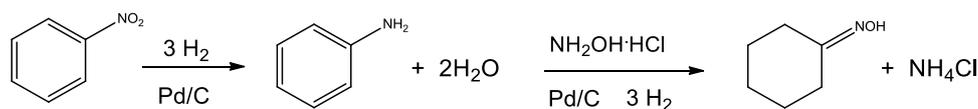
these reasons, the recent studies of nitrobenzene hydrogenation to cyclohexanone oxime appear to open a promising perspective to alternative routes in the COX production, without a complete change of plant layout [14–16]. In Scheme 1 is reported the process from nitrobenzene to caprolactam occurring at very mild condition 338 K and 5 bar.

On the other hand, the reaction proceeds in very high yield, directly starting from aniline [16]. The reaction appears to be highly selective to cyclohexanone oxime, thus aniline hydrogenation to cyclohexanone oxime step is the key for the overall process [16]. In addition, the presence of the hydroxylamine is necessary not only as the reagent for the formation of the COX, but it appears to be a promoter in the hydrogenation of the aniline itself [16]. In fact, formation of COX occurs on the catalyst surface by the reaction of a Pd-imine complex with the hydroxylamine [16]. Then, a further improvement on the overall process could be the use of aniline as starting reagent. In fact, the production of the cyclohexanone oxime, integrated with a process of benzene amination may represent a step forward in the sense of a more sustainable process [17, 18].

A comparison of the overall yield from benzene to caprolactam (CPL) of the main industrial process could be useful to focus on the sustainability of the various procedure [1, 11–13, 19]. Table 1 reports the data available for the different processes [1, 11–13, 19]. It is evident that the direct conversion from benzene to CPL is accompanied by a large amount of byproducts and several steps (6 in all the process), mainly due to the synthesis of cyclohexanone [1, 11–13, 19]. Nitrobenzene process shows the best performance in the reduction of the number of steps and the overall yield from benzene, but lacks in reduction of byproducts.

A further drawback of a process via benzene nitration is that, such a reaction is poorly sustainable and definitely not

**Scheme 1** Cyclohexanone oxime process from nitrobenzene



**Table 1** Comparison of some industrial CPL process with a TFA Nitrobenzene based CPL process

Process	Ref	CON process	BR process	Steps from benzene	Benzene based yield (%)	Max T (K)	CPL byproducts ratio <sup>a</sup>	Corrosion problems
Basf	[1, 19]	CyH ox	Oleum	6	40–70	453	4.1	High
HPO-Fibrant	[11]	Phenol	Oleum	6	58	393	1.5	High
HPO-Fibrant	[1, 19]	CyH ox	Oleum	6	40–70	453	1.5	High
Sumitomo-Eni	[1]	CyH ox	Gas phase	6	40–70	600	0.1	Low
Nitrobenzene	[14–16]	–	TFA	3	90	373	3 <sup>b</sup>	Moderate

<sup>a</sup>Comprised the  $(\text{NH}_4)_2\text{SO}_4$  obtained in the  $\text{NH}_2\text{OH}$  and the wastes of CON synthesis

<sup>b</sup> $\text{NH}_2\text{OH}$  synthesis from conventional Rashig process is about 2.5, 0.5 derive as  $\text{NH}_4\text{Cl}$  from Hydrogenation of nitrobenzene

green. For this reason, its substitution with a single step amination reaction is an ambitious target for the aromatic amines industry [17]. The use of huge amounts sulfuric acid, with the consequent acid dilution and re-concentration stages necessary in the purification of the product, causes corrosion, environmental and economic concerns [13]. Undoubtedly, a new process, where a step starts with such a problem, is not appealing for the revamping of existing plants, since its sustainability is not entirely justified from purely economic perspective. Actually, the reduction of reaction steps does not gain a substantial benefit from an environmental point of view [14, 16]. Even though, benzene amination is a valuable alternative for aniline production it is not an easy way [17]. In fact, in the early work of Kovacic and Bennet reactions took place at 373 K and using strong Lewis acid with low amines yield [18]. More recently are reported yields of 60% in aniline at 353 K, in the presence a high load of V(IV) as the catalyst, with TONs of 30–40 after 4 h of reaction, these evidences suggests that reaching high yields in this reaction is a hard target [20]. In fact, aniline synthesis appears to be the key step of a benzene to caprolactam process via aniline, but it is sustainable when amination reaches a yield comparable to those of nitration-reduction steps, thus avoiding the nitrobenzene synthesis. Furthermore, amination of benzene with hydroxylamine could be sustainable in an optic of an integrated process. Hydroxylamine acts as amination and oximation agent but its production in large amount by salt free processes is necessary for the sustainability of the process. In fact, aniline synthesis appears to be the key step of a benzene to caprolactam process via aniline, but it is sustainable when amination reaches a yield comparable to those of nitration-reduction steps, thus avoiding the nitrobenzene synthesis.

Recently, the cyclohexyl amine oxidation route to CPL has been repropose, such an interesting reaction needs, however the synthesis of such an amine which is a not straightforward. Actually, aniline hydrogenation is not easy and the yield to cyclohexyl amine are obtained by using more severe conditions than that employed in the hydrogenation of AN to COX [21–23].

During the last decades have appeared in literature some papers where the Beckmann rearrangement of oximes occur easily in high yield at temperature of 353–373 K in the presence of trifluoroacetic acid [24–28]. The kernel of these processes is the use of a mixture of trifluoroacetic acid and acetonitrile, which gives high yield in the amides [24–28]. More recently has been introduced a one-pot process where ketones oximation and Beckmann rearrangement were carried out in the same reactor in one-step in the presence of TFA and hydroxylamine hydrochloride in the same range of temperature of the Beckmann rearrangement [29–33]. In addition, we pointed out that the two reactions, at higher temperature (383–393 K), proceeds also in absence of

trifluoroacetic acid (though in lower yield) and hydroxylammonium salt is self-catalyzes the reaction [33].

Nevertheless, in all the processes until described, the elimination of hydrochloric acid or ammonium chloride is certainly their major limit. Recently, we showed that the use of the ionic liquid hydroxylammonium trifluoroacetate instead of an inorganic hydroxylamine salt, results in salt free process giving high yield of caprolactam starting from cyclohexanone [34]. In this case, the purification from hydrochloric or from other mineral acids is avoided, so that resulting in a more efficient process both from environmental and industrial point of view [34].

