Alkylation of phenols and naphthols on silica-immobilized triflate derivatives

Bogdan C. Gagea[a,*], Andrei N. Parvulescu[a], Vasile I. Parvulescu[a], Aline Auroux[b], Paul Grange[c],
and Georges Poncelet[c]

[a] *Department of Chemical Technology and Catalysis, University of Bucharest, B-dul Regina Elisabeta 4-12, Bucharest 70346, Romania*
[b] *Institut de Recherches sur la Catalyse—CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
[c] *Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud, 2/17,
B-1348 Louvain-la-Neuve, Belgium*

Received 27 August 2003; accepted 11 September 2003

Immobilized triflate derivatives ($La(OTf)_3$, AgOTf, *tert*-butyldimethylsilyltrifluoro-methanesulfonate), and triflic acid were found to be effective in the alkylation of phenol and naphthols with *tert*-butanol. The acidic strength and type of acidity (Lewis or Brønsted) are key factors controlling the conversion and product distribution.

KEY WORDS: $La(OTf)_3$; AgOTf; triflic acid; *tert*-butanol.

1. Introduction

Alkylations are electrophilic reactions in nature and many processes for the production of fine chemicals and pharmaceuticals have, as an intermediate step, a Friedel–Crafts-type reaction [1]. Alkylation of aromatics gives rise to valuable intermediates like 1,3,5-trialkylbenzenes, the starting materials for the synthesis of agrochemicals and useful as high-temperature solvents; 4,4′-dialkylbiphenyl, an intermediate in the production of high-performance polymers and with liquid crystal applications; and 2,6-dialkylnaphthalene, a raw material for the manufacture of high-quality polyester fibers and plastics [2]. In the same category of compounds, 2-*tert*-butylphenol (2-TBP) is an intermediate for pesticides, fragrances, and antioxidants; 4-*tert*-butylphenol (4-TBP) is used in the manufacture of phosphate esters, oil field chemicals, demulsifiers, phenolic resins, and polymerization inhibitors, whereas 2,4-di-*tert*-butylphenol is important in the production of antioxidants and UV stabilizers [3–5]. The isomeric O-alkylated phenols also have numerous industrial applications in the production of dyes and agrochemicals [6].

Many of these chemicals are produced in the presence of liquid acids (HF, H_2SO_4) or metal halides ($AlCl_3$, BF_3) as catalysts [7–11]. Although the reaction occurs with good yields and high turnover numbers, the toxic aqueous waste resulting from the catalyst represents an increasing problem from the environmental point of view. Switching from those hazardous materials to solid-acid catalysts presents many additional advantages such as corrosion reduction, easy filtration, reusability, and higher selectivity.

This study reports results of alkylation of phenol and naphthols with *tert*-butanol using as catalysts various silica sol–gel incorporated triflate derivatives ($La(OTf)_3$ (La); AgOTf (Ag); *tert*-butyldimethylsilyltrifluoro-methanesulfonate (BDMST) and triflic acid (HOTf)).

2. Experimental

The catalysts were prepared by sol–gel incorporation of $La(OTf)_3$, AgOTf or *tert*-butyldimethylsilyltrifluoro-methanesulfonate in a silica matrix using a described procedure [12]. Series (1) corresponds to silica supports prepared without surfactant, and series (2) to mesoporous silicas prepared in the presence of $(CH_3)_3C_{16}H_{33}NBr$. HOTf was immobilized by reaction with sol–gel incorporated $Si\text{-}(CH_2)_3\text{-}NH_2$ units. In this case, the support was prepared using the following molar gel composition: TEOS : $Si\text{-}(CH_2)_3\text{-}NH_2$: ethanol : H_2O of 0.05 : 0.05: 0.45 : 0.4. Immobilization of triflic acid was carried out by mixing a solution of 30% HOTf in heptane with the solid containing NH_2 groups in a 1 : 1 ratio for 24 h at room temperature. All the catalysts contained 15 wt% triflate.

The catalysts were characterized by py-FTIR, microcalorimetry of ammonia adsorption, and XPS. Py-FTIR absorption spectra were collected with a Brucker IFS 88 spectrometer (100 scans with a resolution of $1\,cm^{-1}$) in the $4000–400\,cm^{-1}$ range. The powders were pressed into self-supporting disks (12 mg, 13 mm in diameter),

---

[*] To whom correspondence should be addressed.

placed in a glass IR cell with NaCl windows, and treated under vacuum at 200 °C for 2 h before analysis. Then, the sample was exposed to pyridine vapor at room temperature for 30 min. Spectra were recorded after evacuation (9×10^{-3} Pa) for 1 h at room temperature, 100, 200, and 300 °C. The microcalorimetric studies of ammonia adsorption were performed in a heat-flow calorimeter (C80 from Setaram) linked to a conventional volumetric apparatus and equipped with a Barocel capacitance manometer for pressure measurements. Ammonia used for the measurements (Air liquid, >99.9%) was purified by successive freeze-pump-thaw cycles. XPS spectra were obtained with an SSI X probe FISONS spectrometer (SSX-100/206) with monochromated AlKα radiation. The spectrometer energy scale was calibrated using the Au $4f_{7/2}$ peak (binding energy of 84.0 eV).

