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Environmentally friendly hydrogenation of nitrobenzene to *p*-aminophenol using heterogeneous catalysts

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ABSTRACT

Nitrobenzene was converted to *p*-aminophenol at 353 K, using water as solvent and a bi-functional catalyst composed of a mechanical mixture of supported Pt catalyst with zirconium sulphate calcined at 773–923 K. The performance of this system is independent of the support used for Pt, and various supports, such as pure or sulphated zirconia and titania, carbon, MgLa mixed oxide, give similar results. At low Pt content, the reaction rate is first order relative to nitrobenzene, and the slow step is the partial hydrogenation of nitrobenzene to phenylhydroxylamine, which requires only minute amounts of Pt. At higher Pt loadings, the rate of hydrogenation of nitrobenzene to phenylhydroxylamine and consequently to aniline takes over that of the acid-catalysed Bamberger rearrangement of phenylhydroxylamine to *p*-aminophenol. The selectivity of this step depends critically on the solid acid: strong acids such as sulphated zirconia or zeolites give poor selectivities because they tend to decompose the hydroxylamine intermediate. This process does not require sulphuric acid or additives such as DMSO or alkylsulphides, thereby simplifying the downstream processing.

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1. Introduction

The selective catalytic hydrogenation of nitrobenzene (NB) to p-aminophenol (PAP) is a reaction of industrial importance since PAP is an important pharmaceutical intermediate for the manufacture of paracetamol, a widely used analgesic drug. Two-step processes have been reported for the preparation of PAP, in which nitrobenzene is first partially hydrogenated to phenylhydroxylamine (PHA), followed by the Bamberger rearrangement of PHA to PAP in acidic conditions. Platinum is considered as the best noble metal, and carbon the best support, for the hydrogenation of nitrocompounds [1]. Higher selectivity to PHA has been reported by the addition of sulphur compounds such as dimethylsulphoxide (DMSO) [2], sulphides [3], or basic additives such as pyridine [4], phosphines [5] or phosphates [6]. When basic additives are used, a two-step process has to be used for the synthesis of PAP, involving the isolation of PHA after the partial hydrogenation and addition of sulphuric acid after the hydrogenation step [7] to effect the rearrangement. Using DMSO or sulphides, the process can be converted to one pot synthesis. After 3 h of reaction, a 75% conversion of nitrobenzene has been reported with a PAP selectivity of 79% using 27 mL of concentrated sulphuric acid for 57 mL of nitrobenzene in 406 mL of water [7]. The PAP thus formed needs to be isolated by neutralising the acid. This leads to the production of salts as effluents, with more complex separations. Most patents also report the addition of surfactants [8] which increase the area of contact between nitrobenzene and water, usually used as solvent.

A few attempts have been made to substitute sulphuric acid by a solid acid. For instance, Chaudhari et al. [9] reported the use of zeolites and acid resins for this reaction. The results were, however, disappointing since starting from 93.4 mmol of nitrobenzene, the conversion was 97% but the yield was only 14%. Very recently, a bi-functional Pt on highly acidic sulphated zirconia was used also with relatively poor results since the PAP yield was below 30% [10]. Indeed, the authors investigated the Bamberger rearrangement separately and observed selectivity lower than 45% at full conversion for this step, using highly acidic solid acids. It is important to note here that as reported by Groscova et al. [11] or Wang et al. [10], the Bamberger rearrangement can yield not only PAP but also aniline and azoxybenzenes. There is therefore an interest for processes, which would be highly selective towards PAP, would not produce salts as effluents, and could avoid complex separation, particularly of the additives required to promote selectivity.

It can be pointed out that this is a difficult task since the coupling of hydrogenation with acid-catalysed rearrangement is rather uncommon in organic synthesis. The formal reaction



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Scheme 1. Simplified reaction scheme.

scheme, reported in Scheme 1, has some common points with the bi-functional isomerisation of paraffins, with the major difference that in paraffin isomerisation, the concentration of the olefin intermediate is governed by the thermodynamic equilibrium of hydrogenation, while here all steps are controlled by kinetics. An obvious conclusion that can be drawn from Scheme 1 is that the rate of rearrangement of PHA to PAP (k_3) and that of the complete hydrogenation of PHA to aniline (AN) (k_2) are the critical factors in determining the selectivity towards the formation of PAP. Thus, for the catalyst system to be highly selective for PAP, k_3 needs to be substantially higher than k_2 . On the other hand, AN would be the main product if k_2 is substantially higher than k_3 .

