

Mononitration of Benzene on Solid Catalysts without Using Sulphuric Acid

OLEG V. BAKHVALOV

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

E-mail: bakhval@nioch.nsc.ru

(Received January 31, 2002)

Abstract

A review of scientific and patent literature reflecting the newest methods of benzene nitration on solid catalysts for the purpose of obtaining nitrobenzene. The published research results are analysed from the viewpoint of possibility of using them for development of a new technology for obtaining nitrobenzene on the basis of heterogeneous catalytic nitration of benzene.

INTRODUCTION

Obtaining nitrobenzene is a large-scale industrial production with a world volume of about 1 mln t per year [1]. Despite the century and a half long history of this production, its chemical, and in many plants also the instrumentation and technological, circuits have not undergone any considerable changes. Benzene nitration is carried out, as before, with nitric acid in sulphuric acid medium which plays two roles – that of a catalyst and that of a diluent accumulating the reaction heat and preventing its uncontrollable course. The most considerable improvement of the traditional technology of continuous benzene monitoring with a mixture of acids in a cascade of capacity reactors at 60–70 °C goes in two directions – nitration under adiabatic conditions with a rise of temperature to 140 °C due to the exothermic effect of the reaction, and nitration with distillation of water in the form of azeotropic mixture with benzene at a temperature above 120 °C [2]. These modifications of benzene nitration have their advantages and drawbacks, but they do not eliminate the main drawback of the homogeneous catalytic nitration – the

presence of a great amount of non reacting substance – concentrated sulphuric acid – in the reaction medium. Its circulation in the process or its utilization create considerable instrumental, technological and ecological difficulties. The mass of such worked-out acid with a concentration of no less than 70 % amounts to 0.9–1.0 t per 1 t of commercial nitrobenzene [3, 4]. Technology of nitration of aromatic compounds by a mixture of acids has also some other drawbacks [5].

Radically new ways of benzene nitration are such conditions of running this reaction under which catalysts are solid substances. Variants of heterogeneous-catalytic nitration in which sulphuric acid is not used are mentioned in some reviews [6–10], considered in some papers and proposed in some patents. The potential technological and ecological advantages of sulphuric acid-free nitration are obvious: operations involving sulphuric acid become superfluous, which diminishes the amount of sewage waters, improves the ecological situation of the working zone and can decrease the materials consumption of the ready product. The catalyst can be used many times, and in many cases it is cheap and non-

toxic. An increase of nitration selectivity and therefore of nitrobenzene purity is possible. Conditions for modern automated production can be created.

In the present paper, publications issued within the last 15 years, including the first half of 2001, are considered. Unlike the earlier published reviews, studies of only benzene nitration are analysed, because in this case the most important is creation of a radically new modern technology, since nitrobenzene is a large-scale nitroaromatic product. A peculiarity of the present review is also a critical analysis of the proposed methods of benzene nitration using solid catalysts from the viewpoint of their suitability for technological realisation.

ZEOLITES

These have been checked more often than any other solid catalysts, which witnesses to their promising characteristics. A short summary of data on zeolite catalysts that have been proposed for benzene nitration is presented in Table 1. In Table 2, results of nitration achieved in the presence of these catalysts are given.

An analysis of the data of Tables 1 and 2 witness to the fact that, despite the great diversity of benzene nitration conditions in the presence of zeolites, it is difficult to choose a method which could be transformed into a technology. For this purpose, several basic requirements must be met: firstly, achievement of good technological parameters that can be maintained during a long-term service of the catalyst; secondly, use of available cheap reagents at not large assortment; thirdly, explosion and ignition safety and absence of a harmful influence on the human organism. Other undesirable characteristics of the nitration stage can also be mentioned, *e. g.* high temperature which makes difficult the use of equipment under the conditions of aggressive media.

One may assume that the first criterion is met by the results of works [18, 23, 27–29]. However, the conditions mentioned in [23] and [29] do not meet the second criterion (the use of acetic anhydride) and in some degree also the third one (the use of concentrated nitric

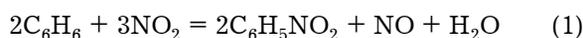
acid). The use of oxygen, and under pressure at that, in [18] creates a risk of explosions and fires. Besides, in three latter works nitration was carried out in a periodic regime which is unacceptable for such a large-scale process as nitrobenzene production. In this way, only data of [27, 28] approach at a maximum a technology suitable for benzene nitration on zeolite catalysts.

