Mechanistic studies of the role of formaldehyde in the gas-phase methylation of phenol

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ABSTRACT

The gas-phase reaction between phenol and formaldehyde was studied using Brønsted acidic and basic catalysts to gain insight into the components of phenol methylation with methanol. Formaldehyde and methylformate form from methanol during phenol methylation over basic catalysts. In the basic-catalyzed methylation of phenol with formaldehyde, the prevailing phenolic products were *o*-cresol and 2,6-xylenol; the same products were obtained in the methylation with methanol. When formaldehyde was used with the acidic catalyst, the distribution of products was similar to that obtained over basic catalysts. Comparing these results with those of methylation with methylformate, methyliodide, and methanol shows that with basic catalysts, formaldehyde was the true methylating agent in the reaction between phenol and methanol. This indicates that the transformation of methanol differentiates the reaction pattern in phenol methylation over basic or acidic catalysts. The role of the catalyst is to generate the methylating species; the nature of the latter then determines the type of products obtained in phenol methylation, whereas the catalyst type (either acidic or basic) has little influence on it.

1. Introduction

The methylation of phenol and of phenol derivatives is very significant from an industrial standpoint [1]. The products of phenol and diphenol alkylation are intermediates for the synthesis of resins and novolacs, dyes, antiseptics, antioxidants, vitamins, skin protection agents, and food additives. Methylation can be carried out in either the liquid phase (homogeneous or heterogeneous) or the gas phase. The catalysts used for this reaction can be subdivided into two groups: (i) catalysts with acidic characteristics (often modified with alkali or alkaline earth metal ions and oxides to infer basic characteristics) and (ii) catalysts with basic features.

Among catalysts with Brønsted-type acidic characteristics, the most studied are (i) metal phosphates (e.g., AlPO$_4$, RE phosphates, BPO$_4$) [2–14]; (ii) γ-Al$_2$O$_3$, either as such or doped with alkali or alkaline earth metal ions [15–22]; and (iii) zeolites in acidic form or sometimes also exchanged with metal ions [23–36]. Catalysts with Brønsted-type acidic characteristics are very active, and high conversion of the aromatic substrate can be reached at moderate temperatures (300–350 °C). The main characteristic of these materials is the preferred formation of the product of *O*-methylation, especially for less-acidic catalysts; for example, when phenol is the reactant, anisole is the prevailing product at low temperature. Generally, it is accepted that *C*-alkylation requires stronger acidic sites than *O*-alkylation [24,32,37–39], and indeed less acidic zeolites are more selective to anisole than to cresols [23,34,40–42].

The characteristics of catalysts with basic features when used for phenol methylation are very high regioselectivity in *C*-methylation, because the *ortho/para*-methylation ratio is always much greater than 2, and high chemoselectivity, because the *O*/*C*-methylation ratio (a function of the basic strength of the catalysts) generally is very low. The very high regioselectivity is explained through the widely accepted model proposed by Tanabe [43,44], which describes the adsorption of the phenolate anion orthogonal to the oxide surface due to the repulsion between the highly nucleophilic O^{2-} anions and the aromatic ring. This makes the para position less accessible by adsorbed methanol, whereas ortho positions, being closer to the surface, are readily accessible. All models described in the literature later refer to the Tanabe model and thus are focused mainly on the mode of phenol adsorption. Methanol is assumed to adsorb on the surface, develop a methoxy species, or be activated by interaction with the acid–base pairs [45,46]. In most cases, however, no hypothesis regarding the role of the reactions of methanol with regard to the mechanism of phenol methylation is reported.

In previous work [47], we reported that the transformation of methanol is the main factor determining the performance in phenol methylation when catalyzed by either basic or acidic catalysts. Specifically, catalysts that activate methanol through an acid-type

mechanism led to the formation of anisole, which reacted further to yield cresols through an intramolecular rearrangement. At high temperature, the formation of polymethylated compounds was preferred. In contrast, the catalysts with basic features dehydrogenated methanol to formaldehyde, which in turn formed other intermediates (formate and methylformate) and then decomposed to yield CO, CO_2, H_2, and CH_4. Evidence was found indicating that with these catalysts, dehydrogenation of methanol is essential to obtain alkylation of phenol; in this case, the main product was *o*-cresol [47].

In the present work, we report a study of the reaction of phenol with compounds formed by methanol dehydrogenation (i.e., formaldehyde and methylformate), highlighting their role as possible methylating agents in the reaction of methanol with phenol. We investigated the following catalysts: MgO, the main component in alkaline earth metal oxide-based catalysts used in the General Electric process for the synthesis of *o*-cresol and 2,6-xylenol [48], magnesium–iron mixed oxide (sample Mg/Fe/O), and a commercial H-mordenite. Fe oxide is claimed to be the main component in the optimal catalyst for the selective ring methylation of phenol and 1-naphthol [49,50], whereas Mg/Fe/O catalyzes the liquid-phase and the gas-phase methylation of both *m*-cresol [51] and phenol [52,53].

2. Experimental

Three catalysts were investigated; MgO, magnesium–iron mixed oxide (sample Mg/Fe/O), and a commercial H-mordenite with a Si/Al atomic ratio of 20, supplied by Süd-Chemie AG. The MgO and Mg/Fe/O samples were prepared by precipitation from an aqueous solution containing corresponding metal nitrates. Details regarding the preparation and characterization of catalysts both before and after reaction are available elsewhere [47]. Before activity testing, the catalysts were equilibrated in the reactant mixture at 390 °C for 10 h, to obtain a stable catalytic performance.

Catalytic tests were carried out by vaporization of an aqueous phenol/formaldehyde solution containing 20.6 wt% formaldehyde, 0.4 wt% methanol, 17.5 wt% phenol (supplied by Sigma–Aldrich, 99 + % purity), and the balance water in a N_2 stream (N_2 gas flow 20 Nml/min). The aqueous formalin solution was prepared to contain the minimal amount of methanol, which is usually added in commercial formalin solutions to limit formaldehyde polymerization. The reactor feed composition was as follows (in molar fractions): nitrogen, 89.3%; formaldehyde, 1.7% (considering all the formaldehyde oligomers as being in the monomeric form); methanol, 0.03%; phenol, 0.46%; and water, 8.5%.

Overall gas residence time was 2.7 s, at a $GHSV_{phenol}$ of 6.2 h^{-1}. Total pressure was 1 bar. These conditions resulted in the same residence time as in tests on phenol/methanol reactivity [47], but this implies a phenol/formaldehyde molar ratio (1/3.7) different from that applied previously (1/10). The gas/vapor stream was fed into a stainless steel reactor containing 1 cm^3 of catalyst shaped either in 30- to 60-mesh particles (catalyst weight: MgO 0.85 g, Mg/Fe/O 0.95 g), or in 1/16-inch extrudates (H-mordenite 0.64 g). Tests with the H-mordenite were carried out in a glass reactor to minimize dehydrogenation due to the reactor wall.

Additional tests were carried out by vaporization of a phenol/methylformate (molar ratio 1/1) solution in a N_2 stream (N_2 gas flow 20 Nml/min). The feed composition was as follows: N_2, 90.5%; methylformate (supplied by Carlo Erba Reagenti, 97% purity), 4.7%; and phenol, 4.7%. The overall gas residence time was 2.7 s.

Finally, tests were carried out while feeding a phenol/methyliodide solution (molar ratio 1/10) composed of N_2, 89.0%; methyliodide (supplied by Sigma–Aldrich), 10.0%; and phenol, 1.0%. The overall gas residence time was 2.7 s.

Blank reactivity tests performed at 390 °C with the empty steel reactor and with the phenol/formaldehyde mixture gave a phenol conversion of 2% (with formation of *o*-cresol and 2,6-xylenol) and an overall yield of light compounds (from formaldehyde decomposition) of 10–15% at 390 °C. This indicates that the reactor wall provided a small, but nonnegligible, contribution to the reactivity. Indeed, it also was found that the catalytic effect of the wall was greater when a steel reactor was used in which the protective passive coating had been removed due to the prolonged exposure to a methanol-containing stream under dehydrogenating conditions. In this case, the blank test at 390 °C led to a phenol conversion of 7% and to a relevant decomposition of formaldehyde. When conducting the same tests in a glass reactor yielded a phenol conversion of 1%, and a formaldehyde decomposition of 5%.

The reactor outflow was condensed in HPLC-grade acetone. Gases (CO, CO_2, H_2, CH_4) were analyzed by sampling the gaseous stream with a syringe at the reactor outlet before bubbling into acetone, and then injecting the sample into a GC 4300 Carlo Erba gas chromatograph, equipped with a TCD and a Carbosieve SII column. The GC oven temperature was programmed from 55 to 220 °C at a heating rate of 10 °C/min. Products condensed in acetone were analyzed by gas chromatography, using a GC 6000 Carlo Erba instrument equipped with a FID and a HP-5 column. The GC oven temperature was programmed from 50 to 250 °C at a heating rate of 10 °C/min. The same GC was also equipped with a CP-Poraplot Q column (FID detector) for the separation of methanol, dimethylether, formaldehyde, methylformate, and formic acid; in this case, the GC oven was programmed from 50 to 250 °C at a heating rate of 10 °C/min.

