# The transformations involving methanol in the acid- and base-catalyzed gas-phase methylation of phenol

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## Abstract

The alkylation of phenol with methanol was studied using a Brønsted-type acid catalyst (a H-mordenite) and basic/dehydrogenating catalysts (MgO, $Fe_2O_3$ and Mg/Fe/O), with the aim of investigating the reaction mechanism. The main difference between the two classes of catalysts concerned the transformations occurring on methanol. Specifically, in the former case the acid-type activation of methanol led to the development of an electrophylic species that gave rise to the formation of anisole and of *C*-alkylated compounds. With basic catalysts, methanol dehydrogenated to formaldehyde, which then underwent transformation to methylformate and to decomposition products, i.e., CO, $CO_2$, $CH_4$ and $H_2$. In this case, the prevailing compounds obtained by reaction with phenol were *o*-cresol and 2,6-xylenol. The dehydrogenation of methanol was found to be the key-step in the generation of the active methylating species with basic catalysts.
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## 1. Introduction

The methylation of phenol and phenol derivatives has been widely investigated, and several papers report about the effect of the catalyst characteristics on the nature and distribution of products. The reaction has a great relevance from the industrial point of view [1]; for instance, 2,6-xylenol is the monomer for the production of poly-(2,6-dimethyl)phenylene oxide resin; 2-methylphenol (*o*-cresol) is the monomer for the synthesis of epoxycresol novolacks; 2,5-dimethylphenol is the intermediate for the synthesis of dyes, antiseptics and antioxidants, and 2,3,6-trimethylphenol is the starting compound for the preparation of vitamin E. The products of *O*-methylation of phenol (anisole) and of diphenols (e.g., guaiacol) are intermediates in the production of skin protection agents and food additives.

Preferred alkylating agents are methanol and dimethylcarbonate, while more conventional reactants, such as methylchloride and dimethylsulfate, although still employed industrially, are nowadays less attractive due to environmental concerns [2–4].

The *C*-methylation of phenol aimed at the production of *o*-cresol or of 2,6-xylenol is industrially carried out with methanol as the alkylating agent and with catalysts possessing basic characteristics [5–13]. Catalysts are made of either (i) supported and unsupported alkali and alkaline-earth metal oxides [14–18], or (ii) transition or post-transition mixed metal oxides [19–33], or (iii) mixed oxides containing both alkaline-earth metals and transition metal ions [34–44]. They are used in prevalence for gas-phase methylation, since under liquid-phase conditions a low conversion is generally achieved. This is attributed to the lower reaction temperature, and to the stronger interaction that develops between the catalyst and phenol in the condensed phase.

The strongest basic catalysts are alkali and alkaline-earth metal oxides, which however may deactivate by interaction

with weak acid molecules, included carbon dioxide and water. Therefore, preferred basic materials for industrial applications are transition metal oxides (e.g., supported V/Fe mixed oxides [45], or Cr oxide [46]) that are claimed to exhibit medium-strength basic properties [1,45–47]. Similar reactivity is exhibited by those mixed oxides that couple the $O^{2-}$ nucleophilicity, typical of alkali or alkaline-earth metal oxides, with the coordinating properties of transition metal oxides [1,47–49]. One example is MgO, in which the $H^+$-abstracting properties are modulated through the introduction of host cations [35,44]. The addition of increasing amounts of $Fe^{3+}$ to MgO in samples prepared by thermal decomposition of hydrotalcite-like precursors, with Mg/Fe atomic ratio between 2 and 6, lead to the formation of solid solutions having general composition $Mg_{1-x}Fe_xO_{1+0.5x}$ and medium-strength basic sites [50]. The latter derived from the higher electronegativity of $Fe^{3+}$ as compared to $Mg^{2+}$, that decreased the charge density on the neighboring $O^{2-}$ and made the latter less nucleophilic than O atoms in MgO [50].

Characteristics of catalysts possessing basic features when used as catalysts for phenol methylation are: (i) the very high regio-selectivity in *C*-methylation, since the *ortho/para*-methylation ratio is in all cases largely higher than 2, and (ii) the high chemo-selectivity, since the *O/C*-selectivity ratio, a function of the basic strength of catalysts, is, in general, very low. A selectivity to *o*-cresol + 2,6-xylenol as high as 98% is reported in many patents [1].

One major problem of the industrial process of phenol methylation is the low yield with respect to methanol, due to its decomposition; consequently, a large excess of methanol is usually fed in order to reach an acceptable per-pass conversion of phenol. Various solutions have been proposed to minimize this side reaction (see, for example, [48]), amongst which the co-feeding of water seems to be the most effective [45,49]. This aspect, however, is often forgotten in scientific literature, and only few papers take into consideration the methanol decomposition [19,34,51–53] and the transformations that occur on the alkylating alcohol. On the other hand, a wide literature demonstrates that methanol undergoes different transformations on metal oxides, depending on the catalyst surface properties [13,54,55].

In the present work we correlate the catalytic performance in the gas-phase methylation of phenol with the transformations that occur on methanol, for one acid (H-mordenite) and three basic catalysts (MgO, $Fe_2O_3$ and Mg/Fe mixed oxide), also possessing dehydrogenating properties. More specifically, the aim was to determine if the nature of the methylating species can be different when either acid or basic systems are used, and which implications this may have on the catalytic performance in phenol methylation.

## 2. Experimental

Fe/O, Mg/Fe/O and Mg/O catalysts were prepared by precipitation from an aqueous solution containing the corresponding metal nitrates. For instance, to obtain 15 g of MgO, 96.15 g of $Mg(NO_3)_2·6H_2O$ (Carlo Erba Reagenti, 99% purity) were dissolved in 375 ml of distilled water. The solution was drop-wise added to another solution containing 39.75 g of $Na_2CO_3$ (Carlo Erba Reagenti) dissolved in 375 ml of distilled water. While adding the first solution to the second one, the pH was continuously adjusted, in order to keep it close to 10.0. Under these conditions the precipitation of $Mg(OH)_2$ occurred. The so obtained slurry was left under stirring for 40 min; then the precipitate was separated from the liquid by filtration, and washed with 6 L of distilled water at 40 °C. The solid was then dried at 110 °C overnight, and calcined at 450 °C for 8 h in air. The preparation of $Fe_2O_3$ was carried out with the same procedure, using $Fe(NO_3)_3·9H_2O$ (Carlo Erba Reagenti) as starting material. The same protocol was also used for the preparation of the Mg/Fe mixed oxide, using the corresponding amount of the two salts to obtain the desired atomic ratio between components.