Besides, it is noteworthy that, with the exception of patents [27–29], in the mentioned works there is no scheme of the catalysate processing, and in [29] the scheme contains technologically inefficient operations – elimination of acetic acid by distillation and especially distillation of the target product at the residual pressure of 0.2 mm of mercury column. These complications of the process are determined by the introduction of the activator – acetic anhydride – into the reaction medium.

Out of the zeolites checked in [27, 28], the most efficient turned out to be zeolite beta (No. 18 in Table 2), although the technologically acceptable zeolite ZSM-5 (No. 17 in Table 2) has also shown sufficiently good results under mild conditions (84 °C, and 80 % excess of 69.3 % HNO₃). A heightening of nitration temperature to 120–130 °C makes the technological nitration parameters on ZSM-5 and on zeolite beta converge.

The good technological parameters presented in [17, 20] turned out to be short-lasting.

One has to comment on the methods of benzene nitration by nitrogen dioxide in the presence of oxygen and ozone (Kyodai process). The role of the latter consists in a more complete use of the nitrating agent due to oxidation of NO that is formed as a result of introducing a nitro group into the benzene ring:



The attractiveness of these methods is due to the low nitration temperature [22, 24]. However, the authors failed to achieve efficient conditions which could possibly arise as the temperature increased (*cf.* [18]), which, however, increased the explosion hazard of the process.

TABLE 1

Zeolite catalysts of benzene nitration and the conditions of their use

No.	Catalyst	Nitration agent	Temperature, °C	Nitration agent/benzene molar ratio	Nitration regime	Other conditions
1	Zeolite ZSM-5	HNO ₃ (61 %)	75	1.89	Periodic	
2	Molecular sieve of crystalline SiO ₂ with the pore diameter of 5–6.5 Å	Aqueous HNO ₃	75	1.9		
3	Modernized mordenite in H-form with the module of 96	HNO ₃ (65 %)	170	0.5	Continuous	Nitrogen as the carrier gas
4	Clinoptilolite	HNO ₃ (conc. >50 %)	27–250	0.5	»	The same
5	Clinoptilolite, zeolites NaY, ZSM-5 in Na-form, mordenite with the module of 6–9, cryst. 85 %	HNO ₃ (65 %)	170	0.5	»	Nitrogen as the carrier gas, volume rate in terms of benzene 1.0 h ⁻¹
6	Modified mordenite	HNO ₃ (65 %)	170	0.5	»	Nitrogen as the carrier gas
7	Zeolite ZSM-5 with a module of less than 83	HNO ₃ (56 %)	140–170	2–3	»	Preliminary treatment of the catalyst with HNO ₃
8	Zeolites MCM, mordenite in Na form, NaY	NO ₂ + O ₂	45	2.0	Periodic	O ₂ pressure is 2.8 gage atmosphere
9	Amorphous aluminosilicate, zeolites Y, ZSM-5 in H-form	PhCOONO ₂	30	0.1	»	
10	Zeolites ZSM-5 with modules of 30, 60, 70, 100 containing ions of B, Fe, Ti; zeolite ZSM-12	NO ₂	150	On the average 4.6	Continuous	Nitrogen as the carrier gas
11	Zeolites Y and ZSM-11 in H-form	HNO ₃ , AlkCOONO ₂	30	<1	Periodic	Hexane as solvent
12	Ag ₂ O + zeolite 4A	NO, N ₂ O ₃ , NO ₂ + O ₃	-10	Excess of nitration agent	»	
13	Zeolite beta	HNO ₃ (90 %)	~20	1.0	»	Acetic anhydride, 1.5 mole per 1 mol of benzene
14	Zeolite beta in H-form	N ₂ O ₄ + O ₂	0	32	»	Dichloroethane as solvent

TABLE 1 (end)

No.	Catalyst	Nitration agent	Temperature, °C	Nitration agent/benzene molar ratio	Nitration regime	Other conditions
15	Mordenites in H-form with modules of 12, 40, 100 containing less than 0.5 % Na ₂ O	HNO ₃ (65 %)	127-250	5.0, 0.5	Continuous	Nitrogen as the carrier gas
16	Clinoptilolite with crystal size of less than 1000 nm	HNO ₃ (>50 %)	27-250	0.5	»	The same
17	Zeolites ZSM-5, ZSM-11 in H-form	HNO ₃ (65-70 %)	76-85	1.4, 1.8, 4.2, 4.5	»	
18	Zeolites beta and mordenite in H-form	HNO ₃ (68-70 %)	105-130	1.8	»	In one of variants, partial anisotropic distillation of water
19	Zeolite SS in H-form with modules of 2 to 80	HNO ₃ (90 %)	from 0 to 20	1.0	Periodic	In the presence of excess of acetic anhydride
20	Zeolites Y modified by treatment with NH ₄ NO ₃ or HNO ₃	HNO ₃ (65 %)	170	0.5	Continuous	Nitrogen as the carrier gas

