

# The effect of some transition metal ions exchanged with zeolites on benzaldehyde, benzophenone and cyclohexanone phenylhydrazones

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## Abstract

Phenylhydrazone derivatives of benzaldehyde, benzophenone and cyclohexanone under the catalytic effect of exchanged zeolite NaY (NaA and HS in some cases) with transition metal ions of chromium (III), iron (III), manganese (II), nickel (II) and copper (II) in refluxing benzene resulted in the formation of benzaldehyde, benzophenone and cyclohexanone respectively. Side products like benzonitrile and biphenyl were also identified.

*Keywords:* Zeolites; Phenylhydrazone derivatives; Transition metals

## 1. Introduction

Phenylhydrazones, tosylhydrazones and semicarbazones are important derivatives of aldehydes and ketones. These compounds are either used for characterization and protection of aldehydes and ketones or to serve as precursors to carbenes, olefins and other compounds [1]. Our literature survey showed that many different methods of oxidations–reductions, acidic and basic conditions have been used for the regeneration of aldehyde and ketones from these derivatives in liquid phase [2]. Unfortunately, cleavage of these nitrogen derivatives in

the presence of heterogeneous catalysts has been rarely carried out [3]. We believe that using heterogeneous catalysts, especially those readily available like zeolites with their unique properties such as their acidity and shape selectivity, can be good candidates for these reactions [4]. However, to our knowledge, the application of zeolites in this way has been limited to the Beckman rearrangement of cyclohexanone oxime to caprolactam [5] which is an important raw material for the production of synthetic fibers. In this work, we have studied the effect of several transition metal ions exchanged with zeolite NaY (and in some cases with NaA and HS) [6–8] on regeneration of benzaldehyde, benzophenone and cyclohexanone from their phenylhydrazone derivatives.

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## 2. Experimental

### 2.1. Preparation of zeolite catalyst: general procedure

100 ml of 0.1 N solution of metal salt ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) was added to 6.0 g of zeolite in a 250 ml flask. The mixture was stirred for 24 h and then filtered. The solid was washed with enough water until the filtrate became colorless and then dried at room temperature.

### 2.2. Regeneration of carbonyl compounds from phenylhydrazones; general procedure

Phenylhydrazone (30 mmol) in 50 ml benzene was added to 1.5 g zeolite in a 100 ml flask. The solution was degassed several times with nitrogen under vacuum, then refluxed for 6 h under nitrogen atmosphere. After filtration and washing with solvent, the filtrate was concentrated on a rotatory evaporator and then subjected to GC and GC-MS analysis using a Philips PU4400 chromatograph (1.5 m 3% OV-17 column) and Varian 3400 chromatograph (25 m DB-5 column) coupled with a QP Finnigan mass INCOF50, 70 eV, respectively.

## 3. Results and discussion

On the basis of GC-MS analyses, it was concluded that transition metal ions Cr, Mn, Fe, Ni and Cu exchanged on zeolite NaY were active on regeneration of benzaldehyde. The results are shown in Table 1. From this table, it is apparent that benzaldehyde has been formed under the effect of all catalysts although its yield depends on the metal ion. According to Fig. 1, Cr–NaY shows the highest activity for regeneration of benzaldehyde, whereas NaY has the lowest activity. Other products such as benzonitrile, biphenyl, benzaldehyde phenyl imine and another unidentified compound were also formed.

Table 1

Effect of NaY and M–NaY zeolites on benzaldehyde phenylhydrazone

Catalyst	Conversion (%)	Yield (%) <sup>a</sup>				
		1	2	3	4	5
NaY	86.48	14.39	1.49	4.43	11.87	5.14
Cr–NaY	91.58	83.79	trace	1.70	4.02	trace
Mn–NaY	34.44	29.64	–	1.29	trace	1.54
Fe–NaY	94.44	41.14	7.35	4.02	4.84	12.42
Ni–NaY	47.06	32.65	–	1.16	1.32	1.82
Cu–NaY	87.75	24.40	27.63	5.75	trace	10.32

<sup>a</sup> (1) Benzaldehyde, (2) benzonitrile, (3) biphenyl, (4) benzaldehyde phenyl imine, (5) unidentified.

