

# Alkylation and acylation of phenol with methyl acetate

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## Abstract

The feasibility of effecting both methylation and acylation of phenol with a single reagent, methyl acetate was investigated over MgZSM-5, MgY and Mg $\beta$  zeolites at 200, 250, 300, 350, 400 °C with a feed ratio 1:2 (phenol:methyl acetate). The major products were anisole, 2,6-dimethylphenol (2,6-DMP), 2,4-dimethylphenol (2,4-DMP), *o*-cresol and phenyl acetate. Phenol conversion increased with increase in reaction temperature from 200 to 350 °C but decreased at 400 °C over Mg $\beta$ . Selectivity to anisole also exhibited similar trend. High selectivity to 2,6-DMP, *o*-cresol and phenyl acetate was noted at 350 °C. Selectivity to 2,4-DMP was not as high as 2,6-DMP. Increase in methyl acetate content in the feed increased the conversion, but a decrease in conversion was noted at the feed ratio 1:7. The activity of the catalysts at 400 °C followed the order Mg $\beta$  > MgZSM-5  $\approx$  MgY which was also the order of Lewis acidity. Increase in WHSV decreased the conversion. The study of time on stream showed decrease in conversion with increase in stream.

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**Keywords:** Acylation; Zeolites; Methyl acetate; Phenol; Methylation

## 1. Introduction

Acylation reactions are largely employed in fine chemical industry to produce a variety of synthetic fragrances and pharmaceuticals [1,2]. The acylation of aromatics has been generally carried out with Bronsted or Lewis acid catalysts [3,4]. Hydroxyacetophenones, which are required in the production of pharmaceuticals, stand out among the aromatic products. These compounds can be obtained by direct C-acylation of phenol with acetic acid or rearrangement of phenyl acetate. Obviously, the first route is more interesting since it employs readily available and less expensive raw materials. Due to the greater electron density of phenolic oxygen, the formation of hydroxyacetophenones occurs essentially through O-acylation and ester formation. Several authors have studied this route in liquid phase [5] or gas phase [6]. In both cases, the primary product is phenyl acetate and *o*-hydroxyacetophenone (OHAP) is the secondary product. Additionally, for kinetic reasons, the phenyl acetate formation is

much faster than its isomerisation. Acylation has been done with acetic acid [7,8], acetic anhydride [9] and acetyl chloride [10,11] over acid–base catalysts. Lewis acid catalysts such as AlCl<sub>3</sub>, BF<sub>3</sub> and ZnCl<sub>2</sub> are the commonly used catalysts in this reaction [1,2]. But, Lewis acid catalysts have drawbacks because they produce heavy inorganic wastes necessitating disposal problems. Hence the use of solid acid catalysts such as zeolite is advantageous for both acylation and alkylation as they are ecofriendly. The use of acetic acid is also not advantageous for acylation as it would leach out framework aluminium. Similarly acetic anhydride is also not advantageous as acetic acid is produced as one of the products. In the present study, the feasibility of effecting simultaneously both methylation and acylation of phenol using methyl acetate over Mg<sup>2+</sup> ion-exchanged ZSM-5, Y and  $\beta$  zeolites was investigated and the results are discussed in this paper.

## 2. Experimental

The parent NaY, Na $\beta$  and NaZSM-5 zeolites were provided by Sud chemie India Ltd. These catalysts were sub-

