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Silica-Embedded *tert*-Butyldimethylsilyltrifluoromethanesulfonate Catalysts as New Solid Acid Catalysts

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Silica-embedded *tert*-butyldimethylsilyltrifluoromethanesulfonate catalysts were synthesized by a sol-gel method in acidified CCl_4, using hexadecyltrimethyl-ammonium bromide as a surfactant. The catalysts were characterized by nitrogen adsorption–desorption isotherms at 77 K; TG-DTA; ^1H, ^{13}C, and ^{29}Si solid state MAS/NMR; XRD; XPS; Raman spectroscopy; and FTIR after adsorption of NH_3. The characterization data indicated mesoporous solids in which most of the silyl-triflate derivative keeps its integrity. The catalytic tests performed with the methyl ester of 1-cyclopentenylacetic acid in various solvents showed that the reaction selectively leads to 3-methylbenzaldehyde and is sensitive to the solvent accepting ability. © 2001 Academic Press

INTRODUCTION

Alkylsilyltrifluoromethanesulfonates are known as exceptionally strong silylating agents (1–3). The silylation reaction occurs in homogeneous conditions in the presence of triethylamine or triethylamine and carbon tetrachloride as solvents. However, up to this day, nothing on the homogeneous or heterogeneous catalytic behavior in acid-assisted reactions of these compounds has been reported. On the other hand, the use of triflates or triflic acid as homogeneous acid catalysts has received a keen interest because of the electron-withdrawing effect exerted by the trifluoromethanesulfonyl group. Since heterogeneous catalysis is more versatile for practical applications, several studies have been reported in the past few years on the heterogeneization of triflic acid (4) and various triflates by impregnation (5, 6) or polymer incorporation (7, 8), and on selective acid-catalyzed reactions using these materials. Silica-supported triflates or triflic acid are active and selective catalysts in the rearrangement of α-pinene oxide to campholenic aldehyde, polymerization and depolymerization of cyclic ethers, Friedel–Crafts reactions, alkylation of isobutane with *n*-butene (4–8), etc.

This study is devoted to the embedding of *tert*-butyldimethylsilyltrifluoromethane sulfonate in a silica sol-gel matrix and the catalytic performances in the reaction of the *methyl* ester of the 1-cyclopentenylacetic acid.

EXPERIMENTAL

The catalysts were prepared by embedding *tert*-butyldimethylsilyltrifluoromethanesulfonate in a silica sol-gel matrix. Since the silyl triflate derivative is only soluble in carbon tetrachloride and triethylamine (9), the sol-gel synthesis was carried out in inert atmosphere (Ar), using an adapted route in which the silica sol was obtained by acid hydrolysis of a solution of tetraethoxyorthosilicate (TEOS) (10.4 g) in acidified CCl_4 (TEOS : CCl_4 molar ratio of 4, pH 1.5 with HCl 37%). Water was then added to the acidic solution in TEOS : H_2O molar ratio of 1 : 10 (samples A1 and A2) or 1 : 4 (sample A3), and the mixture was refluxed at 70°C for 2 h. After cooling the silica sol solution at room temperature, the silyl triflate derivative (0.38 ml) was added under vigorous stirring as a 0.3 M solution in CCl_4 (samples A1 and A3) or as such (sample A2). Hexadecyltrimethyl-ammonium bromide, as a surfactant, was then introduced (surfactant : TEOS ratio of 0.1) and the gelation was carried out at 90°C for 2 days in a Teflon cylinder within an autoclave (samples A2 and A3) or at room temperature for 6 days (sample A1). The resulting gel was dried under vacuum, first at room temperature for 24 h and then at 100°C for 6 h. Samples without surfactant were prepared as well. Using this procedure, samples with 15 wt% triflate were obtained.

The catalysts were characterized using nitrogen adsorption–desorption isotherms at 77 K; TG-DTA; ^1H, ^{13}C, and ^{29}Si solid state MAS/NMR; XRD; XPS; Raman spectroscopy; and FTIR after adsorption of NH_3. The surface area of the samples containing the surfactant was measured after extraction of the surfactant using the procedure of Hitz and Prins (10).

