Esterification and Intramolecular Acylation Reactions with Transition Metal/Zeolites

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Abstract

Transition metal/Y zeolites were prepared by microwave solid state and aqueous solution ion exchange methods. The activity of these zeolites was investigated in the intramolecular acylation of 4-phenyl butyric acid and phenoxy acetic acid. The yield of acylation increased in the order of CoY < FeY < VY < NiY < NaY < CrY < CuY < MnY < ZnY for both methods. The yield in intramolecular acylation increased when microwave solid-state ion exchange was used. A yield in the range of 62–65% was observed for acylation reactions with ZnY zeolite. The activity of these ion exchange zeolites was also investigated in the esterification of benzyl alcohol and isoamyl alcohol with acetic acid and isoamyl alcohol with butanoic acid. The yield increased in the order of MnY $\cong$ FeY < VY < CoY < NaY < CrY < NiY < CuY < ZnY. The aqueous solution ion exchanged zeolites showed higher activity in comparison to the solid-state exchange. About 90% yield was observed for the esterification reaction with ZnY zeolite.

Introduction

In spite of extensive research regarding the carbonium ion intermediates that are catalyzed by acidic zeolite, such as Friedel-Craft [1, 2], cracking [3], isomerization [4] and estrification [5], the nature of the acidic sites in zeolites has not been fully clarified and further studies can be fruitful [4, 6]. The zeolite acidity could be due to Bronsted sites arising from hydroxyls in the zeolite pore structure, or Lewis sites, such as $Al_xO_y^{n+}$ species on the zeolite surface [7]. It is well known that the dehydration reaction occurs above 875 K, which decreases the proton sites and increases the Lewis sites [8]. The Bronsted and Lewis sites can be present simultaneously in the structure at high temperature.

In addition to the Si/Al ratio, which affects the acid properties of zeolite [9], the exchange of monovalent ions with polyvalent cations creates very strong acidic centers by the hydrolysis phenomenon and improves the catalytic property [10]. The ion exchange properties of zeolite are important for the acid catalyst reaction. Most of the studies, which refer to ion exchange, are performed in aqueous solution. On the other hand, it has been known since 1972, that ion exchange between zeolites and metal containing species can be carried out in the solid-state phase at elevated temperature. However, this solid-state exchange requires a long time [11, 12]. Recent work shows that the exchange time can be reduced significantly by microwave irradiation [13]. The metal/zeolites prepared by the thermal method are interesting in many respects, such as their ability to decom-pose nitrogen oxide to nitrogen and conversion of carbon monoxide to carbon dioxide, which are important from an environmental point of view [14, 15].

A literature survey on organic reactions catalyzed by zeolite indicates that in the majority of them Bronsted and Lewis acid centers are simultaneously important in the catalytic activity of zeolites. Interestingly, it has been demonstrated that in some reactions such as acylation and alcohol dehydration, the Bronsted sites of zeolite are the active sites [1], and in other reactions such as isomerization, Lewis centers are the active sites [16].

The present study was carried out to understand the effect of the ion exchange method of zeolite on esterification and interamolcular acylation reactions. It will be very fruitful and may allow tailoring zeolites for specific reactions. In this work, transition metal/Y zeolites have been prepared by solution ion exchange and solid-state ion exchange methods. Microwave heating was used for the solid-state ion exchange methods. The activity of these catalysts has been tested in intramolecular acylation and esterification reactions.

Experimental

Preparation of zeolite catalyst

Zeolite YNa was prepared and activated according to the procedure described previously [17]. Two different routes were used to prepare metal/Y zeolites.

A. 200 mL of 0.01M solutions of metal salts (VCl_3, $CrCl_3.6H_2O$, $FeCl_2.4H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,

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NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O and ZnCl$_2$) was added to 2 g of zeolite YNa in a 250mL flask. The mixture was stirred for 24 h and then filtered. The obtained solid was washed with water and a colorless filtrate observed, which indicated that in the exchange process all the metal ions used were absorbed. The final zeolites were dried at room temperature.

B. 2 g of zeolite and 2 mmol of the above metal salts were mechanically mixed, ground and heated in a microwave oven for 10–20 min with 900 W power. The temperature in the solid-state ion exchange is estimated around 700 °C. The XRD pattern showed no metal salt remained and the solid state ion exchange was complete.

Intramolecular acylation reactions

1 g of zeolite was added to a stirred solution of the acid compounds (3 mmol) in dry chloroform (40 mL) and the mixture was refluxed for 7 h. The zeolite was filtered and washed with a few mL of chloroform. The collected organic phase was diluted with chloroform (10 mL) and then washed with a 10% NaHCO$_3$ aqueous solution in order to remove unreacted acids. Chloroform was removed under reduced pressure and α-tetralone and benzotetrahydrofuranone were obtained as the sole products for acylation of 4-phenyl butyric acid and phenoxy acetic acid, respectively. Products were characterized by ^{13}C, ^{1}H-NMR, IR and mass spectroscopies and yields quantified by weight. Control experiments showed no product formed in uncatalyzed acylation reactions.