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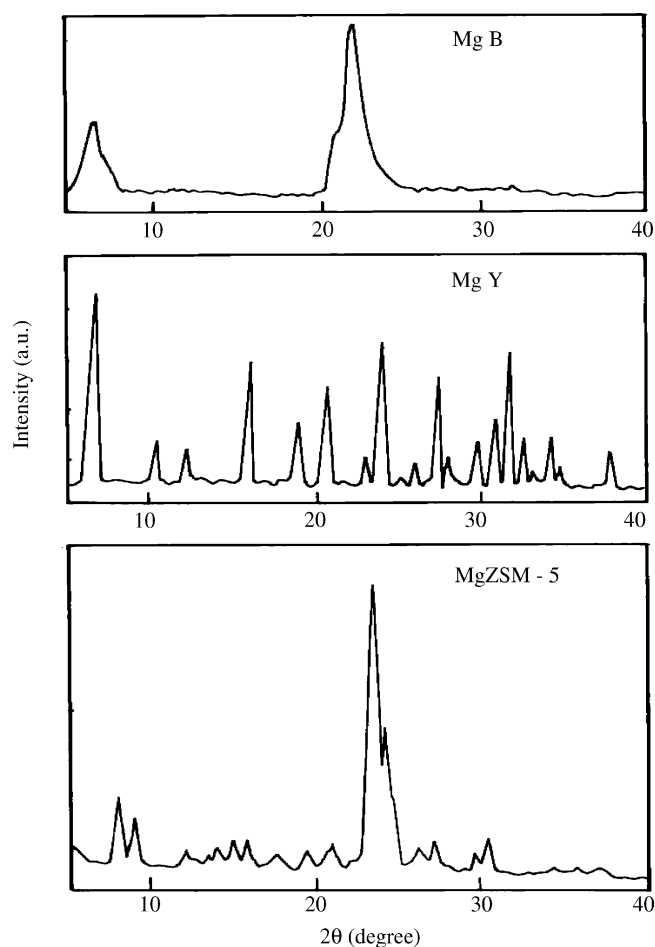


Fig. 1. XRD patterns of modified zeolites.

jected to ion exchange with  $\text{Mg}^{2+}$  by wet chemical method [12]. The dried catalysts were calcined at  $500^\circ\text{C}$  for 6 h and characterised by XRD, FT-IR, TGA and BET techniques.

## 2.1. Characterization

### 2.1.1. X-ray diffraction

The powder X-ray diffraction patterns of the ion-exchanged zeolites were recorded on Siemens D5005 diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation. The X-ray diffraction patterns of Mg forms of Y,  $\beta$  and ZSM-5 zeolites are shown in Fig. 1. The diffractograms of  $\beta$  zeolite show two major characteristic peaks located at  $2\theta = 7.8^\circ$  and  $22.6^\circ$  which coincides with the reported data [13]. The appearance of both peaks in the pattern has been ascribed to structural faulting in zeolite beta. The existence of stacking faults in zeolite precludes the derivation of structural data by conventional methods. Nevertheless, the degrees of planar faulting can be gauged by simulation of powder diffraction pattern [13,14]. In addition, the diffractogram indicates high crystallinity. However, decrease in relative intensities is observed in all the ion-exchanged Y zeolites. The XRD patterns of MgZSM-5 appear very much similar to the parent NaZSM-5.

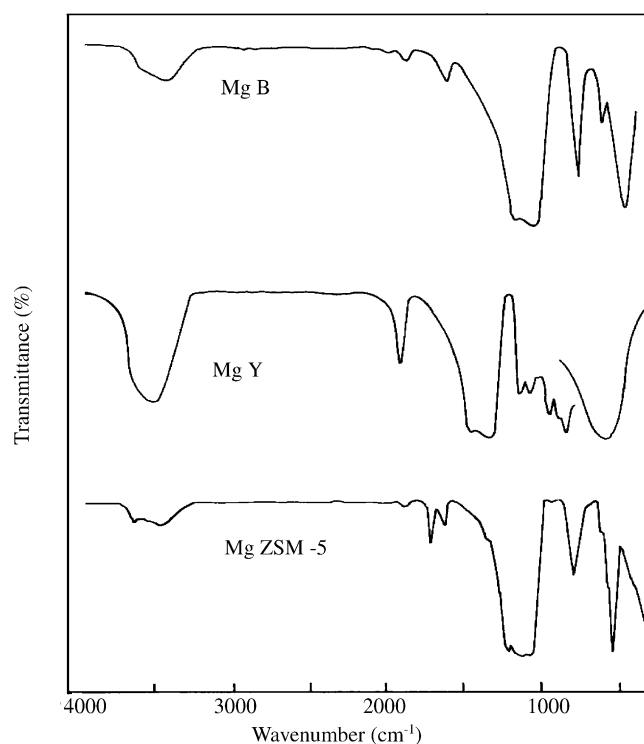


Fig. 2. FT-IR spectra of modified zeolites.

