Catechol *O*-methylation with dimethyl carbonate over different acid–base catalysts

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Received (in Montpellier, France) 7th April 2006, Accepted 21st June 2006
First published as an Advance Article on the web 14th July 2006
DOI: 10.1039/b605053k

A series of meso and microporous materials, previously described and characterised, were tested in the catechol *O*-alkylation process using methanol (MeOH) and dimethyl carbonate (DMC) as alkylating reagents. In this regard, interesting results in terms of catalytic activity and selectivity to the desired monomethylated product (guaiacol) compared to the dimethylated one (veratrole) were found for the majority of the catalysts. Moreover, DMC is a better methylating agent than methanol with respect to the conversion ratio of catechol and guaiacol. The presence of n-type nucleophilic centres (oxygen from the OH groups) together with π-type ones (aromatic ring) in catechol led only to *O*-alkylated (guaiacol and veratrole), whereas no *C*-alkylated products were found under the reaction conditions. $AlPO_4$ and, especially, $AlPO_4$–Al_2O_3 systems showed the best performance in this alkylation process in comparison with silicoaluminophosphates (SAPO) and some acidic commercial zeolites (H-Y, H-β and H-ZSM-5).

Introduction

Alkylation reactions are among the most important reactions in organic chemistry.[1–3] In this regard, while heterogeneously catalysed alkylations are widely employed in the production of alkylbenzenes (ethylbenzene, toluene, xylenes, *etc.*), the use of stoichiometric reagents is still the common alkylation procedure in the majority of the processes. The most common methods use dimethyl sulfate or alkyl halides as alkylating agents in a reaction usually carried out in liquid phase. These agents exhibit some problems associated with toxicity, corrosiveness, the need for stoichiometric amounts of base, salt waste and separation and recovery procedures. So, an important issue deals with the replacement of stoichiometric reactions by catalytic ones, where the use of heterogeneous catalysis with vapour-phase reactants is strongly preferred.

These important drawbacks can be overcome by replacing stoichiometric reagents with non-toxic ones such as methanol (MeOH) and/or dimethyl carbonate (DMC), even though these reagents are not as reactive as the previous ones, and also replacing stoichiometric reactions by catalytic reactions.

The development of cleaner processes is of special interest in order to meet global competition and conform to environmental specifications. The use of solid acids to replace waste generating soluble acids attained vast interest in recent years due to its non-corrosiveness, environmental benign nature, reusability as well as minimization of undesired toxic wastes. Materials can also be tuned to give higher activity, selectivity and longer catalyst life.

Thus, solid materials are preferred, acid and/or basic catalysts being the best candidates for these reactions due to their easy separation and recycling after the reaction workup. Recently, an increasing interest in developing new synthetic routes for high added value chemicals, minimising the waste production as well as employing heterogeneous catalysis has arisen.[4] The methylation reaction of catechol, a typical acid-catalyzed reaction, is of both industrial and academic relevance as well as an example of this type of process, using MeOH or DMC rather than an alkyl halide, over heterogeneous catalysts. The distribution of products (*O*-/*C*-methylation ratio) is largely dependent on reaction parameters such as temperature, reactant concentration, acid–base properties and the pore size of the catalyst used.

The main products that can be obtained in the methylation process are guaiacol and veratrole, ring-methylated products (methylguaiacols and methylveratroles) as well as other products (heavies), which come, mainly, from the condensation of two or more catechol molecules (Scheme 1). Moreover, *O*-alkyl-catechols [guaiacol (gua) and veratrole (ver)] are important as chemicals and chemical intermediates, in the fine chemistry industry for the synthesis of flavouring agents, fragrances, agricultural chemicals and pharmaceuticals,[5] guaiacol being of special value.

Guaiacol and veratrole have been commonly synthesized from catechol and guaiacol methylation, respectively, either using corrosive and toxic reagents such as dimethyl sulfate and NaOH as homogeneous catalyst[5–7] or using an alkyl halide (methyl iodide) and NaOH in THF at room temperature.[5–8]

In homogeneous conditions, guaiacol has also been synthesized using dimethyl carbonate and NaOH/NaI.[8]

A wide range of materials have been investigated as catalysts for the process. These included pure and doped metal oxides, mixed metal oxides, sulfates, metal phosphates and zeolites.[9–18] The activity–selectivity patterns as well as

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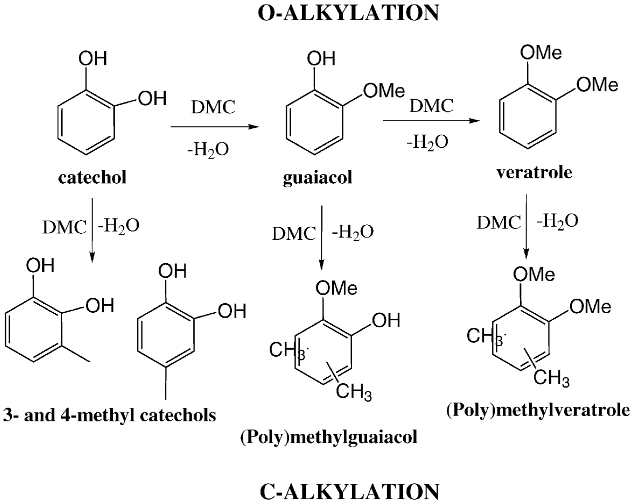

Scheme 1 Catechol alkylation reaction scheme.

optimum reaction temperature of the catalyst is primarily governed by its acid–base properties and by the methylating agent used, MeOH or DMC. Recently, some authors have reported the vapour-phase alkylation of catechol with DMC[9–12] and MeOH,[13–18] which leads, mainly, to the mono- and di-methylated products. In this way, DMC was reported to be a potential harmless and versatile methylating agent.

