



Letter

An improved acylation of phenol over modified ZSM-5 catalysts¹

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Abstract

The acylation of phenol with acetic anhydride was carried out over different modified ZSM-5 catalysts. Co, Cu, and Ce showed a promoting effect. The best temperature and weight hourly space velocity for this reaction were found to be 250°C and 0.5 h⁻¹, respectively. ZSM-5(30) was found to be a better catalyst than ZSM-5(150) and ZSM-5(250) in the acylation of phenol. A plausible reaction mechanism is also discussed.

Keywords: Cerium; Cobalt; Copper; Phenol acylation; Zeolites; ZSM-5

1. Introduction

O-hydroxyacetophenone (*o*-HAP) and *p*-hydroxyacetophenone (*p*-HAP) are very useful intermediates for the manufacture of agrochemicals and pharmaceuticals, and are generally synthesized by the very popular Fries rearrangement or direct acylation of phenol [1-6]. The most widely used catalyst for Fries rearrangement is AlCl₃, but the inherent disadvantage is that it is required in equimolar ratio and involves a tedious work-up. Changing over to zeolites instead of using the environmentally hazardous AlCl₃ is more acceptable, because of their activity, selectivity and reusability and they do not pollute the environment [7-9]. Recently, Guisnet et al. have reported the vapour-phase acylation of phenol by taking acetic acid as acylating agent but the yields were not up to the mark [1,2]. Herewith, we

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¹ The authors dedicated this paper to Dr. A.V. Rama Rao on his 60th birthday.
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Table 1
Acylation of phenol over different modified ZSM-5 catalysts^a

S.No.	Catalyst	TOS (h)	Conversion of phenol	PA	<i>o</i> -HAP	<i>p</i> -HAP	Others ^b	<i>o</i> -HAP: <i>p</i> -HAP
1	H-ZSM-5(30)	1	72.55	29.05	41.76	0.64	1.1	98.5:1.5
2	Zr-ZSM-5	2	73.41	32.0	37.62	3.27	0.52	92.0:8.0
3	V-ZSM-5	1	69.74	29.95	39.02	0.5	0.27	98.7:1.3
4	Ce-ZSM-5	2	74.56	30.0	42.7	1.45	0.41	96.7:3.3
5	Pd-ZSM-5	1	71.9	31.24	37.32	2.04	1.3	94.8:5.2
6	Cr-ZSM-5	1	68.36	27.9	39.66	0.53	0.23	98.7:1.3
7	La-ZSM-5	1	68.11	30.3	35.36	1.76	0.69	95.3:4.7
8	Rh-ZSM-5	2	70.85	32.86	35.56	2.16	0.27	94.3:5.7
9	Co-ZSM-5	2	72.2	29.12	41.9	0.9	0.28	97.9:2.1
10	Cu-ZSM-5	1	68.36	24.47	42.56	1.13	0.06	97.4:2.6

^a Catalyst = 4.0 g; WHSV = 0.5 h⁻¹; Temperature = 250°C; Phenol to Ac₂O mol ratio = 1.

^b Others = aromatics.

catalysts (M = Zr, V, Pd, Cr, La and Rh) did not improve the resultant yield of *o*-HAP, where as the M = Co, Cu and Ce enhanced very little the *o*-HAP. In phenol acylation, the C- and O-acylation ratios at 70% conversion of phenol are 1.5, 0.94, 1.06, 1.59, 1.06, 0.94 for the catalysts ZSM-5(30), Cu-ZSM-5, Cr-ZSM-5, Ce-ZSM-5, Rh-ZSM-5 and Co-ZSM-5, respectively. These values show that the modification of ZSM-5(30) is leading to O-acylation except in the case of Ce-ZSM-5. Ce shows a promoting effect in C-acylation.

The reaction of phenol with Ac₂O was carried out over ZSM-5 catalysts with different Si/Al ratio (Table 2). The ratio of SiO₂/Al₂O₃ had a remarkable influence on the acylation reaction. When the reaction was catalyzed by H-ZSM-5(30), H-ZSM-5(150), H-ZSM-5(280) the yield of *o*-HAP was 41.76, 39.70 and 15.12, respectively. An increase in the ratio of Si/Al resulted in a decrease of *o*-HAP, and on the other hand the O-acylation was increased. It means that C-acylation requires more Brønsted acidity and lower acidity leading to phenyl acetate. The *ortho* selectivity was not influenced by the ratio of Si/Al. The non-zeolitic SiO₂/Al₂O₃ acid catalyst (S.No.4) gave mostly phenyl acetate and there was no isomer selec-