### 2.1.2. Infrared spectroscopy

Fourier-transform infrared spectra of the zeolites were recorded on a Nicolet (Avatar 360) instrument with a resolution of  $2 \text{ cm}^{-1}$  using KBr pellet technique (Fig. 2). A portion of the sample (15 mg) was pressed (under a pressure of  $2 \text{ ton/cm}^2$  for 30 min) into a self-supported wafer of 16 mm in diameter. All the spectra of ion-exchanged samples irrespective of their modification give similar peaks in the region from  $200$  to  $1300 \text{ cm}^{-1}$ . From the IR spectra of Y,  $\beta$  and ZSM-5, it is inferred that there is a regular decrease in the intensity of O–H stretching vibration of water due to increase in Si/Al ratio which follows the order  $\text{Y} < \beta < \text{ZSM-5}$ . The decrease in the intensity of the peak due to  $\text{OH}_2$  bending mode around  $1620 \text{ cm}^{-1}$  also evidently proves decrease in the water content of the zeolites in the order  $\text{Y} > \beta > \text{ZSM-5}$ .

### 2.1.3. TGA–DTA analysis

The thermogravimetric analysis (TGA) and differential thermal (DTA) analysis of zeolite materials were performed simultaneously on a high-resolution Mettler TA 3000 thermogravimetric analyser. The samples were heated in air at a heating rate of  $20^\circ\text{C}/\text{min}$  for all data collections from  $30$  to  $1050^\circ\text{C}$ . In the thermograms of MgY and MgZSM-5, there is a weight loss below  $100^\circ\text{C}$  due to loss of water (Fig. 3). The DTA also shows an endothermic peak below  $100^\circ\text{C}$  which coincides with loss of water in the TGA trace. The DTA traces also show origin of broad exothermic peak at about  $540^\circ\text{C}$ , which is assigned to the structural collapse [15]. But, the value is less than the corresponding ion-exchanged Mg $\beta$  zeolite.

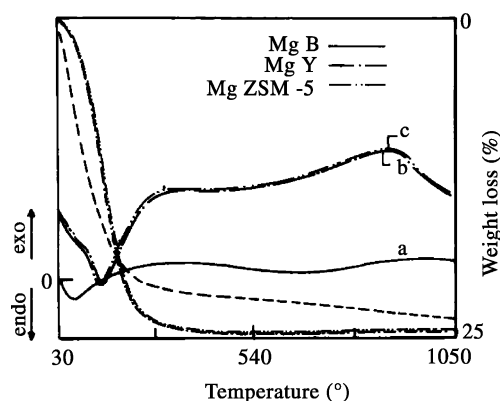


Fig. 3. TGA–DTA curves of modified zeolites.

#### 2.1.4. Surface area measurement

The surface area of zeolite materials was determined by nitrogen physisorption at  $-196^{\circ}\text{C}$  with an ASAP-2010 (Micrometrics Corporation, Norcross, GA) volumetric adsorption analyser. The results are depicted in Table 1 along with the percentage of crystallinity. The surface area decreases in the order  $\text{Mg}\beta > \text{MgY} > \text{MgZSM-5}$ . The decrease in surface area is due to structural distortion but not due to structural destruction.

#### 2.1.5. Chemical analysis

The  $\text{Mg}^{2+}$  content in  $\text{Mg}\beta$ ,  $\text{MgY}$  and  $\text{Mg-ZSM-5}$  was derived from atomic absorption spectroscopy (Labtum plasma 8440). Using this value the content of all other elements was computed based on their unit cell composition. The values are presented in Table 1.