In this paper, we wish to join the latest contributions to this field, presenting a greener approach to this process in which heterogeneous catalysis and more environmentally friendly reagents (DMC) have replaced the homogeneous conditions as well as the stoichiometric reagents.

Experimental

Synthesis of materials

$AlPO_4$ catalysts (designed as AP-X) were obtained by precipitation, from aluminium chloride and H_3PO_4 aqueous solutions, with aqueous ammonia (X = A), ethylene oxide (X = E) or propylene oxide (X = P).[19] A mixture of 79.2 g $AlCl_3 \cdot 6H_2O$, 23.2 mL H_3PO_4 (85 wt%) and 334 mL distilled water were gently stirred and cooled at 273 K, followed by the dropwise addition of an aqueous solution of either ammonia (AP-A), propylene oxide (AP-P) or ethylene oxide (AP-E), respectively. The addition was continued until complete precipitation of the $AlPO_4$ (pH ~ 7). After 24 h, the material was filtered, washed thoroughly with 2-propanol, oven dried at 393 K for 24 h and subsequently calcined at 923 K for 3 h. Therefore, the AP-A material obtained was an $AlPO_4$ material obtained after precipitation with aqueous ammonia (-A). Thus, the use of ethylene (-E) and propylene (-P) oxides instead of aqueous ammonia as precipitating reagents led to materials named AP-E and AP-P, respectively.

$AlPO_4$–Al_2O_3 catalysts (15 and 25 wt% Al_2O_3, respectively) were obtained by adding $Al(OH)_3$ to a reaction medium where the precipitation of the $AlPO_4$ (from $AlCl_3 \cdot 6H_2O$ and H_3PO_4) was initiated by the addition of aqueous ammonia. A mixture of 156 g $Al(NO_3)_3 \cdot 9H_2O$ and 498 mL distilled water were gently stirred and cooled at 273 K, followed by the dropwise addition of an aqueous solution of either ammonia until complete precipitation of the aluminium hydroxide. On the other hand, a mixture of 238 g $AlCl_3 \cdot 6H_2O$, 70 mL H_3PO_4 (85 wt%) and 1000 mL distilled water were stirred and cooled at 273 K, again adding an ammonia aqueous solution until the aluminium phosphate, initially precipitated, was not able to redissolve into the reaction medium (pH 4). Both solutions were then mixed and more aqueous ammonia was added until complete precipitation of the $AlPO_4$–Al_2O_3 system. After 24 h, the gel obtained was washed thoroughly with 2-propanol, oven dried at 393 K for 24 h and finally calcined at 923 K for 24 h.

These materials were designed as APAL-A-Y, where A was, as for the $AlPO_4$ materials, the precipitating H_3PO_4 solution (aqueous ammonia) and Y is a number that refers to the alumina wt% content in the materials (either 15 or 25). Therefore, the APAL-A-15 material prepared was an $AlPO_4$–Al_2O_3 material (APAL) obtained after precipitation with aqueous ammonia (-A) with a 15 wt% of alumina (-15).

Likewise, a fluorine modified $AlPO_4$–Al_2O_3 material (APAL-A-15FM was synthesized by stirring the APAL-A-15 in an NH_4F water–methanol solution for 20 min, containing 2.5 wt% of F^-. Both materials ($AlPO_4$ and $AlPO_4$–Al_2O_3) were calcined at 923 K for 3 h.[19] Al_2O_3 and MgO were obtained after thermal decomposition of the hydroxide precursors, generated from the nitrate aqueous solutions followed by precipitation with ammonium hydroxide up to pH 7.

Microporous SAPO were obtained from fumed SiO_2, boehmite and H_3PO_4, in the presence of different amines such as tri-*n*-propylamine (SAPO-5), di-*n*-propylamine (SAPO-11 and SAPO-31 and diethylamine (SAPO-41) by a hydrothermal procedure at 473 K for 24 h followed by calcination in air at 873 K.[20]

H-Y, H-ZSM-5, and H-β zeolites were commercially available from Zeolyst Inc. Textural properties of all catalysts are summarised in Table 1.

Characterisation

Materials have been previously synthesized and characterised as reported in the literature.[19,20]

Surface acid–basic measurements. The surface acidity was measured in a dynamic mode by means of the gas-phase adsorption of pyridine (Py) at 473 and 573 K, respectively, using a pulse chromatographic technique.[21] The surface basicity was measured by means of the liquid-phase (298 K) adsorption of benzoic acid (BA) and phenol (PH) using a spectrophotometric method.[22] Data is presented in Tables 2 and 3, respectively.

