

GENERAL RESEARCH

A Continuous-Flow O-Methylation of Phenols with Dimethyl Carbonate in a Continuously Fed Stirred Tank Reactor

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A new continuous-flow methodology is reported for the selective O-methylation of phenol and *p*-cresol by using dimethyl carbonate as the methylating agent. The reaction has been performed by a continuously fed stirred tank reactor filled with a catalytic bed of poly(ethylene glycol) 1000 and K₂CO₃ as a base. Thus, operating at atmospheric pressure and at temperatures of 160–200 °C, the phenols have been transformed into their corresponding O-methylated derivatives (anisole and *p*-methylanisole, respectively) with substantially quantitative yields: under gradientless conditions, a space velocity of up to $9 \times 10^{-2} \text{ h}^{-1}$ was achieved.

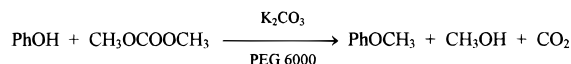
Introduction

O-Methylated phenols (anisoles) are widely utilized in different industrial branches: among other uses, they find major applications as antioxidants in oils and greases manufacture, as stabilizers for plastics, and as starting materials in the production of agrochemicals and dyes.¹ By far, the most common method for the preparation of anisoles is the well-known Williamson ether synthesis,² which is largely employed also for commercial productions through a number of relatively old processes.³ Accordingly, the methylation of phenols is basically performed under liquid-phase conditions by the use of dimethyl sulfate (CH₃OSO₃CH₃; DMS) as the alkylating agent in the presence of a stoichiometric amount of base, usually NaOH. Although synthetically efficient, such procedures pose a serious concern from both the environmental and process safety standpoints; in fact, DMS is a very harmful compound,⁴ and the need for a stoichiometric base results in sizable amounts of inorganic salts as byproducts to be disposed of.

Many alternative methods report the methylation of phenols with methanol under vapor-phase conditions.^{5–10} However, in most cases the O-methyl selectivity (yielding anisoles) is severely limited by the ring methylation (affording cresols); only a few of such procedures claim relevant selectivities (80–90%) in the O-methylation though at relatively low conversions (10–30%).^{11,12}

Instead, a highly selective continuous-flow (c.-f.) transformation of phenols into the corresponding anisoles can be attained by the use of dimethyl carbonate (DMC) as the methylating agent. Such a possibility was

Scheme 1



recognized for the first time by our group some years ago;¹³ we reported that under gas–liquid phase-transfer conditions (GL-PTC),¹⁴ when a mixture of phenol and DMC (in a 1:2 molar ratio) is allowed to flow once over a 100 g catalytic bed composed of 5% PEG 6000 and 95% K₂CO₃ at 180 °C (residence time ~ 10 s), anisole is obtained as the sole product (100% conversion; 100 g of phenol are converted in about 1 h; Scheme 1).

The DMC-mediated c.-f. methylation of phenols has also been reported by different authors describing the use of a number of basic catalytic beds.^{15,16} In all cases, the formation of anisole has been claimed with a very high selectivity at a substantially quantitative conversion of the substrate. For instance, Fu and Ono reported that anisole could be obtained in 91% yield (phenol conversion of 95%, WHSV = 1.85 h⁻¹) at 280 °C and over a sodium-exchanged zeolite (NaX) as a catalyst.^{15a}

Besides the excellent O-methyl selectivity, it is noteworthy that the methylation procedures based on DMC have a relevant environmental significance: DMC is a nontoxic compound, and the reactions can be carried out catalytically so that no wastes are formed.

We report here a new c.-f. methodology for the alkylation of both phenol and *p*-cresol with dimethyl carbonate in a continuously fed stirred tank reactor (CSTR).

