Synthesis of alkoxy- and aminosilanes over solid-base catalysts

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Solid-base catalysts, such as KF loaded on alumina, selectively gave alkoxysilanes through the reaction of alkylsilanes not only with alcohols but also with aldehydes or ketones at around 300–340 K. Solid-base catalysts also catalyzed a reaction of trimethylacetylene with amines to form aminosilanes.

KEY WORDS: solid-base catalyst; alkoxysilane; aminosilane; alkylsilane; alcohol; aldehyde; ketone; amine.

1. Introduction

Preparation of alkyl silyl ethers (alkoxysilanes) has been helpful in various synthetic situations. For example, a silyl ether moiety can be used as a linker for solid-phase synthesis in a combinatorial approach [1–3]. Alkoxysilanes are usually synthesized by the reaction of chlorosilanes with corresponding alcohols. In this preparation method, a stoichiometric amount of bases such as pyridine as an acid-trapping agent, with toluene or benzene as solvent should be used. Furthermore, equimolar salt is inevitably formed and has to be disposed of in an appropriate manner. Thus, this procedure has the disadvantage of requiring removal by filtration of salts, such as pyridine hydrochloride, prior to evaporation of the solvent and distillation of the product. To avoid these disadvantages, a new preparation method should be developed to obtain alkoxysilanes by using solid-base catalysts because they are environmentally benign, present fewer disposal problems, and allow easier separation.

We have already reported that KNH_2 loaded on alumina (KNH_2/Al_2O_3) and KF loaded on alumina (KF/Al_2O_3), which were heated under vacuum at around 700 K, catalyze the dehydrocoupling of alkylsilane ($R_3Si\text{-}H$) with 1-alkyne ($R^1C{\equiv}CH$) and give silyl alkynes ($R_3Si\text{-}C{\equiv}CR^1$) and hydrogen [4].

$$R_3Si\text{-}H + R^1C{\equiv}CH \rightarrow R_3Si\text{-}C{\equiv}CR^1 + H_2 \qquad (1)$$

$$R_3Si\text{-}H + R^1\text{-}OH \rightarrow R_3Si\text{-}OR^1 + H_2 \qquad (2)$$

KF/Al_2O_3 is also excellent in the activation of aldehydes and ketones without proton transfer. For example, it was an effective catalyst for the Tishchenko reaction of benzaldehyde and gave benzyl benzoate [5].

These catalytic properties of solid-base catalysts such as KNH_2/Al_2O_3 and KF/Al_2O_3 encouraged us to examine the reaction of alkylsilanes, not only with alcohols but also with aldehydes (R^1CHO) or ketones (R^1COR^2), to obtain alkoxysilanes by using various solid-base catalysts. In these reactions expressed by equations (3) and (4), atom utilization is 100%.

$$R_3Si\text{-}H + R^1CHO \rightarrow R_3Si\text{-}OCH_2R^1 \qquad (3)$$

$$R_3Si\text{-}H + R^1COR^2 \rightarrow R_3Si\text{-}OCHR^1R^2 \qquad (4)$$

We also used solid-base catalysts to synthesize aminosilane through the reaction of amines ($R^1\text{-}NH^2$) with silylacetylenes.

$$R_3SiC{\equiv}CH + R^1\text{-}NH_2 \rightarrow R_3Si\text{-}NHR^1 + HC{\equiv}CH \quad (5)$$

In this work, we would like to show that solid-base catalysts are effective in the formation of Si–O and Si–N bonds.

2. Experimental

2.1. Catalyst preparation

Alumina, obtained from Shikishima Inc., had a surface area of 131 m^2/g, and an average pore diameter of 15 nm. KNH_2 was loaded on alumina from an ammoniacal solution of potassium metal followed by heating under vacuum at 573 K, as reported in [6]. The amount of KNH_2 was 2.6 mmol per 1.0 g of alumina (KNH_2/Al_2O_3). KF loaded on alumina was prepared by an impregnation method from its aqueous solution followed by drying the catalyst at 393 K for 12 h [4,5]. Prior to the reaction, the catalyst was heated under vacuum at 673 K. The amount of KF on alumina was 5 mmol per 1.0 g of alumina (KF/Al_2O_3). K_2CO_3 loaded on alumina (K_2CO_3/Al_2O_3) was prepared as

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described for KF/Al_2O_3 except that the amount of K_2CO_3 on alumina was 2.5 mmol per 1.0 g of alumina. MgO was prepared by heating $Mg(OH)_2$ at 773 K under vacuum, while CaO was prepared by heating $MgCO_3$ at 973 K under vacuum.

2.2. Reaction procedure

The purified reactants were put into a glass tube, which was then attached to the side arm of the quartz reactor and degassed with a freeze–thaw method. The reaction was started by transferring the reactants into the reactor containing the catalyst prepared as described above. The products were identified with ^{1}HNMR and/or GC-MS. The reactant conversions and the product yields were determined with a gas chromatograph by using an internal standard. The yields of reaction products were expressed by percentage yields based on the silanes employed.