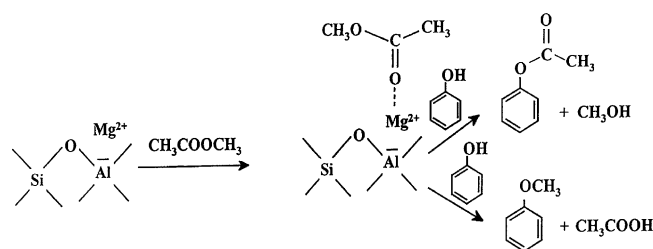
#### 2.1.6. Acidity measurements by DRIFT method

The acidity of the catalysts was determined by in situ DRIFT-pyridine adsorption and desorption technique. Nicolet Avatar 360 FT-IR spectrometer with provision for DRS analysis was used. The dehydrated sample ( $\approx 10\text{ mg}$ ) under  $10^{-5}\text{ mbar}$ , at  $500^{\circ}\text{C}$  was brought down to room temperature and contacted with pyridine vapours. The physically adsorbed pyridine was removed by heating the sample at  $300^{\circ}\text{C}$  under vacuum ( $10^{-5}\text{ mbar}$ ) for 30 min, the removed material was cooled to room temperature, and the spectrum was recorded. The peak area corresponding to Lewis acid site adsorbed pyridine was collected at  $1445\text{ cm}^{-1}$ . The relative peak areas were calculated for all the catalysts and are presented in Table 1. The relative peak areas are in the order 1:8:1.5 which is also the order of Mg content for  $\text{MgY}$ ,  $\text{Mg}\beta$  and  $\text{MgZSM-5}$ , respectively.

Table 1  
Physical properties of the catalysts

Catalyst	Surface area ( $\text{m}^2/\text{g}$ )	Crystallinity (%)	Si/Al ratio	Unit cell composition	Number of moles of Mg	Acidity <sup>a</sup>
$\text{MgZSM-5}$	385	85	75.2	$\text{Mg}_{0.305}\text{Na}_{0.65}\text{Al}_{1.26}\text{Si}_{94.73}\cdot 2\text{H}_2\text{O}$	0.3	1.5
$\text{Mg}\beta$	480	86	15.0	$\text{Mg}_{1.4}\text{Na}_{1.2}\text{Si}_{60}\text{Al}_4\cdot 5\text{H}_2\text{O}$	1.4	8.0
$\text{MgY}$	480	86	2.6	$\text{Mg}_{1.7}\text{Na}_{1.9}\text{Si}_{139}\text{Al}_{5.3}\cdot 9\text{H}_2\text{O}$	0.2	1.0

<sup>a</sup> Relative area of peaks due to Lewis acid site adsorbed pyridine at  $300^{\circ}\text{C}$ .



Scheme 1.

## 2.2. Catalytic reaction

Phenol acylation was performed in a fixed-bed gas phase flow reactor from  $200$  to  $400^{\circ}\text{C}$ . About  $1\text{ g}$  of the catalyst was loosely packed in a borosil glass reactor tube of  $40\text{ cm}$  length and  $2\text{ cm}$  internal diameter. The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The feed was prepared by mixing the required amount of phenol and methyl acetate and fed from the top of the reactor using a syringe infusion pump (Electronic Engineering Corporation). The liquid products were analysed using gas chromatograph (Shimadzu GC-17A) with FID detector equipped with a  $25\text{ m}$  capillary column (cross-linked 5% phenylmethyl polysiloxane). Nitrogen was used as the carrier gas at a flow rate of  $20\text{ ml/min}$ . The products were confirmed by GC–MS (Perkin Elmer Auto System XL Gas Chromatograph with Turbo Mass Spectrometer). After each catalytic run of  $1\text{ h}$ , the catalyst was regenerated by heating at  $500^{\circ}\text{C}$  by passing moisture- and carbon dioxide-free air through the reactor.