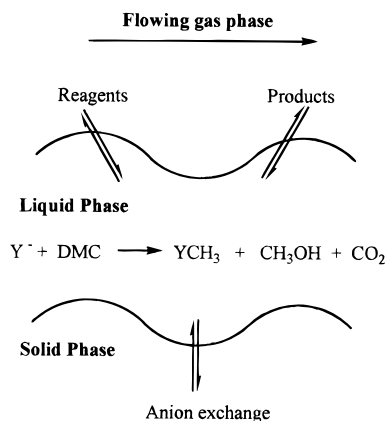
Results and Discussion

As a general rule, c.-f. processes are to be preferred for the case of reactions having low contact times and involving large liquid volumes.^{14,17} On this basis, we were prompted to investigate how the high reaction rate

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Scheme 2. Under GL-PTC Conditions, Reaction Takes Place in the Liquid Film of PEG Covering the Solid Particles of the Base



observed for the methylation of phenols with DMC could be exploited by conceiving different c.-f. conditions, and the starting idea was to realize a system that could perform such reactions by taking advantage of the basic concepts of the GL-PTC.^{13,14}

It seems here convenient to remember that the GL-PTC alkylations through DMC are properly run in a plug-flow (fixed-bed) reactor by feeding continuously a mixture of the reactants over a catalytic bed made up of a high molecular weight poly(ethylene glycol) (PEG) and a solid inorganic base such as K_2CO_3 . While the base is necessary to produce the reacting nucleophiles (Y^-), PEG acts as an anionic activator and it constitutes the appropriate aprotic polar environment in which the reaction takes place (Scheme 2).

At the reaction temperature ($\geq 180^\circ\text{C}$), the PEG is a liquid film covering the solid particles of the base. PEGs are well thermally stable catalysts: in fact, lifetime tests for the methylation of PhOH by DMC in the presence of PEG 6000 (and K_2CO_3) have shown that only at a very high temperature (280°C) does the substrate conversion slightly decrease (from 100 to 95%) after 140 h.¹⁴

According to the configuration of Scheme 2, an applicable alternative to the fixed-bed reactor (the GL-PTC one) seemed to us a CSTR. Stirred tanks are, in fact, particularly suitable to operate also for a three-phasic (gas–liquid–solid) system though in such a case a good agitation must be provided to allow the global uniformity of the reaction parameters and, most of all, the homogeneous stirring of the solid particles.

Thus, a cylindrical entirely glass-made stirred reactor was used (for details, see the Experimental Section). Before each reaction, it was filled to about $\frac{1}{3}$ of its height with the catalytic bed (PEG 1000 and K_2CO_3 , see below) and heated at the desired temperature (160 – 200°C). Under such conditions, the PEG melted and the so-obtained slurry was mechanically stirred at about 2000 rpm. Then, at atmospheric pressure, a mixture of the reagent (phenol or *p*-cresol and DMC) was sent to the CSTR in a way that it continuously bubbled through the catalytic bed. The products were collected by condensation at the outlet of the system (see Chart 1 in the Experimental Section).

Catalytic Bed. The choice of the catalytic bed was done on the basis of our previous experience on the GL-PTC methylations by DMC; accordingly, it was decided to prepare the bed by mixing potassium carbonate as

Table 1. Formation of Anisole in a CSTR at 160°C by Using a Mixture of Phenol and Dimethyl Carbonate in a 1:5 Molar Ratio^a

flow rate (Q), mL/h	time of flowing, h	phenol converted, g	WHSV $\times 100$, ^b $\frac{\text{g}_{\text{prod}}}{\text{g}_{\text{bed}} \text{h}}$
19	2	6.6	1.2
22	5	19.0	1.4
30	2.5	12.9	2.0
50	2	17.3	3.3
70	2.5	30.3	4.5
90	2	31.1	5.8
110	4	76.0	7.1
130	2.5	56.2	8.4
total	22.5	249.4	

^a All reactions were carried out over a catalytic bed of PEG 1000 (300 g) and K_2CO_3 (6 g) using the reactor described in Chart 1.

^b The weight hourly space velocity (WHSV) is defined as the grams of anisole obtained hourly per gram of catalyst.

the base and a PEG. Moreover, to be suitable for the CSTR unit, PEG should have two basic requisites: (i) a low vapor tension (i.e., a rather high MW) to avoid its vaporization during use and (ii) a relatively low viscosity (at the reaction temperature) to allow uniform stirring and contact among the reagents. PEG 1000 ($MW_{\text{av}} = 1000$) adequately answered to the scope. Thus, the catalytic bed for methylation of both phenol and *p*-cresol was prepared as a mixture of PEG 1000 (300 g) and K_2CO_3 (2 wt %, 6.0 g).