The acid catalyst was a commercial H-mordenite, having an atomic Si/Al ratio equal to 20, shaped in 1/16″ extrudates (binder alumina). This sample was supplied by Süd-Chemie AG.

The XRD powder patterns of the catalysts were taken with Ni-filtered $CuK\alpha$ radiation ($\lambda = 1.54178$ Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. Surface area was measured by means of the BET single-point method ($N_2$ adsorption at the temperature of liquid $N_2$), using a Sorpty 1750 Fisons Instrument.

Temperature-programmed-reaction tests were performed with a TPDRO 1100 ThermoQuest Instruments, by saturation of a He stream with methanol at 6 °C, and feeding the gaseous stream continuously to the reactor, while heating the catalyst from 200 to 450 °C (heating rate: 10 °C/min). The effluents were analyzed by means of a VG quadrupole. The intensity of the following ion current signals were recorded: $H_2$ ($m/z = 2$), $H_2O$ (18), CO (28), $CO_2$ (44), $CH_3OH$ (31 > 32 > 29 ≫ 30), $CH_4$ (16), HCOOH (46), $CH_3OCOH$ (60) and $H_2CO$ (29 > 30 > 28). The most intense $m/z$ signals of formaldehyde (29 and 30) are also typical of methanol; therefore, the pressure of $H_2CO$ was extrapolated from the comparison of the intensity profiles for signals at $m/z = 29$ and 30, with that one of $m/z = 31$.

Catalytic tests were carried out by vaporization of a methanol/phenol liquid mixture (methanol/phenol molar ratio: 10/1; liquid flow: 0.0061 ml/min; phenol supplied by Sigma Aldrich, 99+% purity; methanol supplied by Carlo Erba Reagenti) in a $N_2$ stream (gas flow: 20 N ml/min). The composition of the feed gas was the following (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Overall gas residence time was 2.68 s. Total pressure was atmospheric. A high methanol/phenol feed ratio (10/1) was used in order to better evidence the parallel reactions occurring on methanol, (i) dehydrogenation and decomposition with basic catalysts, and (ii) formation of alkylaromatics with zeolites. Some tests were also made with a methanol/phenol feed ratio equal to 5/1. For tests made in absence of phenol, the inlet stream of methanol was maintained the same as that one used in phenol methylation tests.

The gas/vapors stream was fed to a stainless steel reactor (length: 30 cm, internal diameter: 3/4″), containing 1 cm³ of catalyst (catalyst weight: Mg/O 0.85 g, Mg/Fe/O 0.95 g,

Table 1
Main characteristics of catalysts employed in the present work

| Catalyst (atomic ratio) | Surface area (BET), $m^2/g$, before reaction; after reaction | Crystalline phases (XRD) before reaction; after reaction |
|---|---|---|
| Mg/Fe/O (Mg/Fe = 0.19) | 112; 66 | $Fe_2O_3$ and $MgFe_2O_4$; $Fe_3O_4$ and/or $MgFe_2O_4$ |
| Fe/O | 36; 32 | $Fe_2O_3$ hematite; $Fe_3O_4$ magnetite |
| Mg/O | 68; 60 | $Mg(OH)_2$ brucite + hydroxymagnesite $Mg_5(CO_3)_4(OH)_24H_2O$; MgO periclase |
| H-mordenite (Si/Al = 20) | 372; 56 | H-mordenite |

Fe/O 1.10 g and H-mordenite 0.64 g) shaped either in 30–60 mesh particles (Mg/O, Fe/O and Mg/Fe/O) or in extrudates (H-mordenite). Catalyst particles were prepared by pressing the calcined powder to obtain pellets that were then broken into smaller granules. During catalytic measurements, the reactor exit stream was condensed in 25 ml of HPLC-grade acetone for 1 h, maintained at 6 °C. Products condensed in acetone were analyzed by gas chromatography, using a GC6000 Carlo Erba instrument equipped with a FID and a HP-5 column. The GC oven temperature was programmed from 50 to 250 °C, with a heating rate of 10 °C/min. Non-condensable gases (CO, $CO_2$, $H_2$, $CH_4$) were analyzed by sampling the gaseous stream with a syringe at the reactor exit, before condensation in acetone, and by injecting the sample in 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, with a heating rate of 10 °C/min.

Before carrying out the reactivity tests, Mg/O, Fe/O and Mg/Fe/O catalysts were "equilibrated" in the reaction feed at 390 °C for 10 h, in order to obtain a stable catalytic performance. With the H-mordenite, tests were run without any preliminary equilibration, because this catalyst exhibited a slow, continuous deactivation and it was not possible to reach a stable catalytic performance.

Yields are expressed as follows:

- Yield to products of phenol methylation: $\frac{\dot{n}^{out}_{product}}{\dot{n}^{in}_{phenol}}$, where "product" stands for *o*-cresol, *p*-cresol, 2,6-xylenol, 2,4-xylenol, anisole and polyalkylated phenols.
- Yield to products of methanol decomposition: $\frac{\dot{n}^{out}_{product}}{\dot{n}^{in}_{methanol}}$, where "product" stands for CO, $CO_2$ and $CH_4$.
- Yield to products of methylformate decomposition: $\frac{\dot{n}^{out}_{product}}{2\dot{n}^{in}_{metylformate}}$, where "product" stands for CO, $CO_2$ and $CH_4$.
- Yield to $H_2$ from methanol or from methylformate decomposition: $\frac{\dot{n}^{out}_{H_2}}{2\dot{n}^{in}_{methanol\ or\ methylformate}}$.
- Yields to alkylaromatics from methanol: $\sum_i \alpha_i \frac{\dot{n}^{out}_{product_i}}{\dot{n}^{in}_{methanol}}$, where "product$_i$" stands for: toluene, dimethylbenzenes, trimethylbenzenes, tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene; $\alpha_i$ is the number of C atoms for each compound.

