HIGHLY ACTIVE AND REUSABLE HETEROGENEOUS CATALYSTS FOR ACYLATION OF ANISOLE

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In the present study, non-conventional solid acid catalysts such as NaY, metal ion exchanged zeolite NaY (Zn^{2+}, Fe^{3+}, Ce^{3+}, La^{3+} and Nd^{3+}), H-mordenite, H-β and HZSM-5 were used in order to overcome the disadvantages of conventional Friedel-Crafts catalysts for the acylation of anisole with acetic anhydride. Among the various zeolites studied, the HY zeolite shows an intermediate activity. Zeolite containing transition metal ions (Zn^{2+} and Fe^{3+}) are less active and zeolite NaY is nearly inactive. The catalysts exhibit the activity in the order H-β>transition metal ions (Zn^{2+} and Fe^{3+})>HY>NaY zeolite. The highest catalytic activity of H-β could be due to its larger pore size. The type of acidity and the acid strength in zeolite Y were determined by FTIR and differential scanning calorimetric (DSC) studies on the pyridine adsorbed catalysts. The correlation of catalytic activity with acidity reveals that Brönsted acid sites in zeolite promote the acylation of anisole.

Keywords: anisole acylation, DSC, FTIR, p-methoxyacetophenone, surface acidity, zeolite catalysis

Introduction

Acylation is of considerable industrial importance in producing aromatic intermediates, which are used in the manufacture of insecticides, perfumes and other commercial products. Acylation of aromatics have traditionally been carried out using homogeneous acid catalysts such as $AlCl_3$, $FeCl_3$, $ZnCl_2$ and HF, etc. It has been observed that conventional catalysts cause problems such as corrosivity, toxicity and effluent disposal in addition to the complication in the process. Hence, the homogenous catalytic process needs to be replaced by a more effective, heterogeneous catalytic method from the view point of environmental friendliness, ease of separation of products and ease of regeneration of catalyst. In this context, the use of solid acids for the acylation of anisole is worth considering.

Liquid phase acylation of anisole with acetic anhydride has been successfully demonstrated by numerous research groups by using a variety of catalysts [1–9]. Zeolites are extensively used as shape-selective solid acid catalysts in many industrial processes [10]. The successful application of zeolite catalysts to the Friedel-Crafts acylation of aromatics has already been described in the literature [11–13]. Rhodia have commercialized the production of acetoanisole and acetoveratrone from anisole and veratrole, with HY and H-β zeolites as catalysts in a fixed bed process but deactivation is reportedly a problem [14, 15]. It is possible to control the total number and strength of the acid sites in a zeolite by modifying the chemical composition of the framework. This makes it possible to prepare tailor-made catalysts for a particular acidity. Although the acidity of zeolites is not as strong as that of anhydrous $AlCl_3$ or liquid mineral acids, they were found to be quite promising catalysts for acylation reactions of activated aromatic compounds. It can be expected that the combination of strong acidity with shape selectivity favours the formation of the required para-product. The strong Brönsted sites on the zeolites are able to generate acylium ions which are the active intermediates in the acylation of aromatic substrates.

The present paper deals with the systematic investigation of the catalytic activity of solid acid catalysts such as NaY, metal ion exchanged NaY (Ce^{3+}, La^{3+} and Nd^{3+}), H-mordenite, H-β and HZSM-5 for the acylation of anisole with acetic anhydride. The nature of acidic sites is investigated by pyridine adsorption followed by infrared spectroscopy and differential scanning calorimetric studies.

Experimental

Materials

Preparation of catalysts

The hydrothermal synthesis of zeolite NaY consists of preparation of seed materials, gel and their mixing followed by heating in an autoclave at 383 K for 8 h. The zeolites HY, $Nd^{3+}Y$, $Ce^{3+}Y$, $La^{3+}Y$, $Zn^{2+}Y$ and $Fe^{3+}Y$ were prepared by ion exchange method. Other

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zeolite materials were purchased from Zeolyst International.

Preparation of HY

NaY zeolite (20 g) was refluxed with 1 M ammonium chloride at 353 K for 3 h. This was filtered, washed and dried in an oven. This process was repeated thrice. The sample obtained by ammonium chloride exchange was calcined at 773 K for 12 h.

Preparation of metal ion exchanged NaY-Zeolite

The metal ion (Nd^{3+}, Ce^{3+}, La^{3+}, Zn^{2+} and Fe^{3+}) exchanged NaY zeolite was prepared according to the procedure in the literature [16]. The zeolite in sodium form was soaked in 1 N aqueous solution of the respective metal chloride. The solid was then filtered thoroughly, washed and dried at 383 K for 6 h. The dry solid was finely powdered and calcined at 573 K for 12 h.