Reaction of Phenol. An initial test was performed at 160°C by reacting a mixture of phenol and DMC in a 1:5 molar ratio. The flow rate was 19 mL/h. Under such conditions, the system rapidly reached a steady-state situation. In fact, at the reactor outlet, the gas chromatographic (GC) analysis of the mixture did not reveal any variation of its composition with time: a quantitative conversion was already observed after the first 30 min, yielding anisole as the sole product (100%). This result remained unaltered even when the flow rate was progressively increased from 19 to 130 mL/h. Yet, the steady state was quickly achieved, affording only anisole without any modification of the composition of the outlet mixture with time. On the whole, the system was utilized as reported in Table 1; a total of 249.4 g of phenol was converted into anisole in 22.5 h, with a space velocity (WHSV) spanning over the range of $(1.2\text{--}8.4) \times 10^{-2} \text{ h}^{-1}$.¹⁸

Moreover, because a CSTR is "gradientless" and, in principle, it allows a perfect mixing of the reagents, when a suitable feeding rate is used, a constant product concentration (with time) should be observed in a way that the composition of the outlet mixture should be equal to that present inside the reactor itself.^{14,17}

Bearing this in mind, we checked the composition of the mixture in the reactor: at intervals during the reaction, small samples (0.2–0.3 g) of the catalytic bed were withdrawn and analyzed. Regardless of the flow rate, the only detected product was anisole in all cases: under the explored conditions, the system was working in the absence of intrareactor gradient concentration.

The reaction was then investigated by increasing the phenol/DMC molar ratio (R) from 0.2 (1:5) to 0.5 (1:2); it was carried out over the same bed used for the first test. Thus, at 160°C , the reagents' mixture was sent to the reactor at different flow rates (Q) of 60, 80, 120, and 140 mL/h. During this run, the bed processed a total of 720 g of phenol (2644 g of the mixture of PhOH and DMC) and it worked for about 18.5 h (see ref 18). The steady state was always quickly reached.

Table 2. Formation of Anisole in a CSTR at 200 °C by Using a Mixture of Phenol and Dimethyl Carbonate in a 1:1.05 Molar Ratio^a

flow rate (<i>Q</i>), mL/h	time of flowing, h	mixture composition, % by GC ^b			
		PhOCH ₃		PhOH	
		outlet	cat. bed	outlet	cat. bed
50	3	100	87	0	13
60	2.5	100	75	0	25
70	2	98	67	2	33
80	2.5	97	52	3	48

^a All reactions were carried out over a catalytic bed of PEG 1000 (300 g) and K₂CO₃ (6 g) using the reactor described in Chart 1. ^b The percent amounts (by GC) of anisole and phenol were determined both in the outlet mixture (outlet) and in the catalytic bed (cat. bed).