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The catalytic tests were carried out in a round-bottom flask at atmospheric pressure in flowing dry nitrogen at temperatures in the range 25–60°C. The catalyst (40 mg) was first added to the reactor. After purging the reactor with dry nitrogen for 10 min, 30 ml of the solution of the methyl ester of 1-cyclopentenylacetic acid in the solvent (with a molar ratio of methyl ester to solvent of 1 : 60) was added. Cyclohexene, benzene, toluene, *ortho*- and *para*-xylene were used as solvents. After addition of the reaction mixture, the system was vigorously stirred using a magnetic stirrer. The reaction temperature was controlled within 0.3°C. Separate catalytic tests were carried out using the same number of moles of active species, but instead of the embedded silyl triflate derivative, aluminum chloride, free triflic acid, or mixtures of catalysts without surfactant and surfactant. The reaction products were analyzed in a gas chromatograph coupled with a mass spectrometer (MS). The purity of the products was checked by ^{1}H and ^{13}C NMR.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns indicated amorphous materials, which, according to the nitrogen adsorption–desorption isotherms, corresponded to mesoporous solids. The pore diameter was the same for all the catalysts (2.8 nm) but the surface area varied in the order A1 (483 m^2 g^{-1}) > A2 (461 m^2 g^{-1}) > A3 (412 m^2 g^{-1}). The surface area of the catalysts without surfactant followed the same order order: A1 (572 m^2 g^{-1}) > A2 (549 m^2 g^{-1}) > A3 (508 m^2 g^{-1}), exceeding the values of the samples with surfactant. The pore diameter determined for these samples was around 1.8 nm. Raman spectra indicated the same position of the terminal S=O stretch (967 cm^{-1}) for both embedded and pure silyl triflate derivative. The integrity of the silyl triflate derivative in the embedded catalysts was also supported by the thermal decomposition of the embedded materials compared with pure silyl triflate. The surfactant also remained unaffected as shown by ^{1}H and ^{13}C-NMR analysis. In addition, the signals of C_{14}–C_{16} atoms in single pulse experiments were narrow compared with the same resonance in the cross-polarized spectra, which may suggest a certain mobility of the surfactant in the silica matrix. The XPS Si : S atomic ratios varied in the order A1 (18.2) > A3 (16.8) > A2 (15.4), indicating a slight difference in the superficial distribution of the triflate species. These ratios were very close to the analytical ones, indicating a good dispersion of the derivative in the silica matrix. Slight differences in the S–O bond population could also be appreciated from the FTIR analysis (Fig. 1), as inferred from the differences in the relative intensity of the bands located at 942, 1028, and 1073 cm^{-1}, corresponding to S=O vibrations in various binding modes. The XPS S : F atomic ratios were near 1 : 3 for all the catalysts, in agreement with the chemical formulas. The ^{13}C-CP/MAS NMR spectra exhibited the signals of the CF_3 group at 118 and 123 ppm. However, NH_3-FTIR spectra indicated the presence of Lewis acid sites, as inferred from a band at 1611 cm^{-1}, but also of Brønsted acid sites (bands in the range 1460–1490 cm^{-1}) (Fig. 2). These latter bands may indicate that part of the Si–O–S bond in the silyl-derivative is hydrolyzed, leading to chemisorbed triflate.

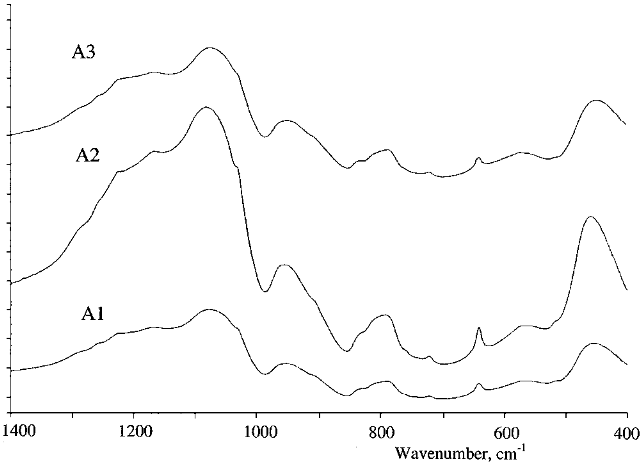


FIG. 1. FTIR spectra of the investigated catalysts.

