

Chrysotile-Supported Transition Metal Salts as Friedel-Crafts Catalysts

Roseli O. Pinho, J. Augusto R. Rodrigues,*

Paulo J. Samenho Moran and Ines Joekes

Instituto de Química, Universidade Estadual de Campinas,
13083-970 Campinas - SP, Brazil

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Ácidos de Lewis ($ZnCl_2$, $CoCl_2$, $FeCl_3$, $NiCl_2$, $CrCl_3$) foram imobilizados em crisotila (um silicato de magnésio fibroso tipo amianto). A atividade catalítica desses ácidos suportados foi estudada para realizar reações de alquilação de Friedel-Crafts entre benzeno e cloreto de benzila para produzir difenilmetano com rendimentos entre 60 e 75%. A reação de acilação entre anisol e cloreto de acetila catalisada por esses catalisadores suportados forneceu *para*- e *orto*-acetilanisol em uma relação de 70:30, respectivamente com rendimento entre 25 e 35%. Esses catalisadores podem ser reutilizados em reações posteriores sem afetar significativamente o rendimento dos produtos.

Lewis acids ($ZnCl_2$, $CoCl_2$, $FeCl_3$, $NiCl_2$, $CrCl_3$) were immobilized on chrysotile (a fibrous asbestos-type magnesium silicate). The catalytic activity of these supported acids was studied by a Friedel-Crafts reaction of benzene and benzyl chloride to give diphenylmethane in 60 to 75% yields. The acylation reaction of anisole and acetyl chloride which was catalyzed by these supported acids gave *para*- and *ortho*-acetylanisole in a ratio of 70:30. These catalysts can be reused in further reactions without a significant reduction in the chemical yield of the products.

Keywords: supported Lewis acids, chrysotile as catalyst support, Friedel-Crafts alkylation, Friedel-Crafts acylation

Introduction

Considerable progress has been made in developing new, more environmentally acceptable Friedel-Crafts catalysts¹. Interest has been focused on zinc chloride supported on acid-activated K.10 montmorillonite as a catalyst to replace the conventional homogeneous reagents, such as $AlCl_3$ and sulfuric acid, which present operational problems due to corrosion and the separation of the products. These supported catalysts, often prepared by cation-exchanging montmorillonite², have attractive features such as ease of handling, low cost and regeneration, and are environmentally safe catalysts in that they prevent the production of aluminum waste. However, many of these reactions require relatively high temperature and pressure, and the products are often isomeric mixtures. Since the results have

mostly been published in patents, detailed experimental procedures are not ready available.

The clay montmorillonite ($Al_4Si_8O_{20}(OH)_4$) possesses smectite-like structures in which the crystallites are composed of negatively-charged silicate sheets with charge-balancing cations located between the sheets. Interlayer cations (mainly Na^+ , Ca^{2+} , K^+) are readily exchangeable and the interlamellar space occupied by the charge-neutralizing cation may swell upon the sorption of water, alcohols and a variety of other organic molecules on the large internal surface area ($700\text{ m}^2\text{ g}^{-1}$)³. Chrysotile has the formula $Mg_3(Si_2O_5)(OH)_4$, and is the only known member of its type with a cylindrical structure have a hexagonal close packing arrangement of the oxygen and hydroxyl groups, forming the $(SiO_4)^{2-}$ tetrahedrons of the silicate layer and the brucite- $Mg(OH)$ octahedrons. The fiber can

also be represented as a hollow tube with its external surface covered with hydroxyl groups (brucite layer) and the inner layer made up of bridging oxygen atoms (silicate layer)⁴. The chrysotile used, which came from the Cana Brava mine in Uruaçu - Go, Brazil was washed with water, filtered in a sieve with a 250 mesh, and dried in an oven. We report here the use of chrysotile, which is very abundant in the central region of Brazil, as a support with a high potential for substituting the well-known K.10 montmorillonite, and its application in the monoalkylation of benzene and high *para*-selective acylation of anisole with an easy workup procedure.

Experimental

All the reagents and the montmorillonite K.10 were purchased from Aldrich. The chrysotile used came from the Cana Brava mine in Minaçu - Go, Brazil and was washed with water in a sieve with a 250 mesh. The fibers were filtered off and dried in an oven (110 °C) for at least 1 h before being used in the reactions. Solvent and reagents were purified before use by the recommended procedures⁷. IR spectra were recorded on a Perkin-Elmer Model 1430 spectrometer. X-ray fluorescence was obtained on a Tracor Northern Spectrace 5000 spectrometer. HPLC was done with a Hewlett-Packard instrument model 1090 with UV detector (Diode Array) using a column of Bondesil CN from Analytichen International (0.5 m, 4.6 mm, 250 mm), and eluted with a mixture of 9:1 dichloromethane: hexane with a flux of 1.0 mL/min flow.