A study of the effect of HY zeolite [9] on benzaldehyde phenylhydrazone did not show considerable activity for the regeneration of benzaldehyde (4.09%) although benzonitrile was obtained as the major product (28.49%).

On the basis of our results, it seems that M–NaY catalysts present the desirable acidic and nucleophilic conditions for hydrolysis of phenylhydrazone, whereas the HY catalyst has the least tendency for this reaction. Although HY zeolite has been used as a Brønsted acid to protonate organic molecules [10], its inactivity in our reaction might be due to low protonating power of this stable superacid at reaction temperature [11] and also its low water contents available inside the network, since this zeolite is usually prepared from thermal decomposition of the corresponding  $\text{NH}_4^+$ -zeolite at 400°C which removes the majority of water molecules. On

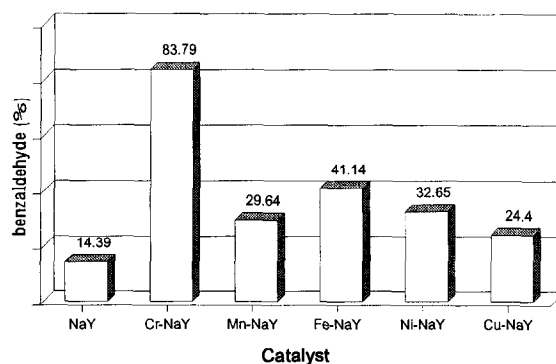
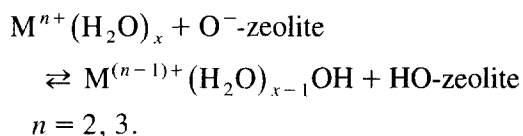


Fig. 1. Effect of NaY and M–NaY zeolites on regeneration of benzaldehyde from its phenylhydrazone derivative.

the other hand, the M–NaY catalysts contain enough water inside their network because the exchange process is carried out in aqueous solution at room temperature. Since addition of water to HY zeolite and subsequent drying at room temperature did not show any improvement in hydrolysis activity, one might conclude that this catalyst can not protonate the phenylhydrazone substrate at reaction conditions.

The presence of metal cation in zeolite increases the HO-zeolite sites via the hydrolysis of hydrated ion according to the following mechanism [12]:



Therefore, zeolite containing metal ions should provide stronger Brønsted acidity to substrate. As can be seen from Table 1, all metal ions exchanged with zeolite NaY produce a greater percentage yield of benzaldehyde than NaY catalyst. Since maximum and minimum aldehyde regeneration occur in the presence of Cr–NaY and Cu–NaY respectively, it might be possible to conclude that hydrated chromium cation would strongly be hydrolyzed in zeolite and produce the highest number of acid sites, while hydrated copper cation has the lowest tendency for hydrolysis and therefore less acidic centers are available for phenylhydrazones. This

Table 2

Effect of time and ratio of catalyst (Fe–NaY) to substrate (benzaldehyde phenylhydrazone)

	Conversion (%)	Yield (%)				
		1	2	3	4	5
<i>Time (h)</i>						
3	43.79	22.14	5.72	2.88	trace	2.04
6	94.44	41.14	7.35	4.02	4.84	12.42
9	96.12	50.09	12.08	10.84	9.04	11.19
<i>Catalyst / substrate</i>						
2	49.57	30.42	7.12	3.94	2.74	2.21
3	94.44	41.14	7.35	4.02	4.84	12.42
4	94.67	56.10	7.63	5.23	3.10	5.09