We report here a novel reaction system, which permits the substitution of sulphuric acid and selectivity promotors and gives reasonable yields with high selectivity [12].

2. Experimental

2.1. Catalyst preparation

A series of sulphated zirconias were investigated. Two samples (reference numbers 922-1 and 999/1) were supplied by MEL Chemicals, UK, and one was supplied by Loba Chemie (Mumbai, India). These were sulphated with a 1 N solution of sulphuric acid. A laboratory-made zirconia was prepared by hydrolysis of ZrOCl₂ (Aldrich) at pH 10. This solid obtained after filtration was sulphated by treatment with a 1 N solution of sulphuric acid (15 mL 1 N sulphuric acid for 1 g zirconia, stirred 15 min), followed by drying at 393 K and calcination at 923 K with a ramp of 1–2 K/min (denoted as ZrSAD-1). The sample 999/1 was received in a sulphated form and used as such.

Another sulphated catalyst, ZrSAD-3, was prepared as follows. Forty-eight grams zirconyl chloride (ZrOCl₂·xH₂O, MW: 322.249) was dissolved in 375 mL water, and Zr hydroxide was precipitated at constant pH = 10 by adding ammonium hydroxide. The precipitate was aged at 353 K for 12 h after which it was separated by centrifugation and washed several times with hot water to remove the excess ammonia and chloride ions. The wet precipitate was transferred to a conical flask. A solution of 21 mL concentrated sulphuric acid in 150 mL water was prepared and added to the conical flask. The slurry was stirred for 1 h at room temperature. Within this time, most of the precipitate dissolved and a turbid solution was obtained. This solution was fed to a rotary evaporator, and water was evaporated at 353 K. At the end, a white precipitate appeared almost instantaneously. The precipitate was then transferred to a glass pan and dried overnight at 393 K. After drying, it was sieved and stored in a bottle. Before use, the sample was calcined at the desired temperature with a ramp of 1-2 K/min.

Main cha	racteristics	of	the	acid	catalysts.	
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Catalyst	Supplier	Calcination temperature (K)	Surface area $(m^2 g^{-1})$	'S' content (wt%)
BEA (Si/Al = 22)	Zeolyst	723	720	-
ZrSAD-3	Home made	Uncalcined	2.7	17.8
ZrSAD-3	Home made	898	11	4.2
ZrSAD-3	Home made	923	15	4.3
ZrSAD-1	Home made	923	122	2.6
MEL-999/1	MEL	898	318	1.4
MEL-922/1	MEL	Uncalcined	309	-
Loba (sulphated)	Loba Chemie	898	20	0.4
Sulphated TiO ₂	Home made	773	110	1.9

The zirconium sulphate (ZrSAD-3) was calcined in air at different temperatures between 823 and 923 K. The catalysts, Loba-S and MEL-999/1, were used after calcination in air at 898 K for 2 h. The final calcination temperature was obtained with a linear programming rate of 2 K/min. The BET surface areas and the sulphur contents of these solid acids are reported in Table 1.

Supported Pt catalysts were prepared using zirconia, sulphated zirconia, titania, or a MgLa mixed oxide as carrier. In this series of supports, zirconia and titania are amphoteric oxides, sulphated zirconia is a strong acid, and MgLa mixed oxide has been shown to be a strong solid base [13]. Using aqueous solutions of chloroplatinic acid on the oxide carriers and amine salt for sulphated carriers, 0.1-2% Pt was introduced by the method of impregnation at incipient dryness. After impregnation, the resulting solids were dried overnight at 383 K, calcined in air at 673 K, and finally reduced in H₂ flow at 523 K. A commercial 1% Pt/C was used as received.