Esterification reactions

0.5 g of zeolite was added to 3–5 mL of acids containing 3 mmol of alcohol. The mixture was refluxed with stirring and the progress of the reaction was monitored by TLC until esterification was completed (2 hours). The zeolite was filtered and washed with several portions of ether. The collected organic phase was diluted with ether (30 mL) and then was washed with a 10% aqueous solution of NaHCO$_3$ in order to remove unreacted acids. Ether and unreacted alcohol were removed under reduced pressure and the ester obtained as the sole product and yields quantified by weight. Esters were characterized by ^{13}C, ^{1}H-NMR, IR and mass spectroscopies. Uncatalyzed esterification reactions showed only a trace amount of product.

Characterization of the products

All products obtained from the esterification and acylation reactions were characterized by ^{1}H, and ^{13}C nuclear magnetic resonance, infrared and mass spectroscopies. The infrared spectra were recorded on a Shimadzu 470 grating spectrophotometer and mass spectra were obtained on a Shimadzu spectrometer model GCMS-QP 1000 EX instrument, operating under EI conditions (70 eV). ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker advanced DPX-250.

Microwave solid state ion-exchanged zeolites were fully characterized and results will be reported in our forthcoming paper.

Results

Table 1 shows the results of the intramolecular acylation reactions for 4-phenyl butyric acid and phenoxy acetic acid. The zeolite, which was used as catalyst in these reactions, was ion exchanged by microwave in the solid state and aqueous solution. The level of ions exchanged in zeolites by the two methods was the same according to the XRD results of solid state ion exchanged zeolites and the concentration of ions in the filtrate of the solution of ion exchanged zeolites. The infrared spectra of the products showed that the peak of the hydroxyl band of the acid disappeared and a strong band at about 1730 cm^{-1}, characteristic of a cyclic ketone stretching vibration, appeared. Phenoxy acetic acid was converted to ketone and was identified by mass spectrometry: m/z (134, 13%); (106, 50%); (76, 75%) and (43, 90%). ^{1}H-NMR in CDCl$_3$: 7.15–7.27 (m, 2H); 6.84–6.97 (m, 2H); 4.62 (s, 1H) and ^{13}C-NMR in CDCl$_3$: 198.09 (CO); 156.78, 128.58, 120.88, 120.53, 120.71, 113.61 (C$_6$H$_4$) and 64.38 (aliphatic C). The spectroscopic data for α-tetralone are well matched with the data in the literature.

Table 2 shows results for the esterification of benzyl alcohol with acetic acid, isoamyl alcohol with acetic acid and butanoic acid. The infrared spectra indicated that the peak of the hydroxyl bands of the alcohol and acids disappeared on completion of the reactions.

Discussion

Table 1 shows the following catalytic activity for ion-exchanged zeolite: CoY < FeY < VY < NiY < NaY < CrY < CuY < MnY < ZnY, with ZnY showing the highest activity for the two sets of catalyst. The yield for these reactions is higher when the microwave solid-state ion-exchanged zeolite was used. It seems that Lewis acid sites are the active centers in the intramolecular acylation reaction. In the solid-state ion-exchange under anhydrous conditions, the transition metal salts transport to the channels and cages of zeolite after dissociation and may also react with T-OH (T = Si, Al) groups. Recently, these sites were characterized and measured by FT-IR spectroscopy [18]. It has been reported that in thermal ion-exchanged zeolite the intensity of the hydroxyl bonds vibration at 3745 cm^{-1} decreased [19] and a metal-oxygen band formed at 890 cm^{-1} [20]. In this investigation, when microwave heating was used for ion exchange, thermal dehydration probably occurred and the Lewis acid sites increased. The following mechanism may be proposed for the acylation reaction with metal zeolite.
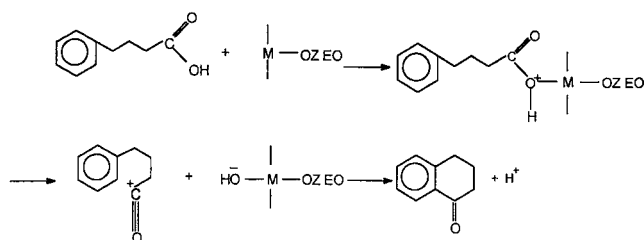
Table 1. Acylation yields of 4-phenyl butyric acid and phenoxy acetic acid[a]

		VY	CrY	FeY	MnY	CoY	NiY	CuY	ZnY	NaY
4-phenyl butyric acid	Aq[b]	25.9	37.3	25	41.8	18	30.9	40	43	30
	M.W[c]	30	42.8	29.5	52.9	22	42	50	62	
Phenoxy acetic acid	Aq[b]	30.7	40	29	43.8	22.3	34.9	41.5	49	35
	M.W[c]	35	45	34.5	54	25	42.3	51	65	

[a] All products characterized by ^{13}C, ^{1}H-NMR, IR and Mass spectroscopies.
[b] Ion-exchanged in aqueous solution.
[c] Ion-exchanged in the solid state by microwave.

