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Direct reductive hydrolysis of nitriles to aldehydes over Ru- and Pt-loaded zeolites

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Bifunctional Ru- and Pt-loaded zeolite catalysts produce aldehydes in a single step from the corresponding nitriles using hydrogen and water.

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1. Introduction

The selective conversion of nitriles to the corresponding aldehydes over Raney nickel in sulphuric acid or formic acid medium has been studied previously [1,2]. Recently, precipitated nickel or iron or aluminium has also been reported for the reductive hydrolysis of nitriles to aldehydes [3]. The conventional Raney nickel catalyst has its own disadvantage as it dissolves in sulphuric acid or formic acid medium during the reaction. Platinum or ruthenium loaded crystalline microporous zeolites catalyse a number of hydrocarbon reactions including isomerization and hydrocracking [4]. However, the potential of Ru- or Pt-zeolite catalysts in the reductive hydrolysis of nitriles to the corresponding aldehydes has not been exploited yet. The catalysts are of a dual functional nature, exhibiting both hydrogenation and acidic activities. In the present paper, we report the first example of the catalytic conversion of the nitrile group of organic molecules to the corresponding carbonyl group over bifunctional Pt-loaded acidic zeolites.

2. Experimental

The detailed synthesis and characterization of zeolite beta, ZSM-5 and ZSM-22 have been reported elsewhere [5–7]. Na-Y and H-mordenite were obtained from ACC, Bombay, India. All samples were found to be highly crystalline. These zeo-

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lites were calcined at 773 K for 16 h in the presence of air and converted into their ammonium form by repeated exchanges with solution of NH_4NO_3 (1 M solution, 10 ml/g zeolite, temperature = 353 K, duration = 6 h, pH = 7–8, three exchanges). The Ru- and Pt-loaded zeolites were prepared by impregnating NH_4-zeolites with the aqueous ammonical solution of $RuCl_3$ and $Pt(NH_3)_4Cl_2$, respectively. The resultant catalysts were calcined in flowing air at 773 K for 16 h. Before measuring catalytic properties of the catalyst, it was treated in situ in a flow of hydrogen at 673 K for 2 h. Catalytic tests were performed at atmospheric pressure in a tubular fixed bed quartz flow reactor. The catalyst sample (1.5 g) was sieved into particles with dimension in the 0.2–0.4 mm range. Nitrile, hydrogen and water were mixed together before entering the heating zone of the reactor. Analysis of products was carried out using a gas-chromatograph (Hewlett Packard model 5890 series II) equipped with a flame ionization detector and a 50 m × 0.2 mm capillary column with methyl silicone gum film. A few samples were also analysed with a Shimadzu GC-MS spectrometer (model GC-MS-QP 2000 A).

3. Results and discussion

The catalytic activity of various zeolites in the reductive hydrolysis of benzonitrile is illustrated in table 1. In all experiments, benzaldehyde was the predominant product. Benzyl alcohol, toluene, benzene and others [$C_6H_5CH_2NH_2$, $(C_6H_5CH)_2NH$] were also found in the product. Similar products have been reported earlier using nickel on iron and aluminium as catalysts [3].

The reductive hydrolysis of nitriles to aldehydes may undergo several side reactions. The formation of aldimine (R–CH=NH) takes place by the hydrogenation of the nitrile group (R–CN) which subsequently hydrolyses to the corresponding aldehydes (R–CHO), scheme 1 [3]. The further reduction of aldehyde may give the corresponding alcohols and hydrocarbons. The intermediate aldimine may undergo further reduction to the corresponding primary ($R–CH_2NH_2$) and secondary amines $(RCH_2)_2NH$, scheme 1 [3].

Various zeolites have been studied to ascertain their yields for benzaldehyde in the reductive hydrolysis of benzonitrile. The results show a strong influence of different catalysts on the conversion, turnover rates and product distribution under identical conditions. The conversion of benzonitrile (24.2 wt%) over 1.0% Pt-H-ZSM-5 was found to be higher compared to the other zeolites. However, 1.0% Ru-H-beta gave higher yields (> 90.0%) for benzaldehyde than other catalysts. The higher conversion over 1.0% Pt-H-ZSM-5 may be attributed to the better hydrolysing nature of H-ZSM-5 due to its stronger acid sites [8]. The influence of different amounts of Pt loading (0–1 wt%) over NH_4-beta was seen in the reductive hydrolysis of benzonitrile to benzaldehyde. The conversions of benzonitrile over H-beta, 0.2% Pt-H-beta, 1.0% Pt-H-beta and 1.0% Ru-H-beta were found to be 0, 3.2, 15.9 and 7.1 wt%, respectively. The inactivity of H-beta indicates that platinum or

Table 1
Reductive hydrolysis of nitriles[a]