## 3. Results and discussion

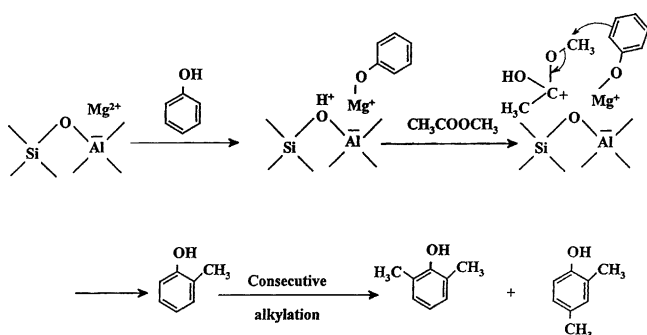
### 3.1. Influence of temperature

The feasibility of effecting both alkylation and acylation of phenol with methyl acetate over  $\text{MgZSM-5}$ ,  $\text{MgY}$  and  $\text{Mg}\beta$  zeolites was examined at  $200$ ,  $250$ ,  $300$ ,  $350$  and  $400^{\circ}\text{C}$  with phenol to methyl acetate feed ratio 1:2 and WHSV  $3.92\text{ h}^{-1}$ . The results are presented in Table 2. The major products were anisole, 2,6-DMP, 2,4-DMP, *o*-cresol and phenyl acetate. Phenol conversion is very meagre over  $\text{MgZSM-5}$  up to  $350^{\circ}\text{C}$  but at  $400^{\circ}\text{C}$  it is high. Anisole was the only product observed up to  $350^{\circ}\text{C}$  but at  $400^{\circ}\text{C}$  all the other products were also observed. Formation of anisole requires nucleophilic attack of phenol on the alkoxy methyl group of methyl acetate adsorbed on  $\text{Mg}^{2+}$  as shown in Scheme 1.

Table 2  
Influence of temperature<sup>a</sup>

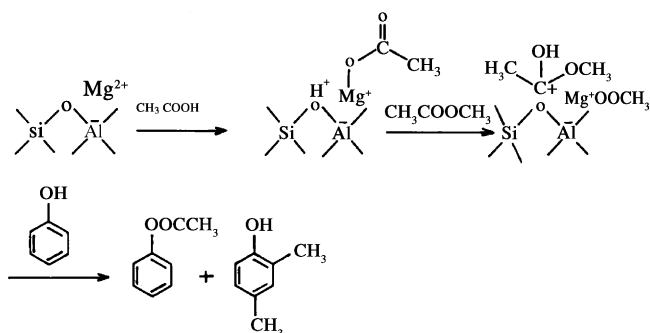
Catalyst	Temperature (°C)	Phenol conversion (%)	Product selectivity (%)				
			Anisole	2,6-DMP	2,4-DMP	<i>o</i> -Cresol	Phenyl acetate
MgZSM-5	200	–	–	–	–	–	–
	250	1.0	100.0	–	–	–	–
	300	1.4	100.0	–	–	–	–
	350	2.7	100.0	–	–	–	–
	400	12.6	46.8	20.6	11.9	11.1	9.5
Mgβ	200	8.8	100.0	–	–	–	–
	250	11.7	86.3	13.7	–	–	–
	300	18.9	61.4	18.0	5.3	9.5	5.8
	350	25.8	55.4	19.0	5.4	10.1	10.1
	400	18.4	61.9	17.4	6.0	9.2	5.4
MgY	200	–	–	–	–	–	–
	250	2.0	100.0	–	–	–	–
	300	7.2	52.7	29.2	–	–	–
	350	10.8	34.2	33.3	–	–	–
	400	10.6	33.0	29.2	10.4	27.4	–

<sup>a</sup> Reaction conditions: catalyst weight, 1 g; feed ratio, 1:2; WHSV, 3.92 h<sup>-1</sup>.



Scheme 2.

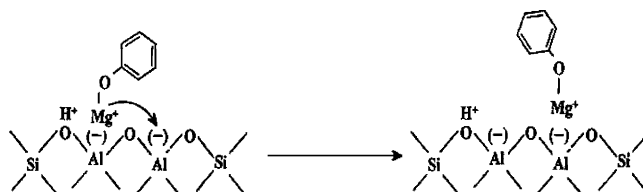
Similarly, formation of phenyl acetate requires nucleophilic attack of phenol on the carbonyl carbon of the ester. Dissociative adsorption of phenol on Mg<sup>2+</sup> releases proton, which is adsorbed on the bridging oxygen as shown in Scheme 2. This may be required to form *o*-cresol, 2,6-DMP and 2,4-DMP. The formation of *o*-cresol and 2,6-DMP may still be favoured if both phenol and methyl acetate are chemisorbed on the same Mg<sup>2+</sup> as the ortho positions of the ring are brought very close as shown in Scheme 3. When phenol is disso-



