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Synthesis of 3-Aminopropyltriethoxysilane via Catalytic Hydrogenation of 2-Cyanoethyltriethoxysilane

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Activation of the industrial cobalt catalyst consisting of 24.8 wt% cobat, 0.3 wt% thorum and 1.2 wt% aluminium (in the form of the oxides supported on silica) modified by potassium corbonate makes it suitable for use in a very effective hydrogenation of 2-cyanoethyltriethoxysilane leading, under optimum conditions (150 °C, 5.1 MPa H_2), to a quantitative synthesis of 3-aminopropyltriethoxysilane, the commonest silane coupling agent with nitrogen functionality. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

3-Aminopropyltriethoxysilane, by far the commonest silane coupling agent with functionality based on the nitrogen atom,[1] can be obtained by three different methods: ammonolysis of 3-chloropropyltrialkoxysilane;[2] direct catalytic hydrosilylation of allylamine with triethoxysilane (in this case both α and β adducts are obtained);[3–5] and hydrogenation of the nitrile group in 2-cyanoethyltriethoxysilane.[2] The latter can be synthesized effectively by hydrosilylation of acrylonitrile with $HSiCl_3$, followed by alcoholysis (ethanolysis).[6] 3-Aminopropyltriethoxysilane is widely used in the modern plastics industry, foundries, the glass-fibre industry, fabric treatment, personal care products, etc., and has been produced by several chemical companies all over the world,[1,6,7] as the commercial products A-1100 (OSi-Specialties–Witco), SC-3900 (General Electric Silicones), APS-E (Chisso), AMEO (Hüls) and KBE-903 (Shin-Etsu).

Hydrogenation of nitrile groups in organic compounds can be carried out in the presence of transition-metal-based catalysts, mainly containing iron, cobalt and nickel groups,[8–12] both in homogeneous (in the form of complexes) and in heterogeneous (as metals supported on alumina or silica) forms. Several catalytic systems, such as Raney nickel or the cobalt catalyst reported here, as powders, in liquid ammonia,[13] or rhodium, platinum (5 wt% of metal on active carbon or Al_2O_3) and palladium (5 wt% of metal on active carbon) systems,[14] were applied to hydrogenation of the nitrile group of carbosilanes leading to aminoalkyltrialkoxysilanes. However, the yield and selectivity (primary, secondary and tertiary amines are produced) are usually low; besides, relatively high pressures (up to 12.2 MPa) and temperatures (up to 300 °C) are needed. Nickel supported on silica (Kieselguhr, 50 wt% metal) applied in the process under study yielded 84% 3-aminopropyltriethoxysilane (150 °C, 5 MPa H_2).[14] The cobalt catalyst supported on silica (67 wt% metal) or alumina (34.1 wt% metal) seems to be the most useful catalytic system, characterized by good performance (high activity and selectivity — conversion up to 89%) and operating under practically mild conditions (50–250 °C, 1.4–14 MPa H_2).[15] The aim of this paper is to demonstrate the high yield and selectivity of the industrial cobalt catalyst (24.8 wt% cobalt, 0.3 wt% thorium, 1.2 wt% aluminium in the form of the oxides, supported on silica), especially after its modification with potassium carbonate, in the hydrogenation of 2-cyanoethyltriethoxysilane.

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EXPERIMENTAL

Materials

2-Cyanoethyltriethoxysilane was prepared by catalytic hydrosilylation of acrylonitrile with trichlorosilane,[16] followed by ethanolysis (C. Pietraszuk, unpublished results). Commercial dihydrogen (99.9%), anhydrous ethanol and potassium carbonate were used as reagent, solvent and catalyst modifier, respectively.

Catalysts

The starting catalysts for the experiments were the following.

(a) Catalyst 1: industrial cobalt catalytic system (24.8 wt% Co, 0.3 wt% Th, 1.2 wt% Al in the form of the oxides, supported on silica) from the ‘Dwory’ Chemical Works, Poland (grains 0.4–0.8 mm in diameter);
(b) Catalyst 2: cobalt oxide catalyst (67.0 wt% Co, supported on silica), prepared according to the described procedure;[15]
(c) Catalyst 3: modified catalyst 1 modified further with aqueous 0.01 M K_2CO_3 solution, and calcined in an oven (contained 0.3 wt% potassium).[17]

$$\underset{\mathbf{1}}{(EtO)_3SiCH_2CH_2CN + 2H_2} \xrightarrow{Co/SiO_2} \underset{\mathbf{2}}{(EtO)_3SiCH_2CH_2CH_2NH_2} \qquad (1)$$

Catalytic procedure

Prereduction

The cobalt catalyst was reduced with dihydrogen at 300 °C in a flow reactor (quartz tube) for the desired time or introduced to the reaction vessel directly under nitrogen. The modified catalyst (with potassium) was reduced with dihydrogen at 450 °C (6 h) and transferred under dinitrogen to the reactor. Completion of the reduction was monitored by the cessation of water evolution and decay of the pink colour of the catalyst grains.