Catalytic testing

The vapour-phase alkylation of catechol with DMC was carried out in a vertical down-flow reactor (5 mm, i.d.) at atmospheric pressure and at temperatures in the range 573–623 K. Temperature was measured with an iron–constantan thermocouple placed in the middle of the catalyst bed. The catalyst samples (*ca.* ~30 mg) were pretreated at 573 K for 1 h in an N_2 flow (50 mL min^{-1}). The catechol–DMC mixture (2 M, 40 μL min^{-1}) was fed from the top through a syringe

Table 1 Textural properties [surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) of different meso- and microporous materials

Catalysts	S_{BET}/ $m^2\ g^{-1}$	D_p/Å	Vp/ mL g^{-1}	$S_{\mu p}{}^a$/ $m^2\ g^{-1}$	$V_{\mu p}{}^a$/ mL g^{-1}
AP-A	109	17.6	0.48	—	—
AP-P	228	13.6	0.75	—	—
AP-E	242	8.6	0.52	—	—
APAL-A-25	244	6.2	0.37	—	—
APAL-A-15	267	11.8	0.77	—	—
APAL-A-15FM	165	17.0	0.70	—	—
MgO	23	—	0.09	—	—
Al_2O_3	151	8.2	0.31	—	—
SAPO-5	183	—	0.08	128	0.12
SAPO-11	110	—	0.07	65	0.06
SAPO-31	115	—	0.08	63	0.03
SAPO-41	91	—	0.07	117	0.04
SAPO-34	119	—	0.06	83	0.06
H-Y-5.2	660	—	—	—	—
H-β-75	650	—	—	—	—
H-ZSM-5-30	400	—	—	—	—

[a] Microporous surface area and volume obtained from the Harkins and Jura method.

pump (Hardward 4400-001) at a space velocity (W/F) of 220 s and was vaporized prior to passing it through the catalyst bed in the presence of a flow of nitrogen carrier gas (50 mL min^{-1}). In order to prevent any condensation of reactant and products, all connections were heated at 548 K. Blank runs at 723 K showed that under the experimental conditions used in this work, thermal effects could be ignored.

The products were sampled on-line and analysed in a FISONS GC 8000 series by using a column (2m × 3mm) of 10% OV-1 on Chromosorb WS DMCS 80/100. The alkylated catechols were also characterized by GC-MS, finding the guaiacol and veratrole as main products. Under the reaction conditions, no C-alkylated products (3 and 4-methylcatechols) were found.

Finally, response factors of the reaction products were determined with respect to catechol from GC analysis using known compounds in calibration mixtures of specified compositions.

Table 2 Surface acidity properties [pyridine (Py) and 2,6(DMPy) titration at different temperatures] of different meso- and microporous materials

Catalyst	Py at 473 K/ μmol g^{-1}	Py at 573 K/ μmol g^{-1}	DMPy at 573 K/ μmol g^{-1}
AP-A	81	15	4
AP-P	166	23	16
AP-E	240	33	29
APAL-A-25	118	41	17
APAL-A-15	156	61	50
APAL-A-15FM	201	99	30
MgO	—[a]	—[a]	—[a]
Al_2O_3	18	10	—
SAPO-5	—	145	—
SAPO-11	—	95	—
SAPO-31	—	65	—
SAPO-41	—	10	—
SAPO-34	—	17	—
H-Y-5.2	—	326	—
H-β-75	—	278	—
H-ZSM-5	—	373	—

[a] No base adsorption.

Table 3 Surface base properties of the $AlPO_4$ and $AlPO_4$–Al_2O_3 systems (15–25 Al_2O_3 wt%), and the metal oxides (MgO and Al_2O_3) for the benzoic acid (BA) and phenol (PH) titration in liquid phase at 473 K

	Basicity/μmol g^{-1}	
Catalyst	BA	PH
AP-A	200	81
AP-P	166	56
AP-E	266	120
APAL-A-25	535	166
APAL-A-15	402	161
APAL-A-15FM	395	148
MgO	—[a]	—[a]
Al_2O_3	556	194

[a] Not measured.

Results and discussion

Previous results of experiments performed using a pulse chromatographic method showed that DMC was an efficient methylating agent compared to MeOH, since the alkylation reaction can be carried out at relatively lower temperatures with improved selectivity to the desired *O*-alkylated products (Table 4).[11,12,23] Also, the molar ratio catechol : DMC is an important issue to consider, increasing markedly the selectivity to guaiacol at lower molar ratios (1 : 2 *vs.* 1 : 4).[12,23]

Similarly, DMC has been reported as a non toxic and environmentally benign chemical,[24] as the lowest photochemical ozone creator potential (POCP) among common volatile organic compounds (VOCs) (2.5, ethylene = 100),[24,25] stressing the greenness of our protocol.