The use of sulfonated resins as catalyst or absorber is well known for long time. For instance, these type of materials as catalysts for ethers and esters are commonly used in the synthesis of methyl tert-butyl ether or in transesterification of vegetal oil in biodiesel production. [35, 36]. O-alkylation of phenol with cyclohexene shows the need of a protic molecule thus allowing the proton exchange between the resin and the olefin in order to form a surface polarized adduct, which is responsible of the catalysis [37]. Besides, in the hydration of olefins promoted by TFA the sulfonated resin as esterification and hydrolysis catalyst grants an enhancement in the yield of the desired products [38].

In this paper, we want to show some results on the use of hydroxylammonium salts in the benzene amination catalyzed by various metals. In addition, we propose the selective Hydroxylation of nitrobenzene and aniline to cyclohexanone oxime catalyzed by Pd/C catalyst. Finally, the Beckmann rearrangement of the cyclohexanone oxime in TFA demonstrates the feasibility of a benzene CPL process in three steps. The formation of ammonium ion as byproduct of the process is a drawback, but it could be the base for a regenerative ammonium nitrate/nitric acid/trifluoroacetic acid exchange process to be used in a modified HPO process, which we have reported some preliminary results in a previous paper [34].

## 2 Experimental

All solvents and reagents were employed as received without further purification. Trifluoroacetic acid 98% (TFA) Carlo Erba, cyclohexanone 99% (CON), cyclohexanone oxime (COX), caprolactam (CPL), aniline 99% (AN), Nitrobenzene 99% (NB), hydroxylamine hydrochloride (HA·HCl) 99%, hydroxylamine Sulfate 99% (HA·H<sub>2</sub>SO<sub>4</sub>), hydroxylamine phosphate 99% (AH·H<sub>3</sub>PO<sub>4</sub>), acetonitrile, ethanol (EtOH) and diethyl ether (DEE) were all Merck solvent grade products. Iron and cuprum powder are Carlo Erba PA products, Ammonium vanadate 99%, Sodium vanadate a Merck product. Pd/C 5% is an Engelhard (now

Basf catalyst) Escat 10. Amberlyst 15 and 36 (4.7 and 5.8 meq  $\text{H}^+$ /g, respectively) are Merck products.

Hydroxylamine trifluoroacetate ( $\text{HA}\cdot\text{TFA}$ ) were synthesized by an exchange procedure in aqueous solution. A typical preparation were carried out as follow: hydroxylamine sulfate was dissolved in water (c.a. 10 wt%). A solution of  $\text{Ba}(\text{OH})_2$  is neutralized with TFA plus an addition of a small excess of TFA until pH 3, this is useful to complete the exchange of the sulfate ions in the second step. The slowly addition of the hydroxylammonium sulfate solution allow the precipitation of the  $\text{BaSO}_4$  and in solution remains  $\text{HA}\cdot\text{TFA}$ . The separation of the supernatant by centrifugation it allows recovering  $\text{HA}\cdot\text{TFA}$  after the evaporation of the water by a rotary-evaporator at 343 K under vacuum (mechanical pump 1000 Pa). The resulting viscous oil is then left at 343 K under higher vacuum (0.2 Pa) for 6 h. A previous paper reports the characterization of  $\text{HA}\cdot\text{TFA}$  by NMR, and electric conductivity [34].

The amination reactions have been carried out in a in an autoclave equipped with a glass insert, stirred by magnetic agitation and fluxed with nitrogen and/or air, then heated in a thermostated oil bath at the reaction temperature (353 K). In a typical reaction, 5 mmol of hydroxylamine and 0.1 mmol of catalyst were dissolved in 10 mL of water/acetic acid 1/9 solution as a solvent. Then 5 mmol of substrate is added to the solution at the temperature of reaction. Some reactions with  $\text{HA}\cdot\text{TFA}$  were carried out in the absence of water, since it is soluble in neat acetic acid. After 4 h of reaction, the solution is neutralized with NaOH, extracted with DEE, finally analyzed by GC, HPLC and GC–MS.

All the hydroxylation reactions were carried out in an autoclave equipped with a glass insert, stirred by magnetic agitation, thermostated at temperatures comprised between 323 and 353 K, containing weighed samples of catalyst, promoter, solvent and reagents. Typically 10 mmol of nitrobenzene or aniline, 30 mmol of  $\text{HA}\cdot\text{X}$  where  $\text{X} = \text{CF}_3\text{COOH}$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , 10 mL DEE as the solvent, 2 g of sulfonated styrene–divinylbenzene copolymers, 50 mg of Pd/C 5%, finally the volume of reaction is about 12 mL.

The Beckmann rearrangement step were carried out in the same reactor used for the oximation step plugged into a 20 mL autoclave in order to accomplish Beckmann rearrangement at temperature of 383 K, which is higher than that of the boiling point of the solvent (acetonitrile 355 K). A typical experiment consists on removing the solid by filtration and the solvent by evaporation at 298 K overnight. Finally 20 mL TFA (30 mmol) in acetonitrile was added to the residue, the autoclave is closed, washed with nitrogen, and finally heated at 383 K for 2 h. The reaction solution were neutralized with  $\text{NaHCO}_3$  before the analysis. In some experiments, we distilled the solvent and recovered both TFA and acetonitrile.

Analysis of reaction products were typically carried by gas chromatograph (GC), gas chromatograph coupled with mass spectroscopy (GC–MS). Besides, we checked products and reagents by high performance liquid chromatography (HPLC).

### 3 Results and Discussion

This work is divided in three part the first one is the amination of benzene, in these experiments the reactivity of various metal catalysts are tested under the run conditions similar to those available in literature [20]. The second part is under many aspects alike to that reported in a recent paper in which the investigation has regarded mainly the conditions of reaction and the stages of the overall process [20]. Here, however, we investigate a different aspect that is the use of the trifluoroacetyl hydroxylamine in the synthesis of cyclohexanone oxime in the presence of a sulfonic resin. In addition, we verify the feasibility of the whole transformation from benzene to CPL by testing the various steps of the process sequentially.