Scheme 3.

ciatively adsorbed on Mg<sup>2+</sup>, the resulting magnesium phenoxide migrates to the next adjacent bridging oxygen where the aluminium site carries the negative charge as depicted in Scheme 4. If methyl acetate is immediately adsorbed on the Bronsted acid site, then ortho alkylation of phenol would also be possible. On the other hand, if there is any time lag either magnesium *o*-methyl phenoxide or just magnesium phenoxide could diffuse to the neighbouring basic site. If methyl acetate adsorption is delayed on the Bronsted acid site, it will favour the formation of 4-methylphenol. However it is not so and hence *o*-alkylation becomes predominant.

As the conversion does not exceed 26%, it is expected that the density of Lewis acid sites play an important role in this reaction. As MgZSM-5 and MgY have very low density of acid sites, they registered less conversion, whereas Mgβ with more density of acid sites registered more conversion. Selectivity to anisole decreases with increase in temperature over all the catalysts, as it is thermally less stable. Selectivity to 2,6-DMP, *o*-cresol and phenyl acetate is high at 350 °C because these products demand high activation energy. The formation of 2,4-DMP is not as much favoured as 2,6-DMP or *o*-cresol as the Bronsted acid adsorbed methyl acetate and Lewis acid site adsorbed phenol (as shown in Scheme 4) are more suited for the formation of the latter compounds than the former. The activity of MgY lies intermediate between MgZSM-5 and Mgβ.



Scheme 4.

Table 3  
Influence of feed ratio<sup>a</sup>

Catalyst	Feed ratio	Phenol conversion (%)	Product selectivity (%)					
			Anisole	2,6-DMP	2,4-DMP	<i>o</i> -Cresol	Phenyl acetate	4-Methyl coumarin
MgZSM-5 <sup>b</sup>	1:2	12.6	46.8	20.6	11.9	11.1	9.5	–
	1:3	16.3	34.4	18.4	21.5	9.2	16.6	–
	1:5	19.2	39.6	17.4	18.2	8.9	15.6	–
	1:7	11.7	53.8	14.5	19.7	–	12.0	–
Mgβ <sup>c</sup>	1:2	25.8	55.4	19.0	5.4	10.1	–	–
	1:3	15.4	69.5	13.0	11.0	–	–	–
	1:5	15.8	54.4	12.7	7.0	–	–	–
	1:7	11.7	81.2	9.4	–	–	–	19.0
MgY <sup>d</sup>	1:2	10.8	34.2	33.3	–	32.4	–	–
	1:3	15.0	45.3	22.0	9.3	14.7	8.6	–
	1:5	10.3	44.7	21.4	13.6	20.4	–	–
	1:7	9.7	42.3	21.6	–	17.5	18.6	–

<sup>a</sup> Reaction conditions: catalyst weight, 1 g; WHSV, 3.92 h<sup>-1</sup>.

<sup>b</sup> Temperature, 400 °C.

<sup>c</sup> Temperature, 350 °C.

<sup>d</sup> Temperature, 350 °C.

### 3.2. Effect of feed ratio

In order to understand the influence of feed ratio (phenol to methyl acetate) on phenol conversion and products selectivity, it was varied as 1:2, 1:3, 1:4, 1:5 and 1:7. The influence of feed ratio on MgZSM-5 was studied at 400 °C whereas the same on Mgβ and MgY was carried at 350 °C. The results are presented in Table 3. The conversion over MgZSM-5 increases from 1:2 to 1:5 but at 1:7 it decreases. It is ascribed to dilution of phenol with increased methyl acetate content in the feed. Selectivity to phenyl acetate is high at high feed ratios compared to 1:2. Selectivity to anisole is higher than other products, although it is thermally unstable. Hence, the Lewis acid sites may not be freely available to adsorb and decompose it at high feed ratios. The selectivity to 2,4-DMP increased with the increase in feed ratio. Selectivity to *o*-cresol is less than that of 2,6-DMP as closely adsorbed

methyl acetate with respect to phenol on the Lewis acid site increases with increase in the feed ratio (Scheme 2).

