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Efficient Solid Catalyst Systems for Cyanosilylation of Carbonyl Compounds with Cyanotrimethylsilane

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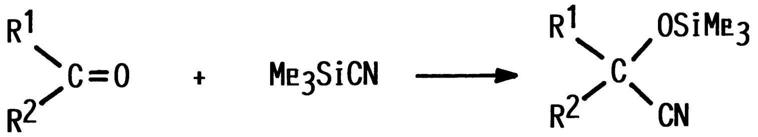
Clay montmorillonite, calcium fluoride, and hydroxyapatite are found to be effective solid catalysts for the reactions of cyanotrimethylsilane with carbonyl compounds. Different catalytic functions of the solid catalysts are also elucidated.

Cyanotrimethylsilane has been widely applied to organic synthesis.1) For instance, its addition reactions to aldehydes and ketones serve as protections of carbonyl functions,2) or as sources of cyanohydrins3) and β-aminoalcohols.4) In 1973, Evans,5) Neef,6) and Sundermeyer7) independently reported the cyanosilylation reactions of carbonyl compounds proceeded thermally or with the aid of Lewis acids such as ZnI_2 and $AlCl_3$. Evans also discovered catalysis of cyanide ions for the cyanosilylation using KCN-18-Crown-6 or $^{n}Bu_4N^+CN^-$.8) These acids and nucleophilic catalysts are soluble in the reaction media.


(1)

We have investigated liquid-phase organic reactions catalyzed by inorganic solid acids and bases such as zeolites9) and clay montmorillonites,10) revealing that not only peculiar catalytic activities of those solids, but also easy separation of the solids from organic products enable us to synthesize labile organic molecules which have hardly been isolated.11)

Here we wish to report two types of solid catalyst systems for cyanosilylation of carbonyl compounds: one is strongly acidic ferric ion-exchanged montmorillonite (Fe-Mont)12) and the other includes non-acidic catalysts, calcium fluoride (CaF_2) and hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$).13)

A typical experiment is as follows: In a flask a solid catalyst (0.2-0.5 g) was dried at 0.5 Torr for 3 h (drying temperature: Fe-Mont, 120 °C; CaF_2, 180 °C; HAp, 180 °C). To a suspended mixture of the catalyst and CH_2Cl_2 (1 ml) was added a mixture of a carbonyl compound (1 mmol) and Me_3SiCN (1.1 mmol) in CH_2Cl_2 (2 ml) at 0 °C, and the resulting mixture was stirred under the conditions shown in Tables. After the consumption of the carbonyl compound, the solid catalyst was filtered off through a Celite pad. The filtrate was distilled to yield α-trimethylsilyloxy nitriles.

Table 1. Cyanosilylation of 2-octanone[a)]

Solid catalyst	S.A./$m^2 \cdot g^{-1}$[b)]	Acid strength[c)]	Time/h	Yield/%
None	--	--	4.5	0
Fe-Mont	37	$-8.2 \geq H_o$	0.2	96
Ca-Mont	--	$+1.5 \geq H_o > +0.8$	4.5	42
CaF_2	6	$+6.8 \geq H_o > +4.0$	4.5	94
HAp	55	$+3.3 \geq H_o > +1.5$	0.5	92
$CaSO_4$	--	$+1.5 \geq H_o > +0.8$	4.5	4
SiO_2	585	$+3.3 \geq H_o > +1.5$	4.5	0

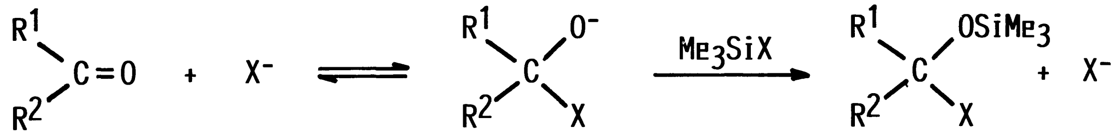
a) Montmorillonite (0.2 g), other solids (0.5 g), 2-octanone (1 mmol), Me_3SiCN (1.1 mmol), in CH_2Cl_2, at 0 °C.

b) Specific surface area.

c) Maximum acid strength determined with Hammett indicators.

Table 1 summarizes the reactions of 2-octanone with Me_3SiCN in the presence of various solids. Fe-Mont has the strongest acid strength among the solid catalysts used, and reveals the highest catalytic activity for the reaction. Compared with Fe-Mont, much less acidic calcium ion-exchanged montmorillonite (Ca-Mont)[12)] gave a poorer yield even in a prolonged reaction time. This result implies that strongly acidic sites on Fe-Mont can promote the cyanosilylation, that is, a carbonyl group of 2-octanone coordinates to the acid site to be activated, followed by addition of Me_3SiCN.

Complexes of 18-Crown-6 with KCN, KN_3, KSCN, and KOMe are effective catalysts for carbonyl cyanosilylation since any anion, X^-, which can directly add to a carbonyl (Eq. 2) or can effect ligand exchange on silicon (Eq. 3), should initiate the reaction.[8)] Similarly, CaF_2 and HAp are assumed to function as nucleophilic catalysts.