Molar yields were calculated as follows ($\dot{n}$ is the molar flow):

- Yield of phenolic products $= \frac{\dot{n}_{product}^{out}}{\dot{n}_{phenol}^{in}}$, where product represents *o*-cresol, *p*-cresol, 2,6-xylenol, anisole, and polyalkylated phenols.
- Yield of light products from formaldehyde: $\frac{\dot{n}_{product}^{out}}{\dot{n}_{formaldehyde}^{in}}$, where product represents CH_3OH, CO, CO_2, and CH_4.
- Yield of H_2 from formaldehyde: $\frac{\dot{n}_{H_2}^{out}}{\dot{n}_{formaldehyde}^{in}}$.

Conversions were expressed as follows:

conversion of phenol or formaldehyde:

$$\frac{\dot{n}_{phenol\ or\ formaldehyde}^{in} - \dot{n}_{phenol\ or\ formaldehyde}^{out}}{\dot{n}_{phenol\ or\ formaldehyde}^{in}}.$$

Selectivity to a compound was expressed as the ratio between the corresponding yield and the reactant conversion.

IR measurements under static conditions were performed with a Perkin–Elmer 1750 FT-IR spectrometer equipped with a DlaTGS detector. For recording spectra, 25 scans were co-added at a resolution of 2 cm^{-1}. MgO samples were pressed into thin, self-supported wafers and activated in situ into the IR cell at 450 °C under vacuum (10^{-5} mbar) for 2 h, until the adsorbed water disappeared. The adsorption procedure involved contacting the vacuum-cleaned sample wafer with vapors of either the single reactants (i.e., formaldehyde [obtained by heating in vacuum of paraformaldehyde, supplied by Sigma–Aldrich] and phenol) or both reactants in a different order of adsorption at room temperature, followed by evacuation at increasing temperatures (i.e., 100, 200, 300, 350, 400, and 450 °C). IR spectra of *o*-cresol (supplied by Fluka, >99,5 purity) and salicylaldehyde (supplied by Aldrich, 98% purity) adsorbed on MgO also were collected for comparison. The IR spectra reported here are difference absorbance spectra of the MgO sample with and without the adsorbed molecules.

3. Results

3.1. Alkylation of phenol with formaldehyde

Figs. 1 and 2 show the results of tests carried out with the MgO and Mg/Fe/O catalysts, respectively. Here the conversion of phenol and the molar selectivity to the phenolic products are plotted as a function of the reaction temperature. The yields of CH_3OH, CH_4, CO, CO_2, and H_2, obtained by the transformation of formaldehyde, also are reported.

Fig. 1 shows that with MgO, the principal product of the reaction between formaldehyde and phenol was o-cresol, with minor formation of p-cresol and xylenols, mainly the 2,6-dimethyl isomer. The selectivity to o-cresol was very high at low temperature and decreased slightly with increasing reaction temperature.

The main C-containing products of formaldehyde transformation were CO_2 and methanol; the two compounds formed with similar yields. The yields of CH_4 and methylformate were <0.5%; the yield of formic acid was nil. These results indicate that due to the presence of a large amount of water in the feed (in the formalin solution), formaldehyde gave formic acid and methanol through the Cannizzaro reaction (reaction (1)),
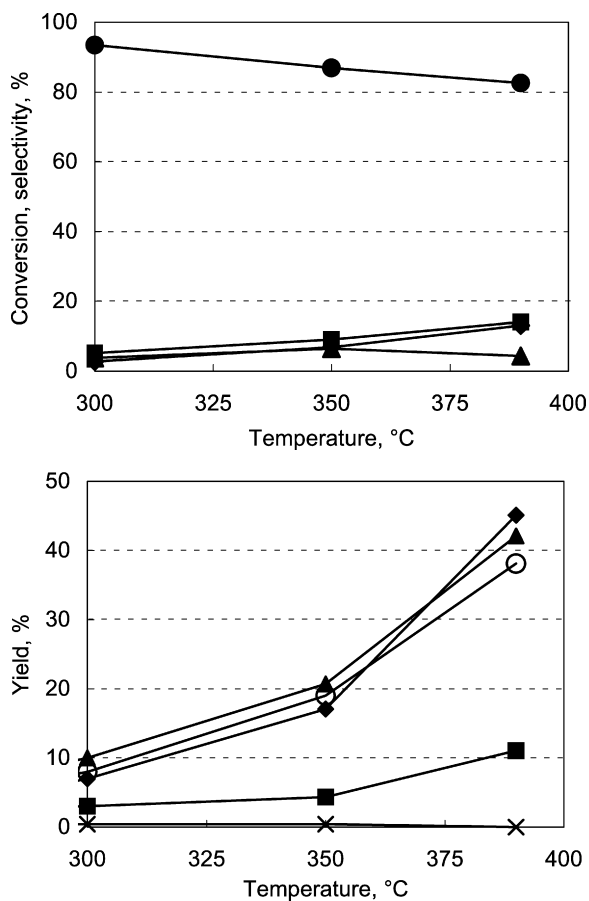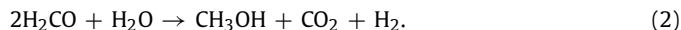
$$2H_2CO + H_2O \rightarrow CH_3OH + HCOOH, \qquad (1)$$

and then formic acid completely decomposed to $CO_2 + H_2$, for an overall stoichiometry (reaction (2)) (reported for mass balance purposes only),

$$2H_2CO + H_2O \rightarrow CH_3OH + CO_2 + H_2. \qquad (2)$$

In fact, the experimental yield of H_2 was similar to that of CO_2. Minor amounts of CO formed either by dehydrogenation of formaldehyde or by decomposition of HCOOH to CO + H_2O; the latter is more likely, because the former reaction would have led to an overall yield of H_2 exceeding that of CO_2. For the same reason, it can be inferred that the dehydrogenation of methanol to formaldehyde also was not extensive.

The overall yield of light C-containing compounds derived from formaldehyde at 390 °C was 92%, because the remaining fraction of formaldehyde was consumed in phenol alkylation. In fact, under these conditions, the conversion of formaldehyde was total.

It is noteworthy that when tests of phenol methylation were carried out with MgO and feeding a methanol/phenol mixture (molar ratio 10/1) [47], the overall conversion of methanol was <10% at 390 °C; the conversion of methanol did not increase when water was added to the feed. Therefore, the lower reactivity of methanol compared with formaldehyde explains why the methanol generated by formaldehyde transformation (Fig. 1, bottom) was not extensively converted to light decomposition compounds.

The negligible formation of methylformate indicates that because of the large excess of water, the reaction between methanol and formic acid to yield the ester was not favored, and that the Tischenko dimerization of formaldehyde to yield the ester was kinetically unfavored with respect to the Cannizzaro disproportion-
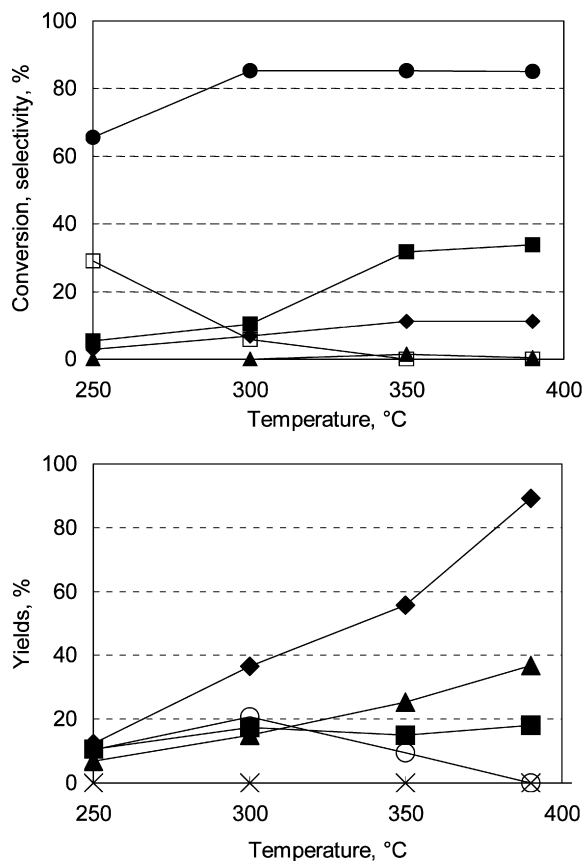

Fig. 1. Top: Conversion of phenol (■), molar selectivity to o-cresol (●), p-cresol (▲) and xylenols (◆) as a function of temperature. Bottom: Molar yield of CH_3OH (○), CO (■), CO_2 (▲), CH_4 (×) and H_2 (◆) as a function of temperature. Feed composition: N_2 89.3%, formaldehyde 1.7%, phenol 0.46%, methanol 0.03% and water 8.5%. Overall gas residence time 2.7 s, $GHSV_{phenol}$ 6.2 h^{-1}; total pressure 1 bar. Catalyst: MgO.