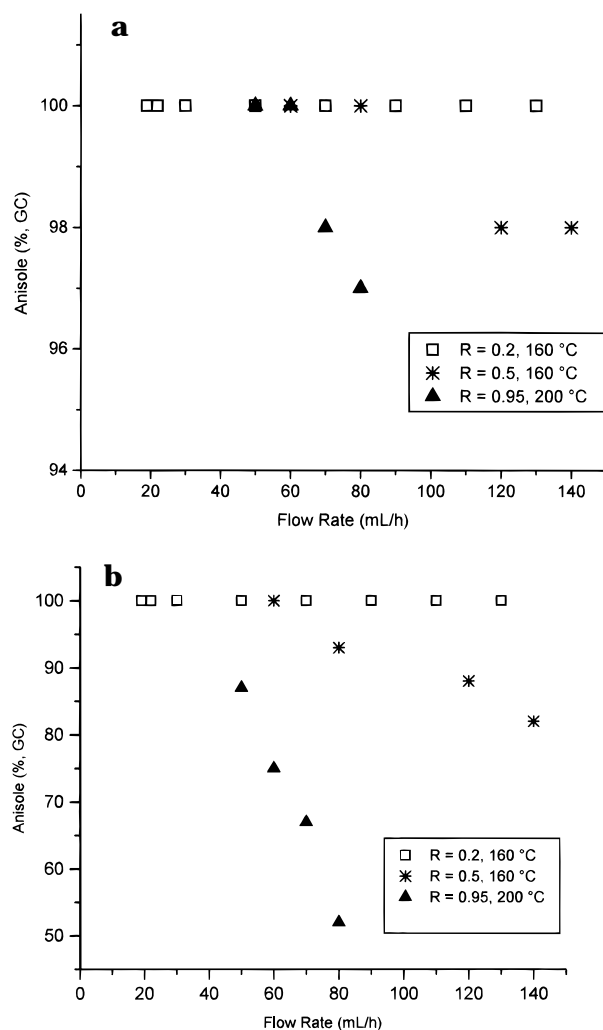
However, when *Q* was increased over 60 mL/h, some unconverted phenol appeared in the GC analyses of both the outlet mixture and the catalytic bed. In particular, the phenol amounts were of 7, 12, and 18% (by GC) inside the bed, and of 0, 2, and 2% in the condensed mixture, at flow rates of 80, 120, and 140 mL/h, respectively, with the remainder being anisole. Moreover, at a *Q* of 140 mL/h, the level of the mixture inside the reactor was visibly raised about 2 cm from the point where it constantly was during the previous runs, when operating at lower *Q* values. At 160 °C and *R* = 0.5, such a flow rate (140 mL/h) appeared to be the upper operating limit of the geometry of the used CSTR though at the outlet anisole was still recoverable in a 98% purity.

The reaction was then carried out at 200 °C and by further increasing the *R* ratio; a new catalytic bed having the composition indicated above (PEG 1000, 300 g; K₂CO₃, 6 g) was used. Two runs were subsequently executed by setting *R* to 0.67 and 0.95 (PhOH:DMC = 1:1.5 and 1:1.05, respectively). In the first case (*R* = 0.67), the flow rate was progressively enhanced from 50 to 70 and 100 mL/h. The latter (100 mL/h) was found to be the upper feeding limit: a visible overloading of the reactor occurred. In the second situation (*R* = 0.95), the end point corresponded to a *Q* of 80 mL/h. The results are reported in Table 2.

Moreover, to get a more direct comparison of the behavior of the CSTR under all of the investigated conditions, Figure 1 reports the anisole amount (percent by GC) detected in both the outlet mixture (Figure 1a) and inside the catalytic bed (Figure 1b) versus the flow rate of the reactants' mixture. The shown trends refer to the three different *R* ratios used (0.2, 0.5, and 0.95). Data indicate that when *R* was 0.2, the CSTR was gradientless under all of the explored range of *Q*, working at a WHSV of up to $8.4 \times 10^{-2} \text{ h}^{-1}$. The same occurred at *R* = 0.5 provided that *Q* was $\leq 70 \text{ mL/h}$; under such conditions, the reactor efficiency was well comparable to the previous one, showing a maximum WHSV of about $9.0 \times 10^{-2} \text{ h}^{-1}$.

Despite the higher reaction temperature (200 vs 160 °C), a significant difference between the internal and external concentrations of the flowing mixture was always manifest at *R* = 0.95. However, anisole could be attained with a complete selectivity in all cases; at the reactor outlet, it ranged from 97 to 100%, with the remainder being unconverted phenol.

Reaction of *p*-Cresol. *p*-Cresol was reacted with DMC at 160 °C on a new catalytic bed (composition was previously described) and using two different *R* ratios of 0.33 and 0.67 (*p*-cresol:DMC = 1:3 and 1:5, respec-

**Figure 1.** Anisole amount (a) at the CSTR outlet and (b) inside the catalytic bed of the CSTR using different PhOH:DMC molar ratios (*R*) and reaction temperatures.**Table 3. Reaction of *p*-Cresol with Dimethyl Carbonate in a CSTR^a**

flow rate (<i>Q</i>), mL/h	time of flowing, h	<i>p</i> -cresol/DMC molar ratio (<i>R</i>)	mixture composition, % by GC ^b			
			<i>p</i> -methylanisole		<i>p</i> -cresol	
			outlet	cat. bed	outlet	cat. bed
50	3	0.33	100	100	0	0
70	5	0.33	97	97	3	3
90	2	0.33	96	96	4	4
70	4	0.67	99	96	1	4
80	4	0.67	98	92	2	8