2.2. Catalyst characterisation

The structures of the catalysts were checked by powder X-Ray diffraction using a Bruker D5005 instrument. The S content was determined at SCA (Service central de micro analyse du CNRS, Solaise) by infrared spectroscopy analysis of the gases evolved upon oxidation at 1623 K in oxygen. The surface properties of the solid acids were characterised by measuring their surface area and acidity. The surface area was determined from the adsorption isotherm of nitrogen at 77 K on samples activated in N₂ flow for 2 h at 523 K. The acid properties were determined by adsorption of NH₃ at 353 K, using microcalorimetry coupled with volumetry. The solid taken in a sample cell was first evacuated up to 10^{-5} torr at 673 K, then transferred to a Tian-Calvet microcalorimeter. Small increments of NH₃ were then introduced into the cell, and differential heat of adsorption was measured. The differential heat represents the strength of the ammonia interaction with the surface, therefore the acid strength, whereas the amount of NH₃ measures the number of acid sites. The dispersion of Pt on zirconia was estimated from electron micrographs obtained by TEM, using a JEOL 2010 LaB6 instrument, and carbon replicas. The resolution of the apparatus is 0.19 nm and permits the detection of particles 0.5 nm in size. The distribution of particles size was obtained from the micrographs taken from different zones of the sample. A surface average size was calculated from this distribution using the formula $d = \sum n_i d_i^3 / \sum n_i d_i^2$.

2.3. Catalytic reaction

The hydrogenation of nitrobenzene to *p*-aminophenol was investigated in a 100 mL autoclave from Autoclave Engineers, filled

at about 80%. The reaction conditions were 353 K and hydrogen pressure 10 bar, reported to be optimum for the process using sulphuric acid [14]. In a typical experiment, 75 mL of water and 3 mL of nitrobenzene (NB) were introduced in the autoclave equipped with an efficient gas induction agitator, temperature sensor, sampling tube, and a baffle. To the above, 0.01 g of 2% Pt/ZrO₂ and 0.5 g of ZrSAD-3A, previously calcined at 923 K for 4 h, were added and the reactor closed. Nitrogen was fed to the reactor (2.5 bar) and purged three times. Then, nitrogen was replaced with hydrogen (10 bar) and purged three times. The agitation was started and maintained at 1200 rpm, and the autoclave was heated to 353 K, under 10 bar H₂. Samples were periodically withdrawn to monitor the progress of reaction. When using nitrobenzene/water ratios higher than 3/75, the reaction medium formed two phases, aqueous and organic: in that case, at the end of the reaction, the reaction mixture was dissolved in ethanol in order to obtain a homogeneous solution and analysed to determine the conversion and selectivities. The reaction produces PAP, traces of PHA, and aniline. The reactants and products were analysed by HPLC using a C18 column and a solution of acetonitrile (30%) in water as eluent. The mass balance was found to be better than 90%. The conversion is classically defined as the fraction of NB disappeared from the reaction mixture, and the selectivity as the molar fraction of PAP in the products.

3. Results and discussion

3.1. Characterisation of the catalysts

The chemical compositions of the solid acids used here are reported in Table 1. Except BEA zeolite and MEL-999/1, all solid acids are mesoporous (average pore size about 3.8 nm), which limits the possibility of intra-particle diffusional limitations. The material called ZRSAD-3 exhibits the composition of zirconium sulphate and the XRD pattern of $Zr(SO_4)_2$, $4H_2O$ (not shown) after drying at oven temperature, and of $Zr(SO_4)_2$ after calcinations at 773 K (Fig. 1). Sulphated zirconias (calcined above 923 K) show by contrast the pattern of tetragonal zirconia.

The results of the thermal analysis of ZRSAD-3 are reported in Fig. 2 for the fresh sample and a sample calcined at 773 K. The fresh sample shows weight losses below 500 K corresponding to dehydration in successive steps, followed by a large weight loss above

773 K due to desulphation. The loss in the range 500-1260 K amounts to 57.6 wt% of the weight of the dry sample, matching with the 56.5 wt% expected for the decomposition of $Zr(SO_4)_2$ into ZrO_2 . The weight loss below 500 K, attributed to the loss of water, permits to calculate a formula $Zr(SO_4)_2$, $3.8H_2O$, which is in agreement with the XRD pattern. After calculation at 773 K and storage in air, a small rehydration occurs, giving a ratio Zr/H_2O about 1.