Immobilization by adsorption from the solution was carried out by refluxing 0.002 mol of the Lewis acid (FeCl₃, ZnCl₂, CoCl₂, NiCl₂, ZnSO₄) with 2 g of the support (chrysotile or montmorillonite K.10) for 20 h in methanol, followed by filtration washing with methanol, drying by evaporation, and calcination at 200 °C for 2 h. Immobilization by evaporation was done by refluxing 0.002 mol of the Lewis acid and 2 g of the support for 20 h in methanol, followed by evaporation of the solvent on a rotatory evaporator and calcination at 200 °C for 2 h. The third immobilization procedure was carried out by grinding 1 g of the support in a mortar with the Lewis acid in the absence of a solvent, followed by calcination for 2 h.

Friedel-Crafts alkylation. 1 g of the supported catalyst prepared as above was stirred with anhydrous benzene (30 mL, 0.337 mol) and freshly distilled benzyl chloride (1.2 mL, 0.01 mol), and refluxed for 3 h. After cooling, the reaction mixture was filtered and the supported catalyst was washed with ether; the solvents were evaporated on the rotatory evaporator. The crude material was purified by column chromatography with silica gel 60, and eluted with a 1:1 mixture of CH₂Cl₂: hexane to give diphenylmethane, which was identified by IR and NMR.

Friedel-Crafts acylation. 1 g of the supported catalyst prepared as above was stirred with dichloromethane (20

mL), anisole (0.5 mL, 0.005 mol), and fresh distilled acetyl chloride (1.0 mL, 0.014 mol), and heated for 4 h at 50 °C. After cooling, the reaction mixture was filtered and the supported catalyst was washed with a solvent (ether or dichloromethane). The crude material was purified by column chromatography with silica gel 60, and eluted with a 1:1 mixture of CH₂Cl₂:hexane to give a mixture of *ortho*- and *para*-acetylanisole which was analyzed by HPLC.

Results and Discussion

Three methods were used for the immobilization of the Lewis acid: i) mixing or grinding the support and the salt in a mortar (without solvent) followed by calcination; ii) immobilization by adsorption: adsorption from the solution by refluxing a methanolic solution of the Lewis acid with the support for 20 h, followed by filtration, washing with methanol, drying by evaporation and calcination at 200 °C for 2 h; and iii) immobilization by evaporation: the support was refluxed for 20 h in a methanol solution of the Lewis acid, followed by the evaporation of the solvent on a rotatory evaporator and calcination at 200 °C for 2 h.

The Friedel-Crafts alkylation was studied using the reaction of benzyl chloride with benzene, which gives diphenylmethane as the major product, as a model. Clark *et al.* reported that montmorillonite-supported zinc and nickel chlorides are highly active and selective reagents for Friedel-Crafts alkylations⁵.

Using 1 g of Zn salt (1 mmol g⁻¹) on chrysotile, 10 mmol benzyl chloride reacted with 30 mL of benzene under reflux for 3 h to give diphenylmethane with the following yields (average of three reactions, isolated yields): ZnSO₄ (67%), Zn(NO₃)₂ (68%), Zn(OAc)₂ (70%), and ZnCl₂ (72%). With ZnCl₂, it was found that the optimum concentration of this salt in reactions with 10 mmol of benzyl chloride was 0.3 g g⁻¹ ZnCl₂/chrysotile (See Table 1), which gave a 73% yield when the molar ratio of benzyl chloride to Lewis acid was 3:57. Thermogravimetric analysis showed that in the range of 250-400 °C chrysotile loses its brucite layer by

Table 1. The effect of the amount of ZnCl₂ supported on chrysotile in the yield of diphenylmethane^a.