Table 2
Phenol acylation over ZSM-5 catalysts with different Si/Al ratio^a

S.No.	Catalyst	TOS (h)	Conversion of phenol	PA	<i>o</i> -HAP	<i>p</i> -HAP	Others ^b	<i>o</i> -HAP: <i>p</i> -HAP
1	H-ZSM-5(30)	1	72.55	29.05	41.76	0.64	1.1	98.5:1.5
2	HSM-5(150)	1	73.5	31.73	39.70	1.59	0.48	96.2:3.8
3	H-ZSM-5(280)	1	56.75	40.91	15.12	0.26	0.46	98.3:1.7
4	SiO ₂ /Al ₂ O ₃	1	77.42	76.22	0.55	0.63	0.02	46.6:53.4
5	ZrO/La ₂ O ₃	1	51.2	46.16	3.9	0.27	0.87	93.5:6.5
6	Zirconia sulphated	1	62.5	58.7	2.0	1.7	0.1	54.0:46.0

^a Catalyst = 4.0 g; WHSV = 0.5 h⁻¹; Temperature = 250°C. Phenol to Ac₂O mole ratio = 1.

^b Others = aromatics.

Table 3
Acylation of phenol: Effect of Ac₂O molar ratio^a

S.No.	TOS (h)	Phenol:Ac ₂ O (mol)	Conversion of phenol	PA	<i>o</i> -HAP	<i>p</i> -HAP	Others	<i>o</i> -HAP: <i>p</i> -HAP
1	1	1:0.5	65.93	28.15	37.76	–	–	100:1.0
2	2	1:1.0	74.56	30.0	42.7	1.45	0.41	96.7:3.3
3	1	1:1.5	79.54	36.67	33.07	8.0	1.8	80.05:19.5
4 ^b	1	1:2.0	84.95	44.39	29.57	9.93	1.06	74.9:25.1
5 ^b	1	1:2.5	91.37	51.76	23.1	14.06	2.45	62.2:37.8

^a Cat. = Cc-ZSM-5(30), Cat. wt. = 4.0 g; WHSV = 0.5 h⁻¹; Temperature = 250°C.

^b = TOS 2 h, the PA is more than 95%.

tivity. It shows that the C-acylation of phenol occurs in the channels of zeolites and not on the surface. The superacid catalyst, sulphated zirconia (682/01, MEL Chemicals, UK) (S.No. 6) was also tested and found sluggish in the acylation of phenol.

The role of the phenol to Ac₂O ratio in acylation was studied (Table 3) in detail. These experiments reveal that the selectivity was governed by the molar ratio of acetic anhydride. Absolute isomeric selectivity was observed when the phenol to acetic anhydride ratio was 0.5 (S.No.1). The ratio of *o*-HAP to *p*-HAP decreases to 1.65 with increase of acetic anhydride (S.No. 5). The molar ratio of Ac₂O was adapted so as to increase the percentage of PA, but not the total percentage of acylated phenols. It shows that the formation of *p*-HAP and AAP depends upon the availability of excess acyl cation and partly proves that the reaction is going by direct C-acylation of phenol and not by Fries rearrangement.

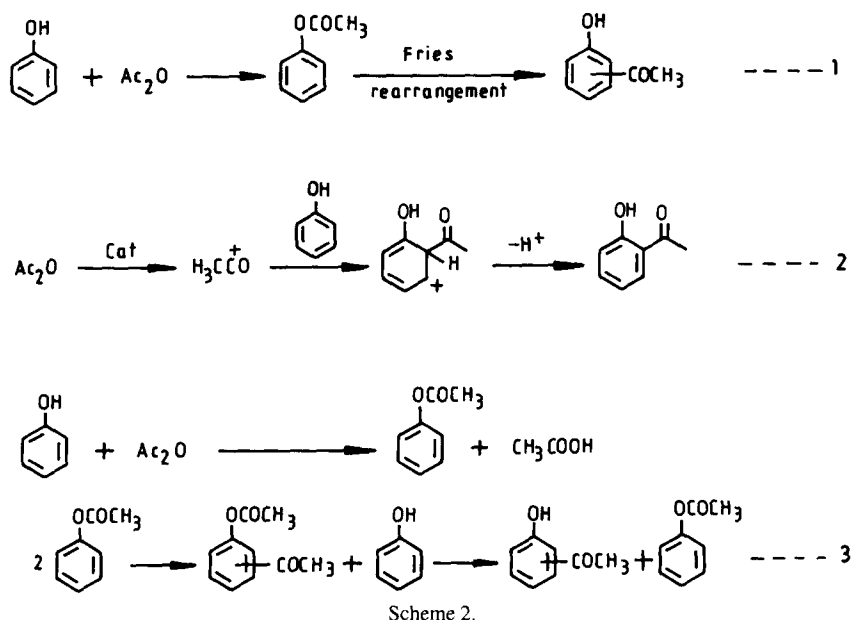
The acylation of phenol at different temperatures is depicted in Table 4. The suitable temperature for C-acylation of phenol is 250°C (S.No. 2). At lower temperature, 200°C (S.No. 1), the major product phenyl acetate comes from O-acylation. When the temperature is raised beyond 250°C the conversion of phenol decreases. This may be due to the decomposition of phenyl acetate, i.e. backward reaction, to phenol. At higher temperatures aromatics were also observed.

