

A Novel Acylative Cyclization Reaction of Phenol over Modified Y Zeolites†

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A novel acylative cyclization reaction of phenol and acetic anhydride to give 4-methylcoumarin (>70%) over CeNaY zeolite is reported.

The applications of zeolites in the synthesis of fine chemicals have been reviewed by Holderich *et al.*¹ and Van Bekkum and Kouwenhoven.² Geneste *et al.* reported^{3,4} the acylation of alkylbenzenes with carboxylic acids, over Y type zeolites. The reaction was carried out at 150 °C in the liquid phase with lower yields for C₁–C₃ carboxylic acids. We report the novel acylative cyclization of phenol with acetic anhydride over CeNaY for the first time.

The reactions were carried out using a tubular, down-flow Pyrex reactor 20 mm in diameter. The reaction mixture was fed from the top using a syringe pump (Sage Instruments, USA). The product was cooled using ice-cooled water and collected at the bottom. The products were analysed by GC

using an SE-30 (30%) column. The analysis was confirmed by mass spectroscopy, GC-MS and NMR spectroscopy. NaY obtained from PQ Corporation (SiO₂/Al₂O₃ = 5.1) was used as the starting catalytic material. Impregnation with cerium phosphate led to exchange of 68% of the Na⁺ for Ce³⁺. About 80% ion exchange was obtained for all the modified Y zeolites.

The reaction of phenol with acetic anhydride (1:1 molar ratio) was carried out over CeNaY (4 g) at 0.5 h⁻¹ space velocity in the temperature range 210–380 °C. The results are in Table 1. At 380 °C, the conversion of phenol was 81% and the yield of 4-methylcoumarin was 75%. The amount of phenyl acetate formed was 62 and 67% at 210 and 250 °C respectively. Byproducts were 2-acetylphenyl acetate and 3-methylcoumarin (<2%). Higher temperatures led to higher yields of 4-methylcoumarin. Above 300 °C, phenyl acetate was

Table 1 Acylative cyclization of phenol over CeNaY^a

T/°C	Time on stream/h	Conversion of phenol (%)	Yield (%)	
			4-Methylcoumarin	Phenyl acetate
210	4	81	11	62
250	4	88	21	67
300	3	63	59	Trace
350	4	65	58	—
380	4	81	75	—

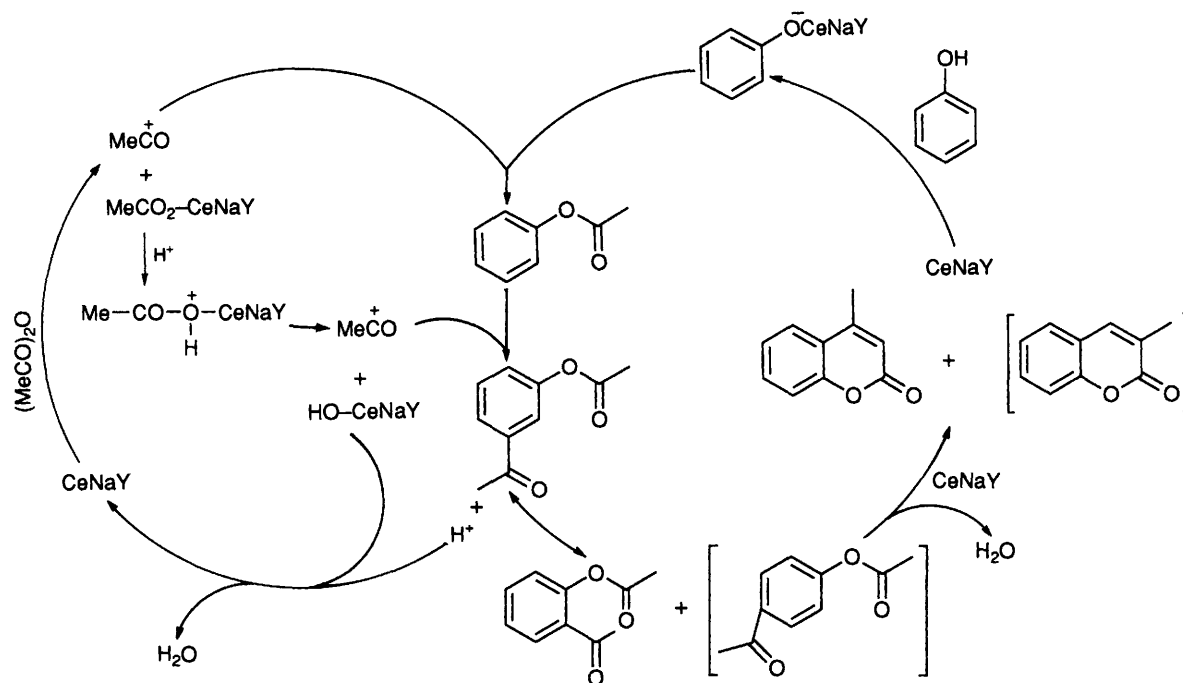
^a The other products were 2-acetylphenyl acetate and 3-methylcoumarin (traces). Weight hourly space velocity (WHSV) = 0.5 h⁻¹; phenol: Ac₂O = 1:1.

Table 2 Acylation of phenol over modified Y zeolites^a

Catalyst	T/°C	Conversion of phenol (%)	Yield of phenyl acetate (%)
CoNaY	350	90	84
CoNaY	300	98	92
CuNaY ^b	350	98	95
CuNaY	350	80	80
CrNaY	350	98	90
LaNaY	350	98	90
HY	350	10	7

^a WHSV = 0.5 h⁻¹; time on stream = 4 h; phenol: Ac₂O = 1:1. ^b In the presence of hydrogen.

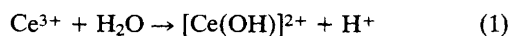
† IICT Communication No. 3212.



Scheme 1

not observed. In the reaction of phenol with acetic anhydride at 140 °C under slurry conditions using CeNaY, 4-methylcoumarin was not observed. In the reaction of 2-hydroxyacetophenone over CeNaY at 350 °C, with or without acetic acid, 10 or 5% of 4-methylcoumarin was formed, with phenol as the major product,⁵ using a fixed-bed reactor.

A plausible reaction mechanism is given in Scheme 1. The formation of phenyl acetate is the first step in the acylative cyclization. CeNaY shows a bifunctional character. The active centres in the supercages of CeNaY, Ce³⁺ ions and Brønsted acidic centres (H⁺ ions), are responsible for the acylative cyclization. Brønsted acidic centres are formed in the dissociation of water as in eqn. (1).⁶



Cerium ion facilitates the electrophilic substitution of phenyl acetate. The formation of phenyl acetate and subsequent acylative cyclization support the reaction mechanism.

The reaction of phenol with acetic anhydride was also carried out over CoNaY, CuNaY, CrNaY, LaNaY and HY zeolites. The results are given in Table 2. The major product

was phenyl acetate. Except for HY, the amount of phenyl acetate obtained was >80%. 4-Methylcoumarin was either found in traces or was absent. Thus, CeNaY was the best acylative cyclization catalyst.

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