Conversions are expressed as follows:

- Conversion of phenol or of methanol:

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

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

## 3. Results

### 3.1. The characterization of catalysts

Table 1 summarizes the main characteristics of catalysts employed in the present work: (i) Magnesium oxide (sample Mg/O) is the main component in alkaline-earth oxides-based catalysts employed in the General Electric process for the synthesis of 2,6-xylenol [47–49]. (ii) Iron oxide (sample Fe/O) is claimed to be the main component in the optimal catalyst for the selective ring methylation of phenol and 1-naphthol [22, 27,56]. (iii) Magnesium-iron mixed oxide (sample Mg/Fe/O) catalyzes the liquid-phase and the gas-phase methylation of *m*-cresol [42,44] and of phenol [35,57]. In the case of the Mg/Fe/O catalyst used in the present work, the choice was for a sample having an excess of Fe, in which the chemical–physical properties of iron oxide are modified by the presence of a low amount of $Mg^{2+}$ [58]; the Mg/Fe ratio, as determined in the calcined sample by SEM/EDX, was 0.19. Finally, the acid catalyst investigated was a commercial H-mordenite, having a Si/Al atomic ratio of 20.

Fig. 1 compares the X-ray diffraction patterns of the three basic catalysts, both before (fresh samples) and after (spent samples) reaction. In the case of Mg/O, before reaction the oxide was strongly carbonated and hydrated (hydroxymagnesite, $Mg_5(CO_3)_4(OH)_24H_2O$, JCPDS file 25-0513, and brucite $Mg(OH)_2$, 44-1482), whereas after reaction the pattern did correspond to that of MgO (periclase, 04-0829). The XRD pattern of the fresh Mg/Fe/O sample was not well resolved, indicating the presence of a large fraction of amorphous compound; reflections corresponding to both $MgFe_2O_4$ (36-0398) and $Fe_2O_3$ hematite (13-0534) were present. After reaction, reflections attributed to $Fe_2O_3$ had disappeared, while those corresponding to either magnetite $Fe_3O_4$ (19-0629) or the spinel phase $MgFe_2O_4$ (the two patterns are almost coincident) were present. The same occurred in the case of the Fe/O sample; the XRD pattern of the sample before reaction was that of $Fe_2O_3$, while after reaction it corresponded to that of $Fe_3O_4$. The partial reduction of hematite in the reaction environment, when used as the cat-
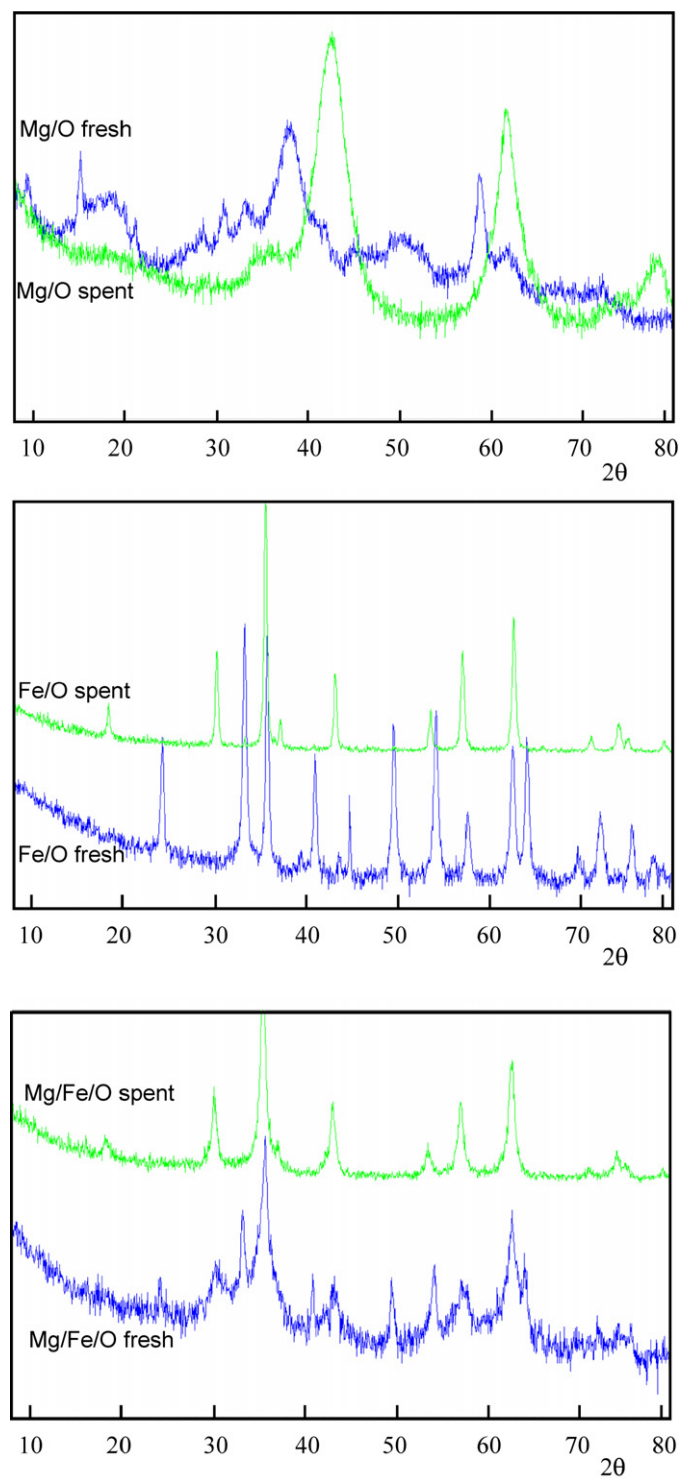
Fig. 1. X-ray diffraction patterns of fresh (calcined) samples and of spent Mg/O, Fe/O and Mg/Fe/O.

alyst for aryl methylation, was also reported by other authors [59,60].