The formation of *p*-HAP and AAP was increased with time on stream. In ZSM-5(150) catalyzed phenol acylation the ortho:para selectivities are 96.2:3.8, 82.6:17.4 and 76.3:23.7 at times on stream of 1, 2 and 3 h, respectively. It must be

Table 4
Acylation of phenol at different temperatures^a

S.No.	Temp. (°C)	TOS (h)	Conversion of phenol	PA	<i>o</i> -HAP	<i>p</i> -HAP	Others	<i>o</i> -HAP: <i>p</i> -HAP
1	200	1	77.2	46.35	30.52	0.31	0.02	99.0:1.0
2	250	1	68.36	27.9	39.66	0.53	0.23	98.7:1.3
3	300	2	63.4	29.9	32.44	1.03	0.03	96.9:3.1
4	350	1	44.56	19.56	14.22	1.33	9.45	91.5:8.5
5	400	1	43.4	20.0	15.77	0.35	7.28	92.0:8.0

^a Cat. = Cr-ZSM-5(30); Cat. wt. = 4.0 g; WHSV = 0.5 h⁻¹; phenol to Ac₂O mole ratio: 1.



underlined that the increase of *para* isomer was because of channel/pore tailoring due to coking.

The plausible mechanistic routes are shown in Scheme 2. Route 3 can be ruled out because, due to the restricted geometry of the channels it should give more *para* isomer and AAP, which is contrary to the obtained results. O-acylation is very facile and based on the ratio of PA to *o*-HAP (3.85) [3] and phenol to *o*-HAP (0.65), it can be concluded that the *o*-HAP is formed by C-acylation (route 2) rather than by O-acylation and subsequent rearrangement, but parallel reactions cannot be ruled out.

In summing up, the modified and unmodified ZSM-5 (30) catalysts were better in selective acylation of phenol to *o*-hydroxyacetophenone. Cerium shows a promoting effect in C-acylation. An increased molar ratio of acetic anhydride to phenol leads to more *para* isomer formation. The formation of *p*-HAP and AAP increased with time on stream due to coking. The best temperature for acylation of phenol was 250°C. Thus the present catalysts, which offer high selectivity, reusability and environmental safety, represent a potential alternative for industry.

References

- [1] I. Neves, F. Jayat, P. Magnoux, G. Perot, F.R. Ribeiro, M. Gubelmann and M. Guisnet, *J. Mol. Catal.*, 93 (1994) 169.
- [2] I. Neves, F. Jayat, Magnoux, G. Perot, F.R. Ribeiro, M. Gubelmann and M. Guisnet, *J. Chem. Soc., Chem. Commun.*, (1994) 717.
- [3] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, *Tetrahedron Lett.*, 34 (1993) 7799.
- [4] A.J. Hoefnagel and H. van Bekkum, *Appl. Catal. A*, 97 (1993) 87.

- [5] C.S. Cundy, R. Higgins, S.A.M. Kibby, B.M. Lowe and R.M. Paton, *Tetrahedron Lett.*, 30 (1989) 2281.
- [6] Y. Pouilloux, N.S. Gnep, P. Magnoux and G. Perot, *J. Mol. Catal.*, 40 (1987) 231.
- [7] W. Hoelderich, M. Hesse and F. Naumann, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 226.
- [8] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, *J. Org. Chem.*, 89 (1994) 3998.
- [9] Y.V. Subba Rao, S.J. Kulkarni, M. Subrahmanyam and A.V. Rama Rao, *J. Chem. Soc., Chem. Commun.* (1994) 1456.