Fig. 2. Top: Conversion of phenol (■), molar selectivity to o-cresol (●), p-cresol (▲), xylenols (◆) and salicylaldehyde (□) as a function of temperature. Bottom: Molar yield of CH_3OH (○), CO (■), CO_2 (▲), CH_4 (×) and H_2 (◆) as a function of temperature. Reaction conditions as in Fig. 1. Catalyst: Mg/Fe/O.
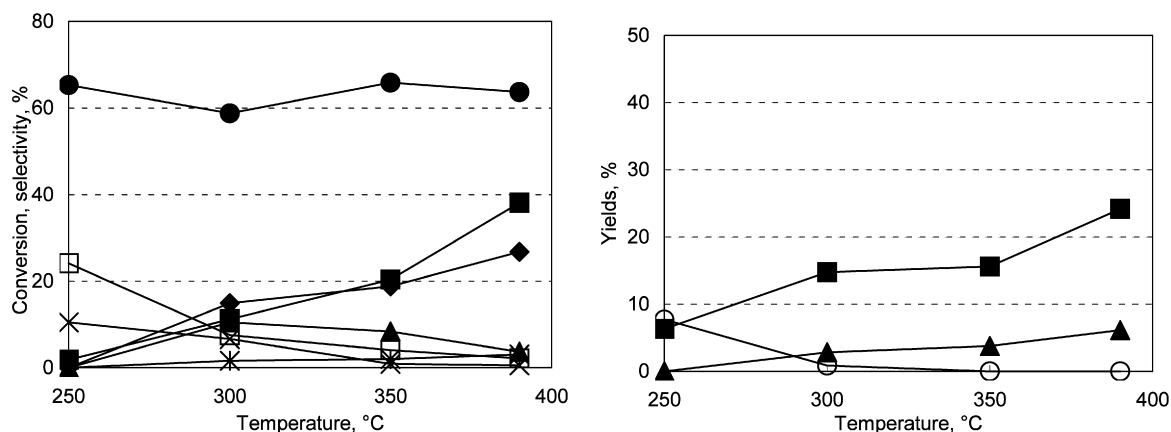
Fig. 3. Left: Conversion of phenol (■), molar selectivity to anisole (×), o-cresol (●), p-cresol (▲), xylenols (◆), salicylaldehyde (□) and polyalkylated phenols (∗) as a function of temperature. Right: Molar yield of CH₃OH (○), CO (■) and CO₂ (▲) as a function of temperature. Reaction conditions as in Fig. 1. Catalyst: H-mordenite.

ation. Indeed, methylformate might have quickly decomposed to methanol + CO; in this case, however, the yield of CO should have been equimolar to that of methanol.

Fig. 2 reports the catalytic performance of Mg/Fe/O. This catalyst was more active than MgO, as it was in the reaction between phenol and methanol reported previously [47]. The phenolic products were o-cresol and 2,6-xylenol; no anisole was formed. The selectivity to p-cresol was very low, whereas this compound was obtained with selectivity >2–3% with MgO; the same difference between the two catalysts was observed in the reaction between phenol and methanol [47]. Below 350 °C, salicyladehyde (2-hydroxybenzaldehyde) also formed; its selectivity was close to 30% at 250 °C and then decreased down to zero at 350 °C, with a corresponding increase in the selectivity to o-cresol. This is the main difference with respect to tests carried out with methanol [47]; in the latter case, salicylaldehyde was not obtained. In the case of MgO, salicyladehyde did not form even in the reaction between phenol and formaldehyde (Fig. 1); this may be due to the fact that this catalyst was less active than Mg/Fe/O and gave nonnegligible conversion of phenol only at temperatures above 300 °C. Under these conditions, salicylaldehyde is likely rapidly transformed to o-cresol.

Concerning the side reactions occurring on formaldehyde, main differences with respect to MgO were as follows: (i) an higher yield of CO, which at low temperature formed in an amount comparable to CO₂; (ii) a much higher yield of H₂, which at 390 °C approached the theoretical limit value of 100%, and (iii) a lower yield of methanol, which had a maximum at 300 °C and became nil at 390 °C. The decreased yield of methanol was accompanied by increased yields of CO₂ and H₂. Also with this catalyst, the yields of formic acid and methylformate were negligible.

The formation of CO can be explained by considering the contribution of formaldehyde dehydrogenation (reaction (3)),

$$H_2CO \rightarrow CO + H_2. \tag{3}$$

However, the relevant yield of H₂ can be explained only by considering a role of H₂O in the WGS reaction (reaction (4)), catalyzed by the Fe cation,

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{4}$$

Another contribution to H₂ formation may derive from methanol reforming (reaction (5)),

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2. \tag{5}$$

Clearly, a significant contribution of these reactions might cause the yield of H₂ to exceed 100%. In fact, the yield of H₂ is dependent on the amount of formaldehyde fed; therefore, additional H₂ formation deriving from a co-reactant (water in this case) may cause it to exceed the theoretical limit for the stoichiometry of formaldehyde dehydrogenation.

The overall conversion of formaldehyde was lower than that obtained with MgO: 70% at 390 °C, considering also the fraction of formaldehyde reacted with phenol. Mg/Fe/O was much more active than MgO in methanol dehydrogenation to formaldehyde in the absence of phenol, but the two catalysts had similar activity when phenol also was present in the stream [47]. This finding was interpreted by assuming competition between methanol and phenol for adsorption over the Fe³⁺ ions, which led to inhibition of methanol dehydrogenation. In the present case, the lower conversion of formaldehyde observed with Mg/Fe/O may be attributed either to the inhibition effect due to the presence of phenol or to the lower activity of this catalyst in the Cannizzaro reaction. With both the MgO and Mg/Fe/O catalysts, no deactivation phenomena were observed at reaction temperatures of 390 °C and lower.

Fig. 3 reports the catalytic performance of the H-mordenite in phenol methylation with formaldehyde. The results differ from those obtained with methanol [47]; in the latter case, at low temperature, the main reaction product was anisole, whereas over 300 °C, the products were o-cresol, p-cresol, and polyalkylated phenols. With formaldehyde, the nature and amount of the products were similar to those obtained with MgO and Mg/Fe/O. At low temperature, the prevailing products were o-cresol and salicylaldehyde, whereas anisole formed with selectivity of 10%. At high temperature, the prevailing products were o-cresol and 2,6-xylenol, with lesser amounts of p-cresol and polyalkylated phenols.

In terms of the formation of light compounds (Fig. 3, right), the prevailing compounds were CO and methanol, which formed in equimolar amounts at 250 °C; no formation of methane or hydrogen was seen. This finding suggests that formaldehyde yields methylformate by dimerization, which is then further decomposed to yield the two light compounds. The possible formation of formic acid, further decomposed to CO and water, cannot be excluded. At temperatures above 250 °C, the yield of methanol decreased whereas that of CO increased; in fact, methanol reacted to yield anisole, alkylphenols, and alkylaromatics [47].

Two other findings are worth mentioning. First, polyalkylbenzenes (mainly pentamethylbenzene and hexamethylbenzene), which were obtained in large amounts from methanol [47], formed with an overall yield <1% from formaldehyde. Furthermore, no short-term deactivation phenomena were observed, whereas they were evident from methanol. In the latter case, it can be suggested that the deactivation was due to the formation of alkylaromatics, precursors of coke formation. This indicates that with formalde-
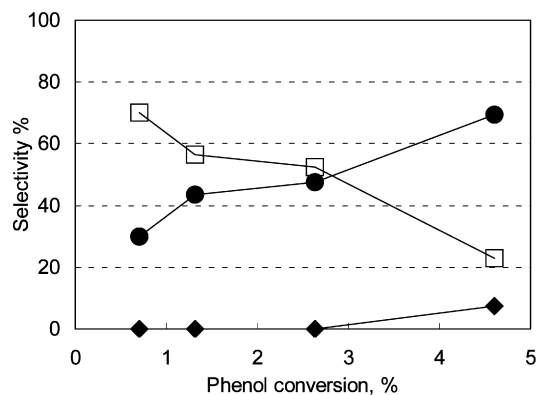
Fig. 4. Molar selectivity to salicylaldehyde (□), *o*-cresol (●) and xylenols (◆) as a function of phenol conversion. Temperature 250 °C; residence time was varied. Other conditions as in Fig. 1. Catalyst: Mg/Fe/O.
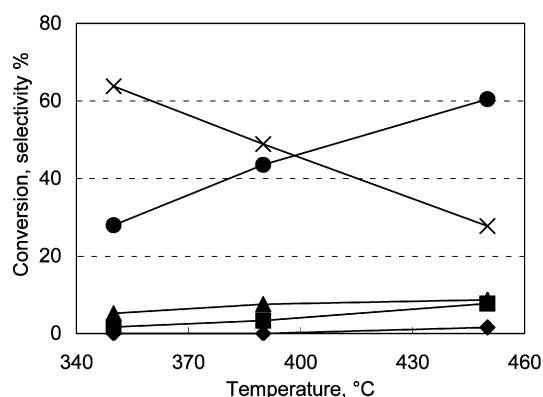

Fig. 5. Conversion of phenol (■), molar selectivity to anisole (×), *o*-cresol (●), *p*-cresol (▲) and 2,6-xylenol (◆) as a function of temperature. Feed composition: N_2 90.5%, methylformate 4.7% and phenol 4.7%. Overall gas residence time 2.7 s; total pressure 1 bar. Catalyst: MgO.

Fig. 6. Conversion of phenol (■), molar selectivity to anisole (×), *o*-cresol (●) and 2,6-xylenol (◆) as a function of temperature. Reaction conditions as in Fig. 5. Catalyst: Mg/Fe/O.

Fig. 7. Conversion of phenol (■), molar selectivity to *o*-cresol (●), 2,6-xylenol (◆), *p*-cresol (▲), anisole (×), 2,4-xylenol (○) and polyalkylated phenols (∗) as a function of temperature. Reaction conditions as in Fig. 5. Catalyst: H-mordenite.

hyde, the formation of coke precursors was hindered, due either to the low amount of methanol generated or to the presence of water, which inhibits the formation of dimethylether.