In the preparation of FeY zeolite, the exchange of NaY was carried out in the presence of ammonium acetate-acetic acid buffer (pH=5).

Methods

The catalysts were characterized by various physico-chemical techniques. The chemical composition was determined by wet chemical analysis. Alumina and silica contents were estimated by the standard gravimetric method. The sodium content was estimated by flame photometry. The amount of lanthanum, cerium and neodymium were estimated gravimetrically by precipitating the metal ions as their oxalates, igniting the oxalates to oxides and weighing as oxides. Zinc was estimated titrimetrically using standard disodium salt of EDTA and iron content by using spectrophotometric method.

BET surface area was measured by nitrogen adsorption-desorption at 77 K using Micromeritics Pulse Chemisorb 2700 instruments. Before each measurement, the catalyst was degassed at 423 K for 4 h to remove the adsorbed impurities.

The vapor phase adsorption of pyridine as probe molecule [17] was adopted to find out the acidity of catalyst samples. The nature of acid sites was characterized on the basis of IR spectral data of pyridine adsorbed catalyst samples. The nature and strength of acidic sites were determined by differential scanning calorimetric studies. Differential scanning calorimetric curves were recorded on Mettler DSC-20 unit with TA-3000 microprocessor. Each pyridine adsorbed sample was subjected to a temperature scan between 30 and 550°C, at a heating rate of 10°C min^{-1}. The nullifying technique [18] was

adopted in which the sample cell contained around 20 mg of pyridine-adsorbed catalyst sample, whereas the reference cell contained an equal mass of the corresponding pyridine-free sample. All the curves were recorded at atmospheric pressure with nitrogen as the carrier gas. The nature of acid sites in the catalyst samples were confirmed by recording the absorption spectra corresponding to various acid sites on a FTIR spectrophotometer (Perkin Elmer 1706).

Catalytic activity

The acylation of anisole catalyzed by zeolite was carried out in a Teflon autoclave under autogeneous pressure at 393 K for 24 h. The products were analyzed by gas chromatographic analysis (Hewlett Packard 5890), using OV-101 column (2 m length, 1/8 inch dia) and FID detector. They were identified and confirmed by GC-MS (Varian star 3400 GC, Column: Varian DB-1 Megapore) and ^{1}HNMR studies. The major product of acylation of anisole was found to be *p*-methoxyacetophenone (almost 95 to 97%) and only 3 to 5% of the *ortho*-substituted product.

Results and discussion

Acylation of anisole with acetic anhydride was carried out over metal ion exchanged zeolite NaY, H-mordenite, H-β and HZSM-5. The effect of catalyst pretreatment temperature and mole ratio of reactant on the conversion of anisole were studied using metal ion exchanged NaY-zeolite. The catalytic activity of various zeolites for the acylation was also investigated.

Effect of activation temperature of the catalyst

The catalysts were subjected to different calcination temperatures in the range of 523–823 K. Since Brönsted
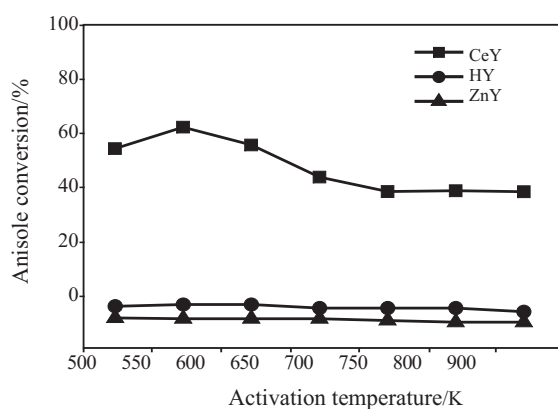
Fig. 1 Effect of activation temperature of zeolite catalysts on the conversion of anisole: Catalyst mass=0.4 g; anisole:acetic anhydride=1:2; reaction temperature=393 K; reaction time=24 h

and Lewis acid sites are created during calcinations, the former by dissociation of water molecules and the latter by dehydroxylation of the lattice at higher temperatures, the nature of the acid sites must depend on the thermal pretreatment. A study of the relation between the catalytic activity and the temperature of activation for the acylation of anisole was undertaken for three modified Y-zeolites, using anisole (20 mM) and acetic anhydride (100 mM) and 0.4 g zeolite at 393 K for 24 h. The results are shown in Fig. 1.