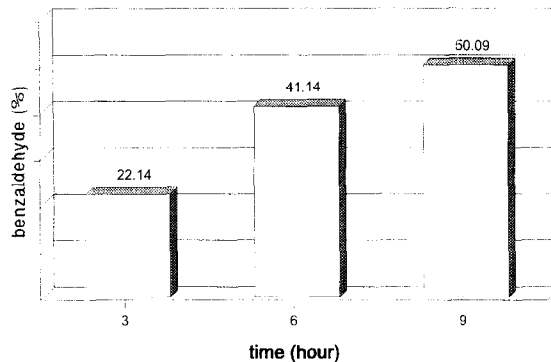


Fig. 2. Effect of time on benzaldehyde yield in the presence of Fe–NaY catalyst.

behavior can be related to the polarizing power of cations [13].

The effect of time and ratio of catalyst to substrate on reaction of benzaldehyde phenylhydrazone with Fe–NaY catalyst are shown in Table 2. This catalyst was chosen for these experiments because all products 1 to 5 were obtained under this condition. As can be seen from Figs. 2 and 3, most enhancement in conversion occurs around 3 h and the ratio of 3, although increasing time and catalyst to substrate ratio will certainly increase the aldehyde regeneration yield.

In order to illustrate the difference in behavior of NaY, NaA and hydrated sodalite HS, three series of experimental results are listed in Table 3. The results obtained allow us to draw

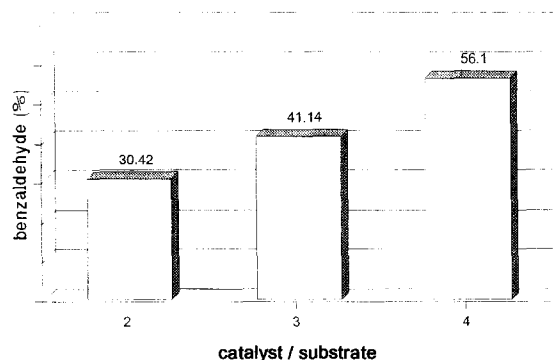


Fig. 3. Effect of catalyst (Fe–NaY) to substrate ratio on benzaldehyde yield.

Table 3  
Effect of NaY, NaA, HS and Cu–NaY, Cu–NaA, Cu–HS on benzaldehyde phenylhydrazone

Catalyst	Conversion (%)	Yield (%)				
		1	2	3	4	5
NaY	86.48	14.39	1.49	4.43	11.87	5.14
NaA	40.59	11.65	–	1.07	trace	trace
HS	95.88	49.21	–	trace	4.26	1.74
Cu–NaY	87.75	24.40	27.63	5.75	trace	10.32
Cu–NaA	92.67	23.46	–	4.96	7.31	3.11
Cu–HS	92.45	16.81	11.22	4.32	1.02	7.84

the following conclusions on the catalyst structures:

(1) The internal channels and cavities of NaY with the pore aperture of 7.4 Å [14] can be accessible to a phenylhydrazone guest. Therefore, the majority of the reactions can be done inside the channels and cavities. This idea can be supported by considering the experimental results listed in Table 1 which shows the catalysts exchanged with different transition metal ions exhibit different capabilities toward aldehyde regeneration.

(2) Zeolite HS has the smallest window size (2.2 Å) [14]. Therefore, the reaction should take place on the outer surface due to the lack of space within the channels or cavities.

(3) Comparison of aldehyde regeneration in the presence of HS and NaY shows that HS is about three times more selective than NaY. Such marked difference might have arisen from the more acid sites (Brønsted and Lewis) available on the outer surface of HS due to its lower Si/Al ratio [unit cell formula:  $\text{Na}_6(\text{AlO}_2)_6(\text{SiO}_2)_6 \cdot 7.5\text{H}_2\text{O}$ ] than the similar ratio in NaY [unit cell formula:  $\text{Na}_{48.2} \text{Al}_{48.2} \text{Si}_{143.8} \text{O}_{384} \cdot 243\text{H}_2\text{O}$ ] [14]. When the Brønsted acidic character of M–NaY is increased by using ions of high polarizing power like chromium cation, selectivity of aldehyde regeneration increases to more than 90% (compare to 49.21% in the case of HS).