Hydrogenation tests

Hydrogenation tests were carried out in a 2 dm^3 Parr reactor, equipped with a stirrer, outlet and inlet gauges and a manometer. The reactor was purged with dry dinitrogen, filled with solvent (ethanol), the catalyst and 2-cyanoethyltriethoxysilane. The reaction mixture was pressurized with dihydrogen several times (up to 1.4 MPa) and then, at a dihydrogen pressure of to 2.0 MPa, heating was started and the reaction mixture was stirred at a given temperature (up to 150 °C). After completion of the process, the reaction mixture was analysed by a GC method, using 3-aminopropyltriethoxysilane as the authentic sample.

The reaction conditions and amounts of reagent are presented in Tables 1–3 and footnotes.

Equipment and analytical measurements

Gas-chromatographic analyses were carried out using a Philips PV 4400 apparatus equipped with a glass column (3 m) filled with 5% DC 200 on Chromosorb WAW DMCS (160 °C, argon) and with a TDC detector.

RESULTS AND DISCUSSION

Hydrogenation of 2-cyanoethyltriethoxysilane (**1**) occurs in the presence of activated cobalt catalysts supported on silica according to the Eqn [1].

All the cobalt catalysts applied in Eqn [1], under the conditions described in the Experimental section and specified in Tables 1–3 below, showed 100% selectivity of the hydrogenation towards the silylamine **2**. The generally accepted hydrogenation route involves, in the first step, the formation of the aldimine RCH=NH and, in the second, its hydrogenation to the amine RCH_2NH_2.[8,18] When the second step is relatively slow, the aldimines react with the resulting amines, leading to secondary and tertiary amines as by-products.[8]

Table 1 presents results illustrating the effect of substrate/catalyst 1 ratio and the time of preliminary reduction of catalyst by H_2 (hydrogen pretreatment) (at 300 °C) on the yield of **2**, compared with the results obtained for catalyst 2.

Hydrogen pretreatment of the heterogeneous cobalt oxide catalysts is a generally accepted

Table 1 Hydrogenation of 2-cyanoethyltriethoxysilane (**1**) in the presence of catalyst 1

Run	Catalyst (g)	Pre-reduction time[a] (h)	**1**/Co mass ratio (g/g)	**1**/Co molar ratio (mol/mol)	Yield of **2** (%)
1	4.09	3	4.8	5.4	100
2	4.20	3	7.7	8.7	54.0
3	4.00	3	10.8	12.2	22.0
4	4.02	1	3.6	4.2	74.2
5	4.20	2	4.0	4.5	94.3
6	4.30	4	4.7	5.3	100
7	4.20[b]	3	8.0	9.1	53.1
8	4.50	None	4.6	5.1	0
9[c]	4.20	3	7.5	8.6	76.0

Reaction conditions: 150 °C, 2 h, ethanol as a solvent (100 cm^3), pH_2 = 5.1 MPa.
[a] Catalyst pre-reduction at 300 °C.
[b] Catalyst pre-reduction at 450 °C.
[c] Catalyst 2.

procedure for their activation for the process of hydrogenation. This pre-reduction leads to low-valent cobalt species as well to metallic forms with metal–hydrogen bonds which are catalytic centres of the hydrogenation reaction.[18,19] The non-hydrogenated catalyst does not exhibit catalytic activity at all (see Table 1, entry 8). Three-hour activation of the catalyst (by hydrogenation) is required to reach the maximum yield (100%). All possible catalytic centres were already created — but at a high mass ratio of **1**/catalyst = 4.8, whereas for the reference **2** a 76% yield was observed for a **1**/catalyst ratio of 7.5. Catalyst 1 is able to transform 2.5 molecules of the substrate per cobalt atom in the catalyst in 1 h. It can be concluded that the industrial catalyst 1 does not improve the efficiency of the process when compared with the catalyst 2, reported previously[15] to show similar activity.