#### 3.1 Some Results on Benzene Amination with Hydroxylamines

Table 2 reports some preliminary results on amination of benzene. In this reaction, catalyst is homogeneous in aerated acetic acid solution. The yield of aniline reaches almost 34% of conversion and 98% of selectivity using  $\text{NaVO}_3$  as a catalyst (entry 1).  $\text{NH}_4\text{VO}_3$  (entry 2) as a catalyst shows lower selectivity and conversion than  $\text{NaVO}_3$ . Fe and Cu both show low conversion compared to V, thus suggesting a lower activity of these metals (entries 3 and 4). An interesting feature of the utilization of  $\text{HA}\cdot\text{TFA}$  instead of  $\text{HA}\cdot\text{HCl}$  is the high solubility of this ionic liquid in organic solvent, thus it is feasible its use neat acetic. In fact, the use of neat acetic acid is most relevant improvement, since all the metals tested show an increasing of their activity by using acetic acid instead of the aqueous acid solution. The reaction carried out in the presence of  $\text{HA}\cdot\text{TFA}$  has, in any case, higher conversion and selectivity than those reactions carried out in  $\text{HA}\cdot\text{HCl}$  (entries 5–10). Despite of these very preliminary results on benzene amination, it appears that the use of  $\text{HA}\cdot\text{TFA}$  together with  $\text{NaVO}_3$  as catalyst gives remarkable yield in aniline thus suggesting the possibilities for a new integrated process,  $\text{HA}\cdot\text{TFA}$ , benzene to caprolactam. The best result is obtained in the presence of  $\text{NaVO}_3$  with  $\text{NH}_2\text{OH}\cdot\text{TFA}$  as amination agent, in neat acetic acid with a conversion of 76%, selectivity of 97% and a TON of 38 (entry 6). To say the truth it is actually a modest utilization of the catalyst, however comparable of what reported in literature [20]. Entry 7 has been carried out in the presence of

**Table 2** Benzene amination in the presence of various metals as catalyst

Entry	NH <sub>2</sub> OH·X	Solvent	Catalyst	Conversion (%)	TON	Selectivity	
						Aniline (%)	Others (%)
1	HCl	AcOH/H <sub>2</sub> O <sup>a</sup>	NaVO <sub>3</sub>	34	17	98	2
2	HCl	AcOH/H <sub>2</sub> O <sup>a</sup>	NH <sub>4</sub> VO <sub>3</sub>	12	6	97	3
3	HCl	AcOH/H <sub>2</sub> O <sup>a</sup>	Fe	5	2.5	97	3
4	HCl	AcOH/H <sub>2</sub> O <sup>a</sup>	Cu	2	1	96	4
5	CF <sub>3</sub> COOH	AcOH/H <sub>2</sub> O <sup>a</sup>	NaVO <sub>3</sub>	40	20	98	3
6	CF <sub>3</sub> COOH	AcOH	NaVO <sub>3</sub>	76	38	97	3
7 <sup>b</sup>	CF <sub>3</sub> COOH	AcOH	NaVO <sub>3</sub>	99	0.99	92	8
8	CF <sub>3</sub> COOH	AcOH	NH <sub>4</sub> VO <sub>3</sub>	18	9	97	3
9	CF <sub>3</sub> COOH	AcOH	Fe	7	3.5	98	2
10	CF <sub>3</sub> COOH	AcOH	Cu	3	1.5	97	3

Run conditions: reaction volume 10 mL, benzene 0.5 mol L<sup>-1</sup>, HA 5 mmol, T 353 K, catalyst 0.1 mmol, time of reaction 4 h

Others: oxidation condensation products of amines and benzene

<sup>a</sup>Reaction carried out in acetic acid/water = 9/1

<sup>b</sup>Used a stoichiometric amount of NaVO<sub>3</sub>

an equimolar amount of V in order to verify if it is possible to achieve high aniline yield. In this case, we obtain almost quantitative conversion and selectivity above 90%, suggesting the possibility of a synthetic application. Further studies need for the reuse of the vanadium catalyst.

The reactivity of other aromatics, the optimization of the run conditions and the study of the mechanism are beyond the scope of the present work.

### 3.2 Nitrobenzene and Aniline Hydrogenation in the Presence of Various Hydroxylammonium Salts

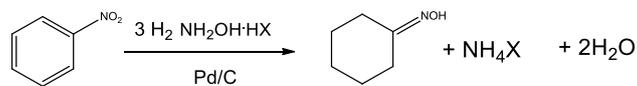
In Tables 3 and 4, we compare the hydrogenation of nitrobenzene and aniline in the presence of several hydroxylammonium salts. As already pointed out in the previous paper, nitrobenzene hydrogenation is faster than that of the COX formation from aniline [16]. The latter derives easily from nitrobenzene but COX needs longer reaction time. The best results are, in any case observed, in the presence of the hydrochloric salt (entries 1 and 2). At difference of the mineral acid hydroxylammonium salts, HA·TFA, in the range studied, is fully soluble in DEE, but the selectivity to COX is negligible. The presence of a soluble hydroxylammonium salt is accompanied by a fast hydrogen consumption (see Sect. 3.3) due to parallel hydrogenation of nitrobenzene and of hydroxylamine, the reaction is highly selective to AN and only in negligible amount to COX (entries 3 and 4). Thus suggesting the fast parallel reaction of hydroxylamine

hydrogenation causes a fast lowering of its concentration, thus determining the low selectivity in COX. On the contrary, the very low selectivity to COX in the presence hydroxylamine sulfate and phosphate compared to the chloride one can be ascribed to the negligible solubility of these salts and likely to the inhibiting effect of sulfate and phosphate anion.

The use of AN as the starting substrate shows low yield in COX, except the reaction carried out in the presence of HA·HCl (Table 4 entries 1 and 2). Such a behavior can be ascribed, as already suggested for NB hydrogenation, to the solubility of the hydroxylamines, which is complete for the HA·TFA being hydrogenated to the ammonium salt, while results negligible for sulfate and phosphate ones. It is noteworthy the lower conversion of the aniline compared to the reactions of Table 3, where aniline is converted to COX after the reduction of the nitro-group [16]. Such a phenomenon can be ascribed to a strong deactivating effect of the AN on the catalyst activity, when Pd directly interact with the amine, as already pointed out in a previous work [16].

