Phenylhydrazine rearrangement revisited over modified ZSM-5 catalysts ☆

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The rearrangement of phenylhydrazine to *o*- and *p*-phenylenediamines was carried out over ZSM-5 and its modified catalysts. Sm and V showed the promoting effect. In presence of ammonia flow Ga and Cr modified ZSM-5 catalysts gave good yields of *o*- and *p*-phenylenediamines. The better temperature and WHSV for this reaction are found to be 400°C and 0.25 h^{-1} respectively. The SiO_2/Al_2O_3 catalyst showed very low ortho–para selectivity when compared with zeolite catalysts.

Keywords: phenylhydrazine; phenylenediamines; rearrangement; zeolite ZSM-5

1. Introduction

o-phenylenediamine (*o*-PDA) and *p*-phenylenediamine (*p*-PDA) are very serviceable intermediates in the synthesis of heterocyclic compounds and polymers. Several methods are available for the synthesis but the acid-catalysed benzidine analogue rearrangement of phenylhydrazine to phenylenediamines looks to be easy and convenient [1]. Zeolites, being acidic/bifunctional, mediated synthesis of fine chemicals and organic transformations is a growing field, due to their characteristic features such as shape selectivity, activity, thermal stability, reusability and pollution free environment [2–5]. Recently, we have reported the rearrangement of phenylacetate to ortho-hydroxyacetophenone over modified ZSM-5 catalysts [6], which prompted us to exploit the use of ZSM-5 catalysts for the rearrangement of phenylhydrazine to *o*- and *p*-phenylenediamines (scheme 1). This report gives the successful completion of our objectives.

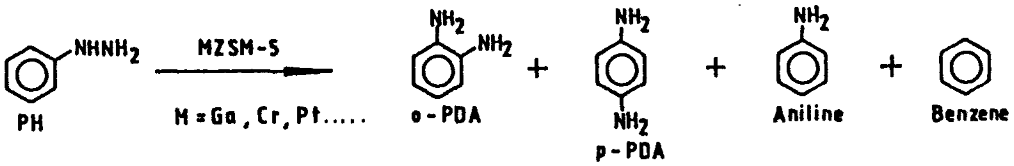
2. Experimental

Modified catalysts were synthesised by impregnation/ion-exchange of 5–10 wt% of metal cation on HZSM-5 (Si/Al = 30, Conteka, Sweden), using 4.0 g in water/methanol (40 ml). The mixture was kept aside for 6 h and stirred occasionally. Finally the water/methanol was evaporated and the solid dried. The ion exchange in HZSM-5 was about 80%. 70–80% of the cations were present in the zeolite and rest on the surface [7]. All the modified catalysts are crystalline as determined by XRD after the reaction.

The rearrangements were carried out in a down-flow, tubular, isothermal, continuous, vapour phase, fixed-bed reactor at atmospheric pressure. The reactor was made up of pyrex glass of 2 cm diameter and 30 cm length. 4.0 g of catalyst was charged in the reactor and activated for 4 h at 450°C, then cooled to 400°C. The phenylhydrazine (PH) was fed by a calibrated syringe pump at a constant feed rate (2 ml/h) through the catalyst bed. The products were condensed by circulating ice-cooled water. A yellow coloured solid settled on the walls of the condenser. After 4 h, this solid was collected in 30 ml of methanol.

3. Results and discussion

The rearrangement of PH over various catalysts is compiled in table 1. The reaction was carried out at the reaction temperature of 400°C and WHSV = 0.5 h^{-1} and 1–4 h on stream. In all the cases > 98% PH conversion was observed. The product was collected in metha-



Scheme 1.

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Table 1
Rearrangement of phenylhydrazine over different catalysts [a]

Sample No.	Catalyst	Conversion of PH (%)	Yield (wt%)				Ortho/para
			benzene	aniline	*o*-PDA	*p*-PDA	
1.	HZSM-5 (30) [b]	98.4	14.49	39.79	27.26	17.14	1.59
2.	HZSM-5 (150) [b]	100.0	14.26	46.35	24.27	14.95	1.62
3.	PtZSM-5	100.0	19.44	42.09	24.15	14.60	1.65
4.	GaZSM-5	99.05	21.60	47.84	18.17	11.50	1.58
5.	CrZSM-5	98.4	21.05	37.95	25.76	13.69	1.88
6.	VZSM-5	100.0	15.75	35.19	31.17	18.05	1.73
7.	SmZSM-5	100.0	13.69	30.70	32.89	22.66	1.45
8.	PbZSM-5	99.54	20.35	40.02	24.50	14.84	1.65
9.	NiZSM-5	100.0	20.93	41.63	23.46	13.92	1.69
10.	CuZSM-5	98.4	20.59	44.74	20.93	12.08	1.73
11.	SiO_2–Al_2O_3 [c]	87.1	18.00	50.90	4.00	6.85	0.58

[a] PH = phenylhydrazine; *o*-PDA = phenylenediamine; *p*-PDA = *p*-phenylenediamine; time on stream = 1–4 h; WHSV = 0.5 h^{-1}; temperature = 400°C; catalyst = 4.0 g.