ZnCl ₂ g	yield, % ^b	reuse, ^c yield, %
0.3	73	68
0.5	63	–
0.8	61	62
1.0	63	–
1.5	56	61

(a) ZnCl₂ supported on 1 g of chrysotile by grinding, followed by activation at 280 °C, 10 mmol of benzyl chloride, 10 mmol of benzene, and reflux for 3 h. (b) Isolated yields, average of 3 runs. (c) The catalyst ZnCl₂ / chrysotile was washed with ether, activated at 280 °C, and reused in another reaction under the same conditions.

dehydroxylation. Table 2 shows the effect of the activation temperature of the catalyst on the diphenylmethane yield. Higher yields were obtained with calcination temperatures of 150 and 400 °C, which shows that dehydroxylation has little effect on the catalytic activity. The reutilization of the catalyst in another reaction is important for economic reasons. With 0.3 g of ZnCl₂ on 1 g of chrysotile, we achieved a 68% yield of diphenylmethane in the first reuse, which is a good result. In the third reuse, the yield was very poor, and the analysis of the catalyst by X-ray fluorescence showed that few Zn²⁺ species were present. For reuse, the catalyst was washed with ether, dried and calcinated again. The ether leached the ZnCl₂, making the catalysts ineffective for further use. To prevent this, it is necessary to employ dichloromethane or toluene as the solvent during the extractions. Using a microwave oven (household, 1.58 kW) to increase the temperature, the same reaction conducted in a Teflon bomb for 30 min gave diphenylmethane in a 50-60% yield. The advantage of microwave heating is that it reduces the reaction time and affords the same product with nearly the same yield. The activities of the other supported metal salts are shown in Table 3. The highest yields were obtained with CoCl₂, ZnCl₂ and FeCl₃ and comparing the supports, chrysotile always gave better yields than montmorillonite. The remarkable activity of the cobalt, zinc and iron supported reagents is in marked contrast to that of unsupported cobalt chloride, zinc chloride and iron chloride, which are generally regarded as the weakest Friedel-Crafts catalysts. A powerful Lewis acid

Table 2. The effect of the ZnCl₂/chrysotile activation temperature on the diphenylmethane yield^a.

temperature °C	150	280	325	400
yield ^b %	75	61	63	73

(a) Reaction conditions: chrysotile 1 g, ZnCl₂ 0.3 g, benzyl chloride 10 mmol, benzene 30 mL, reflux for 3 h. (b) Isolated yields (average of three runs).

Table 3. The effect of Lewis type acid, immobilized on chrysotile or K.10 montmorillonite by adsorption, on the diphenylmethane yield^{a,b}.

Lewis acid	chrysotile, yield %	montmorillonite, yield %
CoCl ₂	72	73
ZnCl ₂	72	69
FeCl ₃	78	64
NiCl ₂	49	45
CrCl ₃	52	53

(a) isolated yield, average of 3 runs. (b) Reaction conditions: 1 g of the catalyst (Lewis acid support) activated at 150 °C, 5.2 mmol of benzyl chloride, 30 mL of benzene, under reflux for 3 h.

Table 4. The acylation of anisole by acetyl chloride in the presence of supported ZnCl₂ and FeCl₃ in CH₂Cl₂ at 40 °C after 4 hours of reaction.

Catalyst ^a	Process of immobilization	yield % ^b	<i>para</i>	<i>ortho</i>
ZnCl ₂ -chrys	adsorption	19	75	25
ZnCl ₂ -chrys	evaporation	35	70	30
ZnCl ₂ -K.10	evaporation	26	70	30
FeCl ₃ -K.10	adsorption	27	72	28

(a) Activated at 280 °C. (b) isolated yields.

catalyst such as a AlCl₃ is less effective as supported reagent than CoCl₂, ZnCl₂ and FeCl₃.

Few examples were found for Friedel-Crafts acylation using supported Lewis acids. Successful examples of solid acid-catalyzed acylations are limited to very active substrates⁶. Table 4 presents our results from the acylation of anisole using solid Lewis acids supported on chrysotile and montmorillonite to give acetylanisoles in 19-35% yields with a *para:ortho* ratio of 70:30. With ZnCl₂ supported on chrysotile by evaporation, a 35% yield of acetylanisole was achieved. This catalyst is ineffective for the acylation of benzene, and our system gave results similar to those obtained by Clark *et al.* using FeCl₃-montmorillonite for 24 h of reaction⁶.

In summary, chrysotile is an excellent support for solid Lewis acids used as catalysts for alkylation and acylation in Friedel-Crafts reactions, and it can be used to substitute the classic procedures employing AlCl₃. The benzylation of benzene with Lewis acid-chrysotile gave good diphenylmethane yields without byproducts, and the catalyst can be used in additional reactions. For acylation reactions, the catalyst is less effective and needs a very active substrate. The acetylation of anisole gave modest yields of *para*- and *ortho*-acetylanisole in a ratio of 70/30. Further studies using these catalysts are in progress.

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