^a All reactions were carried out over a catalytic bed of PEG 1000 (300 g) and K₂CO₃ (6 g), using the reactor described in Chart 1. ^b The percent amounts (by GC) of *p*-methylanisole and *p*-cresol were determined both in the outlet mixture (outlet) and in the catalytic bed (cat. bed).

tively). The results are reported in Table 3. The reaction behaved similarly to that of phenol; thus, when *R* was 0.33, the reactor operated gradientless in the investigated range of flow rates (*Q* = 50, 70, and 90 mL/h). Substantially quantitative conversions of *p*-cresol into *p*-methylanisole were attained (96–100%) with a WHSV of up to $9.5 \times 10^{-2} \text{ h}^{-1}$. However, as *R* was increased to 0.67, the amount of the nonreacted *p*-cresol inside the reactor increased as well, at each *Q*, though the com-

position of the outlet mixture still showed 98–100% of the O-methylated derivative.

Conclusions

The here-reported selective O-methylation of phenols joins the well-known advantages of the c.-f. operating mode to relevant environmentally benign features: (i) the alkylating agent (DMC) as well as the inexpensive poly(ethylene glycol) (PEG 1000) used as an anion activator is a nontoxic compound; (ii) the reaction is truly catalytic, producing no inorganic wastes to be disposed of; (iii) the reaction is properly run at atmospheric pressure and does not originate any dangerous gaseous stream; (iv) the coproduct methanol can be easily separated from anisoles.

The used CSTR can work gradientless, affording a WHSV of up to $\sim 9 \times 10^{-2} \text{ h}^{-1}$ for the methylation of both phenol and *p*-cresol; however, even when the reactor is forced to diverge from such a condition by increasing the *R* ratio (substrate:DMC molar ratio) or the feeding flow rate (*Q*), the O-methylated derivatives are still recovered in a very high purity (96–100%) at the outlet of the reactor.

Under all of the investigated conditions, the used catalytic beds have very good chemical and thermal stabilities: they have been tested for up to 7 days (8 h/day¹⁸), finding no appreciable changes in their efficiency. Moreover, no leaching effects of the catalyst have been observable: the GC analysis of the CSTR effluent has never shown the presence of PEG 1000.

