

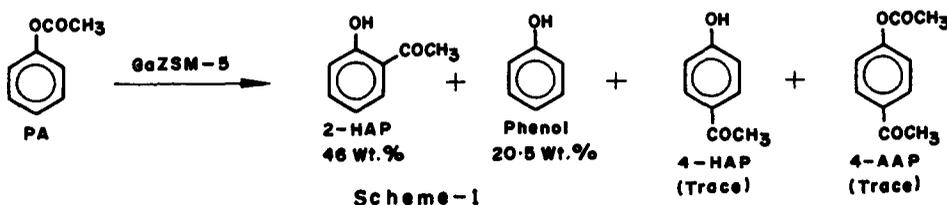
## Highly Selective Fries Rearrangement over Modified ZSM-5 Catalysts<sup>†</sup>

Yarlagadda V Subba Rao, Shivanand J Kulkarni\*, Machiraju Subrahmanyam and A V Rama Rao  
Indian Institute of Chemical Technology, Hyderabad 500 007, India

**Abstract :** In the reaction of phenyl acetate over modified ZSM-5 catalysts, 2-hydroxy acetophenone was obtained in good yields. GaZSM-5 was the better catalyst for Fries rearrangement reactions.

Hydroxyacetophenones and its derivatives can be synthesized via Fries rearrangement. It has been established that this reaction can be catalyzed by a variety of Lewis and Bronsted acids,  $\text{AlCl}_3$  being the most widely used<sup>1</sup>. An equimolar amount of  $\text{AlCl}_3$  is generally required which is consumed during the work-up. Zeolites, being acidic, may prove better catalysts due to their activity, selectivity, and can be used repeatedly and pollution-free environment<sup>2</sup>. But there are very few reports of Fries rearrangement over zeolites<sup>3,4</sup> with low yields at 400°C. We are reporting a highly selective Fries rearrangement of phenyl acetate to 2-hydroxyacetophenone over modified ZSM-5 catalysts (Scheme 1) in good yields at moderate conditions.

The reaction was carried out using tubular down flow pyrex reactor with 20 mm dia. Phenyl acetate was fed from the top using Sage syringe pump. The weight hourly space velocity was  $0.5 \text{ hr}^{-1}$  and the reaction temperature was in the range of 200°-400°C. The product was condensed using ice-cooled water and collected at the bottom. The products were analyzed by GC-Mass, NMR and quantified by GC using SE-30 (5%) column. GaZSM-5 was synthesized by impregnating 2.5 wt% of gallium oxide in HZSM-5 (Si/Al = 30). The amounts of other cations used in the modification were in 2-5 wt%.



The reaction of phenyl acetate (PA) was carried out over various modified ZSM-5 catalysts and the results are depicted in Table 1. The reaction was carried out at the reaction temperature of 250°C and W.H.S.V. =  $0.5 \text{ hr}^{-1}$ . The yields of 2-hydroxy acetophenone (2-HAP) obtained were 46.0, 17.7, 26.4, 27.0, 23.0 and 9.8 for GaZSM-5, NiZSM-5, PdZSM-5, PtZSM-5, SmZSM-5 and WZSM-5, respectively. Phenol formation can be suppressed by adding acetic anhydride in the feed<sup>5</sup>. In case of GaZSM-5, the ortho-selectivity in isomers was > 95% at time on stream = 1 hr. The formation of 2-hydroxy acetophenone was much more than 4-hydroxy acetophenone (4-HAP) in all the reactions. This unusual finding of ortho-selectivity over modified ZSM-5 catalyst may be attributed to the easy migration of acetyl cation to the ortho-position than para, and also the reactive intermediate for the ortho may be more stable. In

the reaction of anisole over GaZSM-5 p-cresol was obtained in good yields (ortho/para = 3.0) which supports the above conclusion.

Table 1<sup>§</sup>

S.No.	Catalyst	Conversion of PA (wt. %)	Yield of		2-HAP/Phenol (molar)
			Phenol (wt. %)	2-HAP (wt. %)	
1	HZSM-5 (30)	49.6	36.5	13.1	0.25
2	GaZSM-5	71.0	20.5	46.0	1.55
3	NiZSM-5	48.3	28.1	17.7	0.44
4	PdZSM-5	78.2	47.0	26.4	0.39
5	PtZSM-5	82.3	47.9	27.0	0.39
6	SmZSM-5	89.4	58.7	23.1	0.27
7	WZSM-5	33.0	18.1	9.8	0.37

§ Catalyst = 4.0 g; Time on stream = 1 hr; WHSV = 0.5 hr<sup>-1</sup>; Temperature = 250°C. In traces of 4-HAP and 4-AAP also observed.

The reaction of phenyl acetate was carried out over GaZSM-5 and HZSM-5 at various reaction temperatures from 200° to 400°C and Si/Al ratios = 30, 150 and 280<sup>5</sup>. The highest yield of 2-hydroxyacetophenone (46 wt%) and 4-hydroxy acetophenone (< 5 wt%) was obtained at 250°C reaction temperature and 0.5 hr<sup>-1</sup> W.H.S.V. and the conversion of phenyl acetate was 71 wt% over GaZSM-5. Under these conditions at 250°C, the molar ratio of 2-HAP/phenol is 1.55, highest, indicating the best conditions for the rearrangement. The deacetylation and disproportionation of phenyl acetate leads to the formation of phenol and 4-acetoxy acetophenone (4-AAP). With the increase of Si/Al ratio from 30 to 280 in HZSM-5, the yield of 2-hydroxy acetophenone decreases from 13.1 to 0.8 wt%. This indicates that as the number of Bronsted acidic centres present at the intersections of HZSM-5 decreases, the extent of rearrangement and the total conversion of phenyl acetate decreases. In case of GaZSM-5, at 250°C and 5 hrs time on stream, the conversion of phenyl acetate was decreased to 27 wt % due to coking and the ortho-selectivity was 50%. The increase of para-selectivity was because of channel/pore tailoring due to the coking but the original activity was obtained after regeneration. Thus compare to AlCl<sub>3</sub>, Zeolite (GaZSM-5) can be reused, selective and noncorrosive catalyst. Gallium in ZSM-5 has shown better promoting effect for Fries rearrangement of phenyl acetate and may be a potential alternative for the commercialization.

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