The characterisation of the acidities of the solid acids has been reported previously [15], and the comparison between dehydrated zirconium sulphate (ZRSAD-3-898 K) and sulphated zirconias is reported in Fig. 3. The two sulphated zirconias have been calcined at 973 K and consist of ZrSAD-1, prepared by impregnation of zirconia by sulphuric acid, and ZrSAD-3. It appears clearly that the modification of the parameters of the preparation allows tuning of the surface properties of sulphated zirconias. In particular, the ZrSAD-3 sample calcined at 893 K shows a much lower number of sites of weaker strength compared to sulphated zirconia.

Representative electron micrographs of two Pt/ZrO₂ catalysts, containing 1% and 2% Pt are reported in Fig. 4. More particles are visible on the 2% Pt sample, but both samples show a similar distribution of particles sizes as illustrated in Fig. 5, the main difference being the presence of a few bigger particles on the 2%Pt sample. The surface average size calculated from these distributions is 2.2 nm for the 1%Pt sample and 2.3 nm for the 2%Pt sample.

3.2. Definition of the conditions of reaction

An exploratory study was first performed on the possible substitution of sulphuric acid by solid acids using ZrSAD-1 sulphated zirconia calcined at 923 K and DMSO as promoter. The results obtained for the reaction of 3 mL of NB in 75 mL of water are reported in Table 2. In the presence of DMSO, PAP is formed both on Pt/C and on Pt/TiO₂ (entries 1 and 2), showing that these supports indeed exhibit some acidity. The selectivity is significantly increased on Pt/TiO₂, and PHA is also detected with a selectivity of about 12%, which indicates that the acid-catalysed rearrangement of PHA is slow and controls the overall process.

The number of acid sites can be increased by adding a solid acid in a mechanical mixture. This strategy was applied first using DMSO as additive. The reaction rate is slightly promoted by the addition of an acidic zeolite such as BEA (entry 3). The interesting point is that using a sulphate as solid acid, DMSO can be omitted. As illustrated in Table 2, the yield of PAP is significantly improved



Fig. 1. Powder XRD pattern of ZRSAD-3 after calcinations at 623 K.



Fig. 2. Differential gravimetric analysis of ZrSAD-3 fresh or calcined at 923 K.



Fig. 3. Comparison of the acid properties of zirconium sulphate (ZRSAD-3-898 K) and sulphated zirconias.

(entries 4 onwards). This result suggests a partial reduction of sulphates in the conditions of reaction, resulting in a promotion of PHA selectivity.

The coupling of reactions requires a respect of the balance of the two functions. The comparison of results with different amounts of Pt in the catalyst shows that a large amount of Pt favours the hydrogenation of NB to aniline, with a large loss of selectivity to PAP (comparison of entries 7 and 8). In general, the support of Pt has little importance, as long as Pt is well dispersed. It can be chosen from a large variety of supports, hydrophobic, such as carbon, acidic or basic.

Another aspect was the choice of the solvent. The original work of Rylander et al. [1] on the hydrogenation of NB to PHA was performed in ethanol as solvent, and this solvent was therefore investigated. The results were very poor, since the conversion in a mixture of ethanol/water = 70:30 reached only 6.6% after 1 h of reaction, with a selectivity to PAP of 77%, compared to 30% of conversion and 83% selectivity in pure water. The isomerisation of PHA is therefore much slower in ethanol, and this inhibition is attributed to the fact that ethanol masks the acidity of the catalyst by virtue of stronger adsorption on the active sites, when compared to water. The adsorption of water on the other hand gives rise to enhanced Bronsted acidity, which is essential for the Bamberger rearrangement.

3.3. Effect of the amount of Pt on the catalytic properties

If the type of support has little influence on the catalytic results, the balance between metallic/acid sites is very important. The Pt loading on the support was varied from 0.1% to 2% using cationic exchange from Pt amine. The activity was measured at 353 K, 3.8 bars, with different amounts of Pt/ZrS catalyst (0.01, 0.03 and 0.1 g) and ZrSAD-3A calcined at 823 K (0.1 g) as solid acid (Table 3). In order to obtain a homogeneous liquid phase, 1.5 mL of NB in 50 mL of water was used. The initial rate was measured from the conversion after 1 h of reaction, conditions in which the selectivity to PAP was better than 95%. The results are reported in Fig. 6. Using 0.1 g of acid catalyst, the rate first increases linearly with the number of Pt atoms engaged in the reaction, then reaches a plateau. This is the behaviour expected for bi-functional catalysis, in which the overall rate is controlled by the hydrogenation of nitrobenzene at the Pt surface for a low Pt content, then by the acid-catalysed isomerisation of PHA, at the higher Pt loadings. Indeed, when using 0.025 g of catalyst at 2%Pt, increasing the amount of acid catalyst from 0.1 g to 0.25 g induces a proportional increase in the conversion after 1 h from 18% to 36.7%, thus confirming that the overall process is controlled by the acid-catalysed isomerisation of PHA at high Pt loading.