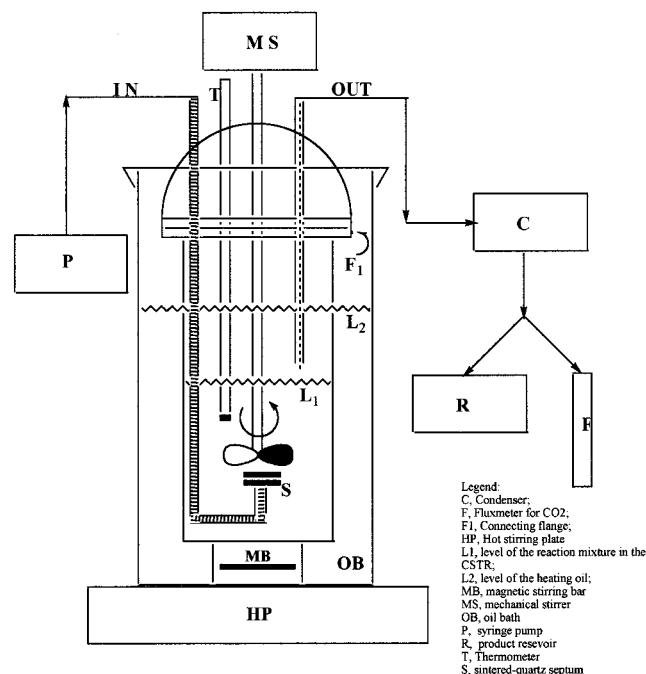
Experimental Section

All of the compounds used were ACS grade and were employed without further purification. In particular, phenols [both phenol (99%) and *p*-cresol (99%)], K_2CO_3 (99%), and PEG 1000 ($MW_{av} = 1000$; Aldrich catalog no. 20, 242-8) were supplied by Aldrich Chemical Co. (Divisione Italiana Aldrich, Milano, Italy) while dimethyl carbonate (DMC; 99%) was a generous gift of Enichem (Ravenna, Italy). GC analyses were performed on a Varian GC 3400 using a 30 m, DB5 capillary column. GC/MS analyses were performed on an HP 5971 mass detector at 70 eV coupled to an HP 5890 series II gas chromatograph fitted with a 30 m, DB5 capillary column.

Features of the CSTR and the General Procedure for the Continuous-Flow Methylation of Phenols by DMC. The stirred reactor used for the experiments is reported in Chart 1. It was entirely built in glass and was constituted by two main units: a cylindrical tank of a capacity of 600 mL ($\Phi_{int} = 200 \text{ mm}$) and a hemispheric cap provided with inlet/outlet glass pipes ($\Phi_{int} = 6 \text{ mm}$), and two conic adapters to receive a thermometer (T) and the bar of a mechanical stirrer (MS), respectively. The two units were coupled by a flange (F_1), which in turn was held in position through two fastening rings and four steel clips. The heating of the reactor was performed by dipping the tank (until $\frac{2}{3}$ of its total height) into a 3 L beaker filled with silicone oil (OB) itself heated at the desired temperature (160–200 °C; the heating took about 1 h) through an electric hot plate (HP; the homogeneity of the bath temperature was assured by keeping the oil under a vigorous magnetic agitation).

The inlet of the reactant mixture (DMC and phenol or *p*-cresol in the reported molar ratio; see Tables 1–3)

Chart 1. Schematic Plot of the CSTR Used for the Methylation of Phenols by DMC



occurred at atmospheric pressure: it was allowed by a syringe pump (P, flow rate of up to 200 mL/h) connected to the inlet pipe. The latter proceeded vertically throughout the length of the reactor and ended with a sintered-quartz septum (S) at about 1 cm over the bottom of the reactor. In this way, at the reaction temperature, the mixture could vaporize and bubble uniformly inside the catalytic bed, which in turn was kept under active stirring (up to 2200 rpm). At the reactor outlet, the gaseous stream passed in a condenser (C): products were condensed and analyzed by GC and GC/MS, while the CO₂ released from the reaction flowed into the fluxmeter (F). At intervals (2.5 h), the condensed mixture was distilled and the yield of anisole determined.

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Literature Cited

- (1) Dorothea, G. Phenol Derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry*; Barbara, E., Stephen, H., Gail, S., Eds.; VCH Verlagsgesellschaft: Weinheim, Germany, 1991; Vol. A19.
- (2) (a) Fener, H.; Hooz, J. Methods of Formation of the Ether Linkage. In *The Chemistry of the Ether Linkage*; Patai, S., Ed.; Interscience Publishers: London, 1967; Chapter 10, pp 445–498. (b) Hiers, G. S.; Hager, F. D. Anisole. In *Organic Syntheses*, 2nd ed.; Gilman, H., Blatt, A. H., Eds.; Wiley: New York, 1941; Collect. Vol. I, pp 58–60.
- (3) McCormack, W. B.; Lawes, B. C. Sulfuric and Sulforous Esters. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley & Sons: New York, 1978; Vol. 22, p 236 and references therein.
- (4) Ono, Y. Dimethylcarbonate for Environmentally Benign Reactions. *Pure Appl. Chem.* **1996**, *68*, 367–75.

(5) KiwiMinsker, L.; Porchet, S.; Doepper, R.; Renken, A. Catalyst Acid/Base Properties to Control the Selectivity in Gas-Phase Methylation of Catechol. *Stud. Surf. Sci. Catal.* **1997**, *108*, 149–156.