3. Results and discussion

3.1. Dehydrogenative silylation of alcohols with diethylsilane

Dehydrogenative silylation of alcohols (R^1OH) with diethylsilane (Et_2SiH_2) was carried out by using KF/Al_2O_3 at 329 K in tetrahydrofuran (THF) as a solvent. The results are shown in table 1.

$$Et_2SiH_2 + 2R^1OH \rightarrow Et_2Si(OR^1)_2 + 2H_2 \qquad (6)$$

$$R^1 = C_3H_8, CH_2{=}CHCH_2, HC{\equiv}CCH_2$$

When propane-1-ol was used as a reactant, it was selectively converted to diethyldipropoxysilane in an 89% yield in 20 h, without any by-products. However, triethylsilane (Et_3SiH) was no less reactive for propane-1-ol under the same reaction conditions, giving triethylpropoxysilane in a 25% yield.

Table 1
Reaction of Et_2SiH_2 with alcohols over KF/Al_2O_3

Alcohol (R^1OH)	Yield of $Et_2Si(OR^1)_2$/%
$CH_3CH_2CH_2OH$	89
$CH_2{=}CH_2CHCH_2OH$	78
$HC{\equiv}CCH_2OH$	66

Note: Reaction temperature: 329 K; reaction time: 20 h; R^1OH: 3 mmol; Et_2SiH_2: 3 mmol; solvent: THF 2 mL.

Dehydrogenative silylation of ally alcohol with Et_2SiH_2 gave diethyldiprop-2-enyloxysilane in a 78% yield, while 1,1,3,3-tetraethyl-1, 3-diprop-2-enyloxydisiloxane was also formed in a 7% yield. For 2-propyn-1-ol, the dehydrogenative silylation reaction proceeded to give diethyldiprop-2-ynyloxysilane in a 66% yield, while 1,1,3,3,5,5-hexaethyl-1,5-diprop-2-ynyloxytrisiloxane was formed as a by-product with a 21% yield. Hydrogenative products such as diethyldipropoxysilane were not obtained, when solid bases were used as catalysts. However, the dehydrogenative silylation of unsaturated alcohols was mediated by certain platinum [7] and rhodium [8,9] catalysts, which give saturated alkoxysilanes as a side or major product depending on reaction conditions.

Alkoxysilanes can be synthesized through the reaction of aldehydes or ketones with alkylsilanes over a solid-base catalyst. The reaction of benzaldehyde (PhCHO) with Et_3SiH was carried out at 303 K. The results are shown in table 2.

$$PhCHO + Et_3SiH \rightarrow PhCH_2O\text{-}SiEt_3 \qquad (7)$$

When *N,N*-dimethylformamide (DMF) was used as a solvent, PhCHO selectively reacted with Et_3SiH to give benzyloxytriethylsilane. Thus, KF/Al_2O_3 gave benzyloxytriethylsilane with a >99% yield in 1 h. However, Tishchenko reaction of benzaldehyde mainly proceeded to give benzylbenzoate with 98% yield and 87% yields, when solvents were hexane and THF, respectively. K_2CO_3/Al_2O_3, KNO_3/Al_2O_3, $KHCO_3/Al_2O_3$, and

Table 2
Alkoxysilanes synthesis through the reaction of alkylsilanes with aldehydes or ketones over solid-base catalysts

Aldehyde or ketone	Silane	Catalyst	Reaction temperature (K)	Reaction time (h)	Yield of alkylsilane (%)
PhCHO	Et_3SiH	KF/Al_2O_3	303	1	>99
PhCHO	Et_3SiH	K_2CO_3/Al_2O_3	303	1	99
PhCHO	Et_3SiH	KNO_3/Al_2O_3	303	1	96
PhCHO	Et_3SiH	$KHCO_3/Al_2O_3$	303	1	90
PhCHO	Et_3SiH	KNH_2/Al_2O_3	303	1	60
PhCHO	Et_3SiH	MgO	303	20	37
PhCHO	Et_3SiH	CaO	303	20	7
PhCHO	$PhMe_3SiH$	KF/Al_2O_3	303	1	97
PhCHO	$(EtO)_3SiH$	KF/Al_2O_3	303	20	31
PhCOMe	$PhMe_3SiH$	KF/Al_2O_3	353	1	74
n-$C_6H_{13}COMe$	$PhMe_3SiH$	KF/Al_2O_3	353	1	32

Note: Catalyst: 0.25 g, amount of K in potassium, salt: 2.6 mmol/g, aldehyde or ketone: 2.5 mmol, silane: 2.5 mmol, solvent: DMF 2.5 mL.

