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Alkylation of hydroquinone with *tert*-butanol over silica-immobilized triflate derivatives

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Silica immobilized La(OTf)$_3$, tertbutyldimethylsilyl-triflate and triflic acid proved to be very efficient catalysts for the hydroquinone alkylation with *tert*-butanol. In solvent free conditons, the conversion was higher than 95% with the dialkylated product (2,5-DTBHQ) formed in high yields. When a polar solvent (1,4-dioxane) was used, the selectivity towards the monoalkylated product (2-TBHQ) increased up to 90%.

KEY WORDS: La(OTf)$_3$; tertbutyl-dimethyl-silyl triflate; triflic acid; alkylation; hydroquinone.

1. Introduction

Alkylphenols are valuable industrial chemicals, among which *tert*-butylated phenols are of particular importance. Among C-alkylation derivatives, 2-*tert*-butylhydroquinone (TBHQ) is an effective storage inhibitor for unsaturated compounds and a highly effective antioxidant for non-food fats, oils, and unstable organic solvents [1,2]. It is also useful as a cook stabilizer for oils and fats [3]. 2,5-di-*tert*-butylhydroquinone (DTBHQ) is useful as an antioxidant for rubber articles, stabilizer against odor and color development in various compositions and as an anti-skinning agent in paints. Generally these derivatives are prepared by alkylation of hydroquinone with isobutylene in the presence of liquid acids catalysts. H_3PO_4 is used for the production of 2-*tert*-butylhydroquinone [4] while for synthesizing 2,5-di-*tert*-butylhydroquinone the reaction occurs in the presence of a sulfonic/H_2SO_4 mixture [5]. 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 to solid-acid catalysts instead of using environmentally hazardous materials brings about many advantages such as corrosion reduction, simple filtration, reusability, and also higher selectivity. Yadav and Doshi reported the alkylation of hydroquinone with methyl-*tert*-butyl-ether and *tert*-butanol in the presence of dodecatungstophosphoric acid (DTP) supported on K10 montmorillonite clay [6]. They obtained good conversions and selectivity in 2-TBHQ when using MTBE as alkylation agent but with *tert*-butanol the results were poor due to catalyst deactivation by the water formed from alcohol dehydration. Recently, another group tested in this reaction a serie zeolites and Al-SBA15 catalysts obtaining good results in terms of selectivity for 2-TBHQ but only at moderate conversions [7].

Metal triflates and other triflate derivatives possess strong Lewis acidity and, in contrast to metal halides, they exhibit a very high tolerance towards water. Therefore, from application point of view, their use may provide more environmentally friendly catalysts. In the recent years, lanthanide trifluoromethanesulfonates (triflates), have been found as very effective Lewis acid catalysts in many organic reactions [8]. Alkyl-silyltrifluoromethanesulfonates were also very active catalysts in a series of reactions catalyzed by Lewis acid sites [9]. Although triflate derivatives proved to be very active Lewis acids there are few reports of their use as Friedel-Crafts alkylation catalysts and to our knowledge only Sc(OTf)$_3$ was used in alkylation with alcohols as alkylation agents [10–12]. Serrano *et al.* reported the use of sulfonic acids (including triflic acid) as catalysts for hydroquinone alkylation using a mixture of alcohol/water as solvent and obtained the 2,5-di-alkyl derivatives [13].

This paper deals with results of alkylation of hydroquinone with *tert*-butanol using as catalysts various silica-immobilized triflate derivatives: La(OTf)$_3$(La); *tert*-butyldimethylsilyl-trifluoromethanesulfonate (BDMST) and triflic acid (HOTf).