(4) When HS and NaY zeolites are exchanged with the least polarizing power of copper ion, the selectivity of Cu–HS catalyst de-

creases sharply, whereas the Cu–NaY shows more selectivity toward aldehyde formation. The decreased effect of Cu–HS might be due to stable complexation of copper ion with surface active hydroxyl groups. Therefore, the availability of acid sites for substrate will be decreased. On the other hand, the complexation inside the NaY cavities increases the HO-zeolite sites via the hydrolysis of hydrated cation. Therefore, the reaction will be facilitated.

(5) The aperture pore of zeolite NaA is 4.2 Å [14]. Therefore, one might expect the surface and cavities to be active simultaneously. Since using the Cu–NaA catalyst increases the percentage yield of aldehyde, it might be possible to conclude that the surface activity of NaA is less important than the role of cavity activity in reaction progress. Such deduction is based on the fact that the presence of Cu intensifies the cavity activity due to the hydrolysis of hydrated cation.

Finally, the effect of catalysts Cr–NaY and Cu–NaY on benzophenone and cyclohexanone phenylhydrazones are summarized in Table 4. We can observe similar behavior with the maximum selectivity of Cr–NaY.

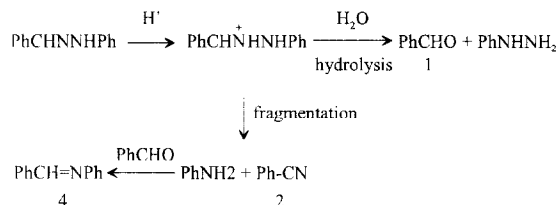
A plausible reaction mechanism for the processes taking place under the effect of zeolite catalyst containing metal ion can be simultane-

Table 4  
Effect of M–NaY zeolites on benzophenone and cyclohexanone phenylhydrazones

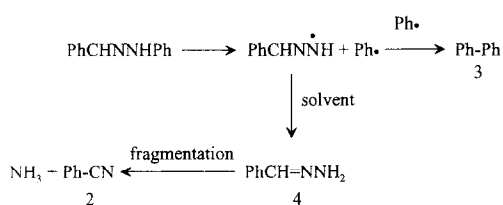
Substrate	Catalyst	Yield (%) <sup>a</sup>		
		6	7	3
Benzophenone phenylhydrazone	Cr–NaY	100.00	–	–
Benzophenone phenylhydrazone	Cu–NaY	65.00	–	–
Cyclohexanone phenylhydrazone	Cr–NaY	—	47.00	trace
Cyclohexanone phenylhydrazone	Cu–NaY	—	39.00	7.0

<sup>a</sup> (6) Benzophenone, (7) cyclohexanone.

ous hydrolysis and fragmentation of phenyl-hydrazone on Brønsted acid sites as follows:



Since decomposition of benzaldehyde and cyclohexanone phenylhydrazones both generate biphenyl as a byproduct, it seems likely that both phenyl groups in biphenyl have come from the phenylhydrazone part. Therefore, biphenyl product might have resulted from the homogeneous cleavage of N–Ph single bond with subsequent coupling of phenyl radicals as follows:



#### 4. Conclusion

The above data can be regarded as experimental evidence for activity of transition metal ions of Cr, Mn, Fe, Ni and Cu exchanged with zeolite NaY for regeneration of aldehydes and ketones from corresponding phenylhydrazones. Since the reaction conditions are quite mild with respect to other methods mentioned earlier and undesirable products are eliminated by using Cr–NaY, we think this catalyst can be regarded as a good candidate for phenylhydrazone derivatives of aromatic aldehydes and ketones. To obtain higher yield of ketones of aliphatic derivatives, reaction time should be increased to more than six hours.