Table 1 compiles the reaction conditions and the yields of 3-methylbenzaldehyde. The reaction selectively produced 3-methylbenzaldehyde with, except for the hydrogenated part of the solvent, the secondary products being in amounts smaller than 1%. These results indicate that the most important factor in this reaction was the chemical nature of the solvent. Based on the chemical analysis of the products, we suggest that the reaction occurred via the route indicated in Scheme 1, in which the first step of the reaction consists of a ring enlargement, typical of acid-catalyzed reaction. The second step involves a hydrogen transfer from the cyclohexene cycle of intermediate **II** to the solvent, resulting in **III**, which finally undergoes a rearrangement to 3-methylbenzaldehyde (compound **IV** in Scheme 1). It is note worthy that in the absence of an adequate solvent, the reaction does not take place (Table 1). The presence of the hydrogen acceptor molecule is therefore the key factor. Based on these data, one can say that the hydrogen accepting ability in this reaction varies in the order: *p*-xylene > *o*-xylene > cyclohexene ≫ toluene, benzene. The chromatographic analysis indicated in all the cases a stoichiometric reduction of the solvent. Steps **III** to **IV** involve both isomerization and oxygen elimination. The reduction of simple aryl triflates by trialkylammonium formate in the presence of Pd(0) as catalyst has already been reported (11, 12). Very recently, Kamochi and Kudo (13) reported another example in which triflate compounds were found as effective reduction catalysts. These authors reported the reduction of carboxylic acids to the corresponding alcohols using samarium triflate. In the present

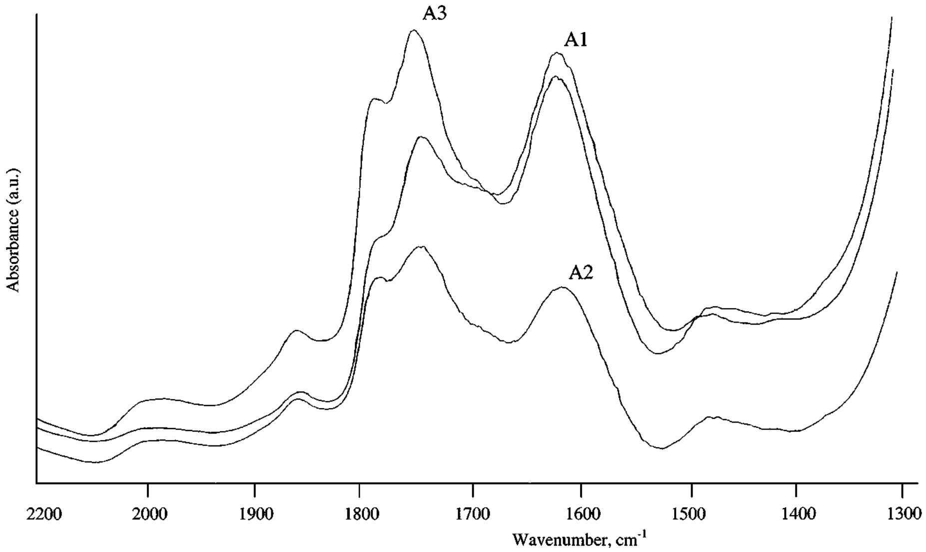


FIG. 2. NH_3-FTIR spectra after the samples were evacuated at 100°C.