Surface acid–basic properties

Starting with the acid properties, $AlPO_4$–Al_2O_3 systems exhibited improved surface acid properties compared to $AlPO_4$ materials, increasing at the same time, in the systems, when decreasing their alumina content (from 25 to 15 wt%). As expected, when increasing the temperature from 473 to 573 K, the materials' surface acidity, as measured by pyridine titration, decreased as a consequence of the activation of the strongest acid sites that are the only ones retaining the adsorbed base (Table 2). In addition, these materials also exhibited surface basic sites (Table 3), thus showing their bifunctional character.[19] In terms of basicity, the Al_2O_3

Table 4 DMC *vs.* MeOH performance [total conversion (X_T) and selectivity to guaiacol (S_{gua})] in the catechol *O*-alkylation reaction over different $AlPO_4$ materials[a]

	MeOH 2 M			DMC 2 M		
Catalyst	Temp./K	X_T	S_{gua}	Temp./K	X_T	S_{gua}
AP-A	573	11.7	87.2	523	24.9	87.8
AP-P		7.3	80.6		32.5	93.1
AP-E		5.5	93.3		27.9	86.0

[a] Pulse chromatographic method (amount = 2 μL).

Table 5 Total conversion (X_T, mol%), product selectivities (S_i, mol%) and reaction rate (k 10^{-4}, s^{-1}) in the catechol *O*-alkylation reaction with DMC over different catalysts (I)[a]

		4 h on stream				12 h on stream			
Catalyst	Temp./K	X_T	S_{gua}	S_{ver}	k 10^{-4}	X_T	S_{gua}	S_{ver}	k 10^{-4}
AP-A	573	2.9	81.9	18.1	1.4	1.8	82.1	17.9	0.9
	623	5.3	90.8	9.2	2.5	3.4	91.1	8.9	1.6
	573Py[b]	3.4	93.7	6.3	1.6	2.9	95.3	4.7	1.4
AP-P	573	5.9	80.1	19.9	2.9	4.0	79.8	20.2	2.0
	623	11.3	80.0	20.0	5.6	7.2	80.5	19.5	3.5
	573Py[b]	7.2	85.6	14.4	3.5	6.9	88.7	11.3	3.3
AP-E	573	8.1	90.0	10.0	4.0	4.0	89.2	10.8	1.9
	623	9.7	89.3	10.7	4.8	5.0	88.4	11.6	2.4
	573Py[b]	8.3	94.1	5.9	4.1	7.2	95.0	5.0	3.5
MgO	573	—[c]	—	—	—	—[c]	—	—	—
Al_2O_3	573	—[c]	—	—	—	—[c]	—	—	—
APAl-A-25	573	5.9	98.9	1.1	2.9	3.9	98.0	2.0	1.8
	623	5.7	98.4	1.6	2.6	3.4	96.7	3.3	1.6
	573Py[b]	—[d]	—	—	—	—[d]	—	—	—
APAl-A-15	573	10.9	98.3	1.7	5.3	8.0	97.7	2.3	3.8
	623	8.2	96.1	3.9	4.0	5.1	93.6	6.4	2.4
	573Py[b]	11.2	100.0	—	5.3	9.0	98.0	2.0	4.2
APAl-A-15FM	573	11.1	97.6	2.4	5.4	6.9	97.4	2.6	3.3
	623	7.5	92.6	7.4	3.6	3.2	82.0	18.0	1.5
	573Py[b]	10.6	100.0	—	5.4	7.9	98.7	1.3	4.0

[a] $F = 1.33 \times 10^{-6}$ mol s^{-1}; W/F = 220 s; 2 M catechol in DMC. [b] Deactivated with pyridine. [c] No reaction under the stated conditions. [d] Not measured.

incorporation to the $AlPO_4$ provided systems $AlPO_4$–Al_2O_3 with a higher number of basic centres in comparison with the $AlPO_4$.

On the other hand, the acidity measurements carried out for the microporous materials (SAPO and zeolites) proved that these materials display a greater number of strong acid sites when compared to $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts (Table 3).

Catechol *O*-methylation

Catechol conversions, reaction rate constants and product selectivities of the alkylation of catechol with DMC are collected in Tables 5 and 6. Moreover, Fig. 1 and 2 showed the deactivation curves of the different catalysts as a function of the reaction time. Under the reaction conditions (including catechol conversion <20%), as we have pointed out before, the main products obtained were the *O*-alkylated ones, that is, guaiacol and veratrole for $AlPO_4$, $AlPO_4$–Al_2O_3, SAPO-5 and commercial zeolites.

Table 6 Total conversion (X_T, mol%), selectivity to guaiacol (S_{gua}, mol%) and reaction rate (k 10^{-4}, s^{-1}) in the catechol *O*-alkylation reaction with DMC over different catalysts (II)[a]

		4 h on stream			12 h on stream		
Catalyst	Temp./K	X_T	S_{gua}[c]	k 10^{-4}	X_T	S_{gua}[c]	k 10^{-4}
SAPO-5	573	—	—	—	—	—	—
	623	1.9	96.9	0.9	1.7	96.5	0.8
SAPO-11	573	2.0	96.4	0.9	1.7	96.0	0.8
SAPO-31	573	—[b]	—	—	—	—	—
SAPO-41	573	—[b]	—	—	—	—	—
SAPO-34	573	—[b]	—	—	—	—	—
H-Y-5.2	573	0.6	99.0	0.4	—	—	—
H-β-25	573	1.0	84.3	0.5	0.7	82.9	0.3
H-ZSM-5-30	573	1.5	95.0	0.7	0.9	94.3	0.4

[a] $F = 1.33 \times 10^{-6}$ mol s^{-1}; W/F = 220 s; 2 M catechol in DMC. [b] No reaction under the stated conditions. [c] The difference to 100 corresponds to the veratrole selectivity (S_{ver}).