### 3.3 Hydrogenation of Nitrobenzene and Aniline in the Presence of Sulfonic Resins

After such a comparative introduction on the reactivity of the various hydroxylammonium salts in the synthesis of COX, we reports in Table 5 some results obtained in the hydrogenation of nitrobenzene also in the presence of a macro reticular sulfonic resin. The use of two different resins show

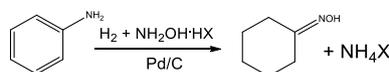
**Table 3** Comparative results on nitrobenzene hydrogenation to cyclohexanone oxime

Entry	NH <sub>2</sub> OH·X	Time of reaction (h)	Conversion (%)	Selectivity					
				AN (%)	COX (%)	CHA (%)	CON (%)	PCA (%)	Others (%)
1	Cl	1	85	44	55	–	–	–	–
2	Cl	20	99	29	64	1	1	4	1
3	CF <sub>3</sub> COOH	1	83	98	1	–	–	–	–
4	CF <sub>3</sub> COOH	20	99	94	4	–	–	1	1
5	H <sub>2</sub> SO <sub>4</sub>	1	88	99	0.5	–	–	–	0.5
6	H <sub>2</sub> SO <sub>4</sub>	20	98	93	5	–	–	0.5	0.5
7	H <sub>3</sub> PO <sub>4</sub>	1	81	100	–	–	–	–	–
8	H <sub>3</sub> PO <sub>4</sub>	20	96	96	3	–	–	–	1

Run conditions: reaction volume 20 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, NH<sub>2</sub>OH·X 30 mmol, T 333 K, Pd/C 5% catalyst 50 mg, H<sub>2</sub> pressure 7 Bar

Entries 1 and 2 and 5–8 data from [16]

AN aniline, COX cyclohexanone oxime, CHA cyclohexylamine, CON cyclohexanone, PCA phenylcyclohexylamine, others: condensation products

**Table 4** Comparative results on aniline hydrogenation to cyclohexanone oxime

Entry	NH <sub>2</sub> OH·X	Time of reaction (h)	Conversion (%)	Selectivity				
				COX (%)	CHA (%)	CON (%)	PCA (%)	Others (%)
1	Cl	1	4	98	–	–	1.5	0.5
2	Cl	20	47	98	0.4	0.8	0.2	0.6
3	CF <sub>3</sub> COOH	1	0.5	–	–	–	–	100
4	CF <sub>3</sub> COOH	20	2	74	T	T	T	25
5	H <sub>2</sub> SO <sub>4</sub>	1	1	T	–	–	–	0.9
6	H <sub>2</sub> SO <sub>4</sub>	20	16	79	–	T	T	20
7	H <sub>3</sub> PO <sub>4</sub>	1	1.5	80	–	–	–	20
8	H <sub>3</sub> PO <sub>4</sub>	20	12	78	–	T	T	21

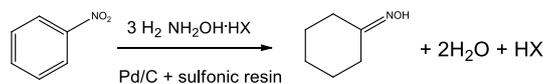
Run conditions: reaction volume 20 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, NH<sub>2</sub>OH·X 30 mmol, H<sub>2</sub>O 20 mmol, T 333 K, Pd/C 5% catalyst 50 mg, H<sub>2</sub> pressure 7 Bar

Entries 1 and 2 data from [16]

AN aniline, COX cyclohexanone oxime, CHA cyclohexylamine, CON cyclohexanone, PCA phenylcyclohexylamine, others: condensation products

similar results suggesting a minor influence of the type of resin on the overall reactivity. As regard the reactions in the presence of HA·HCl (entry 1 and 2) it appears that after 20 h of reaction the reactivity is similar to that observed without the resins, thus suggesting the presence of resin does not change the behavior of the reaction. The reactivity of HA·TFA (entries 3 and 4) is similar to that of HA·HCl but

completely different of that obtained without resin (Table 1 entries 3 and 4). Such a difference can be related to the hydroxylamine adsorption on the resin. In fact, the resin adsorbs hydroxylamine thus reducing its hydrogenation, in turn, the formation of ammonia displace the hydroxylamine from the sulfonic resin, thus allowing its reaction with the surface imine compound that is likely formed on

**Table 5** Nitrobenzene hydrogenation to cyclohexanone oxime in the presence of sulfonic resins

Entry	NH <sub>2</sub> OH·X	Sulfonic resin type	Conversion (%)	Selectivity					
				AN (%)	COX (%)	CHA (%)	CON (%)	PCA (%)	Others (%)
1	Cl	A15	99	58	40	0.1	0.1	0.4	0.4
2	Cl	A36	99	61	38	0.1	0.1	0.4	0.4
3	CF <sub>3</sub> COOH	A15	98	34	64	–	0.5	0.2	0.3
4	CF <sub>3</sub> COOH	A36	98	33	65	–	0.5	0.2	0.3
5	Exchanged	A15	99	70	29	–	–	–	T
6	Exchanged	A36	99	71	28	–	–	–	T
7	H <sub>2</sub> SO <sub>4</sub>	A15	98	99	0.9	–	–	–	T
8	H <sub>2</sub> SO <sub>4</sub>	A36	97	99	0.9	–	–	–	T
9	H <sub>3</sub> PO <sub>4</sub>	A15	97	99	0.7	–	–	–	T
10	H <sub>3</sub> PO <sub>4</sub>	A36	96	99	0.4	–	–	–	T

Run conditions: reaction volume 20 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, NH<sub>2</sub>OH·X 30 mmol, T 333 K, catalyst 50 mg, sulfonic resin 2.5 g, time of reaction 20 h

AN aniline, COX cyclohexanone oxime, CHA cyclohexylamine, CON cyclohexanone, PCA phenylcyclohexylamine, others: condensation products

the Pd catalyst [14]. The adsorption of HA on the resin has been tested by filtering away the resin and adding 10 ml 1 M NaOH solution, which readily displaces the adsorbed base on the sulfonic site of the resin. In fact, the so obtained supernatant reduces a Fe(III) solution to Fe(II), clearly evidenced by the formation of the red complex with the 1,10-phenanthroline. Furthermore, an ionic HPLC analysis of the solution shows the presence of both hydroxyl ammonium and ammonium ion, detailed study on HA adsorption on sulfonic resins is however beyond the aim of this research. It is noticeable that the reaction takes place also in the presence of hydroxylamine exchanged on Amberlyst 15 or 36 (entries 5 and 6). Such evidence suggests the reaction is strongly influenced by the effective concentration of the hydroxylamine, in fact, when hydroxylamine is dissolved into the solvent the reaction does not give COX but reaction stops to AN. This is due to the fast parallel reduction of HA, which is competitive with that of NB hydrogenation, then its consumption determines a negligible selectivity toward COX. Besides, we obtain similar behavior of reactivity for sulfate and phosphate hydroxylammonium salts of those observed without resins (compare Table 3 entries 5–8 with Table 5 entries 7–10).