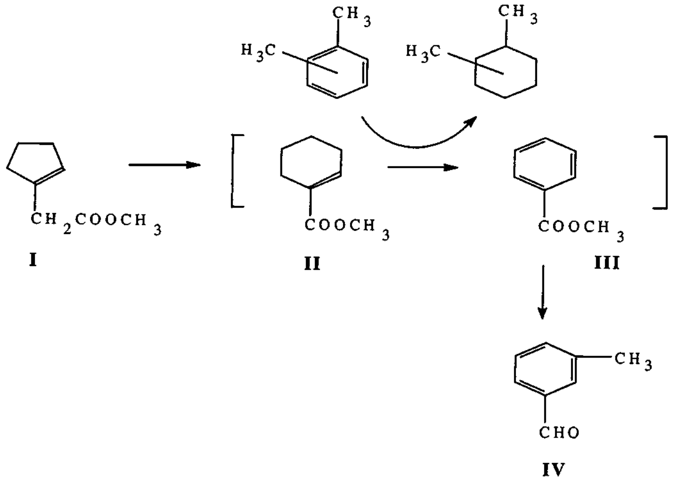
case, neither the noble metal nor the rare-earth element is necessary. During the reaction, aryl triflate may be formed by interaction with the silyl-derivative or cleavage of Si–O–S bonds. The participation of the tetraalkyl ammonium salt in this process can be expected because of its mobility. The reaction may also involve some rearrangements (14) since a compound with $M = 152$ was identified by MS analysis of the by-products.

The analyses did not show the presence of either **II** or **III** intermediates. However, several reasons led us to consider that these intermediates are indeed involved in this reaction. It is already known from the aromatization of alkanes that is easier to dehydrogenate a C6 hydrocarbon than a C5 one, and this step is easily catalyzed by the acid function of the catalysts. This reaction may easily occur in the presence of a Lewis catalyst. Such a behavior has recently been reported for methyl-cyclopentane to benzene on Lewis sulfated zirconia catalysts (15). Therefore, only the passage between **III** and **IV** is a typical and new step for this catalyst. At this moment, we have no explanation for this mechanism,

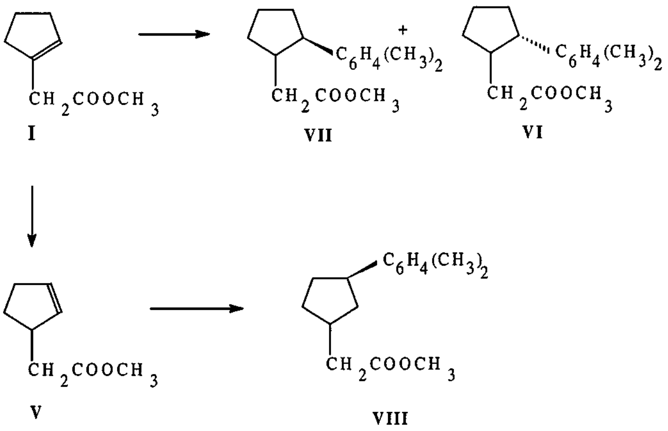
TABLE 1

Conversion and Selectivity to 3-Methylbenzaldehyde

Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion to 3-methylbenzaldehyde (%)	Selectivity (%)
No catalyst	*p*-xylene	60	24	0	0
A1	benzene	25	4	0	0
A1	cyclohexene	60	4	3.2	8.8
A1	cyclohexene	25	24	1.6	97.3
A1	*p*-xylene	60	4	22.8	98.4
A2	benzene	60	4	0	0
A2	*p*-xylene	25	24	11.7	97.8
A2	*p*-xylene	60	4	15.2	98.4
A2	cyclohexene	60	4	2.2	7.1
A3	benzene	60	4	0	0
A3	toluene	60	4	1.2	97.2
A3	*o*-xylene	60	4	5.9	97.3
A3	*p*-xylene	60	4	17.8	98.4
A3	*p*-xylene	60	24	27.8	97.9
A3	cyclohexene	60	4	2.7	7.9
A3 without surfactant	*p*-xylene	60	4	0	0
A3 without surfactant + surfactant	*p*-xylene	60	4	0.5	20.0



SCHEME 1. Reaction route of the methyl ester of the 1-cyclopentenylacetic acid in the presence of embedded *tert*-butyldimethylsilyltrifluoromethanesulfonate and hydrogen acceptor solvent.