(6) (a) Velu, S.; Swamy, C. S. Effect of Substitution of $\text{Fe}^{3+}/\text{Cr}^{3+}$ on the Alkylation of Phenol with Methanol over Magnesium–Aluminium Calcined Hydrotalcite. *Appl. Catal. A* **1997**, *162*, 81–91. (b) Velu, S.; Swamy, C. S. Selective C-Alkylation of Phenol with Methanol over Catalysts Derived from Copper–Aluminium Hydrotalcite-like Compounds. *Appl. Catal. A* **1996**, *145*, 141–153. (c) Velu, S.; Swamy, C. S. Alkylation of Phenol with Methanol over Magnesium–Aluminium Hydrotalcites. *Appl. Catal. A* **1994**, *119*, 241–252.

(7) Landau, M. V.; Kogan, S. B.; Tavor, D.; Herskowitz, M.; Koresh, J. E. Selectivity in Heterogeneous Catalytic Processes. *Catal. Today* **1997**, *36*, 497–510.

(8) Sato, S.; Koizumi, K.; Nozaki, F. Ortho-Selective Methylation of Phenol over CeO_2 Catalyst. *Appl. Catal. A* **1995**, *133*, L7–L10.

(9) Bautista, F. M.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M.; Romero, A.; Navio, J. A.; Macias, M. Anion Treatment (F^- and SO_4^{2-}) of $\text{AlPO}_4\text{--Al}_2\text{O}_3$ (25wt-Percent Al_2O_3) Catalysts. 4. Catalytic Performance in the Alkylation of Phenol with Methanol. *Appl. Catal. A* **1993**, *99*, 161–173.

(10) Agayev, A. A.; Tagiyev, D. B. Alkylation of Phenol by Methanol on Type-Y Zeolites. *Pet. Chem.* **1992**, *32*, 101–105.

(11) Pierantozzi, R.; Nordquist, F. Selective O-alkylation of Phenol with Methanol. *Appl. Catal.* **1986**, *21*, 263–271.

(12) Renaud, M.; Chantal, P. D.; Kalliaguine, S. Anisole Production by Alkylation of Phenol. *Can. Chem. Eng.* **1986**, *64*, 787–791.

(13) Tundo, P.; Trotta, F.; Moraglio, G.; Ligorati, F. Continuous-Flow Processes under Gas–Liquid Phase-Transfer (GL-PTC)

Conditions. The Reaction of Dialkyl carbonates with Phenols, Alcohols, and Mercaptans. *Ind. Eng. Chem. Res.* **1988**, *27*, 1565–1571.

(14) (a) Tundo, P. *Continuous-Flow Methods in Organic Synthesis*; Ellis Horwood: Chichester, U.K., 1991. (b) Tundo, P.; Selva, M. Simplify Gas–Liquid Phase-Transfer Catalysis. *CHEMTECH* **1995**, *25* (5), 31–5.

(15) (a) Fu, Z. H.; Ono, Y. Selective O-methylation of Phenol with Dimethyl carbonate over X-zeolites. *Catal. Lett.* **1993**, *21*, 43–47. (b) Fu, Y.; Baba, T.; Ono, Y. Vapor-Phase Reaction of Catechol with Dimethyl carbonate. *Appl. Catal. A* **1998**, *166*, 425–430.

(16) (a) Bautista, F. M.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M.; Romero, A. A.; Urbano, M. R. Phenol Methylation over CrPO_4 and $\text{CrPO}_4\text{--AlPO}_4$ Catalysts. *React. Kinet. Catal. Lett.* **1997**, *62*, 47–54. (b) Bautista, F. M.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M.; Romero, A. A. Alkylation of Phenol with Dimethylcarbonate over AlPO_4 , Al_2O_3 , and $\text{AlPO}_4\text{--Al}_2\text{O}_3$ Catalysts. *React. Kinet. Catal. Lett.* **1998**, *63*, 261–269.

(17) Carrà, S.; Morbidelli, M. Gas–Liquid Reactors. In *Chemical Reaction and Reactor Engineering*; Carberry, J. J., Varma, A., Eds.; Marcel Dekker: New York, 1987; Chapter 9, pp 545–666.

(18) It has to be noted that the reactant mixture was sent to the reactor for about 8 h/day. After that time, the catalytic bed was cooled to 100 °C and kept under stirring overnight before restarting the reaction the next day.

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