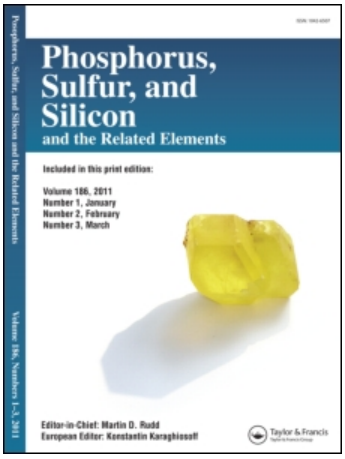

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HY Zeolite as an Extremely Active and Reusable Catalyst in Acylation of Alcohols with Acid Anhydride in a Solventless System

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HY ZEOLITE AS AN EXTREMELY ACTIVE AND REUSABLE CATALYST IN ACYLATION OF ALCOHOLS WITH ACID ANHYDRIDE IN A SOLVENTLESS SYSTEM

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HY Zeolite is a practical and useful catalyst for acylation of various alcohols and phenols.

Keywords: Acylation of alcohols; HY zeolite as catalysts

The acylation of alcohols by acid anhydrides or acyl chlorides is routinely carried out in the presence of tertiary amines such as triethylamine or pyridine.[1,2] Dimethyl amino propylamine is particularly noteworthy as an efficient catalyst for the acylation of tertiary alcohols.[3,4,5] Recently Vedejs and coworkers[3,4,6] reported tributylphosphine to be a similar catalyst for the acylation of alcohols. In addition to the catalysts mentioned above protonic acids such as toluene p-sulphonic acid[7] and Lewis acids such as zinc chloride,[8] cobalt chloride,[9] scandium trifluoromethane-sulfonate,[10] montmorillonite K-10 and KSF[11] are also known to catalyze the acylation of alcohols and phenols. However, none of the above mentioned catalysts is claimed to work in a solventless system and to be reusable.

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After preparation of this article, similar acetylation of alcohols using HSZ-360 zeolite was reported in R. Bollini, G. Bosica, S. Carloni, *Tetrahedron Letters*, volume 39, page 6049 (1998).

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TABLE I Actylation of Alcohols, Phenol, and Naphthol with Acetic Anhydride Catalyzed with H-Y Zeolite

Entry	Substrate	T/°C	Time (hr)	Ratio[a]	Product	Yield (%)
1	Cinnamylalcohol	rt	2	2:1	Cinnamyl acetate	85
2	1-octanol	rt	1	2:1	Octyl acetate	92
3	Cyclohexanol	rt	2	2:1	Cyclohexyl acetate	92
4	Phenol	rt	3	2:1	Phenyl acetate	98
5	β-naphthol	rt	2.5	2:1	Naphthyl acetate	81
6	Menthol	60	2	2:1	Menthyl acetate	89
7	Ethylene glycol	60	2	4:1	Ethane-1,2,dioldi-acetate	100
8	Benzyl alcohol	rt	1	2:1	Benzyl acetate	68

[a]Acetic anhydride: Substrate (mmol:mmol).

Zeolites as catalysts have received considerable attention in recent years because of their characteristic properties such as selectivity, acidity, and thermal stability.[12] Their catalytic potential in petrochemistry and in oil processing is well documented,[13,14] however their application in general organic synthesis has not been fully explored. Recently we have reported the regioselective alkylation of heterocycles using H-Y zeolite.[15] In this article we report that H-Y zeolite serves as an excellent catalyst for acylation of alcohols and phenols in solvent-free conditions.

As shown in Table I a series of alcohols and phenols were acylated with acetic anhydride. Primary and secondary alcohols and phenols can be easily acylated at room temperature. The reaction is clean and the work up procedure is exceedingly simple involving only the filtration of zeolite and removal of solvent to obtain the product in high yield and state of purity.

We next turned our attention towards the possible recycling of the catalyst with the model substrate 1. The catalyst was filtered on a buckner funnel, washed with acetone, dried in air and reactivated by heating it at 500°C. Unexpectedly, after allowing the reaction mixture to stir for 1 h at 25°C, product 2 was obtained in a quantitative yield. Moreover we recycled the zeolite for further five experiments recovering the product 2, with similar high yield. This result indicates that H-Y zeolite is activated after the first cycle and can be therefore reused several times without losing activity.

In conclusion the present note provides a novel, solvent free and general method for acylation of alcohols and phenols in the presence of H-Y zeolite as a reusable catalyst.

$$\underset{\mathbf{1}}{\mathrm{PhCH{=}CH{-}CH_2OH}} \xrightarrow[\text{HY-Zeolite}]{(CH_3CO)_2O} \underset{\mathbf{2}}{\mathrm{PhCH{=}CHCH_2OCOCH_3}}$$

EXPERIMENTAL

All acylated compounds are known and their physical data were compared with those of authentic samples. Yields refer to GC analysis.

Acylation of Alcohols and Phenols with Acetic Anhydride Catalyzed by H-Y Zeolite: A Typical Procedure

In a (50 ml) round bottomed flask equipped with a condenser and a magnetic stirrers a mixture of cinnamyl alcohol (67 mg; 5 mmol), H-Y zeolite (200 mg), and acetic anhydride (1.02 g, 10 mmol) was stirred at room temperature for 2 h. The catalyst was removed by filtration and washed with dichloromethane; the combined liquids were evaporated under reduced pressure to afford the pure product.

Thus a mixture of acetic anhydride and neat alcohols or phenols were mixed with the catalytic amounts of H-Y zeolite to afford the corresponding acyl derivatives. In the absence of H-Y zeolite the reactions are sluggish and considerable amounts of starting alcohols are recovered.

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