The addition of $Mg^{2+}$ to the Fe oxide led to a considerable increase of the surface area, as compared to Fe/O (Table 1); this difference was present also in the spent catalysts. This may derive from the lower crystallinity of Mg/Fe/O as compared to Fe/O. This aspect is typical of Mg/Fe mixed oxides [42],

in which the incorporation of a guest cation in the oxide of a differently charged metal causes the development of structural defects and hence of less crystalline materials. The spent Mg/Fe/O catalyst had a lower amount of amorphous component than the fresh one; the increase of crystallinity led to a decrease of the surface area, that however remained higher than that of Fe/O.

### 3.2. The transformation of methanol with basic catalysts: steady-state performance

The reactivity of catalysts towards methanol was investigated. Tests were carried out by feeding methanol vapors diluted in a $N_2$ stream. Fig. 2 reports the yields of CO, $CO_2$, $CH_4$ and $H_2$ for Mg/O, Fe/O and Mg/Fe/O samples as functions of temperature. There was no formation of either dimethylether or hydrocarbons (with the exception of methane).

Mg/O gave an appreciable conversion of methanol only at 450 °C, while Fe/O was even active at 390 °C; Mg/Fe/O yielded large amounts of decomposition products at 350 °C. From the comparison of the methanol conversion at 390 °C, the following ranking was obtained: Mg/Fe/O > Fe/O ≫ Mg/O. The higher activity of Mg/Fe/O as compared to Fe/O can be attributed to its higher surface area (66 versus 32 $m^2$/g, respectively, for the spent catalysts), but a modification of the dehydrogenating properties of Fe due to the presence of Mg cannot be excluded [27,33,35].

$H_2$ is a co-product in the formation of the $C$-containing compounds. The following stoichiometries can be assumed, for calculation purposes only:

$$CH_3OH \rightarrow CO + 2H_2,$$

$$CH_3OH \rightarrow 1/2CO_2 + 1/2CH_4 + H_2,$$
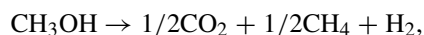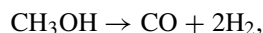
where the first reaction corresponds to methanol decomposition and lumps together the dehydrogenation to formaldehyde and then to CO. The second one is the overall stoichiometry for the transformation of methanol to formaldehyde, followed by dimerization to yield methylformate and decomposition of the latter into $CH_4$ and $CO_2$. Therefore, from a mass-balance point of view, all reactions that lead to the formation of $H_2$ starting from $CH_3OH$ (in the absence of any co-reactant) are included in these two reactions, when the assumption is made that there is no formation of coke on catalysts (the accumulation of which would lead to the additional formation of $H_2$). In other words, the amount of $H_2$ produced should correspond to the sum of $2CO + CH_4 + CO_2$, and the yield of $H_2$ to the sum of yields of $CO + 1/2CH_4 + 1/2CO_2$. An excess of $H_2$ with respect to this sum might be due to the presence of non-decomposed formaldehyde, formic acid or methylformate.

Formic acid may form either through the Cannizzaro reaction

$$2CH_2O + H_2O \rightarrow HCOOH + CH_3OH$$
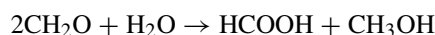
or through oxidation of formaldehyde by a redox-type cation, e.g., $Fe^{3+}$; in the latter case the progressive reduction of the cation would cause a decrease of the contribution of this reaction. In our case, water was not fed to the reactor, neither it
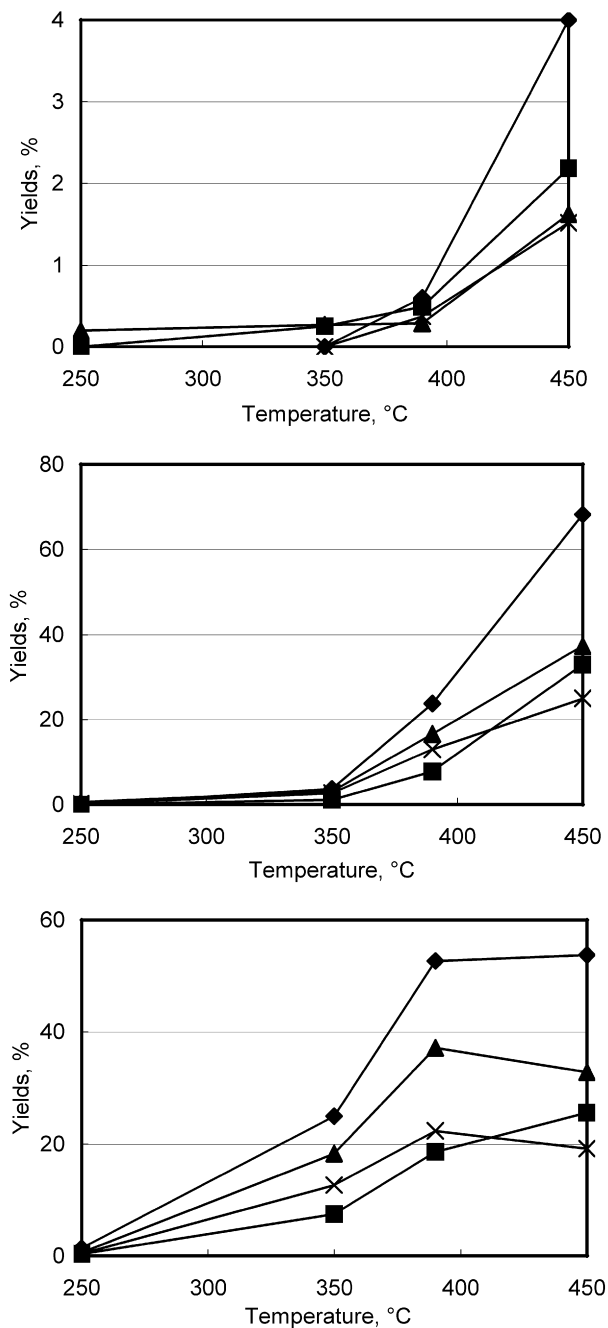
Fig. 2. Yields of CO ($\blacksquare$), $CO_2$ ($\blacktriangle$), $CH_4$ ($\times$) and $H_2$ ($\blacklozenge$) as functions of the temperature. Feed composition (molar fractions): methanol 0.12, nitrogen 0.88. Catalysts: Mg/O (top), Fe/O (middle) and Mg/Fe/O (bottom).