All the reactions were carried out in a 10-mL stainless steel autoclave provided with a magnetic stirrer and a heating source with a temperature control of ±0.3 °C. A typical experiment used 7 mmoles of phenol or 3.5 mmoles of naphthol, 21-mmoles *tert*-butanol, and 30-mg catalyst. The reaction mixture was heated at 150 °C for phenol, or 180 °C for naphthols, with a heating rate of 20 °C/min. The reaction was stopped by cooling at room temperature after 1 h for phenol and 4 h for the naphthols. The catalyst was separated by simple filtration and the products analyzed by GC-MS, and ^{1}H- and ^{13}C-NMR.

3. Results and discussion

Py-FTIR characterization of these materials indicated that samples containing triflates and BDMST behaved as Lewis catalysts while those with HOTf as Brønsted catalysts. The spectra collected for the first group contain bands assigned to pyridine adsorbed on Lewis acid sites (1445 cm^{-1}, adsorption mode 19b), and as species docked via van der Waals (1490 and 1580–1581 cm^{-1}, adsorption modes 19a and 8b) and H-bonds (1490 and 1594–1598 cm^{-1}). Only very small bands assigned to pyridine adsorbed on Brønsted sites have been detected. Spectra collected for HOTf samples also contain bands at 1640 cm^{-1} (adsorption mode 8a) corresponding to a pyridinium ion bonded to a Brønsted site. The Brønsted acidity of the HOTf samples can be explained by the residual acidity left after the neutralization reaction between a weak base ($\equiv$Si-$(CH_2)_3$-NH_2) and a superacid (HOTf; $H_0 = -14.1$).

XPS results indicated the integrity of the embedded triflates. XPS atomic ratios corresponded to the chemical composition of these structures.

Depending on the reaction temperature and acid strength, alkylation of phenol and naphthols can take place at the oxygen atom (O-alkylation) or at the carbon atom (C-alkylation). The O-alkylation requires weak acid sites and low temperatures, while C-alkylation occurs on stronger acid sites and at higher temperatures. The phenols are polar molecules and even the weakest basic sites can bind the H^{+}, giving the phenoxide ion, which is relatively stable and therefore needs a strong acid site in order to interact with the catalytic surface. A strong acid site will create a stronger interaction with the phenoxide ion, liberating the H^{+} that can further generate carbenium-like ions with the adsorbed *tert*-butanol. These will act as electrophilic agents attacking the aromatic ring.

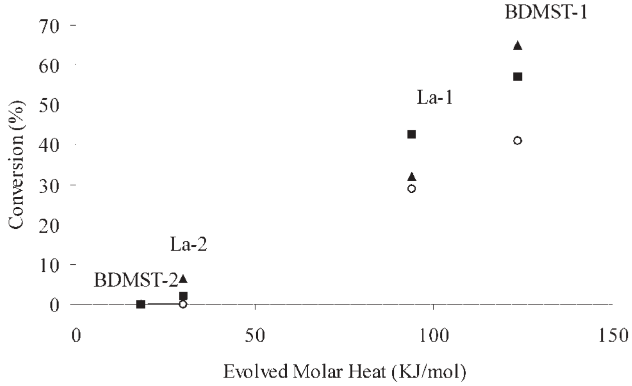

Figure 1. Conversion versus evolved molar heat over Lewis acid catalysts. (▲) Phenol conversion; (○) α-naphthol conversion; (■) β-naphthol conversion.

The strength of the acid sites for all the tested catalysts was determined by microcalorimetry of ammonia adsorption. The results correlated well with the activity of the catalysts in all the alkylation experiments carried out (figures 1 and 2). As expected, an increase of the acidity resulted in a higher conversion. These results indicate that the Brønsted acid catalysts are more effective than the Lewis ones. The presence of the surfactant is detrimental, indicating a direct reaction with triflate derivatives. The acidity of the mesoporous silicas prepared with surfactant is very weak, and, as a consequence, the activity is extremely low.