TABLE 2

Results of benzene nitration in the presence of zeolite catalysts indicated in Table 1

No.	Degree of benzene transformation, %	Nitrobenzene yield, % of theoretical one	Other results	Reference
1		34 within 2 h		[11]
2	22		Dinitro derivatives are not formed	[12]
3		37 in 3 h 35 in 20 h	Selectivity with respect to nitrobenzene 99.9 %	[13]
4		41	Selectivity with respect to nitrobenzene 95 %	[14]
5		42 in 3 h 41 in 20 h	Nitrobenzene yield up to 0.65 kg per 1 kg catalyst per 1 h, selectivity with respect to nitrobenzene up to 98 %	[15]
6	45	39	Nitrobenzene yield 0.62 kg per 1 kg catalyst per 1 h, selectivity with respect to nitrobenzene 99.5 %	[16]
7		At 140 °C: 79 in 0.7 h 39 in 3.9 h At 170 °C 59 in 1.1 h, 45 in 3 h,		[17]
8		More than 99 within 1.5 h		[18]

TABLE 2 (end)

No.	Degree of benzene transformation, %	Nitrobenzene yield, % of theoretical one	Other results	Reference
9		20–50		[19]
10	Up to 74	~ 80	Decrease of catalyst activity with time, admixtures of di- and trinitro derivatives	[20]
11		Less than 20		[21]
12		24 within 3 h		[22]
13	More than 90	About 100 within 0.5 h		[23]
14	55 within 45 h	50 within 45 h		[24]
15		39.5 in 3 h, 38 in 20 h	Selectivity with respect to nitrobenzene more than 99.8 %	[25]
16		41	Selectivity with respect to nitrobenzene 99 %	[26]
17	40 to 85	39 to 82	Dinitro derivatives are not formed; nitrobenzene output up to 1.19 kg per 1 kg catalyst per 1 h	[27]
18	~ 85	Up to 84	Dinitro derivatives content of hundredths of a percent; nitrobenzene yield up to 1.18 kg per 1 kg catalyst per 1 h	[28]
19	About 100	More than 99 within 0.5 h		[29]
20	41 in 4 h, 39 in 20 h	40 in 4 h, 38 in 20 h	Selectivity with respect to nitrobenzene 99.5 %, traces of dinitrobenzenes, some decrease of activity with time	[30]

SHEET CLAYS

Short data on such catalysts tested in benzene nitration reactions and the conditions of their use are given in Table 3. In Table 4, the results attained in the presence of stratified clays are presented.

Not bad results under harder conditions (a heightened temperature and an excess of HNO_3) were achieved in [31, 33, 34], although in the first two of them the increase of duration of the process to 10–20 days resulted in a decrease of parameters, (and) the catalyst lost its activity. This process was determined by the heightened nitration temperature. In [34], a good result was attained due to the use of smoking HNO_3 and azeotropic distillation of a part of water from the reaction medium in periodic nitration regime. Slowing down the dilution of HNO_3 in the course of nitration by means of water distillation is a useful way to intensify the process. However, in the continuous regime of the reaction this leads to a

complication of the instrumental support of the benzene nitration stage.

Interesting are data of [36]. The best result was obtained with a modification of montmorillonite Al^{3+} . On this catalyst a nitrobenzene output of 3.56 g per 1 g of catalyst was achieved at a high volume rate. Impressive is also the conservation of the technological parameters after 480 h of nitration. However, the values of these parameters are not high. A drawback of the proposed method is the use of an almost double benzene/ HNO_3 ratio, which will lead in technology to circulation of a large volume of benzene and to a danger of explosion.

Among the results obtained with “clay catalysts” conspicuous are the data of [36] on catalysts productive capacity. The nitrobenzene output under the conditions of periodic nitration indicated there is possible only at a very high reaction rate and at a small load on the catalyst, which is not confirmed by the materials of the paper.