was produced; in fact, there was no formation of dimethylether. Methylformate may form either by esterification of formic acid with methanol or by direct dimerization of formaldehyde (Tischenko reaction).

In the case of Mg/O (Fig. 2, top), at high temperature the yield of $H_2$ approximately corresponded to the sum of yields of CO + $1/2 CH_4$ + $1/2 CO_2$. Therefore, formaldehyde, formic acid and methylformate were not produced. This indicates that these intermediates are very reactive under the applied conditions and quickly evolve towards the final products. The yields of $CH_4$ and of $CO_2$ were similar, in agreement with the for-

mation of methylformate as the main intermediate, which then decomposed into the two light products.

In the case of Mg/Fe/O and Fe/O, the distributions of products obtained with the two catalysts were similar. Also in this case, the yield of $H_2$ was not much different from the sum: yield CO + $1/2$ yield $CH_4$ + $1/2$ yield $CO_2$. Indeed, very small amounts of formaldehyde and methylformate were detected by GC–MS. Moreover, the yield of $CO_2$ was higher than that of $CH_4$; this points out for an additional mechanism for carbon dioxide formation, for instance the decomposition of formate.

A solution of $CH_3OH$ (30 wt%) in $H_2O$ was vaporized in a $N_2$ stream and fed over the Mg/Fe/O catalyst. A lower selectivity to $CH_4$ and an increased formation of $CO_2$ were observed with respect to results obtained in the absence of water. This indicates that the presence of steam favored the Cannizzaro-type disproportionation of formaldehyde and hence the formation of formic acid; the latter in part yielded methylformate, while in part decomposed to $CO_2$ + $H_2$. On the contrary, in the absence of $H_2O$ the preferred pathway for the formation of formate is likely an oxidation by $Fe^{3+}$, occurring on the fresh, oxidized catalyst; the progressive reduction of $Fe^{3+}$ to $Fe^{2+}$ makes this contribution less and less important.

### 3.3. The transformation of methanol with basic catalysts: non-steady-state performance

With the aim of determining the reaction intermediates in methanol decomposition, and of confirming that the light compounds identified (CO, $CH_4$, $CO_2$ and $H_2$) were due to the dehydrogenation of methanol to formaldehyde and to the consecutive reactions occurring upon the latter, we carried out non-steady-state tests by feeding methanol over the catalyst, while raising the reaction temperature (temperature-programmed-reaction tests). Figs. 3 and 4 show the variation of the pressure for selected products (as evaluated from the intensity of the ion current signal at corresponding $m/z$ values in mass spectra), obtained with Mg/O and Mg/Fe/O, respectively.

In the case of Mg/O, the formation of $H_2$ became relevant above 300–350 °C, in concomitance with the increase of CO. The pressure of $CO_2$ was very low and decreased above 350 °C. No methylformate formed; the amount of HCOOH was very low, since its pressure was 3 orders of magnitude lower than that of CO and $CO_2$. The amount of formaldehyde, as inferred from the comparison of the signals at $m/z = 29$, 30 and 31, was negligible.