[b] The number in brackets indicates the Si/Al ratio.

[c] Other products are 7.4% (not identified).

nol, and analysed by GC mass, NMR and quantified GC using an SE30 (30%) column. Aniline is the major by-product and free ammonia was observed during the reaction. As can be seen from table 1, the total yields (wt%) of *o*-PDA and *p*-PDA are from moderate to good for ZSM-5 catalysts but low for silica–alumina (sample 11). The rearrangement proceeds with low ortho–para selectivity, excluding the SiO_2/Al_2O_3 (84 : 16) (sample 11) which gives more para isomer.

As given in table 1, ZSM-5 catalysts showed better performance for the rearrangement and the rearrangement to deamination ratio is higher for ZSM-5 compared to the SiO_2–Al_2O_3 catalyst. The higher selectivity to the ortho isomer is due to the pronounced stabilization of the intermediate compared to the para isomer [8]. The PH rearrangement reaction was tried with different modified ZSM-5 catalysts (table 1) to improve the total yield of phenylenediamines. All the catalysts show almost the same activity but increased activity was observed for SmZSM-5 and VZSM-5.

Ammonia flow was used to enhance the formation of desired products. Under similar conditions of temperature, WHSV and time on stream, in ammonia flow, the total yield of *o*-PDA and *p*-PDA was increased to 50.8, 69.2 and 60.15 for HZSM-5 (Si/Al = 150), GaZSM-5 and CrZSM-5 respectively. In ammonia flow some catalysts like HZSM-5 (Si/Al = 150), GaZSM-5, show improved para-selectivity as shown in table 2. The synergism may be due to the formation of an active complex by ammonia and cation. On the other hand, the activities of SmZSM-5 and NiZSM-5 decreased under ammonia flow.

The trend in the ratio of the rate of rearrangement reaction to the rate of deamination reaction with respect to cation in the absence of ammonia is: Sm > V > Cr > H^+ > Pt > Pb > Ni > Cu > Ga; in the presence of ammonia, Ga > Cr > Sm > V > H^+ > Pt > Pb > Ni. The activity of GaZSM-5 was improved with respect to the rearrangement reaction in the presence of ammonia.

The reaction of phenylhydrazine over GaZSM-5 with different WHSV, i.e. 0.25, 0.37, 0.5, 0.75 h^{-1}, was studied. The WHSV results reveal that the best yields of *o*- and *p*-phenylenediamines were obtained at 0.25 h^{-1} WHSV. The rearrangement was mild at lower temperatures such as 250 and 300°C. In the case of GaZSM-5 at 400°C and 1–8 h time on stream the conversion decreased to 72%. The decreased activity is due to coking but the original activity was recovered after regeneration. The rearrangement of PH to phenylenediamines

Table 2
Rearrangement of phenylhydrazine over different catalysts under ammonia flow [a]

Sample No.	Catalyst	Conversion of PH (%)	Yield (wt%)				Ortho/para
			benzene	aniline	*o*-PDA	*p*-PDA	
1.	HZSM-5 (150)	96.78	5.06	44.11	27.14	23.69	1.15
2.	GaZSM-5	100.00	–	30.47	39.90	29.33	1.36
3.	CrZSM-5	100.0	2.76	37.03	35.42	24.73	1.43
4.	SmZSM-5	92.41	9.76	38.41	26.91	17.37	1.55
5.	NiZSM-5	91.49	17.25	46.81	18.98	7.82	2.43

[a] PH = phenylhydrazine; *o*-PDA = *o*-phenylenediamine; *p*-PDA = *p*-phenylenediamine; time on stream = 1–4 h; WHSV = 0.5 h^{-1}; temperature = 400°C; catalyst = 4.0 g; NH_3 flow was controlled by needle value and measured by a calibrated flow meter.

was carried out over CrZSM-5 for four times and the same activity and selectivity were found with a variation of 1–2%.

Thus the present catalytic method should serve as a useful addition to synthetic organic chemistry.

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