TABLE 3

Clays as catalysts of benzene nitration and the conditions of their use

No.	Catalyst	Nitration agent	Temperature, °C	Nitration agent/ benzene molar ratio	Nitration regime	Other conditions
1	Montmorillonite with Al, Ti, Zr, Fe, Cr, Bi, La ions or compositions TiO ₂ - MoO ₃ , TiO ₂ - WO ₃ , TiO ₂ - ZnO, ZrO ₂ - WO ₃	HNO ₃ (60-70 %)	140-160	0.5, 0.9	Continuous	Nitrogen as the carrier gas
2	Stratified acid clays containing Al ³⁺ , Bi ³⁺ , Cr ³⁺ , Fe ³⁺ , Zr ³⁺ , or oxides of W, Mo, Zn on TiO ₂ , ZrO ₂		100-300	5.0-0.1		
3	Montmorillonite modified by Al ³⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Fe ³⁺ , Cr ³⁺ , Bi ³⁺ , La ³⁺ , or compositions of Ti, Zr, Hf with oxides of W, Mo, Nb, Zn	HNO ₃ (60-70 %)	140-160	0.5, 0.9	Continuous	Nitrogen as the carrier gas
4	Montmorillonite with Fe ³⁺ or Zn ²⁺	HNO ₃ (conc.)	20, 115	0.4, 1.4	Periodic	Distillation of water
5	Montmorillonite with Fe ³⁺ ions	HNO ₃ (90 %)	70	1.0	»	The same
6	Montmorillonite with Al ³⁺ ions	HNO ₃ (60 %)	70	1.0	»	»
7	Montmorillonite containing on of the following ions: Zr ⁴⁺ , Fe ³⁺ , Cr ³⁺ , Al ³⁺ , Cu ²⁺ , La ³⁺ , Mn ²⁺	HNO ₃ (70 %)	160	0.52	Continuous	Nitrogen as the carrier gas

TABLE 4

Results of benzene nitration in the presence of the clays indicated in Table 3

No.	Degree of benzene transformation, %	Nitrobenzene yield, % of theoretical one	Other results	Reference
1	48, ~85	45, ~85	Nitrobenzene output up to 1.26 kg per 1 kg catalyst per 1 h, selectivity with respect to nitrobenzene 99 %	[31]
2			A high activity, a long-lasting resource	[32]
3	48, ~80	48, ~79	Selectivity with respect to nitrobenzene of up to 99 %, yield of nitrobenzene of up to 1.26 kg per 1 kg catalyst per 1 h	[33]
4	30-93 for 1.5-2 h	30-90 for 1.5-2 h		[34]
5		88	Nitrobenzene output 22.8 kg per 1 kg catalyst per 1 h	[35]
6		48	Nitrobenzene output 0.6 kg per 1 kg catalyst per 1 h	[35]
7		48	Maintenance of the yield of 47 %, that of output of 0.65 kg per 1 kg catalyst per 1 h for 480 h; selectivity with respect to nitrobenzene 98 %	[36]

In this way, the proposed methods of benzene nitration require at least further finishing for development of a new technology.

AMORPHOUS INORGANIC COMPOUNDS

This group includes mainly oxides of metals and metalloids. A part of works [22, 31–33] in which such catalysts were used are considered in Tables 1–4, and the rest of them in Tables 5 and 6.

The first criterion of technological efficiency (see above) is more or less met by the results of [27, 36, 39, 40]. However, each of the methods proposed in these works has its undesirable properties. So, in [27] a very large excess of HNO_3 is required, in [39, 40] expensive catalysts were used. In a part of the cited works, the conditions studied are far from being technologically efficient (periodic nitration regime, a large excess of benzene, lack of catalysate processing schemes). Nevertheless, the long life span of the catalyst $\text{TiO}_2 - \text{WO}_3$ (this

TABLE 5

Amorphous inorganic catalysts of benzene nitration and the conditions of their use