2. Experimental

The catalysts were prepared using a sol–gel procedure described in a previous work [14]. Series (1) cor-

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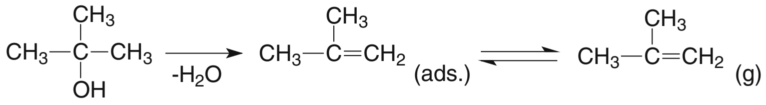
responds to silica supports prepared without surfactant, and series (2) to mesoporous silicas prepared in the presence of $(CH_3)_3C_{16}H_{33}NBr$. HOTf was immobilized by reaction with sol–gel incorporated $\equiv Si-(CH_2)_3-NH_2$ units. A similar method for gererating acid sites into mesoporous materials was reported by Jacobs and co-workers [15]. MCM-41 silicas were first grafted with (3-mercapto-propil)trimethoxysilane and then the thiol functionalities were oxidized into sulfonic groups. Characterization of these materials indicated that samples containing $La(OTf)_3$ and BDMST behaved as Lewis catalysts while those with HOTf as Brønsted catalysts. 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 super acid (HOTf; $H_0 = -14.1$).

Experiments were made in a 10 ml stainless steel autoclave equipped with temperature and pressure measuring devices and a magnetic stirrer. The standard procedure was as follows: 30 mg catalyst with 15% wt. active specie, 7 mmoles hydroquinone (active specie:hydroquinone ratio 1:170 g) and 21 mmoles *tert*-butanol (TBA:HQ molar ratio 3:1) were added in the autoclave. Then the autoclave was introduced in an oil bath heated at 150 °C. The reaction was stopped by cooling at room temperature after 1 h. The catalyst was separated by simple filtration and the products analyzed by GC-MS, and ^1H- and ^{13}C-NMR. In the reaction mixture were identified O-alkylated products (O-*tert*-butylhydroquinone – ether) and C-alkylated derivatives (2-*tert*-butylhydroquinone (2-TBHQ) and 2,5-di-*tert*-butylhydroquinone (2,5-DTBHQ)) along with small amounts of C_8 olefins.

3. Results and discussion

3.1. Reaction mechanism

In the first 5 min of the reaction, the pressure inside the autoclave increased with 6 bar for series (1) catalysts after which it remained constant. When the reaction was stopped by rapid cooling at room temperature, the pressure decreased at 3 bar. For the catalysts prepared with surfactant – series (2), the pressure during the reaction was 3 bar and after cooling only 1 bar. Analyzing samples of gases collected during the reaction proved that *iso*-butylene was the major compound along with vapors of *tert*-butanol. After cooling, the amount of *iso*-butylene in the remaining gases exceeded 95%. Based on these observations we can conclude that the first step is the dehydration of *tert*-butanol with the formation of *iso*-butylene and water. The dehydration reaction is much faster than the alkylation of hydroquinone and the *iso*-butylene produced could not be consumed fast enough until an equilibrium is reached between the *iso*-butylene from the gaseous phase and the *iso*-butylene adsorbed in the *tert*-butanol solution (Scheme 1):



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[-H_2O]{} CH_3-\overset{CH_3}{C}=CH_2\ (ads.) \rightleftharpoons CH_3-\overset{CH_3}{C}=CH_2\ (g)$$

Scheme 1. *Tert*-butanol dehydration.

The amount of water produced from dehydration in the first few minutes of the reaction has been calculated to be 0.8 mmol (series (1) catalysts), which corresponds to an active species (triflate):water molar ratio of 1:50. Thus, water is present in the reaction mixture from the beginning and as the results showed it will not deactivate the Lewis or Brønsted acid sites of the catalysts.

After the dehydration of *tert*-butanol in the reaction mixture two alkylation agents are possible: *tert*-butanol which can generate carbenium like-ions on both Lewis and Brønsted sites and the adsorbed *iso*-butylene which with a H^+ from a Brønsted site forms also carbenium ions. The later mechanism is possible because hydroquinone is adsorbed on the Lewis acid catalysts (La-1 and BDMST-1) as a fenoxid type ion, thus generating H^+ species on the surface which act as Brønsted sites.