Tests were carried out with varying residence times to obtain information on the reaction scheme. A very low residence time (e.g., <0.1 s) and low temperature (250 °C) were used to isolate the intermediates, which were considered highly reactive. Fig. 4 plots the selectivity to the products as a function of phenol conversion for tests carried out with the Mg/Fe/O catalyst. Salicylaldehyde clearly was a primary product, because its selectivity, if extrapolated to nil conversion, exceeded zero; however, it rapidly declined when the conversion was increased. The decreased selectivity to aldehyde led to an increase in selectivity to *o*-cresol; this evidently supports the hypothesis that the latter compound forms by consecutive transformation of salicyladehyde. The further reaction of *o*-cresol gave the formation of 2,6-xylenol, the selectivity of which, however, was <10% under these experimental conditions.

3.2. Alkylation of phenol with methylformate

The results of catalytic tests performed by feeding phenol and methylformate are reported in Figs. 5–7. These figures show the conversion of phenol and the molar selectivity to the phenolic products (i.e., *o*-cresol, 2,6-xylenol, and anisole). With MgO (Fig. 5), the prevailing product was anisole, whereas in tests carried out with either methanol [47] or formaldehyde (Fig. 1), this compound was obtained with selectivity <10%. With Mg/Fe/O (Fig. 6), the formation of anisole was low, as it was in tests carried out with either methanol [47] or formaldehyde (Fig. 2); the main pheno-
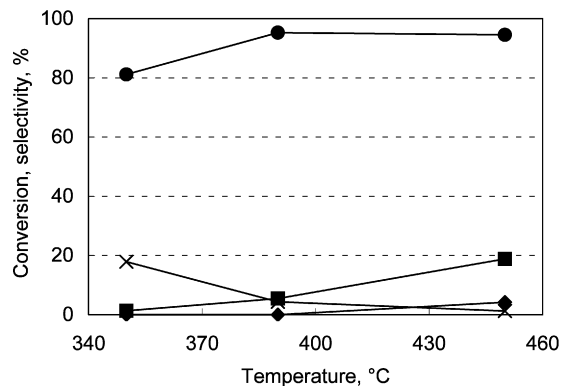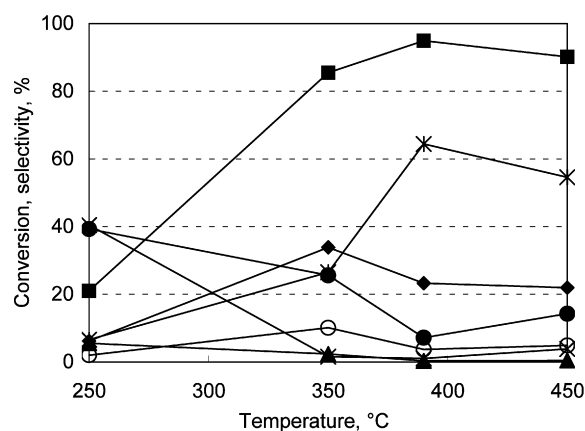
lic products were *o*-cresol and 2,6-xylenol. With both catalysts, the conversion of phenol was low; in fact, most methylformate decomposed, and only a minor fraction of it reacted with phenol.

Fig. 7 shows the catalytic performance obtained with the H-mordenite catalyst. At low temperatures, the products of reaction with phenol were anisole and cresols (mainly *o*-cresol). The same distribution of products was obtained starting from methanol [47], whereas that obtained from formaldehyde (Fig. 3) was different. An increase in reaction temperature led to the formation of xylenols.

In terms of the formation of light compounds (results not reported), with MgO, methylformate decomposed to CO (21% yield at 390 °C) and methanol; the yield of methane was nil. The amount of H_2 generated was relatively low (<1% yield at 390 °C), suggesting a low fraction of methanol dehydrogenated to formaldehyde. With the Mg/Fe/O catalyst, at 390 °C, the yields of CO and CO_2 were similar (19 and 14%, respectively), the yield of methane was 3%, and that of H_2 was 8%. With the H-mordenite, methylformate decomposed mainly to CH_3OH and CO (30% yield at 390 °C); the yields of CH_4 and CO_2 were 3%.

3.3. Alkylation of phenol with methyliodide

To demonstrate the role of the methylating agent, tests were carried out feeding methyliodide and phenol over the Mg/Fe/O catalyst. Results are reported in Fig. 8. The conversion of phenol was low, because of the inefficient activation of methyliodide due to the absence of acidic sites. The nature and relative amounts of the products obtained in phenol methylation were the same as those obtained in tests involving feeding methanol and phenol
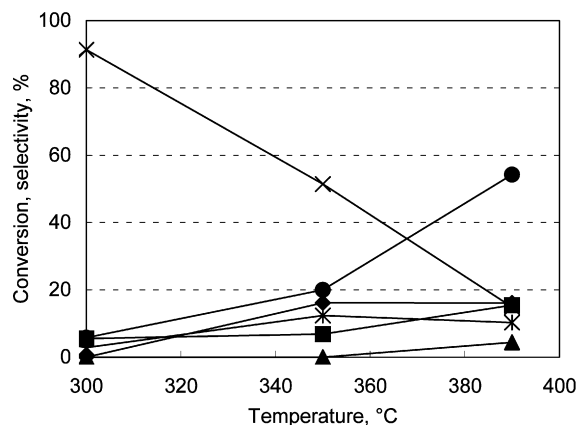
Fig. 8. Conversion of phenol (■), molar selectivity to anisole (×), o-cresol (●), 2,6-xylenol (◆), p-cresol (▲) and polyalkylated phenols (∗) as a function of temperature. Feed composition: N_2 89.0%, methyliodide 10.0% and phenol 1.0%. Overall gas residence time 2.7 s; total pressure 1 bar. Catalyst: Mg/Fe/O.
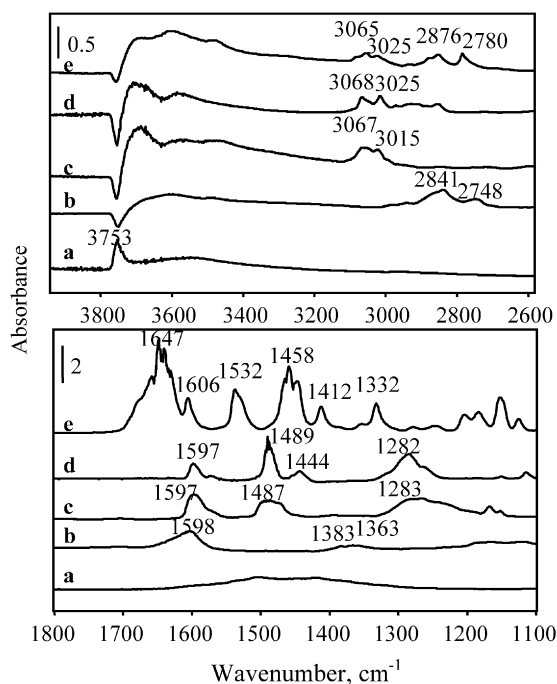

Fig. 9. FT-IR spectra recorded after adsorption at room temperature and evacuation on MgO (a) of: formaldehyde (b), phenol (c), o-cresol (d) and salicylaldehyde (e).

with the H-mordenite [47]. The main product at low temperature was anisole; an increase in the reaction temperature led to the formation of cresols (with the *ortho*-isomer the prevailing one) and polyalkylated phenols.

These findings indicate that when the formation of the aldehyde was not possible, the methylating species generated with the basic catalyst yielded the same phenolic products obtained with methanol and with acid catalysts. These tests demonstrate that the nature of the products obtained in phenol methylation is a function of the type of methylating species generated.

3.4. IR spectra recorded after adsorption and co-adsorption of reactants with the MgO catalyst

Fig. 9 plots the IR spectrum of MgO along with spectra of the sample recorded after the sorption of vapors of formalin, phenol, salicylaldehyde, and o-cresol at room temperature. The spectra of
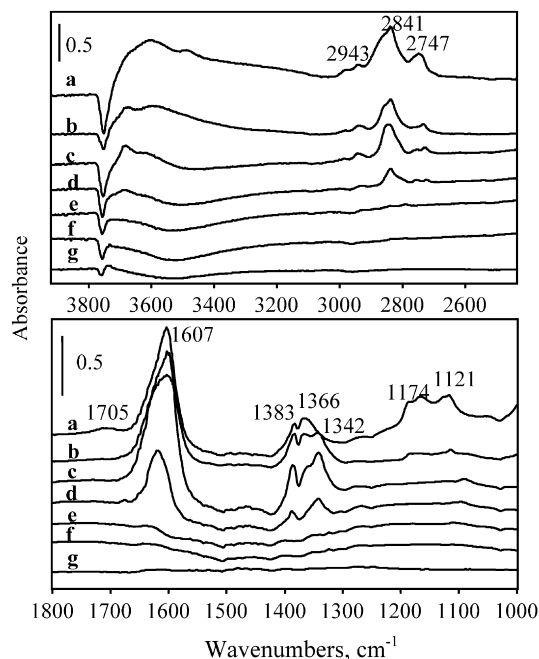

Fig. 10. FT-IR spectra recorded after adsorption of formaldehyde at room temperature on MgO and evacuation, and after heating under vacuum at increasing temperatures. Room temperature (a), 100 (b), 200 (c), 300 (d), 350 (e), 400 (f) and 450 °C (g).