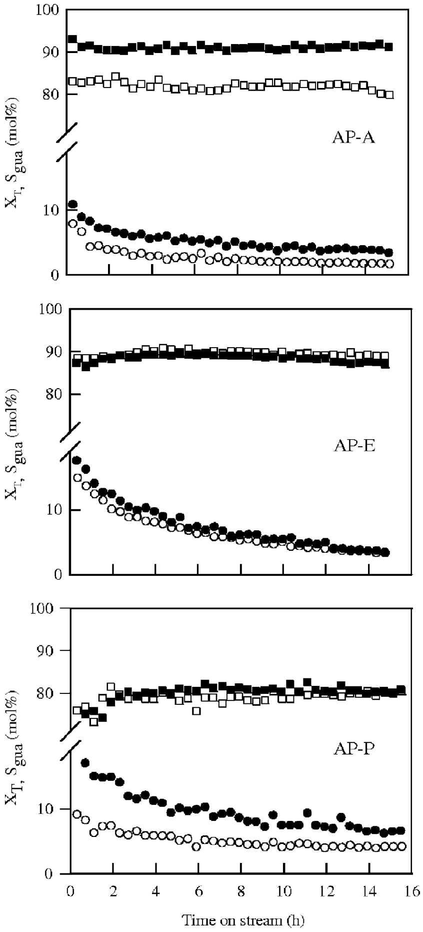

Fig. 1 Deactivation curves with time on stream; conversion (X_T, mol%) and guaiacol selectivity (S_{gua}, mol%) of $AlPO_4$ materials in the catechol *O*-methylation reaction at 573 K (○ = X_T, □ = S_{gua}) and 623 K (● = X_T, ■ = S_{gua}), respectively.

$AlPO_4$ and $AlPO_4$–Al_2O_3 systems. Data summarised in Table 5 manifest that the reaction rate constants follows the order AP-A < AP-P < AP-E on $AlPO_4$ catalysts, as the surface acidity increases in this order, without a noticeable change in terms of selectivity to guaiacol. The incorporation of Al_2O_3 to $AlPO_4$ developed $AlPO_4$–Al_2O_3 systems that exhibited increased activity as compared to $AlPO_4$ catalysts (Table 5). In a similar way as for the $AlPO_4$ materials, the catalytic activity increases when increasing the surface acidity/basicity as well as with the temperature, following the order APAL-A-25 < APAL-A-15 ~APAL-A-15FM. In terms of selectivity, these materials showed an improvement in the guaiacol selectivity, obtaining selectivities close to 100% to the monomethylated product. In spite of the better performance of these $AlPO_4$–Al_2O_3 systems compared to the $AlPO_4$ ones, a temperature increase not only did not improve the catalytic

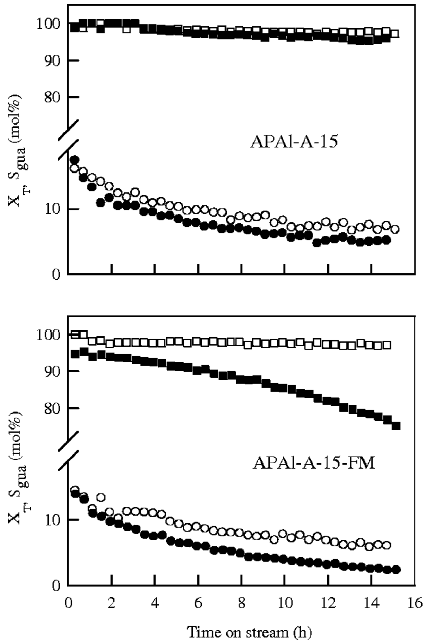

Fig. 2 Deactivation curves with time on stream; conversion (X_T, mol%) and guaiacol selectivity (S_{gua}, mol%) of $AlPO_4$–Al_2O_3 systems in the catechol *O*-methylation reaction at 573 K (○ = X_T, □ = S_{gua}) and 623 K (● = X_T, ■ = S_{gua}), respectively.

