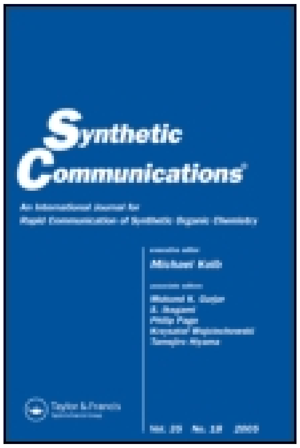

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Divalent Transition Metal Ion-Exchanged Faujasites as Mild, Efficient, Heterogeneous Friedel-Crafts Benzylation Catalysts

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Divalent Transition Metal Ion-Exchanged Faujasites as Mild, Efficient, Heterogeneous Friedel–Crafts Benzylation Catalysts

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ABSTRACT

Ni^{2+}-, Cu^{2+}-, and Zn^{2+}-exchanged faujasite (MY) zeolites efficiently catalyze the Friedel–Crafts benzylation of arenes in a clean and simpler method.

Key Words: Benzylation; Arenes; Substituted benzylchlorides; Lewis acidity of zeolites.

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Zeolites are inorganic solids which find extensive applications in organic transformations[1] and photochemical reactions.[2] Intrazeolite radical reactions,[3] electron-, energy-, and proton-transfer reactions[4] are also extensively reported. In the area of production of fine chemicals, the merits of zeolites, in addition to the usual requisites of mildness, selectivity, and cleanliness, over soluble acidic catalysts are significant and have appeared in several papers and reviews.[5–7] Reduction of salt and waste production, replacement of hazardous acids, prevention of corrosion, availability of variety of structures, and pore dimensions leading to shape selectivity, tunable acidity, and easy regeneration are some of the advantages, which accrue upon their usage as heterogeneous solid acid-catalysts.

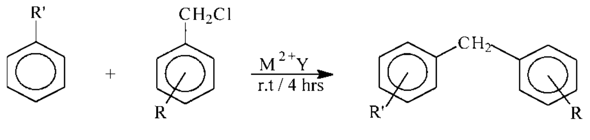
Aluminosilicates-mediated Friedel–Crafts alkylations have received particular attention as the products serve as useful starting materials for synthesis of pharmaceuticals and polymers. Montmorillonite-supported transition metal salts are reported[8,9] as efficient solid Friedel–Crafts alkylation catalysts, which reduce the problems associated with the standard reactions using anhydrous $AlCl_3$. Izumi et al.[10] have shown that, smectites clays with simple exchange of metal ions, particularly Zn^{2+}-exchanged nontronite and montmorillonite, exert much higher catalytic activity for the alkylation than $ZnCl_2$/K10-montmorillonite. Preparation of diphenylmethane from benzyl chloride and benzene using a simple mixture of $ZnCl_2$ and K10/KSF-montmorillonite clays (upon activation by ultrasonic waves) is reported.[11]

These observations, coupled with our interest in exploring aluminosilicates[12,13] as versatile catalysts, have prompted us to study the Friedel–Crafts benzylation of arenes with divalent cation-exchanged zeolites as solid acid catalysts. It is relevant to note here that the H-form zeolites[5–7] and CaY[14] (with an ability to generate Bronsted acidity) are studied in detail in many systems. Friedel–Craft's acylation of toluene and *p*-xylene with carboxylic acid is found[15] to be catalyzed by CeY zeolite and the *para*-isomer is the predominant product. In a recent report,[16] benzyl chloride when included in NaY zeolite, is found to undergo dimerization in a *meta*-selective Friedel–Crafts pathway (in contrast to its reaction in $AlCl_3$, wherein extensive polymerization is observed). However, modulation of zeolite acidity by exchange with transition metal ions, with a subsequent increase in Lewis acidity and much milder reaction conditions has not been explored so far. The present work is directed towards this goal in mind.

In a typical procedure, to a mixture of the arene (0.01 mol) and the substituted benzyl chloride (0.003 mol) taken in a round bottomed flask equipped with magnetic bead, 500 mg of the activated (preheated to 450°C for 6 h in a muffle furnace) zeolite is added and stirred for 4 h at room temperature. After the addition of 15 mL of dichloromethane, the mixture is stirred again overnight, the solvent is removed and evaporated. The reaction mixture is analyzed in a Shimadzu 17A GC (SE-30 10% capillary column, FID detector), unless reported otherwise. In all the cases, retention times of unconsumed benzyl chloride is taken as the internal reference. ^{1}H-NMR spectra of diphenylmethane, isolated in the case of benzene, shows peaks at 6.78 δ (s, 10H) and 3.6 δ (s, 2H). With substituted benzenes and benzyl chlorides, isomeric products are isolated (for Entries 1, 2, and 4 in Table 2) by column chromatography (silica gel; 5% ethyl acetate–95% petroleum ether mixture) and are identified by their ^{1}H-NMR spectra (2H singlet for the methylene group at 3.5–4.0 δ and *para*-isomers by their characteristic AB pattern).