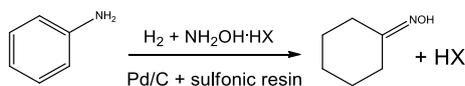
Similar yields in COX are observed starting from AN instead of NB, in the presence of HA·HCl (Table 6 entries 1 and 2). This evidence, as already reported in a previous paper, demonstrates the consecutive nature of nitrobenzene reduction to AN and its further conversion to COX [16]. On the contrary, by comparison data of Table 4 with those of Table 6 we can easily gather that hydroxylamine reduction is a parallel

hydrogenation reaction. In fact, if the sulfonic resin adsorbs HA·TFA from the solution, thus protecting HA from being quickly hydrogenated (compare Table 4 entries 3 and 4 with Table 6 entries 3 and 4). It appears that resin/HA equilibrium permits a concentration of HA sufficient for reacting on Pd surface with the imine intermediate to give COX [16]. Such a hypothesis is supported by the evidence that the reactivity of resins exchanged with hydroxylamine are comparable to those carried out in the presence of HA·HCl-resin or HA·TFA-resin and with comparable yields in COX (compare entries 1–4 with 5 and 6). Nevertheless, HA·H<sub>2</sub>SO<sub>4</sub> and HA·H<sub>3</sub>PO<sub>4</sub>, as already observed without resin, give low selectivity in COX and the type of resin has no influence on the reactivity. Also in this case the reason of this behavior can be ascribed likely to the very low concentration of HA in solution not sufficient to react to give COX, together with a deactivating effect of the anions on the HA reactivity.

As already pointed out in previous papers, the amount of Pd/C catalyst is critical to achieve high yield in aniline [16]. Actually, in an experiment (entry 11) we loaded 4 times the amount of catalyst into the reactor reaching in this way a conversion of 96% and with a selectivity of 95%.

### 3.4 Comparison of the Hydrogen Consumption Rate of Nitrobenzene, Aniline and Hydroxylammonium Salts in the Presence of Sulfonic Resins

In Fig. 1, we compare the hydrogen consumption of nitrobenzene hydrogenation in the presence and without

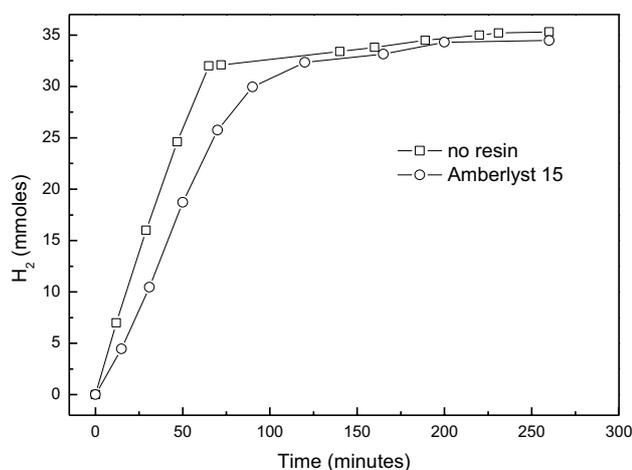
**Table 6** Aniline hydrogenation to cyclohexanone oxime in the presence of sulfonic resins

Entry	NH <sub>2</sub> OH·X	Sulfonic resin type	Conversion (%)	Selectivity				
				COX (%)	CHA (%)	CON (%)	PCA (%)	Others (%)
1	Cl	A15	36	98	–	1	Traces	1
2	Cl	A36	35	98	–	1	Traces	1
3	CF <sub>3</sub> COOH	A15	46	98	–	1	Traces	1
4	CF <sub>3</sub> COOH	A36	45	98	–	1	Traces	1
5	H <sub>2</sub> SO <sub>4</sub>	A15	3	99	–	–	–	Traces
6	H <sub>2</sub> SO <sub>4</sub>	A36	2	99	–	–	–	Traces
7	H <sub>3</sub> PO <sub>4</sub>	A15	0.8	99	–	–	–	Traces
8	H <sub>3</sub> PO <sub>4</sub>	A36	0.6	99	–	–	–	Traces
9	Exchanged	A15	35	98	–	1	–	Traces
10	Exchanged	A36	34	98	–	1	–	Traces
11 <sup>a</sup>	CF <sub>3</sub> COOH	A15	96	95	Traces	1	Traces	4

Run conditions: reaction volume 20 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, NH<sub>2</sub>OH·X 30 mmol, H<sub>2</sub>O 20 mmol, T 333 K, catalyst 50 mg, time of reaction 20 h

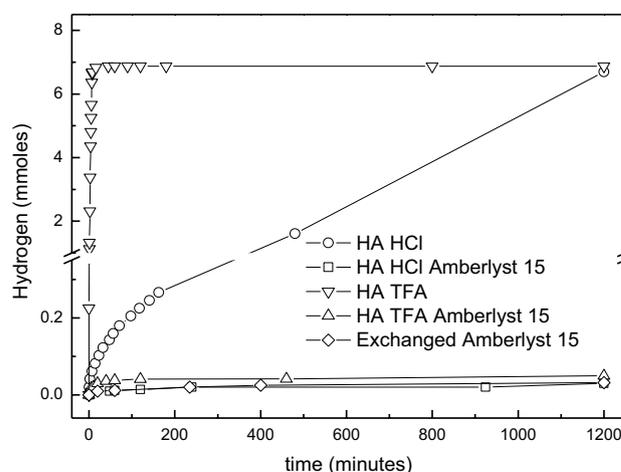
COX cyclohexanone oxime, CHA cyclohexylamine, CON cyclohexanone, PCA phenylcyclohexylamine, others: condensation products

<sup>a</sup>Reaction carried out in the presence of 200 mg of Pd/C to increase the yield of COX



**Fig. 1** Comparison of hydrogen consumption rate of Nitrobenzene hydrogenation. Run conditions: reaction volume 20 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, HA·HCl 30 mmol, H<sub>2</sub>O 20 mmol, T 333 K, catalyst 50 mg, sulfonated resin 2 g

resin. As already pointed out in an earlier paper, two distinct behaviors characterize hydrogen consumption, in the first part we can observe a fast pseudo zero order reaction where nitrobenzene is hydrogenated to aniline and a second slower part, where aniline is converted to COX [16]. The presence of the resins does not modify such a behavior; the main difference with the previous research in the absence of sulfonic resin is a lower hydrogen consumption in the part of the NB



**Fig. 2** Comparison of hydrogen consumption of HA·HCl and HA·TFA hydrogenation in the presence and in the absence of Amberlyst 15 sulfonic resin. Run conditions: reaction volume 20 mL, DEE as a solvent, substrate: HA·X 3.5 mmol, H<sub>2</sub>O 20 mmol, T 333 K, catalyst 50 mg, sulfonated resin 2 g

reduction while in the conversion of AN to COX there is a substantially similar rate of reaction. The adsorption of hydroxylamine on the resin may explain the lower hydrogen consumption rate because of the presence of the resin almost completely stop the parallel hydroxylamine reduction.