Effect of mole ratio of reactants

The effect of mole ratio was studied at anisole to acetic anhydride ratio of 1:1 to 1:5 at a constant volume of the reaction mixture (7.4 mL) and 0.4 g of CeY at 393 K for 24 h. The results are presented in Table 1. The optimum mole ratio was found to be 1:2.

Catalytic activity of various zeolites on the acylation of anisole

Acylation of anisole (24 mM) with acetic anhydride (48 mM) was studied with various zeolites. The results are presented in Table 2. From the results

it can be depicted that the catalytic activity of ion exchanged zeolite NaY was strongly influenced by the nature of the exchanged cation. Rare earth cations (Ce^{3+}, La^{3+} and Nd^{3+}) exchanged zeolites (what zeolite) exhibited the highest activity. The HY zeolite had an intermediate activity. Zeolite containing transition metal ions (Zn^{2+} and Fe^{3+}) were less active and zeolite NaY was nearly inactive. Comparison of the catalytic activity of large pore zeolite H-β with that of medium pore zeolite HZSM-5 towards acylation of anisole indicated that the former was more active due to its larger pore size.

Comparison of the catalytic activity of different framework Si/Al ratio of zeolite HZSM-5 (Si/Al=30 and 150) towards acylation of anisole indicated that the zeolite HZSM-5 (Si/Al=50) was more active. It is well established that higher siliceous materials show a marked hydrophobicity on their surfaces [12]. Therefore, the adsorption of reagents was higher on the more hydrophobic zeolite HZSM-5 (Si/Al=50) which in turn resulted in higher catalytic activity towards acylation of anisole.

Correlation of catalytic activity and surface acidity

The nature, density and strength of acidic sites play an important role in deciding the catalytic activity of a surface towards acylation of anisole. Hence, in the present study IR and DSC techniques were chosen to get information about the nature of acidic sites. Pyridine has been shown to be an excellent probe for solid acids. Its ring vibration modes are very sensitive to their environment and can be used to differentiate Lewis and Brönsted acid sites [19]. Pyridine can interact with Brönsted acid sites to form pyridinium ion and Lewis acid sites to form coordination complex. Though all the infrared bands are due to the C–C ring vibrations, it is possible to distinguish

Table 1 Effect of mole ratio of reactants (anisole:acetic anhydride) on the conversion of anisole

Sample no.	Molar ratio of anisole:acetic anhydride	Conversion of anisole/%
1	1:1	57
2	1:2	66
3	1:3	65
4	1:4	65
5	1:5	61

Catalyst mass=0.4 g: Reaction temperature=393 K; Reaction time=24 h

Table 2 Catalytic activity of various zeolites on the conversion of anisole

Catalyst	Si/Al ratio	Exchange of sodium/%	Surface area/m² g⁻¹	Conversion of anisole/%
NaY	2.5	–	495	3.0
HY	–	95	386	15.9
NdY	–	70	380	21.0
LaY	–	75	376	26.3
CeY	–	72	381	66.0
ZnY	–	81	390	12.0
FeY	–	83	375	14.0
HZSM-5	30	95	389	56.0
HZSM-5	150	96	389	69.0
H-β	150	97	600	81.0
H-mordenite	20	93	486	59.0

Catalyst mass=0.4 g: Anisole:acetic anhydride=1:2; Reaction temperature=393 K; Reaction time=24 h

Table 3 FTIR and DSC data for pyridine adsorbed catalyst samples

Catalyst	Peak temperature/°C			ΔH (exo)/J g^{-1}	IR frequency/cm^{-1}		
	HPY	LPY	BPY	HPY/BPY	HPY	LPY	BPY
NaY	180	–	540	812/1229	1491	–	1638
HY	187	–	–	20.32/–	1491	–	1638
CeY	173	–	–	141.8/–	1443	–	1638
					1491	–	1545