3.2. Influence of acid strength

Depending on the reaction temperature and acid strength, alkylation of hydroquinone can take place at the oxygen atom (O-alkylation) or at the carbon atom (C-alkylation). The O-alkylation requires weak acidic sites and low temperatures while C-alkylation occurs on stronger acid sites and at higher temperatures. 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 (Figure 1). 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 at the same acid strength. The presence of the surfactant is detrimental, indicating a direct reaction with triflate derivatives. The acidity of the mesoporous silicas prepared with surfactant (series (2)) is extremely low and, as a consequence, the activity is extremely poor.

3.3. Influence of reaction temperature

The influence of the reaction temperature was studied over the HOTf-1 catalyst and the results are presented in

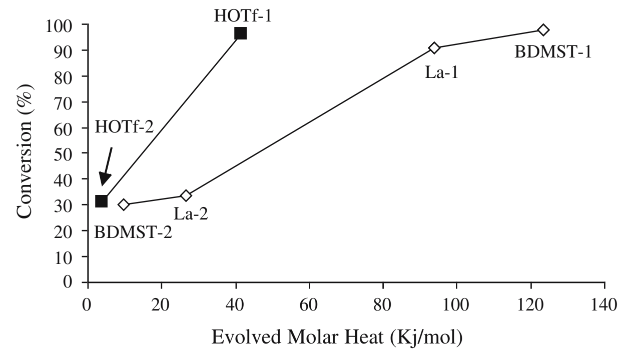


Figure 1. Conversion vs. evolved molar heat over (◇) Lewis and (■) Brønsted acid catalysts ($T = 150$ °C; $t = 1$ h; TBA:HQ = 3:1).

Table 1. At low temperatures (110 °C) the O-alkylated was the main product while the di-alkylated derivate was undetected. The conversion was small, 42.7%, but the selectivity to O-alkylated was high (80.5%) because O-alkylation requires much lower temperatures than the C-alkylation. At higher reaction temperatures, the conversion exceeds 90%, with a maximum of 98.6% at 180 °C and the C-alkylation products are preferred. The major product is 2,5-DTBHQ but at 180 °C the selectivity decreases due to dealkylation and transalkylation reactions.

3.4. *Influence of reaction time*

The reaction time influenced both the conversion and product distribution as shown by the results presented in Table 2 for La-1. The conversion increases with the reaction time reaching a steady value of 90% after 60 min when the thermodynamically equilibrium is reached. The very high TOF, 0.48 mol s^{-1} (calculated after 30 min) indicated that, indeed, the catalyst is very active. The O-alkylated product was found only in traces (less then 1% after 60 min). However, the selectivity was time-dependent. For short reaction times, the major product was the mono C-alkylated one, but as the reaction progressed the second alkylation step was increasing. For a conversion of 90%, 2,5-DTBHQ was about 93%.

Table 1

Reaction temperature vs. conversion and product distribution over catalyst HOTf-1; $t = 1$ h; TBA:HQ = 3:1

Temperature (°C)	Conversion (%)	Product distribution		
		Ether	2-TBHQ	2,5-DTBHQ
110	42.7	80.5	15.6	–
130	92.2	6.2	24.8	69
150	97.5	2.6	18.3	79.1
180	98.6	0.5	39.8	59.7

Table 2

Reaction time vs. conversion and product distribution over La-1; $T = 150$ °C; TBA:HQ = 3:1.

Time (min.)	Conversion (%)	Product distribution		
		Ether	2-TBHQ	2,5-DTBHQ
10	13.9	5.1	67.4	27.5
30	67.5	2.6	54.1	43.3
60	90	0.8	6.2	93
90	90.5	1	29.9	69.1
120	90.6	1.3	38.2	60.5

Water exhibited no effect in this reaction. After 60 min in the presence of 12.3 mmol water, which corresponded to a $La(OTf)_3:H_2O$ molar ratio of 1:1600, the catalyst preserved its activity.