Therefore, taking into consideration the information achieved with steady-state and non-steady-state tests, it can be inferred that Mg/O dehydrogenates methanol to formaldehyde above 300 °C, even though with a very low yield, and that methylformate is rapidly formed through the dimerization mechanism. At the high temperature required for its formation, methylformate immediately decomposes yielding $CO_2$ + $CH_4$. The Cannizzaro reaction, followed by esterification, is another possible mechanism for methylformate formation; however, this reaction is unlikely, due to the fact that water was not fed to the reactor.
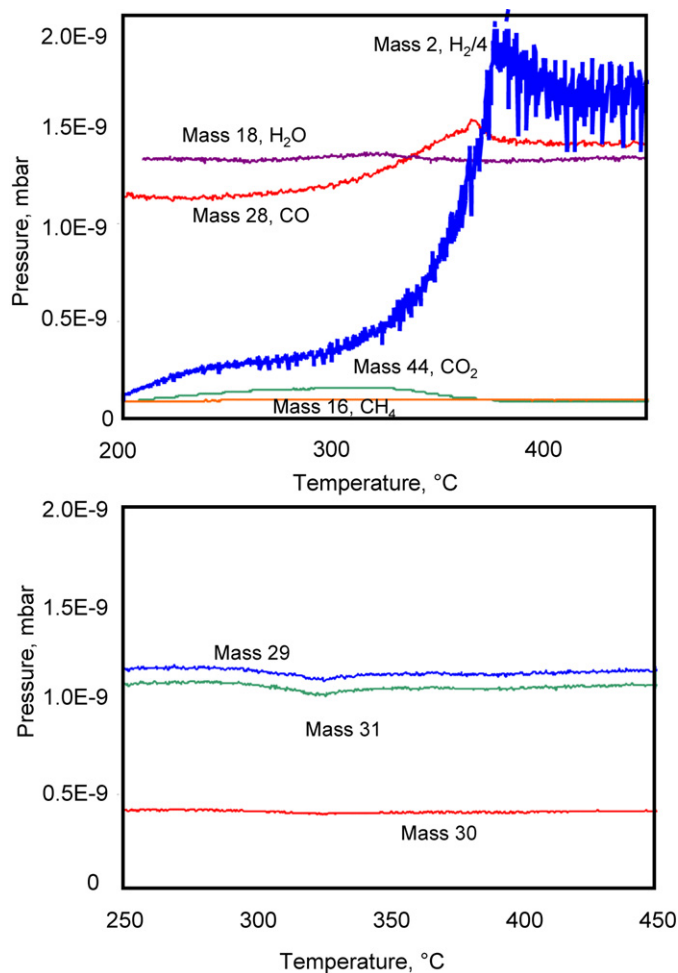
Fig. 3. Pressure of selected molecular ions as functions of temperature in temperature-programmed-reaction tests. Top: selected substances. Bottom: molecular ion and main fragments for methanol and formaldehyde. Catalyst: Mg/O. Feed methanol, carrier He.
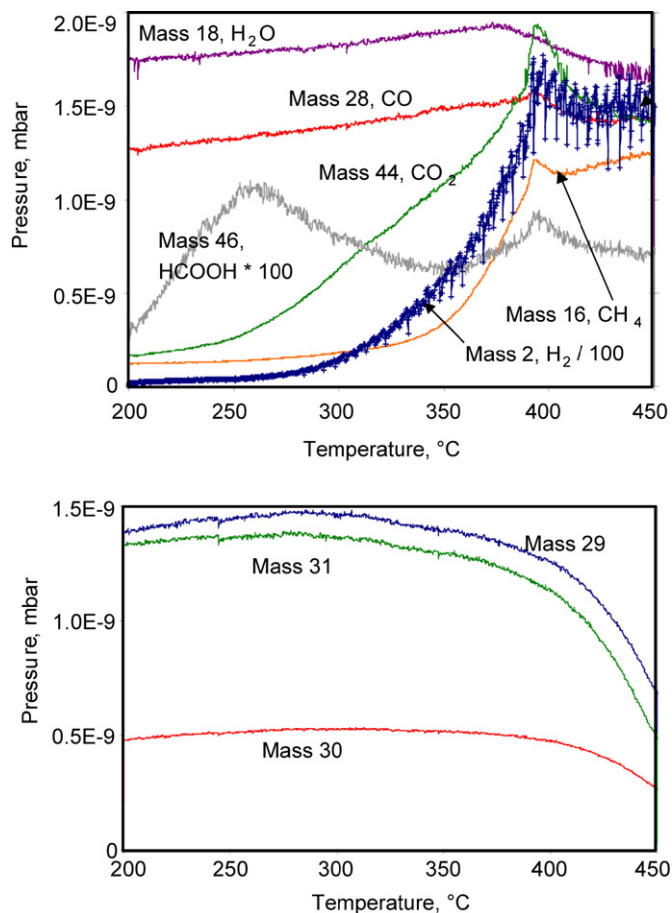


Fig. 4. Pressure of selected molecular ions as functions of temperature in temperature-programmed-reaction tests. Top: selected substances. Bottom: molecular ion and main fragments for methanol and formaldehyde. Catalyst: Mg/Fe/O. Feed methanol, carrier He.

As far as tests with Mg/Fe/O concern (Fig. 4), the amount of each product was higher than that obtained with Mg/O, confirming the results obtained with steady-state tests. $H_2O$ and CO formed in relevant amount even at low temperature, when the formation of HCOOH occurred. Therefore, under these conditions the decomposition of formic acid into $CO + H_2O$ is probable. The detection of formic acid confirms the high activity of Mg/Fe/O in the dehydrogenation or oxidative dehydrogenation of methanol to formaldehyde; the latter was then oxidized by $Fe^{3+}$ to yield the formate species.

The partial pressures of $CO_2$ and $CH_4$ had the same trend above 300–350 °C, confirming the presence of one common intermediate, i.e., methylformate. It is worth mentioning that methylformate was not detected even under non-steady conditions, probably because of its high reactivity and rapid decomposition to light compounds. The decrease of intensity of the $m/z = 31$ signal above 350 °C was due to a relevant increase of methanol conversion. The relative decrease of intensity for signals at $m/z = 29$ and 30 was lower than that of $m/z = 31$; this indicates the presence of low, but non-negligible, amounts of formaldehyde.

### 3.4. The transformation of methanol with the acid catalyst

The tests of methanol transformation were also carried out with the H-mordenite. In this case, two different classes of compounds formed: (i) alkylbenzenes, ranging from toluene to hexamethylbenzene, and (ii) light decomposition products. Fig. 5 (top) plots the conversion of methanol, the overall yield of alkylaromatics and that of light compounds. Fig. 5 (middle) reports the detail of the yields of the light compounds.

Alkylaromatics were the prevailing compounds in the temperature range comprised between 250 and 350 °C; in this range the formation of light decomposition products was nil (only methane formed). In a recent work [61] we reported that in the gas-phase methylation of phenol catalyzed by H-BEA zeolites, the main products of methanol transformation were pentamethyl and hexamethylbenzene; the latter, and polynuclear aromatics as well, were responsible for the progressive catalyst deactivation.