No.	Catalyst	Nitration agent	Temperature, °C	Nitration agent/benzene molar ratio	Nitration regime	Other conditions
1	75 % WO_3 – 25 % MoO_3 , 90 % TiO_2 – 10 % MoO_3 , SiO_2 – Al_2O_3 and other oxide mixtures	NO_2	200	2.3	Continuous	Vapour phase
2	(SiO_2 , Al_2O_3 , MgSiO_3 , MgSiO_4 , kaolin)	$\text{NO}_2 + \text{O}_2$	45	1.0, 1.5, 2.0	Periodic	Repeated use of the catalyst
3	WO_3/MoO_3 , $\text{SiO}_2 + \text{Al}_2\text{O}_3$	NO_2	150–200	2.3	Continuous	Nitrogen as the carrier gas
4	KNO_3 – $\text{BF}_3 \cdot \text{H}_2\text{O}$	HNO_3 , formed from the initial reagents	~20	0.2	Periodic	Purification of the end product by distillation or by recrystallization
5	Salts of heteropoly acids with central atoms P, Si or As, ligands Mo, W, V. The catalyst contains also K, Rb, Cs, Tl	Aqueous HNO_3	140		Continuous	Nitrogen as the carrier gas
6	Glass granules with a size of 1–1.5 mm	HNO_3 (68.6 %)	81–83	4.5	»	
7	Heteropoly acid $\text{H}_3\text{PW}_{12}\text{P}_{40}$ on SiO_2	HNO_3	155–160	0.5		
8	Oxide mixtures TiO_2 – WO_3 , ZrO_2 – WO_3 , TiO_2 – MoO_3 , TiO_2 – ZnO_2 , Al_2O_3 – TiO_2 , ZrO_2 – TiO_2 , SnO_2 – TiO_2	HNO_3 (70 %)	150, 160	0.52, 0.9	Continuous	Nitrogen as the carrier gas

TABLE 6

Results of benzene nitration in the presence of inorganic catalysts indicated in Table 5

No.	Degree of benzene transformation, %	Nitrobenzene yield, % of theoretical one	Other results	Reference
1	~40	40	The most active was WO_3/MoO_3 , the nitrobenzene output was 0.4 kg per 1 kg catalyst per 1 h	[37]
2		With NO_2 /benzene ratio of 1.0, 65 for 2 h; with the ratio of 1.5, 96 for 3 h; with that of 2.0, 99 for 1.5 h	A high reaction rate at NO_2 excess	[18]
3		The best result with WO_3/MoO_3 - 39.5		[38]
4		88		[39]
5	93.7	91.1		[40]
6	~90	75	A low (about 81 %) yield of nitrobenzene per consumed benzene; nitrobenzene output 0.4 kg per 1 kg catalyst per 1 h	[27]
7	~50	45.3		[41]
8		With HNO_3 /benzene ratio of 0.9-72	Nitrobenzene output 1.2 g per 1 g catalyst per 1 h; at HNO_3 /benzene ratio of 0.52, the yield was maintained at 40 %, the output at 0.57 g for 480 h, selectivity with respect to nitrobenzene 96-99 %	[36]

pair gives also better technological results) draws attention, and one could work on it, varying the conditions in order to heighten the technological efficiency of nitration.

ARYLSULPHONATED ACIDS ON SiO_2

Japanese scientists have proposed to use aromatic sulphoacids deposited on silicagel as benzene nitration catalysts [42-46]. On the basis of the available scanty information about this method, one can conclude that nitration was carried out mainly with nitrogen dioxide in gaseous phase within the temperature interval of 0-200 °C, using an inert carrier gas. The nitrating agent/benzene ratio varied from 1.0 to 2.1. Used as catalysts were benzenesulphonic acid, *o*- and *n*-nitrobenzene sulphonic acids, *n*-toluenesulphonic acid, nitrotoluenesulphonic acid, *n*-chlorobenzenesulphonic acid deposited on SiO_2 . The best result was achieved in the presence of *o*-nitrobenzenesulphonic acid [46]. At continuous nitration with the NO_2 /benzene ratio of 1.1, and at the temperature of

170 °C, the nitrobenzene yield varied from 67 to 74 %. Dependent on the reagents proportion was also the degree of benzene transformation which varied from 70 (NO_2 /benzene = 1.1) to 95 % (NO_2 /benzene = 2.1).

The presented results of nitration meet the first technological efficiency criterion, although they should be supplemented with data on the catalyst resources. The estimation of NO_2 as the nitrating agent is equivocal. Its use seems expedient in cases of territorial proximity of the HNO_3 and nitrobenzene production sites, taking into account that NO_2 production technology is shorter (the stage of its absorption by water is eliminated). True, in [43] a diluted HNO_3 is proposed as the nitrating agent.

In the benzene nitration method under consideration, one may be concerned about the high reaction temperature; besides, the possibility and conditions of reiterated use of the catalyst are not clear, and so is the catalysate processing technology. Nevertheless, a technological study of the method seems expedient.