Table 3
Catalytic activities of solid-base catalysts for aminosilanes formation through the reaction of $Me_3SiC{\equiv}CH$ with amines

Catalyst	Amine	Yield (%)[a]	
		Aminosilane	Bis(trimethylsilyl)acetylene
MgO	$PhNH_2$	93	1
K_2CO_3/Al_2O_3	$PhNH_2$	81	8
KNH_2/Al_2O_3	$PhNH_2$	76	1
KF/Al_2O_3	$PhNH_2$	67	9
MgO	n-$C_4H_9NH_2$	45	2
KF/Al_2O_3	n-$C_4H_9NH_2$	11	9

Note: Catalyst: 0.25 g KNH_2 (2.6 mmol/g)/Al_2O_3, K_2CO_3 (2.5 mmol/g)/Al_2O_3, KF (5.0 mmol/g)/Al_2O_3; $Me_3SiC{\equiv}CH$: 4.0 mmol; amine: 8.0 mmol; solvent: DMF 2.0 mL; reaction temperature: 318 K; reaction time: 20 h.
[a]Yield based on $Me_3SiC{\equiv}CH$.

KNH_2/Al_2O_3 also selectively catalyzed the reaction of benzaldehyde with Et_3SiH in DMF, while MgO and CaO showed rather low catalytic activities, and benzaldehyde was formed with 7% and 8% yields, respectively, in 30 h.

Arylsilyl ether moiety is important as a removable linker in solid-phase synthesis [1]. For example, dimethylphenylsilane ($PhMe_2SiH$) was used as a precursor for arylsilyl ether. KF/Al_2O_3 showed a high catalytic activity for the reaction of benzaldehyde with dimethylphenylsilane ($PhMe_2SiH$) to give benzyloxydimethylphenylsilane ($PhCH_2O$-$SiPhMe_2$), whose yield was 97% in 1 h at 303 K, as shown in table 2.

$$PhCHO + PhMe_2SiH \rightarrow PhCH_2O\text{-}SiPhMe_2 \quad (8)$$

KF/Al_2O_3 also catalyzed hydrosilylation of alkylsilanes with ketones. Thus, acetophenone (PhCOMe) reacted with $PhMe_2SiH$ to give (1-phentl-1-ethoxy)dimethylphenylsilane, whose yield was 81% in 20 h at 353 K. When 2-octanone (n-$C_6H_{13}COMe$) was used as a reactant for hydrosilylation of $PhMe_2SiH$, the yield of (2-octyloxy)dimethylphenylsilane was 32%.

$$RCOMe + PhMe_2SiH \rightarrow RMeHCO\text{-}SiPhMe_2 \quad (9)$$
$$R = Ph \text{ or } n\text{-}C_6H_{13}$$

Thus, KF/Al_2O_3 is an effective catalyst for hydrosilylation of alkylsilanes such as Et_3SiiH with aldehydes or ketones.

Onaka *et al.* reported the hydrosilylation of alkoxysilanes with aldehydes or ketones in the presence of CaO or clay montomorillonite, although these catalysts showed rather low catalytic activities for the hydrosilylation of alkylsilanes [10]. These results suggest that catalytic performance of KF/Al_2O_3 is different from that of CaO or clay montomorillonite. F^- anion species on Al_2O_3 possibly activate aldehydes or ketones to react with alkylsilanes, since Fujita and Hiyama have reported that tetrabutyl ammonium fluoride or tris(diethylamino)sulfonium difluorotrimethylsilane as a homogeneous catalyst catalyzed the hydrosilylation of alkylsilanes with aldehydes or ketones in polar solvents [11]. We reported that F^- anion species were possibly basic sites over KF/Al_2O_3 on the basis of the experimental results of 19F MAS NMR measurements [5,12].

Solid-base catalysts were also effective in the Si–N bond formation. Thus, MgO gave *N*-trimethylsilylaniline with a 92% yield in 20 h at 318 K through the reaction of aniline ($PhNH_2$) with trimethylsilylacetylene ($Me_3SiC{\equiv}CH$) (table 3). K_2CO_3/Al_2O_3, KNH_2/Al_2O_3, and KF/Al_2O_3 also showed high catalytic activities. The by-product was bis(trimethylsilyl)acetylene, which was formed by the metathesis of $Me_3SiC{\equiv}CH$ over solid-base catalysts [12].

$$2Me_3SiC{\equiv}CH \rightarrow Me_3SiC{\equiv}CSiMe_3 + HC{\equiv}CH \quad (10)$$

When n-butyl amine (n-$C_4H_9NH_2$) was used as a reactant, the yield of trimethylsilylbutylamine was 11% in 20 h at 318 K.

$$RNH_2 + Me_3SiC{\equiv}CH \rightarrow PhNH\text{-}SiMe_3 + HC{\equiv}CH \quad (11)$$
$$R = Ph \text{ or } n\text{-}C_4H_9$$

In Si–N bond formation, aniline more easily reacted with $Me_3SiC{\equiv}CH$ than n-$C_4H_9NH_2$, since the basicity of n-$C_4H_9NH_2$ ($pK_a = 10.61$) is much higher than that of $PhNH_2$ ($pK_a = 4.62$). The lower pK_a value of $PhNH_2$ presumably facilitates proton abstraction through the basic sites of the catalyst.

In summary, solid-base catalysts, KF/Al_2O_3, MgO, and KNH_2/Al_2O_3, mediate Si–O and Si–N bond formation with saturated and unsaturated alcohols, benzaldehyde, and aniline in the presence of hydrosilanes and ethynylsilane as a silicon component.

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