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#### References

- [1] R.H. Shapiro and M.J. Heart, *J. Am. Chem. Soc.* 89 (1967) 5734; L. Friedman and H. Shechter, *J. Am. Chem. Soc.* 83 (1961) 3159; G.W. Kabalka and S.T. Summers, *J. Org. Chem.* 46 (1981) 1217; L.A. Paquette, W.E. Fristad, D.S. Dime and T.R. Bailey, *J. Org. Chem.* 45 (1980) 3017; G. Rosini and R. Ballini, *Synthesis* (1983) 228; J.E. Mc Murry, *J. Am. Chem. Soc.* 90 (1968) 6821.
- [2] R. Oda, M. Mieno and Y. Hagashi, *Tetrahedron Lett.* 8 (1967) 2363; T.L. Ho and G.A. Olah, *Synthesis*. (1976) 611; T.L. Ho and C.M. Wong, *J. Org. Chem.* 39 (1974) 3453; G.A. Olah, Y.D. Vankar and G.K.S. Parakash, *Synthesis*. (1979) 113; G. Rosini and R. Ballini, *Synth. Commun.* (1983) 137; G. Rosini and R. Ballini, *ibid.* (1982) 228; G.A. Olah and J. Welch, *J. Am. Chem. Soc.* 100 (1978) 5396; H. Firousabadi, M. Seddighi, A. Ahmadi and A.R. Sardarian, *Synth. Commun.* (1989) 3385; R.N. Butler and W.B. King, *J. Chem. Soc., Perkin Trans. 1* (1977) 282.
- [3] J.D. Butler and T.C. Poles, *J. Chem. Soc., Perkin II.* (1973) 1262; P. Laszlo and E. Polla, *Synth. Commun.* (1985) 439.
- [4] P.H.E. Speel, B. Janssens and P.A. Jacobs, *J. Org. Chem.* 58 (1993) 7688; L. Delaude and P. Laszlo, *J. Org. Chem.* 55 (1990) 5260; P. Moreau, A. Finiels, P. Geneste, F. Moreau and J. Solofo, *J. Org. Chem.* 57 (1992) 5040; D.R. Corbin, D.F. Eaton and V. Ramamurthy, *J. Org. Chem.* 53 (1988) 5384; M. Onak, K. Sugita and Y. Izumi, *J. Org. Chem.* 54 (1989) 1116; V. Ramamurthy, D.R. Cobin and L.J. Johnston, *J. Am. Chem. Soc.* 114 (1992) 3870.
- [5] T. Curtin, J.B. Monagle and B.K. Hodnett, *Appl. Catal. (A)*. 93 (1992) 75; A. Aucejo, M.C. Burguet, A. Corma and V. Fornes, *App. Catal.* 22 (1986) 187; M.C. Burguet, A. Aucejo and A. Corma, *Can. J. Chem. Eng.* 65 (1987) 944.
- [6] D.W. Breck, *US Pat.* 3 130 007 (1964).
- [7] R.M. Milton, *US Pat.* 2 882 243 (1959).
- [8] F. Farzaneh, M. Khatamian Oskooie and M.M. Akbari Nejad, *J. Sci. I.R. Iran.* 1 (1989) 23.
- [9] K. Tsutun and H. Takhashi, *J. Catal.* 24 (1972) 1.
- [10] T. Indrasena Reddy, B.M. Bhawal and S. Rajappa, *Tetrahedron Lett.* 33 (1992) 2857; P. Kumar, R.S. Reddy, A.P. Singh and B. Pandey, *Tetrahedron Lett.* 33 (1992) 825.
- [11] B. Gates, *Catalytic Chemistry* (John Wiley and Sons, 1992) pp. 269–272.
- [12] L.M. Kustov, V. Yu. Borovkov and B. Kazanshy, *J. Catal.* 72 (1981) 149.
- [13] J.W. Ward, *J. Catal.* 10 (1968) 34; *J. Phys. Chem.* (1968) 4211.
- [14] D.W. Breck, *Zeolite Molecular Sieves* (John Wiley and Sons, 1974) pp. 133–180.