MgO show the presence of carbonates (1200–1700 cm^{-1} region) and –OH group (3753 cm^{-1}) also after pretreatment at 450 °C.

The spectrum recorded after adsorption of phenol is similar to that reported in the literature [54,55]. The stretching vibrations of C–H in the aromatic ring can be seen in the spectral zone between 3010 and 3070 cm^{-1}. Bands at 1597 cm^{-1} and 1487 cm^{-1} are attributed to C–C ring vibrations; bands at 1170 (and 1074) cm^{-1}, to C–H bending. The band at 1283 cm^{-1} is related to C–O stretching for the phenolate species, evidence of dissociation of the hydroxy group. For the spectrum of salicylaldehyde, bands in the spectral zone between 3000 and 3090 cm^{-1} can be attributed to the stretching of the C–H of the aromatic ring. The bands at 2876 and 2780 cm^{-1} are related to the stretching of the C–H in the aldehydic moiety, with the latter deriving from the Fermi resonance. The band at 1647 cm^{-1} is characteristic of aldehydic C–O stretching. Bands at 1606 and 1532 cm^{-1} are related to the aromatic ring-stretching vibrations. At 1412 and 1458 cm^{-1} lie the bands due to C–H bending, the former attributed to aldehydic C–H. The band at 1332 cm^{-1} is due to the stretching of C–O, whereas that at 1155 cm^{-1} corresponds to the stretching of C–CHO. Additional bands in the spectrum of o-cresol, when compared with the corresponding spectrum of phenol, are attributed to the –C–H vibrations of the methyl group (between 2800 and 3000 cm^{-1}) and to the bending of –CH₃ at 1444 cm^{-1}. The bands at 3400–3800 cm^{-1} are attributed to the interaction between the adsorbed molecules and the –OH groups of MgO.

Fig. 10 shows the spectra recorded after adsorption of formaldehyde at room temperature and heating at increasing temperatures. At low temperature, the typical frequencies of formaldehyde (i.e., 2841, 2748 cm^{-1} [ν CH] and 1383, 1363 cm^{-1} [δ CH]) are present; however, these peaks disappear at temperatures above 300 °C, evidence of complete desorption or decomposition of formaldehyde. The peak at 1342 cm^{-1} in the spectra recorded at 100 and 200 °C is due to the formate species. The main result of this experiment is that formaldehyde was weakly bound to the surface sites of MgO and did not remain adsorbed at those temperatures at which the reaction between phenol and formaldehyde occurred. This sug-
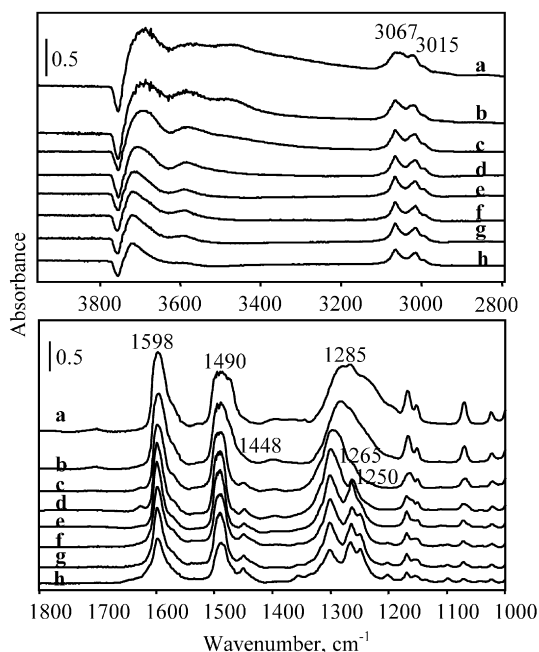
Fig. 11. FT-IR spectra recorded after adsorption at room temperature on MgO of phenol and then of formaldehyde and evacuation, and after heating under vacuum at increasing temperatures. Room temperature (a), phenol and then formaldehyde, room temperature (b), 100 (c), 200 (d), 300 (e), 350 (f), 400 (g), 450 °C (h).

Fig. 12. FT-IR spectra recorded after adsorption at room temperature on MgO of formaldehyde and then of phenol and evacuation, and after heating under vacuum at increasing temperatures. Room temperature (a), formaldehyde and then phenol, room temperature (b), 100 (c), 200 (d), 300 (e), 350 (f), 400 (g), 450 °C (h).

gests that the latter reaction also may occur through a Rideal-type mechanism involving adsorbed phenolate and gas-phase formaldehyde.

Fig. 11 plots the spectra recorded after preadsorption of phenol at room temperature and subsequent adsorption of formaldehyde and heating up to 450 °C. Fig. 12 plots the spectra recorded by inverting the order of reactants adsorption on MgO. In the former case, formaldehyde peaks were not evident, due to the stronger adsorption of phenol over surface sites. In contrast, when phenol was adsorbed after formaldehyde, the aromatic adsorbed on MgO, but there was no substantial variation in the concentration of adsorbed formaldehyde. These data can be interpreted based on previous reports of the adsorption of these molecules over MgO (see also the Section 4). In fact, phenol interacts strongly with Mg–O pairs [54,55]. In contrast, a weaker interaction between the aldehydic O atom and Mg develops with formaldehyde. Therefore, the adsorption of formaldehyde left several Mg–O pairs on the surface available for the adsorption of phenol; the latter did not displace formaldehyde, because a prerequisite for phenol adsorption is the accessibility of free Mg–O pairs. On the contrary, the preadsorption of phenol led to saturation of the surface; because the interaction of formaldehyde with the catalyst was not strong enough to compete efficiently with the aromatic, only a very small amount of formaldehyde was adsorbed.

When the temperature was increased, new bands appeared. In the first case (Fig. 11), the bands at 1448 and 1250 cm^{-1} were due to o-cresol formation, attributed to –CH$_3$ bending and C–O stretching, respectively. This means that the low amount of formaldehyde adsorbed reacted rapidly with the phenolate species. In the second case (Fig. 12), the bands attributed to formaldehyde disappeared at temperatures above 300 °C. Relevant features are the concomitant development of a shoulder at 1642 cm^{-1} (ν C=O) and a peak at 1448 (δ CH) cm^{-1}, both corresponding to the most intense bands of adsorbed salicylaldehyde (Fig. 9). These features disappeared at 300 °C, while bands attributed to o-cresol developed. These results are in agreement with those of the catalytic tests and confirm that in the temperature range of 200–300 °C, salicyladehyde, the intermediate in the formation of o-cresol, can be isolated. In contrast,
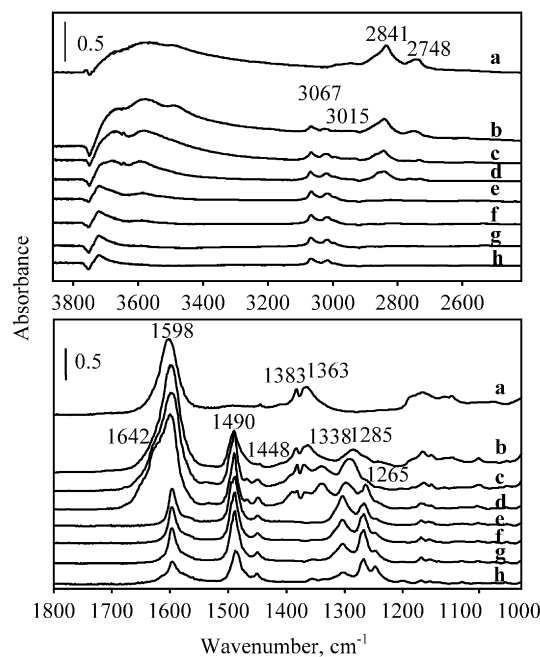
the aldehyde was not isolated at higher temperatures, probably because of its rapid transformation into o-cresol.

4. Discussion

4.1. Formaldehyde as the alkylating agent: A comparison with methanol

Our findings indicate that analogies exist between the gas-phase methylation of phenol with methanol [47] and that with formaldehyde. With basic catalysts, the performance in phenol methylation was similar when either of the two reactants was fed. On the other hand, the catalyst type (either basic or acidic) had little influence on the nature of the products when formaldehyde was used as the methylating agent, whereas the nature of products obtained over the two catalysts was quite different when methanol was the reagent [47]. This finding indicates that the methylating species in phenol methylation with methanol were not the same when basic or acid catalysts were used but were the same when the reaction was carried out with formaldehyde. Furthermore, it implies that not methanol itself, but one of the products of methanol transformation (i.e., formaldehyde or methylformate), plays the major role in the basic-catalyzed methylation of phenol. These hypotheses are discussed more in detail below.