SCHEME 2. Reaction routes on pure triflate and $AlCl_3$.

but the data presented in this study clearly indicate that this is a contribution of a heterogeneous catalyst and, more precisely, of a concerted effect of the close proximity of the silyl derivative and the quaternary ammonium salt.

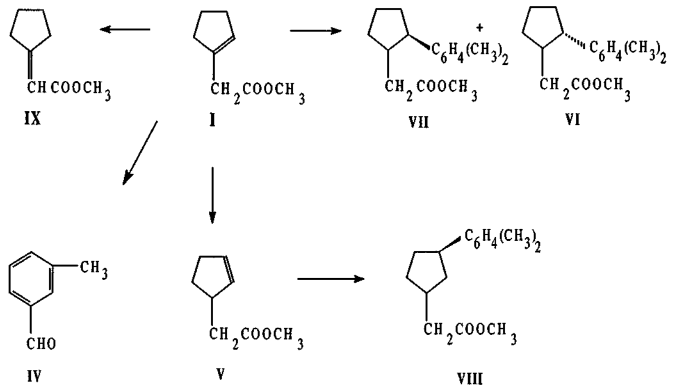
The heterogeneous behavior of the catalysts was confirmed both by the profound dependence of activity on solvent and the analysis of the supernatant resulting after the catalyst separation and another 4 h of reaction. The absence of further reaction is evidence that this reaction is not influenced by the triflate leaching. In addition, because the silyl triflate derivative is insoluble in the solvent used, the supernatant was always a clear solution. It should also be mentioned that catalytic tests done with emulsions of silyl triflate derivative showed that only the Friedel–Crafts alkylation occurred. Additional experiments using $AlCl_3$ as catalyst instead of embedded silyl triflate showed nearly the same results as the pure silyl triflate derivative. The reaction products in this case were the 2-cyclopentenylacetic ester (0.5% for $AlCl_3$ and 9% for triflate) (**V**), *trans*-xylyl-2-cyclopentenylacetic (15.2% for $AlCl_3$ and 16.3% for triflate) (**VI**) and *cis*-xylyl-2-cyclopentenylacetic ester (0.5% for $AlCl_3$ and 9.0% for triflate) (**VII**), and *cis*-xylyl-3-cyclopentenylacetic ester (**VIII**) (63.8% for $AlCl_3$ and 68.4% for triflate) (Scheme 2). The use of free triflic acid as catalyst led to very different results (Table 2). This compound may be expected as a hydrolysis product of silyl triflate derivative during the sol-gel preparation. The analysis of the reaction products indicated that the main reaction routes were exo-isomerization of the double bond and alkylation (Scheme 3). Although small amounts of 3-methylbenzaldehyde were also found, these data show that free triflic acid is not responsible for the results obtained with embedded catalysts; rather it is the silyl triflate derivative in the silica matrix that lies in close proximity to the quaternary ammonium salt.

Additional evidences about the behavior of this catalyst and the contribution of the surfactant to this reaction were provided by the catalytic tests carried out using catalysts without surfactant and mixtures of the catalyst without surfactant and surfactant solved in homogeneous solvent. On the catalysts without surfactant, no 3-methylbenzaldehyde was obtained. The only reaction product was exo-isomerization of the double bond in an amount less than 15%. This is less than we obtained with free triflic acid where, in addition, small amounts of 3-methylbenzaldehyde were also formed. The presence of the surfactant in the reaction mixture led to the formation of 3-methylbenzaldehyde but to a smaller extent than with

TABLE 2

Conversion of the Methyl Ester of 1-Cyclopentenylacetic Acid in the Presence of Triflic Acid (23 mmoles)

Solvent	Temperature (°C)	Time (h)	Conversion to 3-methylbenzaldehyde (%)	Conversion to **IX** (%)	Conversion to alkylated compounds (%)
benzene	60	4	0.3	45.7	3.3
p-xylene	60	4	0.8	15.8	4.8
cyclohexene	60	4	1.6	27.6	9.9



SCHEME 3. Reaction routes on free triflic acid.

the catalyst in which the surfactant was introduced during the synthesis, and comparable with that measured with free triflic acid.