Phenol conversion over Mgβ decreases with increase in the methyl acetate content in the feed. The selectivity to anisole is more over Mgβ than over MgZSM-5. This is due to the difference in the reaction temperature. The reaction was studied at 350 °C over Mgβ whereas the same reaction was studied over MgZSM-5 at 400 °C. As anisole is not thermally stable, its selectivity becomes less over MgZSM-5. The influence of feed ratio on MgY at 350 °C indicates non-linear variation. It gives higher conversion at the feed ratio 1:3 than other ratios. Selectivity to *o*-cresol and 2,6-DMP is higher with MgY than with other catalysts. 4-Methylcoumarin observed only over Mgβ at a feed ratio of 1:5 is an interesting observation in the present study. Absence of this product over MgZSM-5 might be due to pore size restriction. In addition magnesium content is also less. The same logic of less

Table 4  
Influence of WHSV<sup>a</sup>

Catalyst	WHSV (h <sup>-1</sup> )	Phenol conversion (%)	Product selectivity (%)						
			Anisole	2,6-DMP	2,4-DMP	<i>o</i> -Cresol	Phenyl acetate	<i>o</i> -HAP	4-Methyl coumarin
MgZSM-5 <sup>b</sup>	3.82	19.2	39.6	17.7	18.2	8.9	15.6	–	–
	5.8	28.6	19.2	4.9	–	7.7	17.8	50.3	–
	7.6	17.0	42.9	13.5	21.2	6.5	15.9	–	–
Mgβ <sup>c</sup>	3.92	25.8	55.4	19	5.4	10.1	10.1	–	–
	5.88	19.6	61.7	10.7	12.8	5.1	9.2	–	0.5
	7.84	16.9	62.7	11.8	15.4	–	10.1	–	–
MgY <sup>d</sup>	3.86	15.0	45.3	22.0	9.3	14.7	8.6	–	–
	5.8	10.7	39.3	20.6	14.0	16.8	9.3	–	–
	7.7	7.9	40.5	19.0	16.5	13.9	8.9	–	1.3

<sup>a</sup> Reaction conditions: catalyst weight, 1 g.

<sup>b</sup> Feed ratio, 1:5; temperature, 400 °C.

<sup>c</sup> Feed ratio, 1:2; temperature, 350 °C.

<sup>d</sup> Feed ratio, 1:3; temperature, 350 °C.

Table 5  
Time on stream<sup>a</sup>

Catalyst	Time (h)	Phenol conversion (%)	Product selectivity (%)				
			Anisole	2,6-DMP	2,4-DMP	<i>o</i> -Cresol	Phenyl acetate
MgZSM-5 <sup>b</sup>	1	18.0	35.0	15.6	22.2	10.6	16.7
	2	15.8	34.8	15.2	24.1	7.6	18.4
	3	12.9	32.6	14.4	33.5	–	19.5
	4	10.7	31.8	13.1	35.5	–	19.6
	5	10.7	29.9	12.1	37.4	–	20.6
Mgβ <sup>c</sup>	1	24.9	54.9	19.2	5.9	9.9	10.1
	2	18.1	68.5	9.4	13.3	–	8.8
	3	16.2	67.9	8.6	14.8	–	8.6
	4	13.8	65.9	8.0	17.4	–	8.7
	5	12.9	65.9	7.8	17.8	–	8.5
MgY <sup>d</sup>	1	15.2	49.0	20.9	8.5	13.5	8.1
	2	14.1	45.8	19.9	10.5	12.2	11.6
	3	12.9	43.5	19.1	13.5	8.4	15.5
	4	11.8	42.4	17.2	18.9	–	21.5
	5	10.1	38.5	16.5	20.1	–	24.9

<sup>a</sup> Reaction conditions: catalyst weight, 1 g; WHSV, 3.92 h<sup>-1</sup>.