The results obtained in phenol methylation with formaldehyde over MgO and Mg/Fe/O can be explained by considering formaldehyde to be the true alkylating agent in the reaction of phenol methylation with methanol and also with formaldehyde. According to this hypothesis, the dehydrogenation of methanol to formaldehyde is the necessary requisite for methylation with basic catalysts. A large proportion of formaldehyde is then decomposed to light compounds, but a part of it reacts with phenol to yield o-cresol. Therefore, the true molar ratio between formaldehyde and phenol is much lower than the feed ratio (3.7/1) and also much lower than the methanol/phenol feed ratio used in tests with methanol (10/1) [47]. Indeed, the extent of methanol decomposition observed in methanol/phenol reactivity tests was much lower than that of formaldehyde; in fact, the yield of light compounds from

methanol never exceeded 15% [47], whereas with formaldehyde, the extent of formaldehyde transformation was almost total. This difference is due to the higher reactivity of the aldehyde compared with methanol, as well as the presence of a large amount of water, which favors the disproportionation of formaldehyde. Despite this, however, the conversion of phenol with formaldehyde was similar to that with methanol. This indicates that formaldehyde is much more reactive than methanol to the aromatic ring, due to the electrophilic properties of the C atom in the carbonyl moiety.

The nature of the phenolic products and their relative quantities also were quite similar when either of two reactants was used with the basic catalysts. One minor difference concerns the formation of anisole; in the reaction between phenol and methanol over MgO, anisole was obtained with selectivity <10%, whereas in the reaction with formaldehyde it did not form at all. Another difference concerns the formation of salicylaldehyde as the reaction intermediate; this was detected with selectivity close to 30% at low temperature in the phenol/formaldehyde reaction with the Mg/Fe/O catalyst and with the H-mordenite but was not observed at all with these catalysts in the phenol/methanol reaction. This is likely due to the fact that with methanol, the rate-determining step of the reaction is the dehydrogenation of methanol to formaldehyde [47], which then rapidly attacks the aromatic ring; this implies a very low concentration of the adsorbed phenolic intermediates under these conditions. When instead formaldehyde is fed directly, the concentration of the phenolic intermediates is relevant, and the latter may partially desorb into the gas phase.

An alternative hypothesis is that methanol is the true alkylating agent in the reaction of phenol methylation with methanol and also with formaldehyde. In fact, a fraction of formaldehyde is transformed into methanol and formic acid by the Cannizzaro reaction. However, it is noteworthy that in the reaction between phenol and formaldehyde, the concentration of methanol in the reaction environment was low, in the best case equimolar to the amount of CO_2 formed. Therefore, in formaldehyde/phenol tests the effective molar ratio between methanol and phenol is around 1, much lower than that in tests carried out by directly feeding the methanol/phenol mixture [47]. If methanol were the true alkylating agent even in the formaldehyde/phenol tests, then a much lower conversion of phenol than that obtained in methanol/phenol tests would be expected, because the conversion of phenol is greatly affected by the methanol/phenol feed ratio [47]. But at the same temperature and contact time, the conversion of phenol was greater with formaldehyde than with methanol. Finally, it is noteworthy that much of the formaldehyde transformation to methanol (Figs. 1 and 2) was due to the excess of water fed. (Water is a coreactant of the Cannizzaro reaction.) In the tests carried out with methanol, no water was fed, and the amount of water generated in the reaction was comparatively low [47].

All of the data obtained support the hypothesis that in the gas-phase phenol alkylation with methanol catalyzed by basic catalysts, the true alkylating agent is not methanol, but formaldehyde. We next discuss this hypothesis in more detail.

4.2. Formaldehyde as the alkylating agent in the basic-catalyzed reaction between phenol and methanol

In the literature, the direct alkylation of aromatics with aldehydes and ketones has been less studied than the corresponding alkylation with alcohols, alkyl halides, or alkenes, because of the tendency to yield oligomeric byproducts [56–60]. Lercher et al. [61,62] reported that in the basic-catalyzed methylation of toluene to styrene with methanol, the necessary conditions for obtaining side-chain alkylation are the dehydrogenation of methanol to formaldehyde and the development of a strong interaction between the methyl group of toluene and the basic oxygen atoms

to form a partial negative charge on the C atom. An aldol-type condensation occurs, with C–C bond formation. The formation of formaldehyde and an intermediate formate species in the side-chain alkylation of alkylaromatics with methanol also has been proposed by others [63–65].

In terms of the alkylation of activated aromatics with methanol, to the best of our knowledge, the hypothesis that formaldehyde may play a direct role was first cited in a patent [66], which specified alkaline earth oxides as catalysts for the gas-phase reaction between methanol and phenol. In the open literature, some authors have suggested a possible role of aldehydes in the alkylation with alcohols, but no experimental proof has been provided [67–74]. For instance, Gopinath et al. [67] identified formaldehyde, dioxymethylene, and formate by means of IR study when feeding methanol over Cu/Co/Fe/O catalysts; however, they argued that methanol dehydrogenation did not occur in the presence of phenol, due to the competition of the two reactants for adsorption on the same sites. Radhe Shyam et al. [71] suggested that in the vapor-phase alkylation of pyridine with methanol over a Zn/Mn/Fe/O ferrospinel system, formaldehyde attacks intermediate dihydropyridine to yield 3-picoline, but they provided no experimental evidence supporting formaldehyde as the true alkylating agent. Klemm et al. [72] proposed that in the methylation of 1-naphthol catalyzed by alumina, the main methylating agents are either the adsorbed methanol (coordinated to the acidic site) or the methyl carbonium ion, but did not exclude the possibility that either formaldehyde (formed by dehydrogenation of methanol) or the hydroxymethyl carbonium ion ($^+CH_2OH$) might be the true electrophilic agent [73].

Our catalytic tests of phenol methylation with formaldehyde have demonstrated that the nature of the methylating species determines the type of phenolic products. On the other hand, the catalyst affects the type of methylating agent when methanol is the reactant, whereas it has little effect on it with formaldehyde. This finding also supports the hypothesis that in the presence of a basic catalyst, the true active species in phenol methylation with methanol is not the alcohol. This would explain why at low temperature, the main product of the reaction between phenol and methanol with the H-mordenite catalyst is anisole [47], which, conversely, is formed in low yield starting from formaldehyde. In fact, under these conditions, methanol is protonated by the acidic catalyst and reacts either with another molecule of methanol to yield dimethylether or with phenol to yield anisole. When formaldehyde is the reactant, the electrophilic carbonyl bond rapidly attacks the aromatic ring.

Therefore, our findings support the hypothesis that the main role of the catalyst (either acidic or basic) is in generation of the methylating species, whereas it has little influence on the reaction pathway between the adsorbed phenol and the methylating species or on the type of phenolic products finally obtained. If this hypothesis is correct, then the use of a basic catalyst and a methylating agent that does not dehydrogenate should yield the same phenolic products obtained with the acidic catalyst and methanol, that is, anisole at low temperature and cresols/polylakylphenols at high temperature. In fact, with a basic catalyst, methyliodide (the activation of which can occur only by generation of a $CH_3^{\delta+}$ species) gave the same distribution of products (Fig. 8) as obtained with methanol/phenol and H-mordenite [47].

The IR spectra recorded after co-adsorption of phenol and formaldehyde demonstrated the following:

1. Phenol developed a much stronger interaction with the MgO surface than formaldehyde.
2. The reaction between phenol and formaldehyde required the preadsorption and activation of phenol and the development of the phenolate species; however, formaldehyde does not
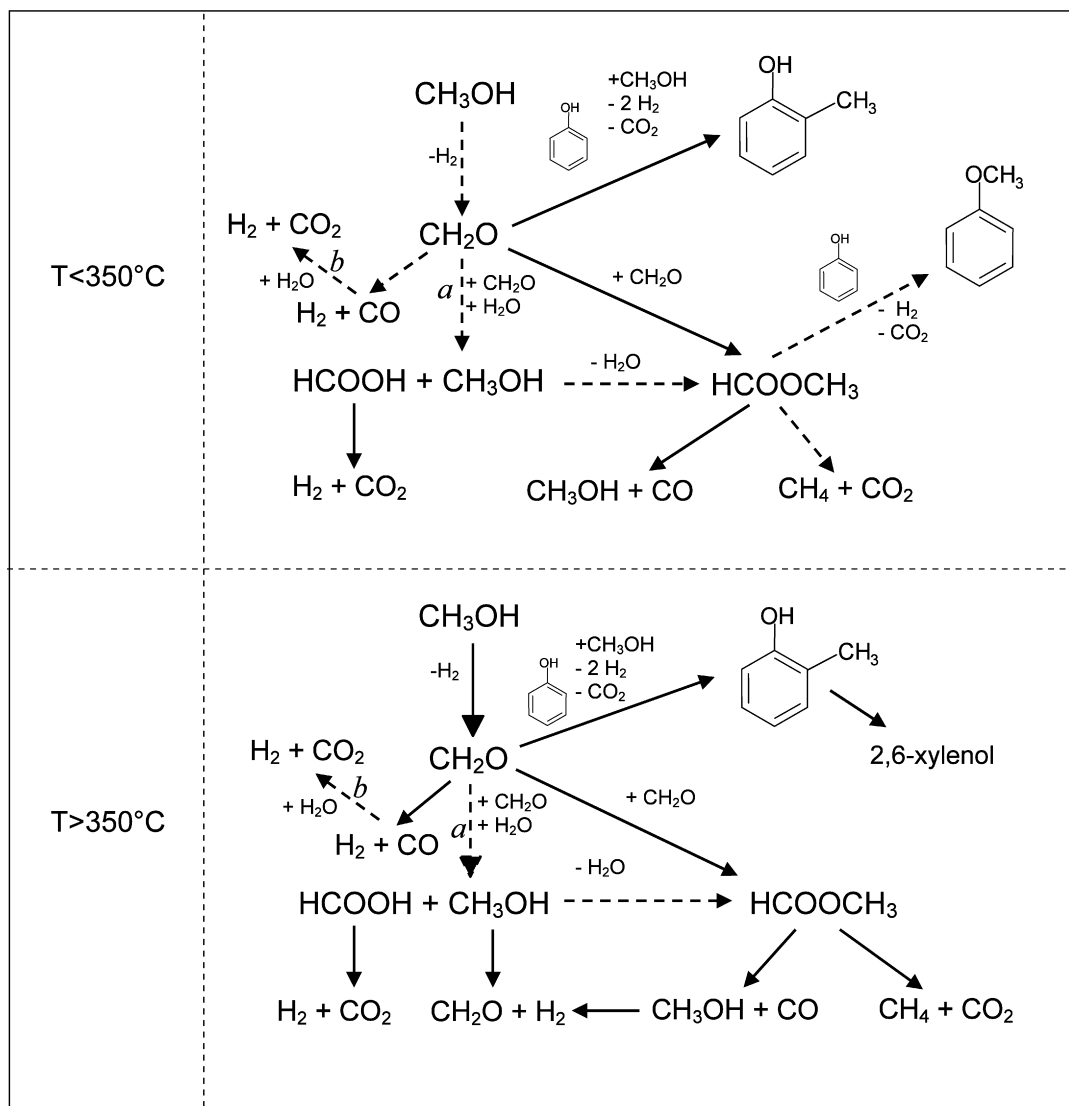
Fig. 13. Schematic representation of the main reactions occurring in the gas-phase methylation of phenol with methanol in basic catalysis. Dotted arrows represent reactions kinetically less favored. *a*: favored in the presence of water (tests with formalin solution). *b*: favored in the presence of water and of Fe.

