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

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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. AlPO₄ and, especially, AlPO₄–Al₂O₃ 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 acidcatalyzed 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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C-ALKYLATION

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 monoand 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

AlPO₄ catalysts (designed as AP-X) were obtained by precipitation, from aluminium chloride and H₃PO₄ aqueous solutions, with aqueous ammonia (X = A), ethylene oxide (X = E) or propylene oxide (X = P).¹⁹ A mixture of 79.2 g AlCl₃ · 6H₂O, 23.2 mL H₃PO₄ (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 AlPO₄ (pH \sim 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 AlPO₄ 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.

AlPO₄–Al₂O₃ catalysts (15 and 25 wt% Al₂O₃, respectively) were obtained by adding Al(OH)₃ to a reaction medium where the precipitation of the AlPO₄ (from AlCl₃ · 6H₂O and H₃PO₄) was initiated by the addition of aqueous ammonia. A mixture of 156 g Al(NO₃)₃ · 9H₂O 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 AlPO₄ 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 AlPO₄– Al₂O₃ material (APAL) obtained after precipitation with aqueous ammonia (-A) with a 15 wt% of alumina (-15).

Likewise, a fluorine modified $AIPO_4-Al_2O_3$ material (APAL-A-15FM was synthesized by stirring the APAL-A-15 in an NH₄F water-methanol solution for 20 min, containing 2.5 wt% of F⁻. Both materials (AIPO₄ and AIPO₄-Al₂O₃) were calcined at 923 K for 3 h.¹⁹ Al₂O₃ 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 SiO₂, 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 N₂ flow (50 mL min⁻¹). The catechol–DMC mixture (2 M, 40 μ L 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	$\frac{S_{ m BET}}{ m m^2~g^{-1}}$	$D_{\mathrm{p}}/\mathrm{\AA}$	$V \mathrm{p}/\mathrm{mL}~\mathrm{g}^{-1}$	${S_{\mu p}}^{a/}_{{ m m}^2}{ m g}^{-1}$	$rac{V_{\mu \mathrm{p}}{}^a}{\mathrm{mL}~\mathrm{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 ₂ O 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				
Η-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 ($2m \times 3mm$) 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

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

Catalyst	Py at 473 K/ $\mu mol~g^{-1}$	Py at 573 K/ $\mu mol g^{-1}$	DMPy at 573 K/ $\mu mol g^{-1}$
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	_
Η-β-75	_	278	_
H-ZSM-5	_	373	_
^a No base adsorp	tion.		

Table 3 Surface base properties of the AlPO₄ and AlPO₄–Al₂O₃ systems (15–25 Al₂O₃ wt%), and the metal oxides (MgO and Al₂O₃) 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.		

known compounds in calibration mixtures of specified compositions.

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, $AIPO_4-Al_2O_3$ systems exhibited improved surface acid properties compared to $AIPO_4$ 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 AlPO₄ materials^{*a*}

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

Table 5 Total conversion $(X_{\rm T}, \text{ mol}\%)$, product selectivities $(S_{\rm i}, \text{mol}\%)$ and reaction rate $(k \ 10^{-4}, \ s^{-1})$ in the catechol *O*-alkylation reaction with DMC over different catalysts $(1)^a$

		4 h c	n strea	m		12 h on stream			
Catalyst	Temp./K	X _T	$S_{\rm gua}$	$S_{\rm ver}$	$k \ 10^{-4}$	X _T	S_{gua}	$S_{\rm ver}$	$k 10^{-4}$
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
	$573 Py^b$	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
	$573 Py^b$	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							
APAI-A-25	573	5.9	98.9	1.1	2.9	3.9	98.0	2.0	1.8
	623 573Pv ^b	5.7 d	98.4	1.6	2.6	3.4 d	96.7	3.3	1.6
APAI-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
	$573 Pv^b$	11.2	100.0	_	5.3	9.0	98.0	2.0	4.2
APAI-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
	$573 Py^b$	10.6	100.0	_	5.4	7.9	98.7	1.3	4.0
$^{a} F = 1.33 \times 10^{a}$ with pyridine. c	⁻⁶ mol s ⁻¹ No reactio	; W/F on und	= 220 er the s	s; 2 M stated	catecho conditio	l in E ns. ^d	OMC. Not n	^b Dea	ctivated ed.

incorporation to the AlPO₄ 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

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

		4 h	on strea	m	12 h on stream		
Catalyst	Temp./K	X _T	$S_{ m gua}{}^c$	$k 10^{-4}$	X _T	$S_{ m gua}{}^c$	$k \ 10^{-4}$
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	_		_
Η-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

 ${}^{a} F = 1.33 \times 10^{-6} \text{ mol s}^{-1}$; 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 AlPO₄ materials in the catechol *O*-methylation reaction at 573 K ($\bigcirc = X_T$, $\square = S_{gua}$) and 623 K ($\bullet = X_T$, $\blacksquare = S_{gua}$), respectively.