The results indicate clearly that benzylation of arenes (Sch. 1) is catalyzed very efficiently (Tables 1 and 2) by divalent cation-exchanged zeolites (NiY, CuY, and ZnY) and there is no reaction with non-acidic zeolites, namely NaY and KY. With CaY the yield has improved significantly, but not as extensive as ZnY and NiY. The reaction is faster with arenes having electron-releasing groups and becomes slower when the arene and benzyl chloride[8] are substituted with electron-withdrawing groups (Table 2). Compared to previous results, zeolites provide much higher isolated yield and lower polyalkylation, which is attributed to their well defined cages and consequent structural characterization.

The reaction is inefficient with benzyl alcohol as evident from the following: treatment with $PhCH_2OH$ and NiY has resulted in only 21% conversion (with 4% of PhCHO, 10% of Ph_2CH_2 and others 7%) and with HY only 3% conversion is observed (1% of Ph_2CH_2 and others 2%). This also rules out the generation of a free benzylic carbonium ion which is also confirmed by carrying out the reaction with NiY/CaY



R' = H, CH_3, OH, Cl, OCH_3, NO_2
R = H, *ortho*-NO_2, *para*-NO_2

Scheme 1.

Table 1. Formation of $(C_6H_5)_2CH_2$ from C_6H_6 and $C_6H_5CH_2Cl$ catalyzed by various cation-exchanged zeolites at room temperature.[a]

				Yield[b] (%) of	
Entry	Zeolite	Time (h)	Conversion of $PhCH_2Cl$ (%)	Ph_2CH_2	Others
1	NaY	4	4	4	—
2	KY	4	3	3	—
3	CaY	4	68	58	10
4	CuY	4	80	80 (75)[c]	—
5	NiY	4	99	99 (85)[c]	—
6	NiY[d]	4	96	96 (84)[c]	—
7	ZnY	1	6	6	—
8	ZnY	2	22	22	—
9	ZnY	4	100	85 (80)[c]	15

[a] 0.01 mol of benzene and 0.003 mol of benzyl chloride in 500 mg of activated zeolite.

[b] GC yield: Error limit ± 5%.

[c] Numbers in parentheses refer to isolated yield (based on the amount of benzyl chloride taken).

[d] NiY reused after three times of benzylation.

Table 2. Benzylation of substituted benzene (C_6H_5R') with $RC_6H_4CH_2Cl$ in the presence of NiY zeolite at room temperature.[a]

					Yield[b] (%) of		
Entry	*R*	*R′*	Time (h)	Conversion of $RC_6H_4CH_2Cl$ (%)	*Ortho*	*Para*	Others
1	H	CH_3	4	100	44	44	12
2	H	–OH	4	100	47	53	0
3	H	–Cl	4	12	3	6	3
4	H	$–OCH_3$	4	100	43	57	—
5	H	$–NO_2$	12	9	—	—	9
6	$2-NO_2$	H	6	No reaction	—	—	—
7	$4-NO_2$	H	6	No reaction	—	—	—

[a] 0.01 mol of substituted benzene and 0.003 mol of substituted benzyl chloride in 500 mg of activated zeolite.

[b] GC yield: Error limit ± 5%.

zeolite in the presence of styrene and benzene in hexane slurry. Only styrene derived products are formed, and the coupled product is absent. Similarly there is no reaction when benzylation is carried out with unactivated NiY/ZnY zeolite, in which the cations of interest are solvated and hence are less readily available. It is likely that the entry into the cage is hindered by water molecules, and the reaction thus takes place on the surface.

The observed results indicate clearly that the Lewis acidity of the transition metal ions in zeolite is mainly responsible for the efficient benzylation. Ni^{2+}, Zn^{2+}, and Cu^{2+} (with ionic radii of 0.72, 0.74, and 0.69 Å, respectively) are all borderline acids according to the HSAB theory of acids and bases and by their ready binding to the covalently linked chloride ion (a borderline base), polarize the carbon–chloride bond in benzyl chloride more efficiently. This is followed by the facile attack of the incipient carbonium ion on the aryl ring. It also explains why the reaction is slow with metal ions as Na^{+}, K^{+} (hard acids), and with Ca^{2+} (though divalent, has a higher ionic radius of 0.98 Å, making it a weaker Lewis acid, compared to NiY, CuY, and ZnY). Izumi et al. have also proposed[10] that only Lewis acidity is responsible for the efficient benzylation by Zn^{2+}-exchanged smectites. It is relevant to note here that in a recent report,[17] zinc-exchanged zeolite BEA is found to be an excellent catalyst for the intramolecular hydroamination of 6-aminohex-1-yne.

Thus the observed results amply demonstrate the efficiency of divalent transition metal cation-exchanged zeolites (NiY, ZnY, and CuY) as versatile Friedel–Crafts alkylation catalysts. Lewis acidity of the metal cations is primarily responsible for this industrially relevant reaction. In addition to ensuring simpler work-up, cleaner, and efficient conversions, the other advantages of employing these solid heterogeneous acid catalysts, are their environmentally benign nature, well defined structural characterization, reduced polyalkylation, much higher isolated yield, presence of basic sites in the framework to trap HCl liberated in the reaction, and reusability (after three times, efficiency of the NiY is still above 95%).

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