Fig. 4. High-resolution electron micrographs of 1%Pt and 2%Pt/ZrO₂ catalysts.



Fig. 5. Distribution of particles sizes for the two 1%Pt and 2%Pt/ZrO₂ catalysts.

3.4. Kinetics of the reaction: effect of the concentration of nitrobenzene

The use of mesoporous supports eliminates the possibility of diffusional limitations by intra-particle mass transfer. The use of a Rushton turbine and hollow holder improves the homogeneity of the reaction medium. The effect of the stirring rate was investigated and it was observed that the reaction rate and selectivity increased with the stirring rate and reached a plateau beyond 1000 rpm, so that the stirring rate was fixed at 1200 rpm.

The initial rate as a function of concentration of nitrobenzene was measured using 2%Pt/ZrSAD-3, 2%Pt/MgLa, and 1% or 2%Pt/ZrO₂ catalysts, which give similar rates normalised to the amount of Pt, mixed with ZrSAD-3 calcined at 823 K. At low NB concentration, the reaction medium is monophasic and it is possible to monitor the conversion and selectivity as a function of time, but above 3 mL of NB, a biphasic system is observed in the absence of stirring. In that case, the reaction was run for 1 h, the reaction medium was dissolved into methanol and analysed. The initial rate was com-

Table 2

Effect	of DMSC	on the	hydrogenation	of	nitrobenzene	at	353 K,	at	10 bar	H ₂ ,	in	the
prese	nce of sol	id acids	s.									

Entry	Catalyst	Without	Without DMSO		ЛSO
		Conv. (%)	PAP sel.	Conv. (%)	PAP sel.
1 2	1%Pt/C (0.1 g) Pt/TiO ₂ (0.1 g)	27.4 ^a 36 ^a	0 27	50.7 ^a 26 ^b	20 68
3	Pt/C (0.13 g) + BEA zeolite (1 g)	50	27	17.8ª	86
4	1%Pt/C (0.01 g) + ZRSAD-3 (0.5 g)	62 ^b	98		
5	2%Pt/ZrO ₂ (0.01 g) + ZrSAD-3 (0.5 g)	85 ^b	83		
6	2%Pt/TiO ₂ (0.01 g) + ZrSAD-3 (0.5 g)	78 ^b	82		
7	2% Pt/MgLa (0.05 g) + ZrSAD-3 (0.5 g)	98.9 ^c	7.9		
8	2% Pt/MgLa (0.01 g) + ZrSAD-3 (0.5 g)	75 ^b	77		

^a Reaction time: 7 h.

^b Reaction time: 6 h.

^c Reaction time: 1 h.

Table 3

Effect of the amount of Pt in the mechanical mixture on the activity measured at 353 K, with different amounts of Pt/ZrSAD-1 catalyst mixed with ZrSAD-3 catalyst as solid acid. Reaction conditions: H₂ pressure 3.8 bars, 1.5 mL of NB in 50 mL.

Entry	Amount of Pt cat (g)	%Pt loading	ZrSAD-3 (g)	Conv. (%) after 1 h	PAP sel. (%)
1	0.025	2	0.1	15.9	96.1
2	0.01	2	0.1	18.8	95
3	0.01	0.5	0.1	6	97.4
4	0.01	0.5	0.1	5.2	97.2
5	0.03	0.5	0.1	17.8	97.9
6	0.1	0.1	0.1	17.8	97.2
7	0.1	0.5	0.1	12.9	95.7
8	0.025	2	0.25	36.7	93.3



Fig. 6. Effect of the amount of Pt in the mechanical mixture on the activity measured at 353 K, with different amounts of Pt/ZrS catalyst mixed with ZrSAD-3A catalyst as solid acid. Reaction conditions: H_2 pressure 3.8 bars, 1.5 mL of NB in 50 mL.