have to be in the adsorbed state to allow an electrophilic attack on the activated aromatic ring.

3. When the reaction was between adsorbed phenol and adsorbed formaldehyde, salicylaldehyde could be isolated as the reaction intermediate at moderate reaction temperatures (i.e., below 300 °C).

4. Salicylaldehyde was the intermediate in *o*-cresol formation.

Reactivity tests conducted with varying residence times (Fig. 4) confirmed that salicylaldehyde was one primary product in the reaction between phenol and formaldehyde, and that salicylaldehyde was consecutively transformed to *o*-cresol. The possible presence of other reactions leading to *o*-cresol cannot be excluded, however.

Salicyladehyde may form by rapid dehydrogenation of salicylalcohol, which, by analogy with the hydroxymethylation reaction, can be assumed to be the initial product of the reaction between phenol and formaldehyde. If salicylalcohol is consecutively transformed before it can desorb into the gas phase, then it cannot be identified as a primary reaction product. Other reactions that may occur on salicylalcohol include condensation with another phenol molecule to yield (PhOH)–CH_2–(PhOH), a possible precursor of cresol [75], and the reduction of the hydroxymethyl to a methyl group by formaldehyde or by hydrogen (the latter formed by de-

hydrogenation of formaldehyde). In this case, a parallel primary formation of *o*-cresol should also contribute to phenol conversion; indeed, the data given in Fig. 4 do not exclude this possibility. The transformation of salicylaldehyde to *o*-cresol also may occur through reaction of the former with either methanol or formaldehyde, leading to reduction of the carbonyl to the methyl group and to oxidation of the reductant to CO_2.

Therefore, the reaction between phenol and methanol in basic catalysis likely includes a reductive step by either methanol or formaldehyde, for an overall stoichiometry,
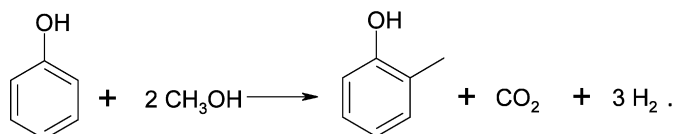
4.3. Methylformate as the alkylating agent: Comparison with methanol

Methylformate is a weak alkylating agent used in the Zerbe–Jage process [76] for the synthesis of anisole from alkali metal phenolate through the classical base-catalyzed Williamson ether synthesis. Methylformate is generated in-situ by reaction between

methanol and CO at 180 °C and high pressure. The reaction between phenol and methylacetate catalyzed by Mg-zeolites also yields anisole as the main reaction product at $T < 350$ °C, whereas o-cresol and xylenols form at higher temperatures [77].

Results obtained in phenol methylation with methanol over basic catalysts [47] demonstrated that with these catalysts, methylformate is a product of methanol transformation that may represent the true alkylating species. Moreover, the yield of the main products obtained by the high-temperature decomposition of methylformate (i.e., CH_4 and CO_2) was significantly affected by the presence of phenol. In fact, whereas in the absence of phenol, the two compounds formed in almost equimolar amounts, the presence of the aromatic led to a substantial decrease in methane formation compared with carbon dioxide. This may be interpreted as being due to the insertion of the methyl group on the aromatic ring from intermediately formed methylformate, with the remaining part of the molecule released in the form of carbon dioxide and hydrogen.

Our findings for the reaction between phenol and methylformate indicate that a very low amount of anisole was formed with the catalyst characterized by the stronger dehydrogenation activity (Mg/Fe/O), whereas anisole was a predominant product of the reaction with MgO. This suggests that methylformate can act directly as the methylating agent, with the introduction of the methyl group to yield anisole and the concomitant release of CO_2. In fact, almost no CH_4 was generated from methylformate decomposition. The C atom of the methyl group in the ester was not sufficiently electrophilic to attack the aromatic ring, whereas it did react with the O atom in the phenolate. Conversely, when methylformate was significantly decomposed to $CH_3OH + CO$ and methanol was dehydrogenated to formaldehyde (i.e., with Mg/Fe/O), the prevailing product was that of C-methylation, o-cresol.

Consequently, our findings demonstrate that with basic catalysts and under mild reaction conditions (at which methylformate was not significantly decomposed), the ester may act as a methylating agent on phenol to yield anisole, but when methanol was the reactant [47], methylformate formed only under those conditions in which the alcohol was dehydrogenated to formaldehyde. The latter then either formed methylformate (which, however, is rapidly decomposed due to the high reaction temperature) or reacted with phenol to yield C-alkylated compounds. In tests involving feeding the formalin solution, methylformate formed only in small amounts, because the Cannizzaro reaction was the preferred path for formaldehyde transformation.

The distribution of products obtained with H-mordenite and methylformate (Fig. 7) was quite similar to that obtained with methanol [47] but different than that obtained with formaldehyde. Therefore, at low temperature, either the methylformate activated by protonation of the carbonylic O atom or the methanol obtained by decomposition of methylformate, reacted with phenol to produce anisole. At high temperature (i.e., $T > 350$ °C), methanol demonstrated ring-substitution to cresols and polyalkylated phenols.

5. Conclusion

Fig. 13 summarizes the results obtained in the present study and in our previous work on phenol methylation with methanol over basic catalysts [47]. In the gas-phase methylation of phenol with methanol, the main role of the catalyst (either basic or acidic) is in generating the methylating agent. With the acidic catalyst, the activation of methanol generates an electrophilic species that reacts with phenol to produce anisole at low temperature, whereas at high temperature, the preferred products of the reaction are C-alkylated compounds. Conversely, with basic catalysts, the dehydrogenation of methanol is a required step in the for-

mation of a more electrophilic species; formaldehyde then either reacts rapidly with phenol to yield o-cresol or gives rise to the parallel formation of methylformate. At low temperature, methylformate may yield anisole by reaction with phenol, but at high temperature, it decomposes to lighter compounds. Salicylaldehyde is the intermediate product in the reaction between phenol and formaldehyde and is the precursor for the formation of o-cresol. Therefore, the nature of the products obtained by reaction between phenol and methanol is governed by the transformations occurring on methanol, which are a function of catalyst type. This also is demonstrated by the results of the reaction between phenol and formaldehyde over the acid catalyst, with the formation of the same products typically obtained in the basic-catalyzed methylation of phenol, and the reaction between phenol and methyliodide over the basic catalyst, with the formation of the same products obtained in the acid-catalyzed methylation of phenol.