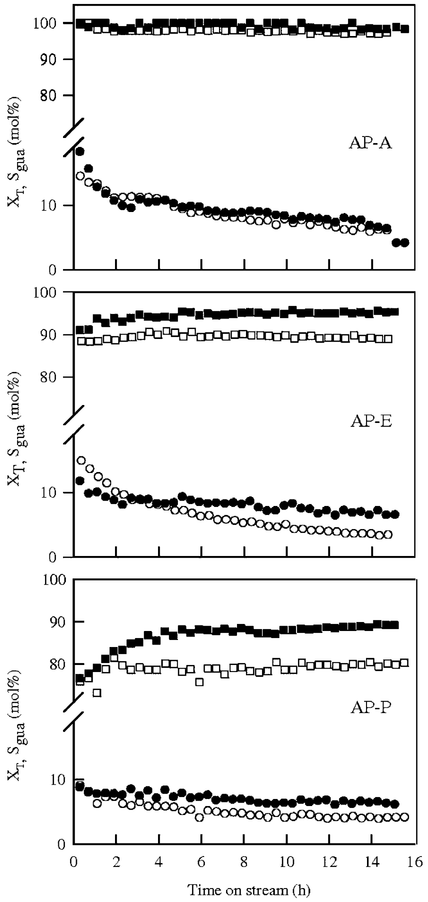

Fig. 3 Deactivation curves with time on stream; conversion (○ = X_T) and guaiacol selectivity (□ = S_{gua}) of fresh $AlPO_4$ materials *versus* (● = X_T) and (■ = S_{gua}) of $AlPO_4$ pyridine treated (20 µL min^{-1}, 15 min) in the catechol *O*-methylation reaction.

activity in the materials but also led to a decrease in the total conversion and the guaiacol selectivity. This decrease was even more perceptible in the more acidic APAL-A-15FM material due to an increase in the coke formation throughout the reaction course. In general, these materials deactivate with time on stream, losing almost 50% of the catalytic activity after 12 h of reaction, particularly the $AlPO_4$ materials (Fig. 1), whereas the $AlPO_4$–Al_2O_3 systems were slightly less deactivated (around 35–40%) after 12 h (Fig. 2).

In any case, the deactivation rate is a function of the reaction temperature as well as of the surface acid/basic properties of the catalysts. In this sense, the higher the reaction temperature and/or the materials surface acidity, the higher the deactivation rate. Nevertheless, in most cases, the product distribution does not change noticeably with time on stream, guaiacol being the main reaction product.

Therefore, in acid/basic materials such as the $AlPO_4$ and $AlPO_4$–Al_2O_3 systems, the *O*-alkylation takes place in acid/basic pairs as has been proposed before,[12,18] whereas the *C*-alkylation takes place, generally, in strong basic sites.

MgO and Al_2O_3 oxides. Moreover, MgO, a basic metal oxide, as well as Al_2O_3, an acid/basic metal oxide, exhibited a poor performance in the *O*-methylating process (less than 3% conversion), being completely deactivated after 3 h of reaction, indicating that the basic or acid properties of the catalysts by themselves (if not strong enough) did not play an important role in the reaction. This may be caused by the strong adsorption of CO_2 at MgO and Al_2O_3 basic sites and due to the low surface area and acidity values for the MgO and Al_2O_3, respectively. Indeed, Jyothi *et al.*[12] have reported that, after the alkylation process takes place *via* nucleophilic attack of the DMC (once activated), the residual methyl hydrogen carbonate decomposes to form CO_2, which is probably adsorbed in the catalysts basics sites, causing the MgO and Al_2O_3 quick deactivation.

So, medium to strong acidic sites are possibly required for the *O*-methylation of catechol with DMC. However, from this evidence, basic sites are also required in addition to acidic sites in order to attain catalysts with high activity.

Microporous SAPO and zeolitic materials. On the other hand, microporous materials such as silicoaluminophosphates (SAPO) and commercial zeolites exhibited a poor performance in the catechol alkylation reaction (Table 6). SAPO materials showed very low conversion values, increasing the catalytic activity, in general, when the surface acidity increases, whilst a temperature increase has no significant effect for these systems. High selectivities were achieved for the monomethylated product. It is noticeable that zeolitic materials proved themselves as very poor catalysts for the catechol alkylation reaction. The extremely low catalytic activity of zeolites is attributed to the rapid deactivation of the catalysts, basically due to their high surface acidity and lower pore diameter in comparison with the mesoporous ones, so that, the pores of zeolites were probably blocked by the oligomeric products.

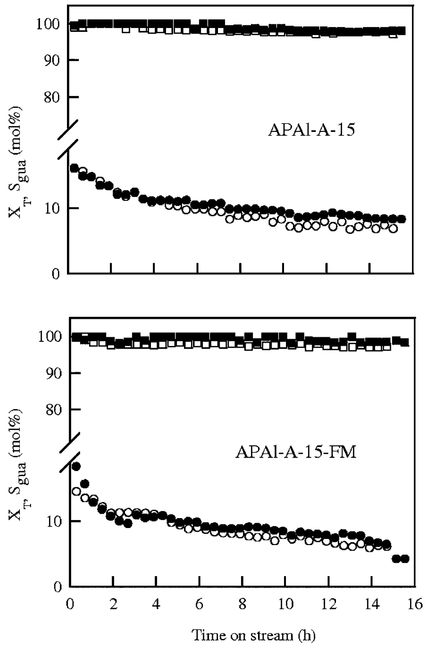

Fig. 4 Deactivation curves with time on stream; conversion (○ = X_T) and guaiacol selectivity (□ = S_{gua}) of fresh $AlPO_4$–Al_2O_3 systems *versus* (● = X_T) and (■ = S_{gua}) of $AlPO_4$–Al_2O_3 pyridine treated (20 μL min^{-1}, 15 min) in the catechol *O*-methylation reaction.