Fig. 7. Variation of the initial rate, as a function of the initial concentration, for reactions at 353 K and 10 bars of hydrogen, using 2%Pt/ZrSAD-3 (point 1), 2%Pt/MgLa (point 2), 1%Pt/ZrO₂ (point 3), and 2%Pt/ZrO₂ (point 4).

puted from the conversion after one hour to determine the reaction order. The results at 353 K are reported in Fig. 7. They show the same reaction rate for Pt on different supports and a first-order dependence of this rate on the NB concentration. Tanielyan et al. [16] reported a constant rate for H₂ pressures above 3.8 bar, for a reaction in water, catalysed by Pt/C and sulphuric acid, and it can therefore be assumed that the reaction is zero order relative to hydrogen at 20 bar. The turnover frequency (rate per surface Pt atom) deduced from this plot is 18 mol s⁻¹.

Boudart and Cheng [17] have applied the test proposed by Koros and Nowak [18,19] for the liquid-phase hydrogenation of cyclohexene on nickel to ensure that the measured rates were not influenced by slow heat or mass transfer. The Koros–Nowak Criterion requires that the values of the turnover rate of a reaction on catalysts with the same metal particle size but different metal loading be the same, for the measured rate to reflect only the chemical process. Here, the same activity is measured when using either 1% or

Table 4

Composition of the reaction mixture for the hydrogenation of nitrobenzene at 353 K, after 1 h in standard conditions (3 mL of nitrobenzene in 75 mL of water, 353 K, hydrogen pressure 10 bars), using 0.5 g of different solid acids used in mechanical mixture with 0.01 g of 2% Pt/MgLa.

Entry	Solid acid	Produ	Products distribution (%)			PAP sel. (%)
		NB	PHA	PAP	AN	
1	ZrO ₂ 922/1	71.8	5.6	2.2	20.3	7.9
2	ZrSAD-3 (calc. 973 K)	24.4	13.9	2.2	20.3	2.2
3	ZrSAD-3 (calc. 948 K)	74.7	5.0	5.6	14.7	22.2
4	ZrSAD-3 (calc. 923 K)	57	0.4	36	6.4	83.6
5	ZrSAD-3 (calc. 823 K)	79.1	0.0	19.7	1.1	94.1
6	TiO ₂ sulf	37.5	5.2	0.5	56.8	0.9
7	Sulf 922/1	68.8	3.6	7.1	20.5	22.8
8	HBEA zeol	76.3	2.1	2.7	18.8	11.5
9	MEL-999/1	18.9	13.6	0.4	66.5	0.5

2% Pt/ZrO₂ of similar dispersions. This suggests that mass transfer limitations are not important. The observation of a high selectivity to PAP also favours this conclusion.

3.5. Comparison of different solid acids

It was reported earlier that the Bamberger rearrangement of PHA to PAP was very sensitive to the nature of the solid acid; therefore, an influence could be expected for the bi-functional hydrogenation of nitrobenzene to PAP. The comparison of a series of solids is reported in Table 4. The results are given after 1 h at 353 K, using a reaction mixture consisting of NB (3 mL), water (75 mL), and 0.01 g of 2% Pt/MgLa mixed with 0.5 g of solid acid. As illustrated in this table, the temperature of calcination has a significant influence on the catalytic properties (entries 2–5). In particular, calcination at high temperature, which induces strong acid properties, is unfavourable in this case, since an increase in conversion is observed at the cost of a selectivity decrease. The low selectivity over sulphated titania and HBEA zeolite was expected from their behaviour in Bamberger rearrangement.

Using the best catalyst, ZrSAD-3A calcined at 823 K, the conversion varies as a function of time as reported in Fig. 8. The final result is comparable to those reported with sulphuric acid as acid catalyst.

The results obtained here for the hydrogenation of NB can be compared to those obtained for the isomerisation of PHA, summarised in Table 5. In both cases, the most selective catalyst is ZrSAD-



Fig. 8. Evolution of the conversion and selectivity into *p*-aminophenol as a function of time at 453 K.