OTHER SOLID CATALYSTS

We considered as belonging to this category naphion-H [37] and triflate with the composition of $[\text{Yb}(\text{H}_2\text{O}_2)]\text{O}_3\text{SCF}_3)_3$ [47]. Data on the conditions of using the first catalyst are contained in Table 5 (No. 3), and technological parameters attained with its use are lower than those presented in the respective line of Table 6. The result of use of triflate presented in [47] witnesses to a low efficiency of this catalyst: by means of nitration with 69 % HNO_3 at 83 °C for 12 h, even without catalyst it is possible to achieve a degree of benzene transformation close to 75 %.

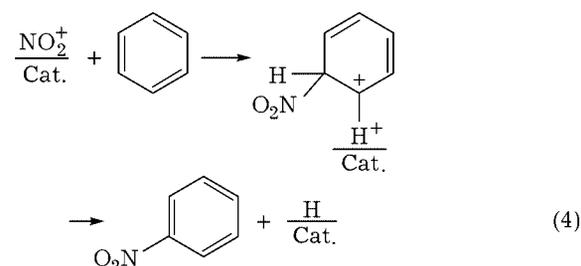
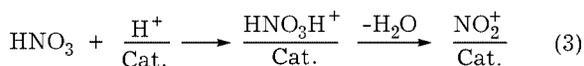
We included in this group also solid catalysts on which a small amount of H_2SO_4 was deposited. Creation of such catalysts may be regarded as the authors' desire to conserve the traditional activator HNO_3 , although in catalytic amounts. Catalysts of this type were prepared by depositing sulphuric acid either on SiO_2 [48] and other carriers (diatomite, sand, silicon carbide, graphite *etc.*) [49], or on metal oxides, *e. g.* $\text{TiO}_2/\text{MoO}_2$ [50], or on hydroxides of Ti, Zr, Fe, Mo, W [51]. The latter, after treatment with sulphuric acid, were calcinated (dehydrated). The nitrating agent in the cited works was aqueous HNO_3 . The reaction was run in gaseous phase (140 °C) in continuous regime with an excess of benzene. The results were as follows: nitrobenzene yield up to 48 % at HNO_3 concentration of 70 % [48, 49], the product output 0.72 kg per 1 kg of catalyst per 1 h [50]. However, a few questions arise. For example, for how long is the sulphuric acid impregnation conserved? If one has to renew it often, then setting up a system for obtaining sulphuric acid is inevitable. How is the acidic phase of catalysate inevitably containing H_2SO_4 processed? What is the proportion of contribution of oxides and H_2SO_4 to the catalytic activity? When SiO_2 was used as the carrier of acid, the result was better [48] than when $\text{TiO}_2/\text{MoO}_2$ was used [50] and when the nitrobenzene yield amounted to 40 %. If so, then why should one use more expensive metal oxides?

The considered literature sources contain not only factual data on benzene nitration, but also results of studies of the regular pattern of this reaction. The fundamental rule consists

in the fact that homogeneous-catalytic nitration (with a mixture of acids) and nitration on zeolite catalysts have similar mechanisms [8, 19–21]. A consequence of this similarity is the similarity of relationship between the acidity of catalysts and their activity [52]. In this work, on the example of ZSM-5, an equation has been deduced which associates the activity with the acidity and with some other characteristics of zeolite. In some studies [8, 9, 20], it is specified that the activity of zeolites is influenced first of all by the protonic acidity, and as the concentration of Brønsted acidic centers increases, so does the degree of transformation of benzene into mononitrobenzene. A diminution of the number of active acidic centres in parallel with the increase of the zeolite module and in its modification by B^{3+} , Al^{3+} , Se^{3+} , and Ga^{3+} ions has been noted. In the latter case, the concentration of Lewis acidic centres increases [52]. The authors of this study assert that a precise distribution of active centres in ZSM-5 gives estimation of activation energy for desorption of ammonia.

It seems that one may consider as a general rule the decrease of activity of zeolite catalysts with time during nitration in gaseous phase (above 140 °C), wherein the deactivation rate increases with temperature [8, 17, 20, 31]. At the same time, the content of di- and trinitrobenzenes and nitrophenols of reaction products increases.