<sup>b</sup> Feed ratio, 1:5; temperature, 400 °C.

<sup>c</sup> Feed ratio, 1:2; temperature, 350 °C.

<sup>d</sup> Feed ratio, 1:3; temperature, 350 °C.

magnesium content in MgY also accounts for the absence of coumarin over this catalyst.

### 3.3. Effect of WHSV

The influence of WHSV on phenol conversion and products selectivity was studied at 3.82, 5.8 and 7.6 h<sup>-1</sup>. The results are presented in Table 4. The conversion increases over MgZSM-5 when the WHSV is increased from 3.82 to 5.8 h<sup>-1</sup>. Hence the increment of 1.98 h<sup>-1</sup> is not adequate enough for the reactants to diffuse fast through the catalyst without much chemisorption. But at 7.6 h<sup>-1</sup>, the conversion is less, suggesting attainment of high rate of diffusion reducing the chemisorption. Small pore diameter of MgZSM-5 might be the cause for such non-linear variation in conversion. The conversion decreases gradually with increase in WHSV over Mgβ and MgY, as these catalysts are large pore materials. Therefore there is a significant increase in the rate of diffusion with increase in WHSV.

### 3.4. Effect of acetic acid in the feed

Acetic acid is one of the products in the reaction. To check whether acetic acid is getting into acylation or not, it is mixed with the feed mixture of phenol and methyl acetate in the ratio 1:2:1 and tested in the catalytic reaction. The study indicated less phenol conversion compared to acetic acid free feed (1:2). Selectivity to anisole was also less whereas selectivity to 2,4-DMP and phenyl acetate was more. The increase in selectivity of the products in the presence of more acetic acid could be based on the reaction shown in Scheme 3. Acetic

acid is dissociatively adsorbed on Mg<sup>2+</sup> with the released proton on the bridging oxygen. Methyl acetate is adsorbed on this Bronsted acid site to produce a species favourable for both alkylation and acylation.

### 3.5. Effect of time on stream

The time on stream was conducted to examine the activity of the catalysts, viz., MgZSM-5 at 400 °C, and Mgβ and MgY at 350 °C. The study was carried out for 5 h and the results are presented in Table 5. Conversion decreases with stream over MgZSM-5. Selectivity to anisole and 2,4-DMP decreases with stream whereas the selectivity to 2,6-DMP and phenyl acetate increases with stream. With increase in time Mg<sup>2+</sup> is coordinatively saturated by chemisorption of acetic acid. The released protons, which will go to bridging oxygen, aid formation of phenyl acetate and 2,6-DMP. Hence, it is suggested that if methyl acetate is adsorbed on Mg<sup>2+</sup> it will favour formation of anisole, 2,6-DMP and *o*-cresol. A change in trend is observed over Mgβ, though conversion exhibits similar trend of decrease with stream as MgZSM-5. Selectivity to anisole and 2,4-DMP decreases with time whereas selectivity to phenyl acetate and 2,6-DMP attains the steady state after exhibiting a decrease at the end of second hour. The sudden decrease in conversion at the end of first hour may be due to blocking of Mg<sup>2+</sup> site by dissociative adsorption of acetic acid formed in the reaction and consequent decrease in the adsorption of methyl acetate. Adsorption of methyl acetate on the Bronsted acid sites then favours anisole formation. The trends in conversion and products selectivity observed over MgY are almost similar to MgZSM-5 catalyst.

#### 4. Conclusions

From this study it is concluded that methyl acetate can be a convenient substitute for alkylation/acylation under appropriate conditions. The less reactive is the acetic acid, the more reactive acetic anhydride and hazardous acyl chloride may be conveniently replaced by methyl acetate for vapour phase alkylation/acylation. Predominance of one reaction over the other depends on the nature of the catalysts employed. The study of influence of temperature indicates that Mg $\beta$  is more active than MgY and MgZSM-5. Lower methyl acetate content in the feed is more favoured than its high content. The study of time on stream indicates the order of the activity of the catalysts as Mg $\beta$  > MgZSM-5  $\approx$  MgY.

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