Table 5

Comparison of a few solid acids for the isomerisation of phenylhydroxylamine at 353 K. 109 mg of PHA added to 7 mL of water reacted in the presence of 0.1 g of solid acid, giving PAP, *o*-aminophenol, aniline and nitrobenzene.

Sample	Reaction time (min)	PHA conv.	PAP sel.
BEA zeolite	30	49.1	61.6
Sulphated TiO ₂ (calc. 773 K)	30	100.0	29.8
ZrS (from LOBA zirconia)	60	33.6	94.8
ZrS-exZrOCl ₂ (calc. 893 K)	30	35.1	99.9
	60	47.3	96.8
ZrSAD-1 (calc. 923 K)	30	23.2	97.0
	60	40.0	92.1
ZrSAD-3 (calc. 893 K	30	100.0	99.6
ZrS MEL-999/1 (calc. 923 K)	30	21.8	94.5
	60	39.1	95.2

Table 6

Experiments in a 700 ml reactor, using a mixture of 2% Pt/ZrO₂ and zirconium sulphate, at 353 K, pressure 20 bar.

Exp.	NB	Water	Time	NB conv.	PAP Sel.	AN Sel.
no.	(mL)	(mL)	(h)	(%)	(%)	(%)
1	40	490	6	33.8	91.9	8.1
2	40	350	8	97	86	14
3	56	490	6	27.2	93.1	6.9
4	56	490	6	22.8	90.8 87.0	9.2
6	56	490	8	86.7	88.1	11.9

Mechanical mixture of catalysts: experiments 1 and 2: 2% Pt/ZrO₂ (0.1 g), ZRS (5 g); experiments 3–6: 2% Pt/ZrO₂ (0.14 g), ZRS (7 g).

3 calcined at most at 923 K. This catalyst can reach high conversion of PHA with high selectivity, and the same behaviour is observed in the hydrogenation of NB. This comparison shows that the loss of selectivity occurs in the second step, the isomerisation of PHA. It is surprising that strong acids such as sulphated zirconias give poor results in the Bamberger rearrangement, when the industrial process uses sulphuric acid. It can be pointed out that the industrial reaction is indeed performed in rather diluted sulphuric acid. It has been reported long ago that Fe^{3+} at ppm levels catalyses the decomposition of PHA by a redox mechanism [20]. It is also well known that radicals can be formed on sulphated zirconias by oxidation [21–24]. It can then be speculated that over sulphated zirconias, the selectivity leak occurs by this oxidation path.

3.6. Experiments in a larger reactor

The scale up of the results obtained in a small reactor to a larger one offers better conditions for the determination of the material balance and is fruitful only when diffusional limitations are negligible; therefore, a few experiments have been performed in a larger reactor (700 mL from Autoclave Engineers), using a concentration of 1 mol L⁻¹ of NB. Due to the separation of the organic/liquid phases at rest, the reactions were run for 6 or 8 h, then the whole reaction mixture was transferred into a 1-l beaker, 100 ml of methanol was added to obtain a homogeneous solution, which was analysed by HPLC (ODH-C18 column, 250 mm, wave length 254 nm, 70:30 water/acetonitrile, flow 1 mL/min). The results reported in Table 6 illustrate the reproducibility of the experiment and show that a good selectivity can be reached at high conversion, as was first observed in the small reactor. Indeed the yield obtained here after 8 h is comparable to that reported for the current industrial process after 3 h [25]. It can be pointed out that the industrial process is based on sulphuric acid and this higher activity can be accounted for by the higher density of protons in sulphuric acid compared to any solid acid. The lower rate of the all heterogeneous process is however compensated by the significant reduction in the e-factor induced by the elimination of the liquid acid and a much simpler separation of the products.

4. Conclusions

An all heterogeneous process for the bi-functional conversion of nitrobenzene into *p*-aminophenol has been described, using the combination of zirconium sulphate and supported platinum. The reaction kinetics is characteristic of a bi-functional mechanism, in which the slow step is the hydrogenation of NB to PHA at low Pt content and the isomerisation of PHA to PAP at high Pt loading. This system requires only very small amounts of Pt, and the support of Pt is not important. The most critical point is the choice of the solid acid, which must be selective for the Bamberger rearrangement. This rearrangement has been shown to be very demanding, and the strong effect of the calcination temperature illustrates this point. Strong solid acids are not good catalysts for this process.

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