The high acid Brønsted sites strength in these materials led to a preferential parallel catechol adsorption over the catalysts surface as shown by Tanabe *et al.*,[26] possibly causing a disrupted interaction between the π-electrons within the aromatic ring and the Brønsted acid sites, therefore leading to the molecule destruction and coke formation. This coke formed deposits over the catalyst surface, thus blocking the active acid centres, which caused the quick zeolites deactivation in the early reaction stages.

In summary, $AlPO_4$ and $AlPO_4$–Al_2O_3 systems showed far higher catalytic activity and guaiacol selectivity than microporous SAPO, and commercial zeolite materials, in spite of their higher acid properties.

Pyridine poisoning experiments. Poisoning experiments were carried out, prior to the alkylation process, by deactivating the materials with pyridine. Pure pyridine (20 μL min^{-1}; 15 min) was passed through the catalyst bed with an N_2 flow of 50 mL min^{-1} at 573 K. The catalyst was later stabilised for 30 min under these conditions, before the *O*-methylation process took place. Data are summarised in Table 5 and Fig. 3 and 4.

In general, we can assert that the pyridine poisoning treatment definitely has an effect over the materials catalytic activity. In terms of activity, in most cases, initial total conversion for the materials remained almost unchanged or slightly diminishes, which makes sense if one considers that pyridine is adsorbed on the acid centres over the catalyst surface, therefore deactivating these centres. However, catalysts treated with pyridine experienced a lower deactivation with time on stream compared to the fresh materials (Fig. 3 and 4). Such a different behaviour became more noticeable when increasing the reaction time (Table 5).

Table 7 Total conversion (X_T, mol%), selectivities to guaiacol (S_{gua}, mol%) and reaction rate constants (k 10^{-4}, s^{-1}) of the $AlPO_4$ reused in the catechol *O*-methylation process[a]

			2 h on stream			6 h on stream		
Catalyst	Temp./K	Carrier	X_T	S_{gua}	k 10^{-4}	X_T	S_{gua}	k 10^{-4}
AP-A	573	Air	4.1	80.5	1.9	2.4	79.4	1.1
AP-P	573	O2	5.2	77.9	2.5	3.2	79.5	1.5
AP-E	573	Air	7.4	88.9	3.7	4.2	88.3	2.0
	623		9.4	88.8	4.7	5.5	88.1	2.7

[a] $F = 1.33 \times 10^{-6}$ mol s^{-1}; W/F = 220 s; 2 M catechol in DMC.

Guaiacol selectivities were also affected, increasing, in general, for the poisoned materials in comparison with the fresh ones. This increase in the guaiacol selectivity was more noteworthy for $AlPO_4$ materials (Fig. 3). Results pointed out that the unavailability of the strong acidic centres over the catalysts surface after the pyridine deactivation, led to an improvement of the total conversion and guaiacol selectivity with time on stream thus supporting the fact that the strong acid/basic centres were basically involved in deactivation processes (coke formation) and di-methylation (veratrole

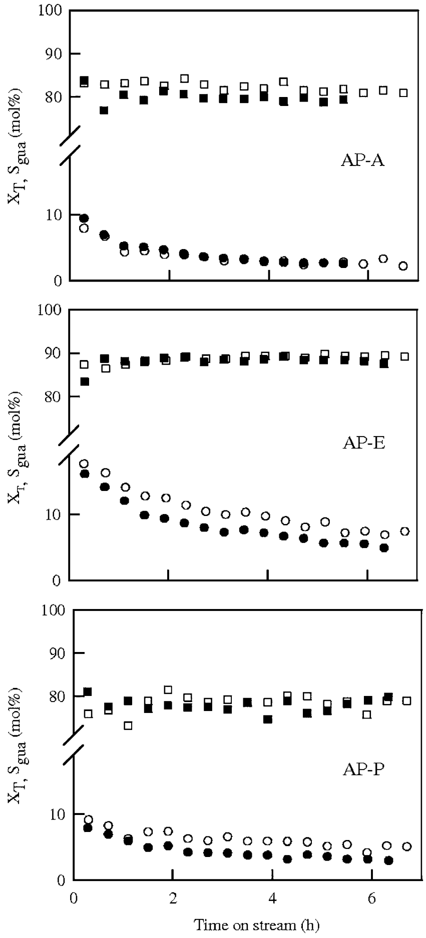

Fig. 5 Reactivation experiments; Conversion (● = X_T) and guaiacol selectivity (■ = S_{gua}) of regenerated $AlPO_4$ *versus* (○ = X_T) and (□ = S_{gua}) fresh $AlPO_4$ materials.

formation), whereas weak to medium strength acid /basic centres were responsible for the mono-methylation process.

Reusability experiments. Reusability experiments were carried out after completion of the *O*-methylation reaction. In this sense, after 20 h on stream, catalysts were regenerated in a carrier (air or oxygen, 50 mL min^{-1}) oxidant flow, increasing the temperature from 573 to 873 K (10 K min^{-1}). After stabilizing the materials at 873 K for 1 h, the methylating process was performed again. Results are shown in Table 7 and Fig. 5, respectively.

As shown in Fig. 5, all $AlPO_4$ materials are regenerated to a variable extent. Thus, the degree of reactivation is higher for the less acidic $AlPO_4$ catalyst (AP-A). On the other hand, selectivities remained almost unchanged with time on stream for both reactivated and fresh materials. Finally, we also found that the catalyst regeneration was independent of the carrier employed in the reactivation procedure.