References

[1] H. Fiege, in: Ullmann's Encyclopedia of Industrial Chemistry, vol. A8, 2002, p. 25.
[2] G. Sarala Devi, D. Giridhar, B.M. Reddy, J. Mol. Catal. 181 (2002) 173.
[3] B.M. Reddy, G. Sarala Devi, P.M. Sreekanth, Res. Chem. Int. 28 (6) (2002) 595.
[4] F.M. Bautista, J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, A. Romero, J.A. Navio, M. Macias, Appl. Catal. A 99 (1993) 161.
[5] V. Durgakumari, S. Narayanan, L. Guczi, Catal. Lett. 5 (1990) 377.
[6] R. Pierantozzi, A.F. Nordquist, Appl. Catal. 21 (1986) 263.
[7] F. Nozaki, I. Kimura, Bull. Chem. Soc. Jpn. 50 (3) (1977) 614.
[8] J.M. Campelo, A. Garcia, D. Luna, J.M. Marinas, M.S. Moreno, Stud. Surf. Sci. Catal. 41 (1988) 249.
[9] L. Calzolari, F. Cavani, T. Monti, C. R. Acad. Sci. IIC 3 (2000) 533.
[10] F. Cavani, T. Monti, in: M.E. Ford (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, 2000, p. 123.
[11] F. Cavani, T. Monti, D. Paoli, Stud. Surf. Sci. Catal. 130 (2000) 2633.
[12] F. Cavani, T. Monti, P. Panseri, B. Castelli, V. Messori, WO Patent 74,485, assigned to Borregaard Italia, 2001.
[13] L. Gilbert, M. Janin, A.M. Le Govic, P. Pommier, A. Aubry, in: J.R. Desmurs, S. Ratton (Eds.), The Roots of Organic Development, Elsevier, Amsterdam, 1996, p. 48.
[14] Y. Shiomi, Y. Nakamura, T. Manabe, S. Furusaki, M. Matsuda, M. Saito, US Patent 5,248,835, assigned to UBE Ind., 1993.
[15] E. Santacesaria, D. Grasso, D. Gelosa, S. Carrà, Appl. Catal. 64 83, 101, 1990.
[16] R. Tleimat-Manzalji, D. Bianchi, G.M. Pajonk, Appl. Catal. A 101 (1993) 339.
[17] Y. Fu, T. Baba, Y. Ono, Appl. Catal. A 166 (1998) 419 and 425.
[18] Y. Fu, T. Baba, Y. Ono, Appl. Catal. A 178 (1998) 219.
[19] L. Kiwi-Minsker, S. Porchet, R. Doepper, A. Renken, Stud. Surf. Sci. Catal. 108 (1997) 149.
[20] S. Porchet, L. Kiwi-Minsker, R. Doepper, A. Renken, Chem. Eng. Sci. 51 (11) (1996) 2933.
[21] L. Kiwi-Minsker, S. Porchet, P. Moeckli, R. Doepper, A. Renken, Stud. Surf. Sci. Catal. 101 (1996) 171.
[22] M.C. Samolada, E. Grigoriadou, Z. Kiparissides, I.A. Vasalos, J. Catal. 152 (1995) 52.
[23] P.D. Chantal, S. Kaliaguine, J.L. Grandmaison, Appl. Catal. 18 (1985) 133.
[24] R. Pierantozzi, A.F. Nordquist, Appl. Catal. 21 (1986) 263.
[25] S.C. Lee, S.W. Lee, K.S. Kim, T.J. Lee, D.H. Kim, J. Chang Kim, Catal. Today 44 (1998) 253.
[26] M. Marczewski, G. Perot, M. Guisnet, Stud. Surf. Sci. Catal. 41 (1988) 273.
[27] M. Marczewski, J.-P. Bodibo, G. Perot, M. Guisnet, J. Mol. Catal. 50 (1989) 211.
[28] L. Garcia, G. Giannetto, M.R. Goldwasser, M. Guisnet, P. Magnoux, Catal. Lett. 37 (1996) 121.
[29] S. Balsamà, P. Beltrame, P.L. Beltrame, P. Carniti, L. Forni, G. Zuretti, Appl. Catal. 13 (1984) 161.
[30] P. Beltrame, P.L. Beltrame, P. Carniti, A. Castelli, L. Forni, Appl. Catal. 29 (1987) 327.
[31] R.F. Parton, J.M. Jacobs, H. van Ooteghem, P.A. Jacobs, Stud. Surf. Sci. Catal. 46 (1989) 211.
[32] S. Namba, T. Yashima, Y. Itaba, N. Hara, Stud. Surf. Sci. Catal. 5 (1980) 105.

[33] Z.-H. Fu, Y. Ono, Catal. Lett. 21 (1993) 43.
[34] M. Renaud, P.D. Chantal, S. Kaliaguine, Can. J. Chem. Eng. 64 (1986) 787.
[35] G. Moon, W. Böhringer, C.T. O'Connor, Catal. Today 97 (2004) 291.
[36] M.D. Romero, G. Ovejero, A. Rodriguez, J.M. Gomez, I. Agueda, Ind. Eng. Chem. Res. 43 (2004) 8194.
[37] R.F. Parton, J.M. Jacobs, D.R. Huybrechts, P.A. Jacobs, Stud. Surf. Sci. Catal. 46 (1989) 163.
[38] J.B. Moffat, Catal. Rev. Sci. Eng. 18 (1978) 199.
[39] A. Corma, H. Garcia, J. Primo, J. Chem. Res. Synop. (1988) 40.
[40] P.D. Chantal, S. Kaliaguine, J.L. Grandmaison, Stud. Surf. Sci. Catal. 19 (1984) 93.
[41] L.B. Young, N.J. Skillman, US Patent 4,371,714, assigned to Mobil Oil Co, 1983.
[42] P. Espeel, R. Parton, H. Toufar, J. Martens, W. Hölderich, P. Jacobs, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites: Fundamentals and Applications, Springer-Verlag, Berlin, 1999, p. 377, chap. 6.
[43] K. Tanabe, T. Nishizaki, in: G.C. Bond et al. (Ed.), Proceed. 6th ICC, The Chemical Society, London, 1977, p. 863.
[44] K. Tanabe, Stud. Surf. Sci. Catal. 20 (1985) 1.
[45] K. Sreekumar, S. Sugunan, J. Mol. Catal. A 185 (2002) 259.
[46] T. Tsai, F. Wang, Catal. Lett. 73 (2001) 167.
[47] N. Ballarini, F. Cavani, L. Maselli, A. Montaletti, S. Passeri, D. Scagliarini, C. Flego, C. Perego, J. Catal. 251 (2007) 423.
[48] US Patent 4,933,509, assigned to General Electric, 1989.
[49] H. Grabowska, W. Kaczmarczyk, J. Wrzyszcz, Appl. Catal. 47 (1989) 351.
[50] H. Grabowska, W. Mista, J. Trawczynski, J. Wrzyszcz, M. Zawadzki, Appl. Catal. A 220 (2001) 207.
[51] F. Cavani, L. Maselli, D. Scagliarini, C. Flego, C. Perego, Stud. Surf. Sci. Catal. 155 (2005) 167.
[52] S. Velu, C.S. Swamy, Appl. Catal. A 162 (1997) 81.
[53] US Patent 6,897,175, assigned to General Electric, 2005.
[54] R.N. Spitz, J.E. Barton, M.A. Barteau, R.H. Staley, A.W. Sleight, J. Phys. Chem. B 90 (1986) 4067.
[55] D.R. Taylor, K.H. Ludlum, J. Phys. Chem. 76 (1972) 2882.
[56] Z. Hou, T. Okuhara, Chem. Comm. (2001) 1686.
[57] A. Corma, H. Garcia, J. Miralles, Microporous Mesoporous Mater. 43 (2001) 161.
[58] J. Tateiwa, E. Hayama, T. Nishimura, S. Uemura, Chem. Lett. (1996) 59.
[59] J. Tateiwa, E. Hayama, T. Nishimura, S. Uemura, J. Chem. Soc. Perkin Trans. 1 (1997) 1923.
[60] T. Nishimura, S. Ohtaka, A. Kimura, E. Hayama, Y. Haseba, H. Takeuchi, S. Uemura, Appl. Catal. A 194 (2000) 415.
[61] A.E. Palomares, G. Eder-Mirth, J.A. Lercher, J. Catal. 168 (1997) 442.
[62] A.E. Palomares, G. Eder-Mirth, M. Rep, J.A. Lercher, J. Catal. 180 (1998) 56.
[63] S.T. King, J.M. Garces, J. Catal. 104 (1987) 59.
[64] H. Itoh, A. Miyamoto, Y. Murakami, J. Catal. 64 (1980) 284.
[65] G. Madhavi, S.J. Kulkarni, K.V.V.S.B.S.R. Murthy, V. Viswanathan, K.V. Raghavan, Appl. Catal. A 246 (2003) 265.
[66] S.B. Hamilton, US Patent 3,446,856, assigned to Schenectady, 1969.
[67] T. Mathew, M. Vijayaraj, S. Pai, B.B. Tope, S.G. Hegde, B.S. Rao, C.S. Gopinath, J. Catal. 227 (2004) 175.
[68] S. Sato, K. Koizumi, F. Nozaki, J. Catal. 178 (1998) 264.
[69] S. Sato, R. Takahashi, T. Sodesawa, K. Matsumoto, Y. Kamimura, J. Catal. 184 (1999) 180.
[70] A.H. Padmasri, A. Venugopal, V. Durgakumari, K.S. Rama Rao, P. Kanta Rao, J. Mol. Catal. A 188 (2002) 255.
[71] A. Radhe Shyam, R. Dwivedi, V.S. Reddy, K.V.R. Chary, R. Prasad, Green Chem. 4 (2002) 558.
[72] L.H. Klemm, J. Shabtai, D.R. Taylor, J. Org. Chem. 33 (1968) 1480.
[73] E.I. Heiba, P.S. Landis, J. Catal. 3 (1964) 471.
[74] A.R. Gandhe, J.B. Fernandes, J. Mol. Catal. A 226 (2005) 171.
[75] I.B. Borodina, E.B. Pomakhina, Ts.M. Ramishvili, O.A. Ponomareva, A.I. Rebrov, I.I. Ivanova, Russ. J. Phys. Chem. 80 (2006) 892.
[76] C. Zerbe, F. Jage, Brennstoff-Chem. 5 (16) (1935) 88.
[77] K. Shanmugapriya, S. Saravanamurugan, M. Palanichamy, B. Arabindoo, V. Murugesan, J. Mol. Catal. A 223 (2004) 177.