(2)

$$Me_3SiCN + X^- \longrightarrow Me_3SiX + CN^- \qquad (3)$$

The catalytic activity per unit surface area of CsF and KF is eight times as large as that of CaF_2, indicating that a fluoride anion is essentially responsible for the catalysis. However, the specific surface area of CaF_2 is much larger than that of CsF and KF, so CaF_2 is recommended as a practical catalyst for the reaction.

Table 2. Cyanosilylation of carbonyl compounds

Substrate	Solid catalyst	Temp/$^{\circ}C$	Time/h	Yield/%
Benzaldehyde	Fe-Mont	0	0.2	96
	HAp	0	0.2	95
2-Octanone	Fe-Mont	0	0.2	96
	HAp	0	0.5	92
	CaF_2	0	4.5	94
Acetophenone	HAp	0	1.3	96
	CaF_2	0	5	98
Benzophenone	Fe-Mont	0	0.7	98
	HAp	20	24	94

Aldehyde or ketone (1 mmol), Me_3SiCN (1.1 mmol), Fe-Mont (0.2 g), HAp (0.5 g), CaF_2 (0.5 g), in CH_2Cl_2.

Concerning metal phosphates, although HAp is an efficient catalyst, $Ni_3(PO_4)_2$, that is more acidic ($+1.5 \geq H_o > +0.8$) than HAp, revealed no catalysis for carbonyl cyanosilylation. This suggests that acid sites on metal phosphates participate little in the promotion of the reaction.14)

In order to elucidate further the difference in catalytic roles between Fe-Mont, CaF_2, and HAp, Me_3SiCN was treated with benzaldehyde dimethyl acetal on those solids in CH_2Cl_2 at 0 °C. Fe-Mont produced 2-methoxy-2-phenylethanenitrile in 83% yield, whereas CaF_2 and HAp gave no adducts, revealing that CaF_2 and HAp show no acid catalysis.

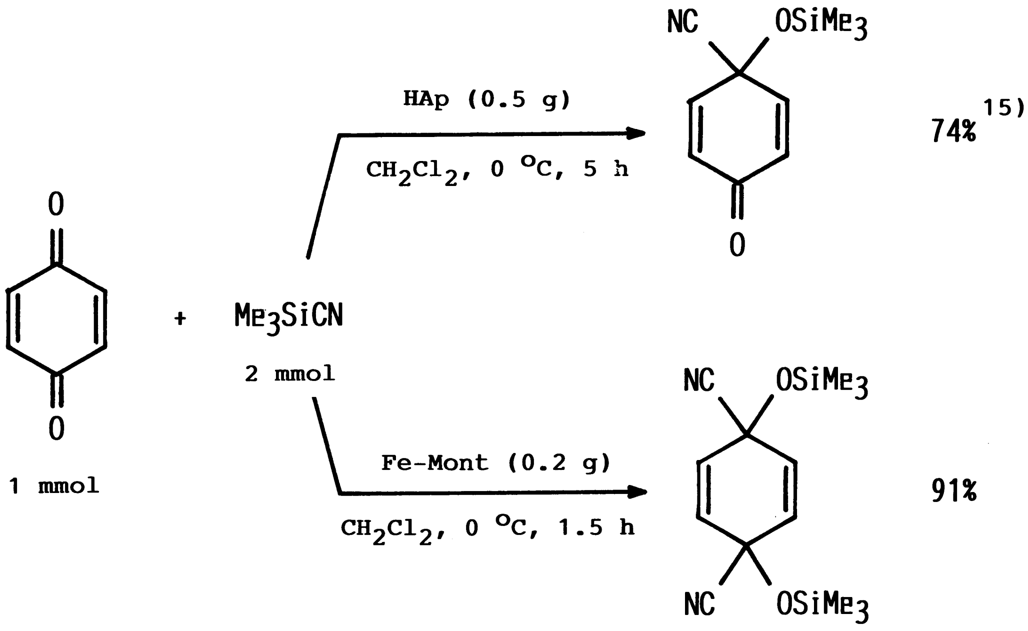
Judging from the results mentioned above, we are assuming that F^- sites on CaF_2 and PO_4^{3-} sites on HAp interact with Me_3SiCN to release a cyanide anion.

Table 2 shows the cyanosilylations of various carbonyl compounds by the present heterogeneous catalyst systems. In all cases, we could isolate the products almost quantitatively.

Using an acidic Fe-Mont or non-acidic HAp catalyst properly enables us to produce a monoadduct or a bisadduct exclusively when we treat p-benzoquinone with 2 equivalents of Me_3SiCN as shown in Eq. 4. It is interesting to note that solid acid, Fe-Mont can catalyze the addition of Me_3SiCN to p-benzoquinone, while Lewis acids such as ZnI_2 and $AlCl_3$ were reported to cause no reaction.8)

Although Fe-Mont, CaF_2, and HAp are very stable solids, in the reaction media they exhibit high catalytic activities comparable to, in some cases superior to, those of homogeneous catalysts, Lewis acid or nucleophilic catalysts.

Further applications of the present solid catalysts to organic synthesis are under way.



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