In order to verify the role of the resin in the reduction of the HA·X we compare (see Fig. 2) the difference in the

hydrogen consumption profile of various hydroxylammonium salts with and without Amberlyst 15 as a sulfonic resin (there are practically no differences with Amberlyst 36). It is noteworthy the reaction does not proceed noticeably in the presence of hydroxylammonium sulfate and phosphate, on the contrary the reaction occurs in the presence of HA·TFA and HA·HCl. The reaction carried out with HA·TFA appears very fast, thus explaining the very high selectivity in COX since hydrogenation of the oxime occurs faster than the reaction with the aniline. The slower reaction observed for HA·HCl is likely due to the lower amount of free HA in solution. In fact, HA·TFA is completely soluble, while HA·HCl is present mainly as a solid in the reaction environment. The presence of the Amberlyst 15 practically suppresses the reaction, as can be observed by the negligible amount of hydrogen consumed. Analogously, hydroxylamine exchanged on the resins shows a similar but very low amount of hydrogen consumption. This evidence suggests the absorption equilibrium of hydroxylamine is displaced toward resin, that is, the large part of the hydroxylamine is not in solution. Besides, by putting together an equimolar amount of Amberlyst 15/HA·TFA in DEE it appears that practically HA neutralizes all the sulfonic groups and the hydroxylamine is almost completely removed from the solution, remaining less than 3% of the initial concentration.

### 3.5 Direct Beckmann Rearrangement of the Hydrogenation Products

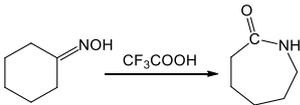
The reacted product of the nitrobenzene and aniline hydrogenation after the solid separation and the removal of the solvent, the latter operation is necessary to adding the solution

of TFA in acetonitrile. Such a mixture of solvents gives the best results in the Beckmann rearrangement at 383 K, while reactions carried out in solution TFA DEE show both low conversion and negligible selectivity [21–23, 34]. Table 7 shows the results of the Beckmann rearrangement of the COX deriving from the hydrogenation reaction mixture. Because of the Beckmann rearrangement at 383 K is quite fast, all reactions have been stopped after 2 h of reaction, and can be considered at completion [23]. As expected the Beckmann rearrangement proceeds in high yield to CPL, the presence of aniline does not influence the reactivity of TFA since the acid is in large excess.

### 3.6 Reactivation of Sulfonic Resins with Nitric Acid and Recovery of Ammonium Nitrate and Pd/C Reuse

The recovery of the resins is a crucial point in the whole process, for this reason we tested the reusability of the resins after the adsorption of the ammonium from the reaction environment. It is noteworthy that the presence of the resin shows that the solid salt, which is coproduced during the reaction, is not observed because it is exchanged with the sulfonic sites of the resin. Washing the resin with 0.1 mol L<sup>-1</sup> nitric acid allows to restore the sulfonic acid sites with negligible loss in acidity of the resin (acidity was tested by titration, and the presence of HA in solution by Fe(III) reduction). The use of nitric acid to restore the acidity of the resins is justified since ammonium nitrate is a byproduct of not negligible value, whose employment as fertilizer is well known, in addition it could be reused in the HPO Fibrant process of hydroxylamine production [4].

**Table 7** Beckmann rearrangement of the hydrogenation products in TFA-acetonitrile



Entry Tables 5 and 6	Initial composition						Conversion (COX) (%)	Yield (CPL) (%)
	AN (%)	COX (%)	CHA (%)	CON (%)	PCA (%)	Others (%)		
1 NB	59	40	0.1	0.1	0.4	0.4	96	38
3 NB	35	64	–	0.5	0.2	0.3	98	62
4 NB	34	65	–	0.5	0.2	0.3	98	64
1 AN	63	35	–	1	Traces	1	95	32
3 AN	53	45	–	1	Traces	1	96	43
4 AN	54	44	–	1	Traces	1	96	42
9 AN	64	34	–	1	–	Traces	95	32
11AN	3	91	1	0.1	1.7	0.2	98	89

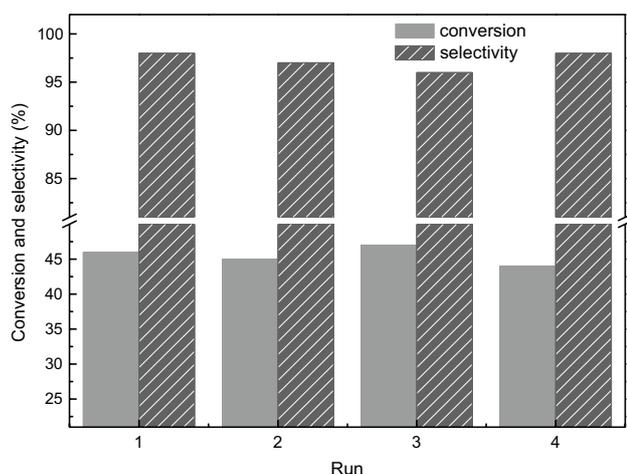
Run conditions: reaction volume 20 mL, acetonitrile as a solvent, TFA 30 mmol, T 383 K, time of reaction 2 h

CHA cyclohexylamine, PCA phenylcyclohexylamine, others: condensation products

Pd/C catalyst is the most expensive component of the whole process for such a reason its reuse in the reaction is of paramount importance for the sustainability of the process. The activity of the catalyst has been maintained after 4 reaction cycles. The Pd/C catalyst is recovered by filtration washed with plenty of water, ether and finally with water and desiccated at 363 K for 24 h before the use. After the operation of washing, which causes some losses, we carried out the reaction at constant substrate/Pd ratio by reducing the reaction volume. Figure 3 shows that activity and selectivity after 4 run are unaffected.