Nitration patterns on non-zeolite solid catalysts have been studied only in two works [36, 37]. In the former, on the basis of the dependence of activity of modified montmorillonite on the electronegativity of the modifier ion, it was concluded that nitration on this catalyst went by the classical mechanism of electrophilic substitution with formation of a nitronium cation:



In the same work, the influence of the content of WO_3 and of its mixture with TiO_2 (25–40 % turned out to be optimal), and of HNO_3 /benzene ratio on the nitration results was checked. An approximate conservation of the nitration rate constant at various proportions of reagents was also demonstrated.

In [37], graphs of dependence of the nitration rate on the acidity of catalysts consisting of two oxides (mainly WO_3 and MoO_3) and on their specific surface are presented. In the same work, data on the dependence of nitrobenzene yield on the temperature and on the dependence of productive capacity of the catalyst on MoO_3 content were obtained.

CONCLUSION

To prevent the reader from getting a false impression of the degree of readiness of nitrobenzene production technology alternative to the currently existing one, let us summarise the peculiarities of most works discussed in the present review. Firstly, in them nitration of several aromatic compounds is considered, the main attention being given to benzene derivatives, because in this case the possibility of studying both the substrate and the regioselectivity of solid nitration catalysts is opened. Secondly, all the works published are laboratory-scale studies. Thirdly, it is only the nitration stage that has been studied, and often under the conditions unacceptable for technology. Even under laboratory conditions, complete technology of obtaining nitrobenzene with characteristics of the end product has not been proposed.

So, if one makes a selection of research works on technological checking, one has to include in their list examples from [27] where zeolite ZSM-5 was the catalyst, from [28] where mordenite was used, [34] (montmorillonite with Fe^{3+} ions), [36] (Al^{3+} montmorillonite and $\text{TiO}_2 - \text{WO}_3$), [46] (catalysis with *o*-nitrobenzenesulpho acid) and [48] (catalyst SiO_2 impregnated with H_2SO_4). Technological study of the enumerated nitration methods has to include first of all a check of resources of catalysts that have been given the form suitable for industrial use (usually granules containing a

binder that gives the active component a mechanical strength). For an economic estimation of the technology, it is important to have the complete scheme of nitrobenzene production. Important are also the questions of selection of a suitable reactor material, especially when the nitration reaction is run at a temperature above 100 °C.

REFERENCES

- 1 A. A. Gaile, V. E. Somov, O. M. Varshavskiy, *Aromaticcheskiye uglevodorody*, Khimizdat, St. Petersburg, 2000.
- 2 M. V. Gorelik, L. S. Efros, *Osnovy khimii i tekhnologii aromaticsikh soyedineniy*, Khimiya, Moscow, 1992.
- 3 V. N. Lisitsyn, *Khimiya i tekhnologiya promezhutochnykh produktov*, Khimiya, Moscow, 1987.
- 4 J. M. Kanhere and S. B. Chandalia, *Chem. Age India*, 30, 5 (1979) 405.
- 5 O. V. Bakhvalov, N. F. Salahkutdinov, K. G. Ione, Pat. 1825358 RF, 1993.
- 6 W. F. Hölderich and van Bekkum, *Stud. Surf. Sci. Catal.*, 58 (1991) 677.
- 7 P. B. Venuto, in: *Microporous Materials*, vol. 2, Elsevier, Princeton, 1994, p. 297.
- 8 L. V. Malysheva, E. A. Paukshtis, K. G. Ione, *Catal. Rev. Sci. Eng.*, 37, 2 (1995) 179.
- 9 K. G. Ione, *React. Kinet. Catal. Lett.*, 57, 2 (1996) 275.
- 10 R. W. Millar, C. M. Eamon, R. P. Claridge *et al.*, Intern. Annu. Conf. ICT 2000, 31st (Energetic Materials), 34/1 – 34/12.
- 11 Pat. 63 225 339 Japan, 1988.
- 12 Application 63225339 Japan, 1989.
- 13 L. E. Berteau, H. W. Kouwenhoven, R. Prins, Intern. Conf. Europcat, Montpellier, Sept. 12–17, 1993, Book of abstr., Vol 1, p. 126.
- 14 H. W. Kouwenhoven, L. Berteau, R. Prins, EP 552130, 1993.
- 15 L. E. Berteau, H. W. Kouwenhoven, R. Prins, *Stud. Surf. Sci.*, 84 (1994) 1973.
- 16 L. E. Berteau, H. W. Kouwenhoven, R. Prins, *Appl. Catal. A*, 129, 2 (1995) 229.
- 17 T. G. Kuznetsova, K. G. Ione, L. V. Malysheva, *React. Kinet. Catal. Lett.*, 63, 1 (1998) 61.
- 18 B.-S. Lee, K.-H. Chung, Y.-S. Lee, Y.-G. Kim, PCT Int. Appl. WO9942, 433, 1999.
- 19 S. M. Nagy, K. A. Yarovoy, M. M. Shakirov, V. G. Shubin, *J. Mol. Catal.*, 64 (1991) 31.
- 20 N. F. Salahkutdinov, K. G. Ione, E. A. Kobzar, L. V. Malysheva, *Zhurn. org. khimii*, 29, 3 (1993) 546.
- 21 S. M. Nagy, K. A. Yarovoy, V. G. Shubin and L. A. Vostrikova, *J. Phys. Org. Chem.*, 7 (1994) 385.
- 22 H. Suzuki, T. Murashima, K. Shimizu, K. Tsukamoto, *Chem. Lett.*, 5 (1991) 817.
- 23 K. Smith, A. Musson, G. A. De Boos, *J. Org. Chem.*, 63, 23 (1998) 8448.
- 24 K. Smith, S. Almeer, S. J. Black, *Chem. Commun.*, (2000) 1571.
- 25 L. Berteau, H. W. Kouwenhoven, R. Prins, Pat. 683918 Switzerland, 1994.
- 26 L. Berteau, H. W. Kouwenhoven, R. Prins, Pat. 683919 Switzerland, 1994.