The aim of this work was to find a way of drastically increasing the catalytic activity of the cobalt catalyst, under milder conditions, and it was reached by using the industrial cobalt catalyst activated by potassium (catalyst 3). The effect of hydrogen pretreatment conditions as well as the reaction temperature and dihydrogen pressure on the yield of **2** is illustrated in Table 2.

The modification of supported oxide catalysts with alkali metal ions, particularly potassium, generally increases the surface area of the metal particles after reduction (producing smaller metal crystallites) and enhances their electron-donor properties. Additionally, potassium ions associated with the support surface enhance desorption of basic products from the catalyst surface. These two effects increase the efficiency of such prepared catalysts; for example, iron oxide catalyst supported on aluminium oxide for ammonia synthesis is promoted by potassium oxide. The modification of the cobalt industrial catalyst by potassium carbonate made hydrogen pretreatment more difficult, so higher temperatures and longer times of prereduction were needed to achieve an active form of the catalyst.

In comparison with previous catalytic systems (catalysts 1 and 2), high yields of **2** were obtained for catalyst 3 at a high molar ratio of the substrate to cobalt (54:1). Additionally, in the presence of the best catalysts reported so far, (both nickel[14] and cobalt[15] species) for the process under study, the highest conversion achieved was only close to 90%. In the case of nickel-based systems, ammonia$_3$ and

Table 2 The effect of hydrogen pretreatment conditions, reaction temperature and H_2 pressure on the yield of **2** in the hydrogenation of 2-cyanoethyltriethoxysilane (**1**) in the presence of catalyst 3

Run	Reaction temperature (°C)	H_2 pressure (MPa)	Yield of **2** (%)
1	120	4.0	0
2	130	4.0	8.2
3	140	4.0	53.1
4	140	5.1	92.1
5	150	5.1	100
6	150	3.5	78.3
7[a]	150	5.1	84.2
8[b]	150	5.1	31.3

Reaction conditions: 2 h, ethanol as a solvent (100 cm^3), 2 g of catalyst, **1**/Co mass ratio = 40:1, **1**/Co molar ratio = 54:1; hydrogen pretreatment 450 °C, 6 h unless otherwise indicated.
[a] Hydrogen pretreatment 450 °C, 4 h.
[b] Hydrogen pretreatment 400 °C, 6 h.

Table 3 Hydrogenation of 2-cyanoethyltriethoxysilane (**1**) in the presence of catalyst 3

Run	Catalyst 3 (g)	**1**/Co mass ratio (g/g)	**1**/Co molar ratio (mol/mol)	Yield of **2** (%)
1	2.2	32.0	43	100
2	2.1	62.0	84	100
3	2.1	97.6	132	100
4	2.0	121.2	164	68.3
5	2.2	148.0	200	44.6

Reaction conditions: 150 °C, 2 h, ethanol as a solvent (100 cm^3), $pH_2 = 5.1$ MPa; catalyst pre-reduction 450 °C, 6 h.

amines should be added to the reaction mixture. Yet, maximum selectivity and yield of the product were observed in this work at an even higher molar ratio of the substrate to cobalt, up to 132 (97.6 g **1**/g Co), which makes this catalyst exceptionally useful in the reaction studied[17] (Table 3).

Regeneration of catalyst 3 is possible by washing with ethanol, but conversion usually declines by *ca* 10% (with no change in the selectivity).

CONCLUSIONS

The results show that the modification of the cobalt catalyst with potassium carbonate increases its catalytic activity in the hydrogenation of organic nitriles. A high selectivity towards primary amines supports the assumption that hydrogenation of aldimines is relatively fast in the presence of the catalyst studied.

Activation of the industrially used catalyst by addition of 0.3% of potassium carbonate makes the resulting catalyst 3 very efficient for the synthesis of 3-aminopropyltriethoxysilane.[17] Under the optimum reaction conditions (150 °C, 2 h, 5.1 MPa H_2) the catalytic hydrogenation of **1** runs quantitatively at an initial mass ratio of **1**/Co catalyst close to 100:1. After the products have been washed off the same catalyst can be used repeatedly in the reaction under study. These results provide a sound basis for elaboration of a synthetic method involving a new effective catalytic system for production of the most common aminofunctional silane coupling agent.

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