### 3.7 Single Reaction Carried Out at Maximal Yield

As can be observed in previous sections we studied the influence of various parameters on the yields of the various steps. The amination carried out in an equimolar amount of catalyst in the presence of HA·TFA and neat acetic acid shows



**Fig. 3** Activity of the reused Pd/C catalyst in aniline hydrogenation. Run conditions: reaction volume 20–17 mL, DEE as a solvent, substrate 0.5 mol L<sup>-1</sup>, HA·TFA 30–25.5 mmol, H<sub>2</sub>O 20 mmol, T 333 K, catalyst 50–40 mg, A15 sulfonated resin 2–1.8 g

**Table 8** Reactions of amination, Hydroxylation and Beckmann rearrangement under conditions of maximal conversion and yield

Step	Catalyst	Reaction temperature (K)	Conversion (%)	Solvent	Yield	
					At the next step (%)	Others (%)
Amination	NaVO <sub>3</sub>	353	99	CH <sub>3</sub> COOH	91	8 <sup>a</sup>
Hydroxylation	Pd/C	338	97	DEE	91	8 <sup>b</sup>
Beckmann rg	CF <sub>3</sub> COOH	373	99	ACN	95	5 <sup>c</sup>

Run conditions: amination, benzene/V/HA·TFA = 1/1/1.1, solvent CH<sub>3</sub>COOH 10 mL reaction time 24 h; Hydroxylation, aniline 5 mmol, DEE 10 mL, HA·TFA 15 mmol, Amberlyst 15 3.2 g, Pd/C 200 mg, reaction time 4 h; Beckman Rearrangements, COX 10 mmol, ACN 10 mL, TFA 30 mmol, reaction time 2 h data from ref [23]

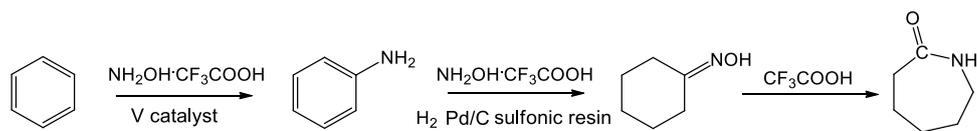
AN aniline, CHA cyclohexylamine, PCA phenylcyclohexylamine, others: condensation products, COX cyclohexanone oxime, CON cyclohexanone, DEE diethyl ether, ACN acetonitrile

<sup>a</sup>Biphenyl, <sup>b</sup>PCA, CON, CHA, <sup>c</sup>CON and CON condensation products

almost quantitative benzene conversion and selectivity to aniline of 92%. The reaction under such a condition appear worth to be used in an amination process despite the stoichiometric use of NaVO<sub>3</sub>. In addition, as already observed in a previous paper, the yield to cyclohexanone oxime in the Hydroxylation step raises, by increasing the amount of Pd/C catalyst [14–16]. Besides Beckmann rearrangement catalyzed by TFA has been extensively studied in previous papers, we report in Table 8 the best result of such a study [23]. In fact, the yield in CPL of the whole process with respect to the starting benzene is about 79% being the synthetic path, which shows the highest overall benzene based yield to CPL. The main industrial processes (see Table 1) have, in any case a lower overall yield because of to the multistep processes from benzene to cyclohexanone. In addition, for a process based on these reactions path, the unwanted salt byproduct is only 0.5 weight ratio with CPL. From this point of view, the main byproduct of salts amount depends for the larger part by the HA·TFA synthesis. For such a reason, in order to improve further the sustainability of this process, we have recently proposed a modified DSM-HPO process for HA·TFA synthesis via nitrate hydrogenation, which gives directly HA·TFA without unwanted byproducts (some preliminary results of this reaction appeared in a previous paper) [16]. Finally, the need of a large excess of HA·TFA in the hydrogenation step is likely the major concern of the process, new selective hydrogenation catalysts may help to overcome such a problem.

## 4 Conclusions

We propose a new reaction path from benzene to caprolactam in three steps as reported in Scheme 2. The first stage is the amination of benzene promoted by V complex. The employ of HA·TFA allows the use of glacial acetic acid as a solvent, thus increasing the yield of AN above 90%, which is likely the highest, reported in literature.

**Scheme 2** New three steps caprolactam process via benzene amination

The hydrogenation of AN to COX in the presence of Pd/C, sulfonated resins and HA-TFA instead of NB looks like a step further for the sustainability of the process, since the use AN, obtained by the previous amination step, allow to overcome benzene nitration. The reaction results selective to COX, but the parallel HA reduction limits its yield. The use of HA-TFA in the presence of a sulfonated resins shows a quite better utilization the HA improving the yield in COX, since the exchange of HA on the resin removes the hydroxylamine from the solution, thus avoiding its hydrogenation. The process may proceed by two simple steps: solvent removal and TFA addition, giving finally the CPL by Beckmann Rearrangement as the target product. The comparison with the actual processes (see Table 1) shows a neat diminish of the reaction steps and a substantial reduction of salts byproducts, without the use of sulfuric and nitric acid. Furthermore, all reactions are carried out in solution at moderate temperatures (333–383 K), thus allowing an easy revamping of the existing plants, since no complex equipment should need for their modification. Further improvements need however on the benzene amination step and on HA-TFA utilization being actually the main limits for the development of a new process.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10562-022-04207-9>.

**Funding** Funding was provided by Ca' Foscari University of Venice ADIR 2019.

## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have an influence on the work reported in this paper.