With the H-mordenite, at above 350 °C, the formation of alkylaromatics decreased considerably and the main product was methane, with minor amounts of CO, $CO_2$ and $H_2$. The plot of methanol conversion as a function of temperature also
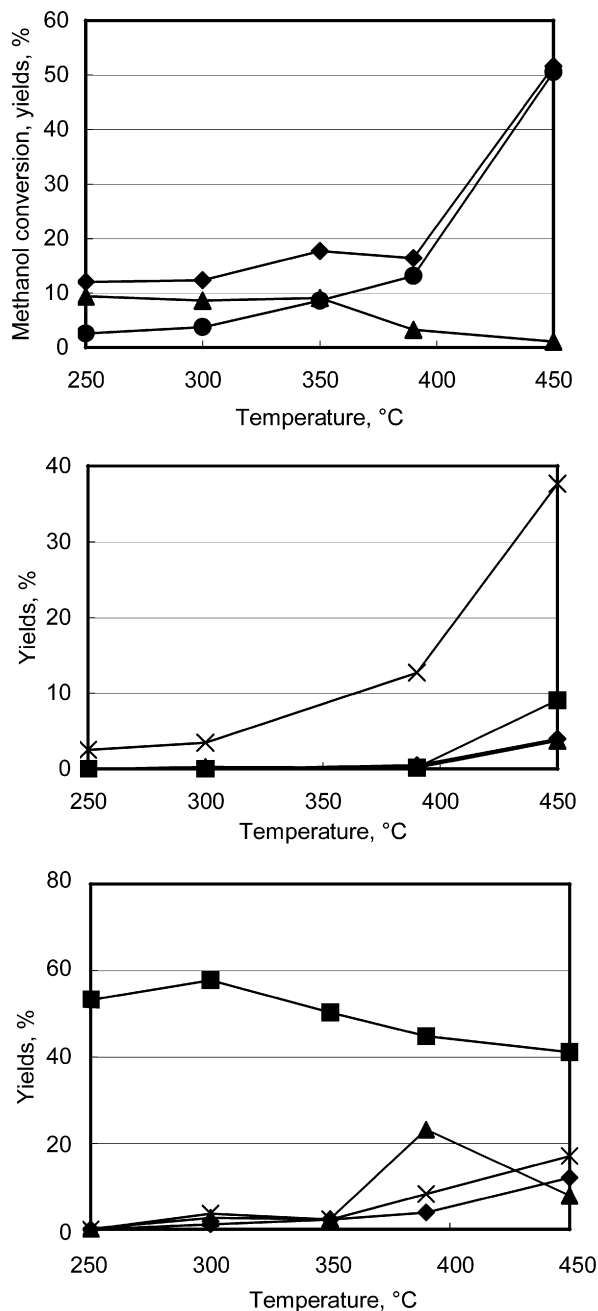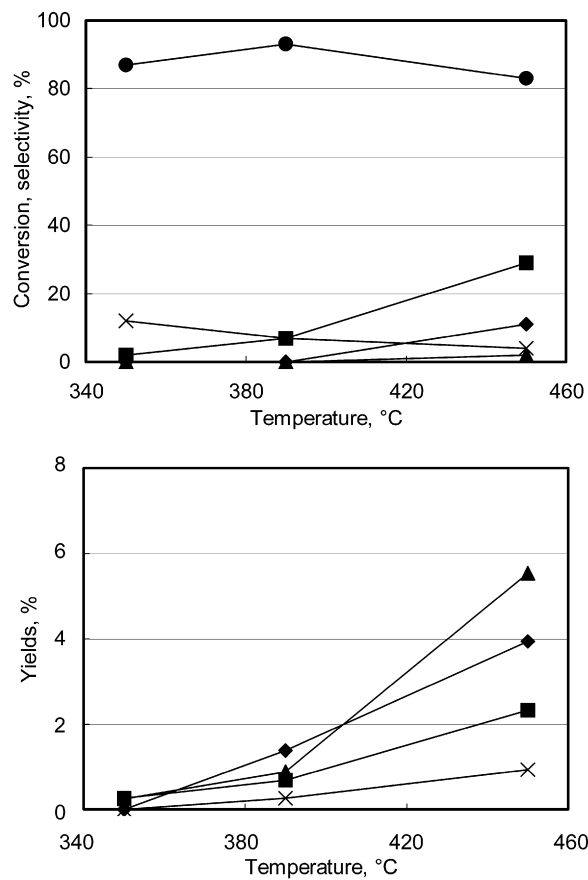
Fig. 6. Top: conversion of phenol (■), selectivity to *o*-cresol (●), *p*-cresol (▲), 2,6-xylenol (◆) and anisole (×) as functions of temperature. Bottom: yields of CO (■), $CO_2$ (▲), $CH_4$ (×) and $H_2$ (◆) as functions of temperature. Feed composition (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Catalyst: Mg/O.

formaldehyde and decomposition; however, methanol yielded small amounts of alkylbenzenes. At higher temperature, methylformate decomposed to $CH_4 + CO_2$. The formation of $H_2$ may derive either from the decomposition of formic acid or from the dehydrogenation of methanol, both formed by hydrolysis of methylformate ($H_2O$ is the co-product in the formation of alkylbenzenes).

### 3.5. The methylation of phenol with the basic catalysts

The performance of Mg/O, Fe/O and Mf/Fe/O catalysts in phenol methylation is shown in Figs. 6–8. For each catalyst the following values are reported as a function of the reaction temperature: (i) the conversion of phenol and the selectivity to the aromatic products, calculated with respect to the phenol converted, and (ii) the yields of the light products ($CO_2$, $CH_4$, CO and $H_2$), calculated with respect to the inlet methanol.

#### 3.5.1. Mg/O (Fig. 6)
The conversion of phenol was low; the main product was *o*-cresol, with small amounts of 2,6-xylenol (at 450 °C) and anisole. *p*-Cresol formed in very low quantity. The conversion of methanol was comparable to that achieved under the same conditions without phenol (Fig. 2, top). However, there were
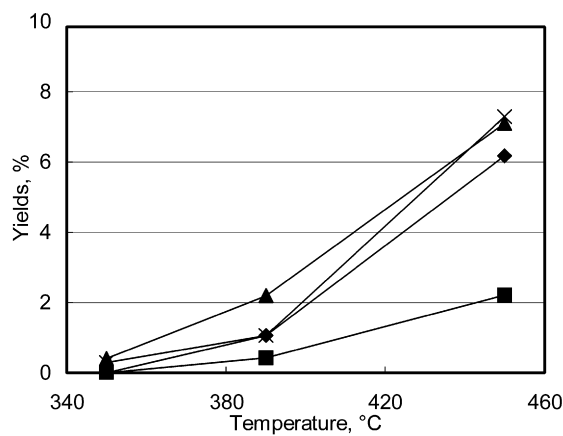






Fig. 5. Top: conversion of methanol (◆), yield of alkylaromatics (▲) and yield of light compounds (●) as functions of temperature. Middle: yields of CO (■), $CO_2$ (▲), $CH_4$ (×) and $H_2$ (◆) as functions of temperature. Feed composition (molar fractions): methanol 0.12, nitrogen 0.88. Catalyst: H-mordenite. Bottom: yields of CO (■), $CO_2$ (▲), $CH_4$ (×) and $H_2$ (◆) as functions of temperature. Feed composition (molar fractions): methylformate 0.12, nitrogen 0.88. Catalyst: H-mordenite.

suggests a change of the prevailing mechanism of methanol transformation at 350–400 °C, with respect to that one occurring at lower temperatures.