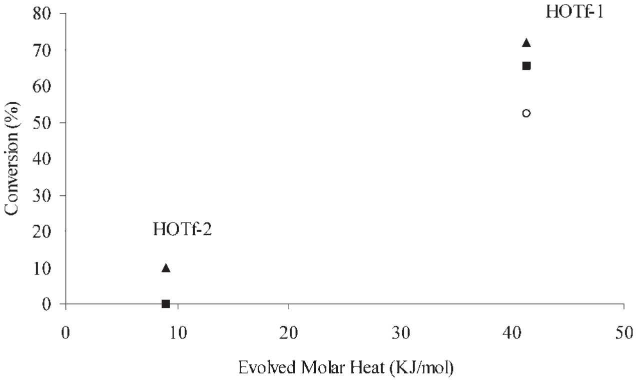

Figure 2. Conversion versus evolved molar heat over Brønsted acid catalysts. (▲) Phenol conversion; (○) α-naphthol conversion; (■) β-naphthol conversion.

Table 1
Product distribution data of phenol alkylation using *tert*-butanol over the catalysts without surfactant[a]

Catalyst	Product distribution of alkyl phenols (mol%)				
	ether	*o*-TBP	*p*-TBP	2,4-DTBP	2,4,6-TTBP
La-1	1.1	40	27.4	30	1.7
Ag-1	0.9	45.7	13	38	2.3
BDMST-1	1.3	45.1	22.9	29.8	0.9
HOTf-1	0.6	24.8	56.7	17.5	0.3

[a]TBA: phenol (molar ratio) = 3 : 1; reaction time = 1 h.

Table 3
Product distribution data of β-naphthol alkylation using *tert*-butanol over the catalysts without surfactant[a]

Catalyst	Product distribution of alkyl naphthols (mol%)		
	ether	3-TBN	3,7-DTBN
La-1	2.8	84	13.2
Ag-1	0.9	83.2	15.9
BDMST-1	1.1	85.8	13.1
HOTf-1	0.6	87.3	12.1

[a]Reaction temperature = 180 °C; TBA: naphthol (molar ratio) = 6 : 1.

At low temperatures, namely, in the range of 50–80 °C, the O-alkylated were the main products, irrespective of the aromatic substrate that was used. The conversion was very small, with a maximum of 10% for phenol and 5% for naphthols, but the selectivity to O-alkylated was higher than 95%. On the Brønsted sites, the phenols adopt an orientation parallel to the surface, thus exposing the *p*-position and the oxygen atom to the electrophilic attack. Such a high selectivity can also be explained because O-alkylation requires much lower temperatures than C-alkylation.

The increase of the reaction temperature above 80 °C led to an increase of the conversion, which reached a maximum at 150 °C for the alkylation of phenol and 180 °C for the naphthols. The C-alkylated products became predominant, while the O-alkylated isomers were found only as traces (tables 1–3). A further increase of the reaction temperature resulted in a decrease of the conversion, because of both the dealkylation and the preponderant reaction of *t*-butanol with itself. Lanthanum, silver, and BDMST catalysts oriented the reaction toward the *o*-isomer, while the catalysts with HOTf produced more *p*-isomers. Tables 1–3 compile the product distribution of the investigated catalysts calculated at 50% conversion for phenol and β-naphthol, and 40% for α-naphthol.

The variation of the selectivity could be explained by the way in which phenol is adsorbed. On Lewis acid sites, adsorption of phenol normal to the surface is more probable [13]. Such an adsorption makes the *o*-position more exposed to the attack of coadsorbed carbenium ions. On Brønsted acid sites, the phenol molecule is adsorbed parallel to the surface, making both the *o*- and *p*-positions equally exposed from a steric point of view. The –OH group kinetically favors the *o*-alkylation. However, because of the steric hindrance, the thermodynamically unfavored *o*-isomer can undergo an isomerization generating the less hindered *p*-isomer. The presence of the bulky *tert*-butyl group in the *o*-position prevents the *o*-isomer to adsorb vertically on a Lewis center. Therefore, for steric reasons the isomerization could not be catalyzed by Lewis sites. The *o*-/*p*-isomerization is possible only on Brønsted sites. Following the same scheme, *o*-TBP could react with TBA to form 2,4-DTBP over strong Brønsted acid sites, while *p*-TBP could perform the same reaction over strong Brønsted or Lewis acid sites. The possibility of a further alkylation to tri-alkylated compounds confirms that the pore size is large enough to allow such a reaction.

Table 2
Product distribution data of α-naphthol alkylation using *tert*-butanol over the catalysts without surfactant[a]

Catalyst	Product distribution of alkyl naphthols (mol%)				
	ether	2-TBN	4-TBN	7-TBN	2,6-DTBN
La-1	1.2	85.6	4.2	3	6
Ag-1	0.1	8	14.4	23.3	54.2
BDMST-1	0.2	20.4	11.4	17.7	50.5
HOTf-1	0.6	40.6	50.2	3.5	5.1

[a]Reaction temperature = 180 °C; TBA: naphthol (molar ratio) = 6:1.