## References

- Tinge J, Groothaert M, op het Veld H et al (2018) "Caprolactam" in Ullmann's encyclopedia of industrial chemistry. Wiley on line Library. [https://doi.org/10.1002/14356007.a05\\_031.pub3](https://doi.org/10.1002/14356007.a05_031.pub3).
- Tonti S, Roffia P, Gervasutti V (1992) Enichem Anic S.p.A., EP 0496385A1
- Holderich WF, Dahloff G, Ichihashi H, et al (2003) Sumitomo Chemical Company US Pat. 6531595 B2.
- Zong B, Sun B, Cheng S et al (2017) Green production technology of the monomer of nylon-6: caprolactam. *Engineering* 3:379–384
- Tullo A (2022) Sumitomo will exit caprolactam business. *C & EN* 100(14):10
- <https://www.fibrant52.com/en/licenses>
- <https://www.mordorintelligence.com/industry-reports/caprolactam-market>
- Cui X (2009) Market analysis of caprolactam at home and abroad. *Fine Special Chem* 17:30–35
- Fisher G (2003) No rooms for new caprolactam plants. *Fibers Text East Eur* 11:14–15
- Van der Linde S, Fisher G (2004) The caprolactam business must change: new production plants cannot be justified. *Fibers Text East Eur* 12:17–18
- Weber M, Weber M, Volker Weber V (2000) Phenol. In: Ullmann's encyclopedia of industrial chemistry. Wiley on line Library. [https://doi.org/10.1002/14356007.a19\\_299.pub3](https://doi.org/10.1002/14356007.a19_299.pub3).
- Weber M, Pompetzki W, Bonmann R, Weber M (2004) Acetone. In: Ullmann's encyclopedia of industrial chemistry. Wiley on line Library [https://doi.org/10.1002/14356007.a01\\_079.pub4](https://doi.org/10.1002/14356007.a01_079.pub4)
- M. Dugal (2005) Nitrobenzene and nitrotoluenes. In: Kirk-Othmer encyclopedia of chemical technology. Wiley on line. <https://doi.org/10.1002/0471238961.1409201801041109.a01.pub2>
- Rubio-Marques P, Hernandez-Garrido JC, Leyva-Perez A et al (2014) One pot synthesis of cyclohexanone oxime from nitrobenzene using a bifunctional catalyst. *Chem Commun* 50:1645–1647
- Corma A, Leyva-Perez AA, Rubio-Marques P (2014) Universitat politecnica de Valencia. WO 191589 A1.
- Pietrobon L, Ronchin L, Sadraoui C et al (2020) Pd/C Catalyzed selective hydrogenation of nitrobenzene to cyclohexanone oxime in the presence of NH<sub>2</sub>OH·HCl: influence of the operative variables and insights on the reaction mechanism. *Appl Catal A: Gen* 598:117570
- Chiara JL (2005) Vinyl- and Arylnitrogen Compounds. In: Katritzky AR, Taylor RJK (eds) *Comprehensive organic functional group transformations II*. Elsevier Science, Amsterdam
- Kovacic P, Bennett RP (1961) Aromatic amination with hydroxylamine-O-sulfonic acid. *J Am Chem Soc* 83:221–224
- Musser MT (2011) Cyclohexanol and cyclohexanone. In: Ullmann's encyclopedia of industrial chemistry. Wiley on line Library. [https://doi.org/10.1002/14356007.a08\\_217.pub2](https://doi.org/10.1002/14356007.a08_217.pub2)
- Zhu LF, Guo B, Tang DY et al (2007) W Sodium metavanadate catalyzed one-step amination of benzene to aniline with hydroxylamine. *J Catal* 245:446–455
- Greenfield H (1964) Hydrogenation of aniline to cyclohexylamine with platinum metal catalysts. *J Org Chem* 29:3082–3084
- Chatterjee M, Sato M, Kawanami H et al (2011) Hydrogenation of aniline to cyclohexylamine in supercritical carbon dioxide: significance of phase behavior. *Appl Catal A general* 396:186–193
- Liu S, You K, Song J et al (2018) Supported TiO<sub>2</sub>/MCM-41 as an efficient and eco-friendly catalyst for highly selective preparation of cyclohexanone oxime from solvent-free liquid phase oxidation of cyclohexylamine with molecular oxygen. *Appl Catal A General* 568:76–85
- Marziano NC, Ronchin L, Tortato C et al (2008) Catalyzed Beckmann rearrangement of cyclohexanone oxime in heterogeneous liquid/solid system: part 2: influence of acid catalysts and organic promoters. *J Mol Catal A Chem* 290:79–87
- Ronchin L, Vavasori A, Bortoluzzi M (2008) Organocatalyzed Beckmann rearrangement of cyclohexanone oxime by trifluoroacetic acid in aprotic solvent. *Catal Commun* 10:251–256
- Ronchin L, Vavasori A, Bortoluzzi M (2008) A DFT study on secondary reaction pathways in the acid-catalysed Beckmann

- rearrangement of cyclohexanone oxime in aprotic solvent. *J Mol Struct Theochem* 858:46
27. Ronchin L, Vavasori A (2009) On the mechanism of the organo-catalyzed Beckmann rearrangement of cyclohexanone oxime by trifluoroacetic acid in aprotic solvent. *J Mol Catal A Chem* 313:22
  28. Quartarone G, Rancan E, Ronchin L et al (2014) Beckmann rearrangement of acetophenone oximes to the corresponding amides organo-catalyzed by trifluoroacetic acid for sustainable NSAIDs synthesis. *Appl Catal A-Gen* 472:167–177
  29. Aricò F, Quartarone G, Rancan E et al (2014) One-pot oximation–Beckmann rearrangement of ketones and aldehydes to amides of industrial interest: acetanilide, caprolactam and acetaminophen. *Catal Commun* 49:47–51
  30. Aricò F, Quartarone G, Rancan E et al (2014) Self-catalyzed direct amidation of ketones: a sustainable procedure for acetaminophen synthesis. *Catal Commun* 54:11–16
  31. Zhang JS, Riaud WAK et al (2014) Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam in a modified catalytic system of trifluoroacetic acid. *Catal Lett* 144:151–157
  32. Zhang JS, Lu YC, Wang AK et al (2013) Novel one-step synthesis process from cyclohexanone to caprolactam in trifluoroacetic acid. *Ind Eng Chem Res* 52:6377–6381
  33. Rancan E, Quartarone G, Ronchin L et al (2015) Acid catalyzed direct-amidation–dehydrocyclization of 2-hydroxy-acetophenones to benzoxazoles by a one-pot sustainable synthesis. *Catal Lett* 145:939–946
  34. Manente F, Pietrobon L, Ronchin, et al (2021) Trifluoroacetic acid hydroxylamine system as organocatalyst reagent in a one-pot salt free process for the synthesis of caprolactam and amides of industrial interest. *Catal Lett* 151:3543–3549
  35. Alexandratos SD (2009) Ion-exchange resins: a retrospective from industrial and engineering chemistry research. *Ind Eng Chem Res* 48:388–398
  36. Harmer M, Sun Q (2001) Solid acid catalysis using ion-exchange resins. *Appl Catal A: General* 221:45–62
  37. Ronchin L, Vavasori A, Toniolo L (2012) Acid catalyzed alkylation of phenols with cyclohexene: comparison between homogeneous and heterogeneous catalysis, influence of cyclohexyl phenyl ether equilibrium and of the substituent on reaction rate and selectivity. *J Mol Catal A: Chem* 355:134–141
  38. Bianchini E, Pietrobon L, Ronchin L et al (2019) Trifluoroacetic acid promoted hydration of styrene catalyzed by sulfonic resins: comparison of the reactivity of styrene, n-hexene and cyclohexene. *Appl Catal A: Gen* 570:130

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