Conclusions

Amorphous $AlPO_4$–Al_2O_3 catalysts exhibited higher catalytic activity and guaiacol selectivity than amorphous $AlPO_4$, microporous SAPO-5 and zeolitic materials. Moreover, $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts exhibited greater activity and selectivity when strong acid sites were deactivated with pyridine. Due to the presence of strong acid sites, H-ZSM-5, H-Mordenite, H-β and H-Y zeolites rapidly deactivate (due to coke formation) in comparison with $AlPO_4$ and $AlPO_4$–Al_2O_3. Consequently, our results indicate that strong acid sites are not required for the *O*-methylation of catechol and that weak to medium strength pairs of acid/basic sites are responsible for the mono-methylation process.

Acknowledgements

This research was subsidized by grants from the Dirección General de Investigación (Projects CTQ2004-21662-E and CTQ2005/04080/BQU), Ministerio de Ciencia y Tecnología, FEDER funds, and from the Consejería de Educación Ciencia (Junta de Andalucía).

References

1 J. Cejka and B. Wichterlova, *Catal. Rev. Sci. Eng.*, 2002, **44**, 375.
2 K. Sreekumar and S. Sugunan, *Appl. Catal., A*, 2002, **230**, 245.
3 C. Perego and P. Ingallina, *Green Chem.*, 2004, **6**, 274.
4 J. H. Clark and D. J. Macquarrie, in *Handbook of Green Chemical Technology*, Blackwell Science, Oxford, 2002.
5 G. Dorothea, in *Phenol Derivatives, Ullmann's Encyclopedia of Industrial Chemistry*, ed. E. Barbara, H. Stephen and S. Gail, VCH, Verlagsgesellschaft, Weinheim, 1991, p. 354.
6 A. Matsukuma, I. Takagishi and K. Yoshido, *Jpn. Pat. Appl.*, 7357935.
7 A. Barbara, N. Stoochnoff and L. Benoiton, *Tetrahedron Lett.*, 1973, **1**, 21.
8 M. M. Marcello, R. Ugo and R. Franco, *Ing. Chim. Ital.*, 1985, **21**, 6.
9 Y. Fu, T. Baba and Y. Ono, *Appl. Catal., A*, 1999, **176**, 201.
10 Y. Fu, T. Baba and Y. Ono, *Appl. Catal., A*, 1999, **178**, 219.
11 M. B. Talawar, T. M. Jyothi, T. Raja, B. S. Rao and P. D. Sawant, *Green Chem.*, 2000, **2**, 266.
12 T. M. Jyothi, T. Raja, M. B. Talawar and B. S. Rao, *Appl. Catal., A*, 2001, **211**, 41.
13 L. Kiwi-Minsker, G. Jenzer, L. Pliasova and A. Renken, *Stud. Surf. Sci. Catal.*, 1999, **121**, 159.
14 F. Cavani and T. Monti, *Catalysis of Organic Reactions*, Marcel Dekker, New York, 2000, p. 123.
15 F. Cavani, T. Monti and D. Paoli, *Stud. Surf. Sci. Catal.*, 2000, **130**, 2633.
16 R. Bal, B. B. Tope and S. Sivasanker, *J. Mol. Catal. A: Chem.*, 2002, **181**, 161.
17 X. M. Li, W. Zhang, G. Liu, L. Jiang, X. Zhu, C. Pan, D. Jiang and A. Tang, *React. Kinet. Catal. Lett.*, 2003, **79**, 365.
18 X. Zhu, X. Li, M. Jia, G. Liu, W. Zhang and D. Jiang, *Appl. Catal., A*, 2005, **282**, 155.
19 A. Blanco, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and A. A. Romero, *J. Catal.*, 1992, **137**, 51.
20 J. M. Campelo, F. Lafont, J. M. Marinas and M. Ojeda, *Appl. Catal., A*, 2000, **194**, 85.
21 J. M. Campelo, D. Luna, R. Luque, J. M. Marinas, A. A. Romero, J. J. Calvino and M. P. Rodríguez-Luque, *J. Catal.*, 2005, **230**, 327.
22 F. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and A. A. Romero, *React. Kinet. Catal. Lett.*, 1998, **63**, 261.
23 (*a*) J. M. Campelo, D. Luna, R. Luque, J. M. Marinas and A. A. Romero, *Proceedings of the 4th Green Chemistry Conference*, Generalitat de Catalunya, Barcelona, Spain, 2002; (*b*) R. Luque, Tesis de Licenciatura, Córdoba, 2003.
24 F. Rivetti, *Green Chemistry: Challenging Perspectives*, ed. P. T. Anastas and P. Tundo, Oxford University Press, 2000, p. 201.
25 M. E. Jenkin and G. D. Hayman, *Atmos. Environ.*, 1999, **33**, 1275.
26 K. Tanabe, in *Catalysis by acid and bases*, ed. B. Imelik, C. Naccache, G. Coudurier, Y. Ben Taarit and J. C. Vedrine, Elsevier, Amsterdam, 1985, p. 1.