The same adsorption mechanism can explain the product selectivity for the naphthols. When the α-naphthol is orientated vertical on a Lewis acid center, the 2- and 7- positions are closer to the surface, allowing a better interaction with the adsorbed carbenium ions. For β-naphthol, the perpendicular interaction between the –OH group and the Lewis site exposes only the 3-position. The secondary alkylation only gives symmetrical derivatives for both naphthols, namely, the 2,6-isomer for α-naphthol and the 3,7- for β-naphthol. The pore size and shape may be responsible for this behavior. While for α-naphthol the 4- position is a *p*-position, in the case of β-naphthol the similar *p*-position is occupied because of the second aromatic ring. This could explain the selectivity to the *p*-isomer in the case of α-naphthol over the HOTf-based catalysts.

The selectivity of these catalysts is conversion dependent. Illustrative is the case of Ag-1, for which a conversion of 46% corresponded to 46% selectivity in *o*-TBP, while the increase of the conversion at 97% corresponded to only 10% *o*-TBP and 78% 2,4-DTBP. The *p*-TBP selectivity remained almost constant on this catalyst.

Zeolite-like catalysts [14,15], H-AlMCM-41 [16], SAPO-11 [17] catalyze this reaction to *p*-isomer. The remarkable point in using such immobilized triflates is that in the case of phenol, by changing the triflate, the selectivity can be tuned from 53.3% *o*-isomer on La-1 to 77.8% 2,4-DTBP on Ag-1 or 56.7% *p*-TBP on HOTf-1 under similar reaction conditions. Also remarkable is the fact that the TOF obtained over those catalysts, both in phenol and naphthols alkylation, exceeded by at least one order of magnitude the values reported for the other types of catalysts.

No leaching of the catalysts was observed. The hot separation of the catalysts followed by keeping the reactants under the reaction conditions for another 2 h indicated no additional conversion. Also, reuse of the catalysts led to the same performances as in the first run, pointing to the absence of destruction of the active sites by water or reaction products, and confirming no loss of active species.

References

[1] G.A. Olah, R. Krishnamurthy and G.K.S. Prakash, in *Comprehensive Organic Synthesis*, B.M. Trost and I. Fleming (eds), Vol. 3 (Pergamon, Oxford, 1991) p. 293.

[2] R.A. Sheldon and H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysis* (Wiley-VCH, Weinheim, 2001).

[3] A. Knop and L.A. Pilato, *Phenolic Resins Chemistry* (Springer, Berlin, 1985).

[4] K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry*, 3rd ed. (VCH, Weinheim, 1997) p. 358.

[5] *The Merck Index*, 11th ed. (1989).

[6] R. Dowbenko, in *Kirk-Othmer Encyclopedia of Chemical Technology*, J.J. Kroschwitz and M. Howe-Grant (eds), Vol. 2, 4th ed. (Wiley, New York, 1992) p. 106.

[7] G.A. Olah and J.A. Olah, J. Am. Chem. Soc. 98 (1976) 1839.

[8] O.N. Tsevktov and K.D. Kovenev, Int. J. Chem. Eng. 6 (1966) 328.

[9] S. van den Bosch, E. van't Land and J. Stoffelsma, US Patent 4,414,233 (1983) to Polak's Frutal Works, B.V.

[10] N. Yukiya, M. Sadao and H. Shigetoshi, JP 56-060290 (1981) to Mitsubishi Gas Chem Co Inc.

[11] K. Shigeaki and I. Sunao, JP 06-080800 (1994) Matsushita Electric Works Ltd.

[12] A.N. Pârvulescu, B.C. Gagea, V. Pârvulescu, V.I. Pârvulescu, G. Poncelet and P. Grange, *Catal. Today* 73 (2002) 177.

[13] K. Tanabe and T. Nishizaki, in *Proc. 6th Int. Congress on Catalysis*, F.C. Tompkins (ed.) (The Chemical Society, London, 1977) p. 863.

[14] R. Anand, R. Maheswari, K.U. Gore and B.B. Tope, J. Mol. Catal. A 193 (2003) 251.

[15] K. Zhang, C. Huang, H. Zhang, S. Xiang, S. Liu, D. Xu and H. Li, Appl. Catal. A 166 (1998) 89.

[16] A. Sakthivel, S.K. Badamali and P. Selvam, Microporous Mesoporous Mater 39 (2000) 457.

[17] S. Subramanian, A. Mitra, C.V.V. Satyanarayana and D.K. Chakrabarty, Appl. Catal. A 159 (1997) 229.