HPY – Hydrogen bonded pyridine, LPY – Pyridine adsorbed on Lewis acid sites, BPY – Pyridine adsorbed on Brönsted acid sites
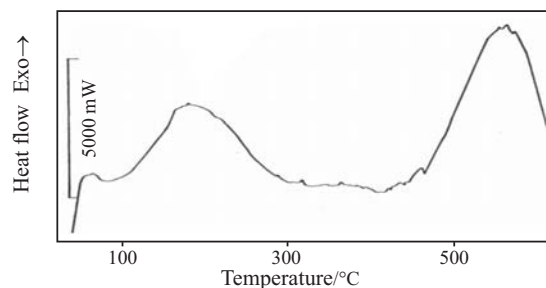
Fig. 2 DSC curve of pyridine desorbed from NaY
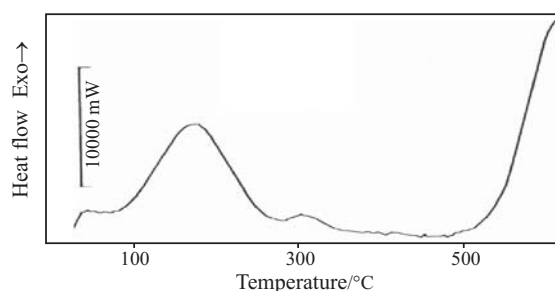
Fig. 3 DSC curve of pyridine desorbed from HY
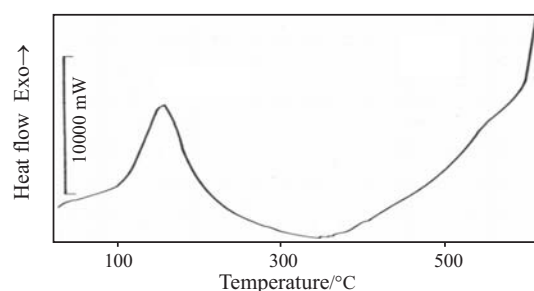
Fig. 4 DSC curve of pyridine desorbed from CeY

between coordinated pyridine, protonated pyridine and physically adsorbed pyridine. The FTIR and DSC data for pyridine adsorbed catalyst samples are presented in Table 3. DSC curve of pyridine desorption from the NaY, HY and CeY catalyst samples are shown in Figs 2–4.

Heterogeneity of the surface acidity has been clearly indicated by the appearance of distinct peaks. All the peaks were exothermic indicating that pyridine had been chemisorbed on the samples. Pyridine desorption occurred from weakly held sites

in the lowest temperature range of 170–190°C. It was apparent that the surface hydroxyl groups were not sufficiently acidic enough to protonate pyridine to form pyridinium ion. The pyridine molecules were probably held by these weakest acidic sites through hydrogen bonding. The presence of hydrogen bonded pyridine has also been confirmed from infrared spectral studies.

The peak in the intermediate temperature range of 200–380°C has been attributed to desorption of pyridine from Lewis acidic sites. The zeolites do not possess Lewis acid sites as confirmed from DSC and FTIR studies. The peak in the higher temperature range (>500°C) has been assigned to desorption of pyridine from Bronsted acidic sites. All the zeolites were found to have desorption temperature in this range and possess Brönsted acid sites. Supporting evidence for the existence of Brönsted acid sites has been obtained from the FTIR studies. The presence of Brönsted acid sites on HY and CeY have been indicated by strong IR absorption bands at 1638 and 1545 cm^{-1} for the pyridine-sorbed samples (figure not shown). For NaY, the desorption of pyridine was observed at 540°C. The desorption temperature of HY and CeY were beyond 600°C. The actual temperature of desorption and the values could not be found out beyond 600°C due to the instrumental limitations. However, from the shape of the curve tending towards the maximum, it could be inferred that CeY possessed larger density of Brönsted acidic sites than NaY and HY.

These results confirmed that Brönsted acid sites were also active for the acylation of anisole. Literature evidence has also indicated that the active sites for dehydration and acylation were identical, suggesting that Brönsted acid sites catalyzed the acylation reaction [16]. These Brönsted acid sites might have been formed through the following mechanism (Eq. (1)) [20].

$$X^{3+}-O\begin{smallmatrix}H\\ \diagdown H\end{smallmatrix} + \bar{O}\text{-Zeolite} \rightleftharpoons X^{2+}-O\diagup^{H} + H^+\bar{O}\text{-Zeolite} \quad (1)$$

Conclusions

The Friedel–Crafts acylation of anisole with acetic anhydride, over zeolite was investigated. The catalytic activity of cation exchanged zeolite NaY is found to be strongly influenced by the nature of the exchanged cation. Rare earth cations (Ce^{3+}, La^{3+} and Nd^{3+}) exchanged zeolite exhibit the highest catalytic activity. The HY zeolite shows an intermediate activity. Zeolite containing transition metal ions (Zn^{2+} and Fe^{3+}) are less active whereas zeolite NaY is nearly inactive. Among the various zeolites studied here H-β exhibits the highest catalytic activity due to its larger pore size. Zeolites NaY, HY and CeY are found to possess weak acid sites and Brönsted acid sites as indicated by FTIR and DSC studies. The correlation of catalytic activity with acidity reveals that Brönsted acid sites in the zeolites promote the acylation of anisole.

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