- 27 O. V. Bakhvalov, K. G. Ione, Pat. 2087463 RF, 1997.
- 28 O. V. Bakhvalov, K. G. Ione, Pat. 2095342 RF, 1997.
- 29 G. A. DeBoos, K. Smith, A. Musson, PCT Int. Appl. WO 96 36, 587, 1996.
- 30 L. E. Berteau, H. W. Kouwenhoven, R. Prins, in: *Heterogeneous Catalysis and Fine Chemicals III*, Amsterdam *etc.*, 1993, pp. 607–614.
- 31 H. Sato, K. Hirose, K. Nagai *et al.*, EP 343048, 1989.
- 32 Application 249755 Japan, 1990.
- 33 H. Sato, K. Hirose, K. Koichi, H. Yoshioka, Pat. 5004846 USA, 1991.
- 34 B. M. Choudary, M. L. Kantam, M. Sateesh *et al.*, EP 949240, 1999.
- 35 B. M. Choudary, M. Sateesh, M. L. Kantam *et al.*, *Chem. Commun.*, 1 (2000) 25.
- 36 H. Sato, K. Hirose, K. Nagai *et al.*, *Appl. Catal. A*, 175, 1–2 (1998) 201.
- 37 H. Sato, K. Hirose, *Res. Chem. Intermed.*, 24, 4 (1998) 473.
- 38 H. Sato, K. Hirose, *Appl. Catal. A*, 174, 1–2 (1998) 77.
- 39 G. A. Olah, Q. Wang, X. Y. Li, I. Bucsi, *Synthesis*, 11 (1992) 1085.
- 40 Pat. 02 300 150 Japan, 1990.
- 41 I.-L. Chen, Q.-S. Lin, L.-H. Lu, T.-X. Cai, *Shiyu Huagong*, 30, 1 (2001) 17.
- 42 Application 1–287063 Japan, 1989.
- 43 Pat. 01287063 Japan, 1989.
- 44 Application 1213256 Japan, 1989.
- 45 Y. Ono *et al.*, Proc. Intern. Congr. 9th, 1988, vol. 4, p. 1688.
- 46 Y. Ono, K. Tohimori, S. Suzuki *et al.*, Proc. Intern. Symp., Poitiers, 1988, p. 75.
- 47 F. J. Waller, A. G. M. Barrett, D. C. Braddock, *Chem. Commun.*, 6 (1997) 613
- 48 H. Sato, K. Nagai, H. Yoshioka, Y. Nagaoka, EP 402207, 1990.
- 49 H. Sato, K. Nagai, H. Yoshioka, Y. Nagaoka, Pat. 5030776 USA, 1991.
- 50 H. Sato, K. Nagai, H. Yoshioka, Y. Nagaoka, *Appl. Catal. A*, 175, 1–2 (1998) 209.
- 51 Pat. 02 300 149 Japan, 1990.
- 52 C. Costa, I. P. Dzikh, J. M. Lopes *et al.*, *J. Mol. Catal. A*, 154 (2000) 193.