Table 2. Esterfication yield of benzyl and isoamyl alcohol with acetic or butanoic acid[a]

		VY	CrY	FeY	MnY	CoY	NiY	CuY	ZnY	NaY
Benzyl alcohol	Aq[b]	43.2	65	46	46	55	60	79.3	90.5	58
Acetic acid	M.W[c]	40	61	39	40	52	50	70	82.3	
Isoamyl alcohol	Aq[b]	40	54	36	37.5	42	62.9	70	89	50
Acetic acid	M.W[c]		33	48	26	25	34	57	65.2	80.1
Isoamyl alcohol	Aq[b]	40.3	57.2	37	35	45.2	65.5	72.2	89.5	52
Butanoic acid	M.W[c]	38	50.2	32	31	40	58.6	69.7	80.1	

[a] All products characterized by ^{13}C, ^{1}H-NMR, IR and mass spectroscopies.
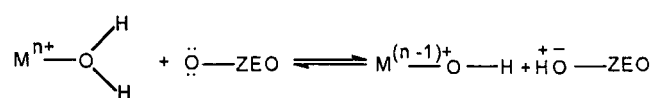[b] Ion-exchanged in aqueous solution.
[c] Ion-exchanged in solid state by microwave.

Furthermore, pervious studies show a synergy between Bronsted and Lewis acid sites, and the number of Bronsted sites increases by adsorption of water on Y zeolite [21]. Interestingly, in the present study, we found that by using hydrated zeolite ion-exchanged with microwave, the yield of the acylation reaction decreased by 5 to 8%. Apparently, in the microwave solid state ion exchange the water bonded to the zeolite decreases at high temperature and consequently the number of Lewis acid sites increases. Therefore, the nature of the acid site is related to the kind of metal centers in addition to the thermal pretreatment.

Table 2 shows the following order of activity for solid state and aqueous solution ion exchange: MnY $\cong$ FeY < VY < CoY < NaY < CrY < NiY < CuY < ZnY, in esterification reactions. ZnY shows the highest activity for the two sets of catalysts but the yield increases when aqueous solution ion-exchanged metal zeolite was used. It seems that these reactions are catalyzed with Bronsted sites. Since, these reactions are catalyzed with acid, the acidity is strongly linked with the kind of cation and will vary with the degree of cation exchange. For small ions such as rare earth or Zn^{2+}, Cu^{2+} ...etc. high degrees of cation exchange are observed. When the zeolite is in the hydrated form, all the metal cations are solvated by water molecules [22]. On the other hand, when the degree of ion exchange increases, more acidic sites develop on the zeolite. In this work, the high degree of exchange with Zn^{2+}, Cu^{2+}, Cr^{3+} ...etc is reflected in their better catalytic activity. Actually, such a conclusion has been reached for rare earth/zeolite in which hydroxyl groups are the centers of activity [23]. Apparently, in these sets of reactions, the origin of these hydroxyl groups is due to the ionization of water molecules by the strong electrostatic field of the cation [24]. It has also been suggested that the increase in acidity is due to an increase of the electrostatic field. This could indicate that the cation itself plays an important role in the formation of acidic function. These Bronsted acid sites are formed through the following mechanism [1]:

The following mechanism may be proposed for the esterification in the present study.
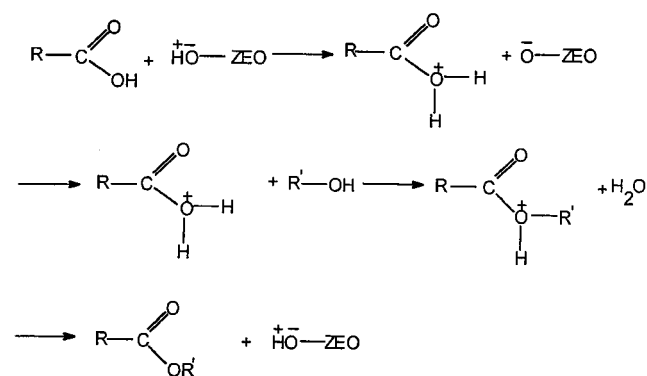
Indeed, in esterification reactions with aqueous solution ion-exchanged zeolites, Bronsted sites are the dominant sites in the esterification.

Conclusion

The nature of cations and the method of exchange influenced the catalytic activities of transition metal cation exchanged zeolites. The good correlation between yields of

intramolecular acylation reactions with different transition metal/zeolite cation exchanged by microwave irradiation, suggested that the active centers are mostly Lewis sites. In contrast, in esterification with transition metal-Y zeolite, which can be achieved by carrying out exchange process in aqueous solution of transition metal salts, the active centers are Bronsted sites.

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