3.5. *Product distribution*

High conversions such 90%, which were obtained for the catalysts of series (1) corresponded to a high selectivity towards the di-alkylated product, 2,5-di-tert-butylhydroquinone. For both La-1 and BDMST-1 catalysts the yield in DTBHQ excepted 90% (Table 3). An exception makes HOTf-1 on which the yield to 2-TBHQ was still ca. 28%. The second C-alkylation reaction occured very rapidly consuming all the mono-alkylated derivate. Series (2) catalysts were unable to afford conversions higher than 35% and the ether was the major product.

3.6. *Influence of the solvent*

A second set of experiments was performed using 1,4-dioxane as a solvent. By using a solvent the TBA:HQ molar ratio could be reduced in order to obtain a higher selectivity in the mono-alkylated product (Table 4). When the TBA:HQ molar ratio is reduced from 3 to 1, 2-TBHQ becomes the major product with a maximum selectivity of 79.5% at 39.1% conversion. Under these conditions only traces of the di-alkylated product resulted. 1,4-dioxane is a weak base due to the electron pairs from the oxygen atoms and therefore can interact with the acid sites reducing their strength. This explains the small conversion rates and why the O-alkylated product is formed in high quantities. All three components (hydroquinone, *tert*-butanol and 1,4-dioxane) compete for the adsorption centers of the catalyst reducing the probability for an efficient adsorption of a

Table 3

Catalyst vs. product distribution; TBA:HQ = 3:1; $T = 150$ °C, $t = 1$ h, catalyst = 30 mg

Catalyst	Product distribution		
	Ether	2-TBHQ	2,5-DTBHQ
La-1	0.8	6.2	93
BDMST-1	2.1	8.6	89.3
HOTf-1	1.2	28.7	70.1

Table 4
Efect of 1,4-dioxane over series (1) catalysts; 2 ml 1,4-dioxane; $T = 150$ °C; $t = 1$ h

Catalyst	TBA:HQ	Conversion (%)	Product distribution		
			Ether	2-TBHQ	2,5-DTBHQ
HOTf-1	3:1	18	57.4	41.8	0.8
HOTf-1	2:1	20.7	32.2	61.9	5.9
HOTf-1	1:1	39.1	18.2	79.5	2.3
La-1	1:1	15.2	48.8	51.2	–
BDMST-1	1:1	68.4	3.3	90.1	6.6

hydroquinone molecule, explaining why the conversion decreased for a higher volume of reactants.

Table 4 compares the catalytic performances of the catalysts in the series 1 for the TBA:HQ molar ratio corresponding to the high conversions. Under these conditions, tert-butyldimethylsilyl-triflate based catalyst (BDMST-1) led to 68.4% conversion and a very good selectivity (90.1%) in the mono C-alkylated derivate, 2-TBHQ. $La(OTf)_3$ based catalyst led only to very poor results in the presence of dioxane. This behavior may be explained by a possible coordination of dioxane molecules at the La^{3+} cation, blocking the Lewis site. However, this catalyst catalyzes the dehydration of *tert*-butanol, proving that, indeed, the dehydration requires less acidic strength than C-alkylation.

4. Conclusions

Silica immobilized $La(OTf)_3$, tertbutyldimethylsilyl-triflate and triflic acid proved to be very efficient catalysts for the hydroquinone alkylation with *tert*-butanol. In solvent free-conditions the conversion was around 90% with the selective formation of 2,5-di-*tert*-butylhydroquinone over the series (1) catalysts. When 1,4-dioxane was used as a solvent the mono-alkylated derivate resulted with 90.1% selectivity for a 68.4% conversion over the BDMST-1 catalyst. In conclusion, by changing the reaction conditions, more precisely the solvent, and the triflate derivate both mono- and di-alkylated products can be obtained with excellent selectivity and high conversions. Water formed as a by-product of the *tert*-butanol dehydration do not deactivate the catalysts.

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