The selectivity to 3-methylbenzaldehyde in the presence of embedded silyl triflate derivative is in good agreement with recent results of Sherman *et al.* (16) on the isomerization of substituted benzenes, showing that, in the presence of a triflate catalyst, *m*-isomers are preferred to *ortho*- or *para*-isomers. The results also show a contribution of the catalyst. Under the investigated conditions, the order of reactivity was A1 > A3 > A2, consistent with the XPS and FTIR data, indicating a proportionality between accessible triflate species and conversion.

In conclusion, embedding of *tert*-butyldimethylsilyltrifluoromethanesulfonate in a silica matrix via a sol-gel carried out in the presence of carbon tetrachloride leads to a heterogeneous catalyst in which most of the triflate derivative remains intact and is homogeneously distributed. This catalyst is able to catalyze selectively (>95%) at low temperature the reaction of the methyl ester of 1-cyclopentenylacetic acid to 3-methylbenzaldehyde. The reused catalysts showed the same activity. The comparison of the embedded catalysts with the pure silyl triflate derivative, $AlCl_3$, or free triflic acid confirms the novelty of these catalysts. Although a partial hydrolysis of the silyl triflate derivative occurs during the synthesis step, the comparative behavior of this catalyst with catalysts without surfactant, and mixtures of the catalyst without and with surfactant, confirms the concerted participation of embedded silyl triflate derivative and surfactant, as an unitary heterogeneous catalyst in this reaction. To the best of our knowledge, both the heterogeneous catalyst and reaction are new.

REFERENCES

1. Murata, S., Suzuki, M., and Noyori, R., *J. Am. Chem. Soc.* **102**, 3248 (1980).
2. Corey, E. J., Cho, H., Rucker, C., and Hua, D. H., *Tetrahedron Lett.* 3455 (1981).
3. Sainte, F., Serckx-Poncin, B., Hesbain-Frisque, A.-M., and Ghosez, L., *J. Am. Chem. Soc.* **104**, 1428 (1982).
4. Clerici, M. G., Perego, C., De Angelis, A., and Montanari, L., Eur. Patent 638 363, 1995.
5. Drysdale, N. E., and Herron, N., WO Patent 9502625, 1994.
6. Wilson, K., Renson, A., and Clark, J. H., *Catal. Lett.* **61**, 51 (1999).
7. Kobayashi, S., and Nagayama, S., *J. Am. Chem. Soc.* **120**, 2985 (1998).
8. Schager, F., and Bonrath, W., *Appl. Catal. A: Gen.* **202**, 117 (2000).
9. Danishefsky, S. J., and Marung, C. J., *J. Am. Chem. Soc.* **107**, 1269 (1985).
10. Hitz, S., and Prins, R., *J. Catal.* **168**, 194 (1997).
11. Peterson, G. A., Kunng, F.-A., McCallum, J. S., and Wulff, W. D., *Tetrahedron Lett.* **28**, 1381 (1987).
12. Chen, Q.-Y., and He, Y.-B., *Synthesis* 866 (1988).
13. Kamochi, Y., and Kudo, T., *Tetrahedron Lett.* **41**, 341 (2000).
14. Effenberger, F., and Gutmann, R., *Chem. Ber.* **115**, 1089 (1982).
15. Pârvulescu, V., Coman, S., Pârvulescu, V. I., Grange, P., and Poncelet, G., *J. Catal.* **180**, 66 (1998).
16. Sherman, S. C., Iretskii, A. V., White, M. G., Gumienny, Ch., Tolbert, L. M., and Schiraldi, D. A., *J. Am. Chem. Soc.*, in press.