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 AlPO₄, AlPO₄–Al₂O₃, SAPO-5 and commercial zeolites.

AlPO₄ and AlPO₄-Al₂O₃ systems. Data summarised in Table 5 manifest that the reaction rate constants follows the order AP-A < AP-P < AP-E on AlPO₄ catalysts, as the surface acidity increases in this order, without a noticeable change in terms of selectivity to guaiacol. The incorporation of Al₂O₃ to AlPO₄ developed AlPO₄-Al₂O₃ systems that exhibited increased activity as compared to AlPO₄ catalysts (Table 5). In a similar way as for the $AIPO_4$ materials, the catalytic activity increases when increasing the surface acidity/basicity as well as with the temperature, following the order APAL- $A-25 < APAL-A-15 \sim APAL-A-15FM$. 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 AlPO₄-Al₂O₃ systems compared to the AlPO₄ ones, a temperature increase not only did not improve the catalytic



Fig. 2 Deactivation curves with time on stream; conversion $(X_{\rm T}, \text{mol}\%)$ and guaiacol selectivity $(S_{\rm gua}, \text{mol}\%)$ of AlPO₄–Al₂O₃ systems in the catechol *O*-methylation reaction at 573 K ($\bigcirc = X_{\rm T}, \square = S_{\rm gua}$) and 623 K ($\bullet = X_{\rm T}, \blacksquare = S_{\rm gua}$), respectively.

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 AlPO₄ materials (Fig. 1), whereas the AlPO₄–Al₂O₃ 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 AlPO₄ and AlPO₄–Al₂O₃ 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 Al₂O₃ oxides. Moreover, MgO, a basic metal oxide, as well as Al₂O₃, 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 CO₂ at MgO and Al₂O₃ basic sites and due to the low surface area and acidity values for the MgO and Al₂O₃, respectively. Indeed, Jyothi *et al.*¹² have reported that, after the alkylation process takes place *via* nucleophilic attack



Fig. 3 Deactivation curves with time on stream; conversion ($\bigcirc = X_T$) and gualacol selectivity ($\square = S_{gua}$) of fresh AlPO₄ materials *versus* ($\bullet = X_T$) and ($\blacksquare = S_{gua}$) of AlPO₄ pyridine treated (20 µL min⁻¹, 15 min) in the catechol *O*-methylation reaction.

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 ($\bigcirc = X_T$) and guaiacol selectivity ($\square = S_{gua}$) of fresh AlPO₄-Al₂O₃ systems *versus* ($\bullet = X_T$) and ($\blacksquare = S_{gua}$) of AlPO₄-Al₂O₃ 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, AlPO₄ and AlPO₄–Al₂O₃ 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 μ L min⁻¹; 15 min) was passed through the catalyst bed with an N₂ 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 ($X_{\rm T}$, mol%), selectivities to guaiacol ($S_{\rm gua}$, mol%) and reaction rate constants ($k \ 10^{-4}$, s⁻¹) of the AlPO₄ reused in the catechol *O*-methylation process^{*a*}

			2 h	on stre	eam	6 h	eam	
Catalyst	Temp./K	Carrier	X_{T}	$S_{\rm gua}$	$k 10^{-4}$	X_{T}	$S_{\rm gua}$	$k 10^{-4}$
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
$^{a} F = 1.33 \times 10^{-6} \text{ mol s}^{-1}; W/F = 220 \text{ s}; 2 \text{ M} \text{ catechol in DMC}.$								

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 AlPO₄ 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 ($\bullet = X_T$) and guaiacol selectivity ($\blacksquare = S_{gua}$) of regenerated AlPO₄ versus ($\bigcirc = X_T$) and ($\square = S_{gua}$) fresh AlPO₄ 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 AlPO₄ materials are regenerated to a variable extent. Thus, the degree of reactivation is higher for the less acidic AlPO₄ 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 AlPO₄–Al₂O₃ catalysts exhibited higher catalytic activity and guaiacol selectivity than amorphous AlPO₄, microporous SAPO-5 and zeolitic materials. Moreover, AlPO₄ and AlPO₄–Al₂O₃ 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 AlPO₄ and AlPO₄–Al₂O₃. 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.

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