Run No.	Catalyst	SiO_2/Al_2O_3 (molar ratio)	Degree of H^+-exchange	Conversion of nitrile (wt%)	TOF[b] (10^{-4} s^{-1})	Product distribution (wt%)[c]				
						R–CHO	R–CH_2OH	R–CH_3	C_6H_6	others[d]
1	H-beta	26.0	> 97		–	–	–	–	–	–
2	0.2% Pt-H-beta	26.0	> 97	3.2	0.9	59.6	8.5	23.5	8.4	–
3	1.0% Pt-H-beta	26.0	> 97	15.9	4.8	65.2	11.2	21.0	–	2.6
4	1.0% Pt-H-ZSM-5	41.0	> 98	24.2	10.9	47.5	5.0	42.2	4.5	0.8
5	1.0% Pt-H-ZSM-22	65.2	> 98	14.7	10.7	61.9	3.4	9.5	25.2	–
6	1.0% Pt-H-mordenite	22.0	> 97	9.3	2.4	72.6	10.5	10.8	6.1	–
7	1.0% Pt-H-Y	4.1	> 97	22.8	6.0	47.3	3.1	45.3	4.3	–
8	1.0% Ru-H-beta	26.0	> 97	7.1	2.1	90.6	–	8.3	1.1	–
9	1.0% Pt-H-beta[e]	26.0	> 97	5.6	1.5	70.3	7.3	10.7	–	11.7

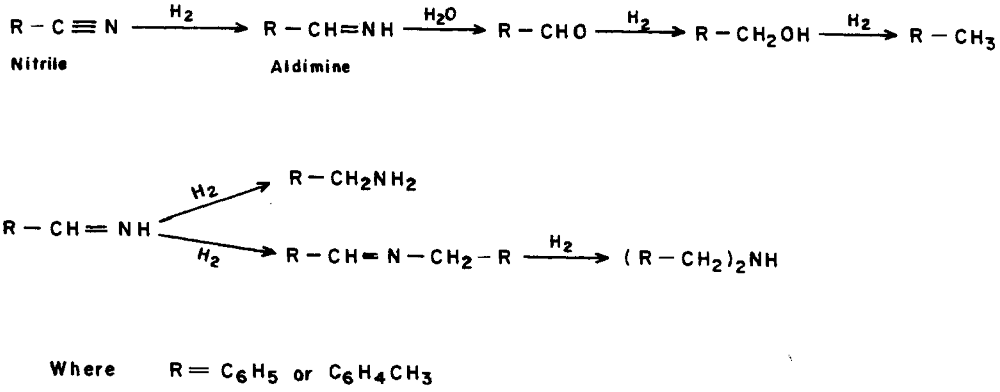
[a] Reaction conditions: catalyst weight: 1.59 g, reaction temperature = 488 K, R–CN/H_2O = 0.08 moles, H_2/R–CN = 4 moles.

[b] Turnover rates are expressed as turnover frequencies (TOF, mol R–CN converted s^{-1} mol Al^{-1}).

[c] R = C_6H_5 for runs 1–8 and $C_6H_4CH_3$ for run 9.

[d] Others = R–CH_2NH_2, $(RCH_2)_2NH$.

[e] Reaction of *o*-tolunitrile.



Scheme 1. Reductive hydrolysis of nitriles to aldehydes.

ruthenium loading over zeolite is responsible for the hydrogenation of nitrile to aldimine intermediate which is subsequently hydrolysed at the acid centers of zeolite.

Larger molecules like *o*-tolunitrile are also found to be converted to *o*-tolualdehyde ($C_6H_4CH_3CHO$), *o*-tolualcohol ($C_6H_4CH_3CH_2OH$), *o*-xylene ($C_6H_4CH_3CH_3$), primary and secondary amines under similar reaction conditions using 1% Pt-H-beta zeolite. The major product of the reaction was found to be the *o*-tolualdehyde (table 1, run 9). *o*-tolunitrile showed lower conversion (5.6 wt%) compared to the benzonitrile (15.9 wt%) over 1.0% Pt-H-beta. The lower conversion of *o*-tolunitrile over Pt-H-beta zeolite may be interpreted in terms of bulkier size of its products than those obtained in the reductive hydrolysis of benzonitrile.

4. Conclusions

The results demonstrate that bifunctional zeolite catalysts can be used in the reductive hydrolysis of nitriles to the corresponding aldehydes whereas H-beta was found inactive. Benzaldehyde is produced selectively (> 90.0%) using 1.0% Ru-H-beta as catalyst. Increase in the Pt-loading over NH_4-beta increases the conversion of benzonitrile. Hindered molecules (like *o*-tolunitrile) can also be converted to the corresponding aldehydes. Finally, the present reaction is merely a model for an approach over bifunctional zeolite catalysts which can be much more wide ranging.

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