When tests were carried out by feeding methylformate (Fig. 5, bottom), CO was the main product below 350 °C, together with methanol, both deriving from the acid-catalyzed decomposition of the reactant. The absence of $H_2$ confirms that the methanol formed did not undergo dehydrogenation to

Fig. 7. Top: conversion of phenol (■), selectivity to $o$-cresol (●), 2,6-xylenol (◆), $p$-cresol (▲) and anisole (×) as functions of temperature. Bottom: yields of CO (■), $CO_2$ (▲), $CH_4$ (×) and $H_2$ (◆) as functions of temperature. Feed composition (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Catalyst: Fe/O.
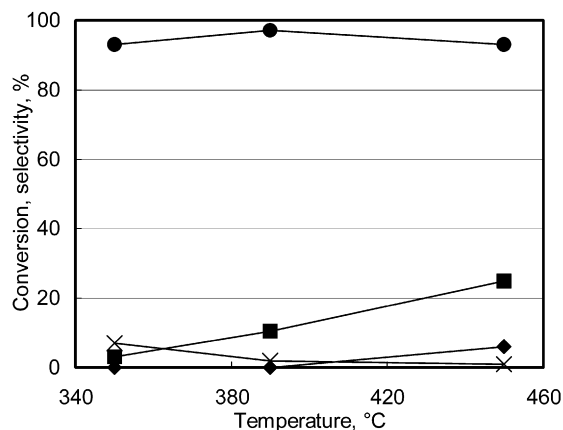


Fig. 8. Top: conversion of phenol (■), selectivity to $o$-cresol (●), 2,6-xylenol (◆), $p$-cresol (▲) and anisole (×) as functions of temperature. Bottom: yields of CO (■), $CO_2$ (▲), $CH_4$ (×) and $H_2$ (◆) as functions of temperature. Feed composition (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Catalyst: Mg/Fe/O.

differences in the distribution of the light products, since the formation of $CH_4$ was lower than that of $CO_2$ in the presence of phenol, whereas the two compounds formed in almost equimolar amounts in the absence of phenol.

### 3.5.2. Fe/O (Fig. 7)

The performance of Fe/O in phenol methylation was similar to that of Mg/O. The prevailing product was $o$-cresol, with low formation of anisole and traces of $p$-cresol. One difference with respect to Mg/O concerns the transformation of methanol; in fact, with Fe/O the conversion of methanol was lower, as demonstrated by the lesser formation of light compounds, with respect to tests done without phenol (Fig. 2, middle). This indicates that methanol and phenol competed for adsorption on the same sites; the presence of the aromatic reactant (even though with a partial pressure which was 1/10th that of methanol) inhibited the dehydrogenation of methanol. The presence of a competitive effect between phenol and methanol indicates a relevant role of the Fe–O Lewis acid–base pair in the interaction with O and H atoms, respectively, of the hydroxy group of the two molecules. The relative distribution of the light compounds also changed with respect to that one obtained in the absence of phenol; the main effect was the decrease of the selectivity to CO, with also a slight increase of the selectivity to $CH_4$.
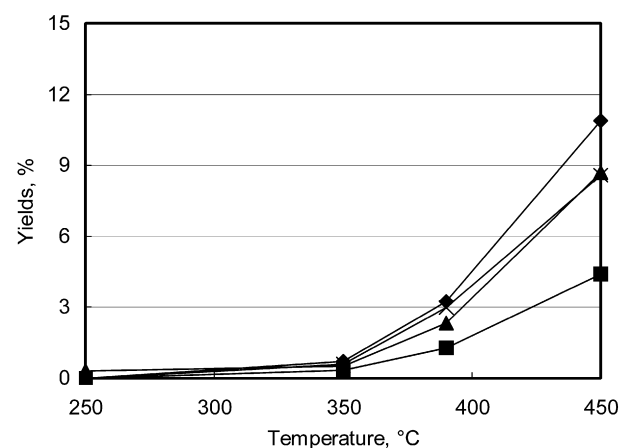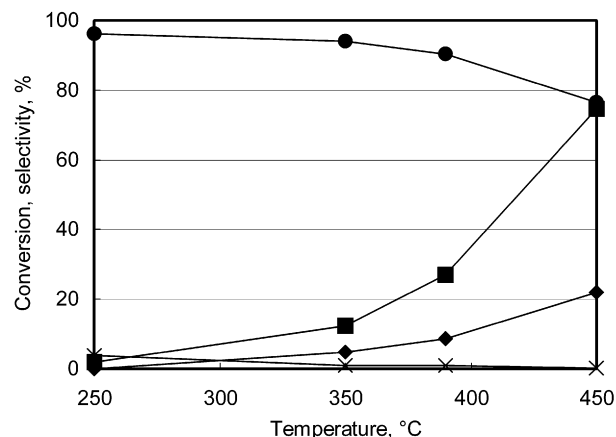
### 3.5.3. Mg/Fe/O (Fig. 8)

The catalyst was more active than Mg/O and Fe/O in phenol and methanol conversion. The surface area of Mg/Fe/O was almost twice that of Fe/O (Table 1); this may explain the difference in reactivity between these two catalysts. By contrast, the surface area of Mg/O was higher than that of Fe/O, but the activity of the two samples was comparable. This points out for an important role of the Fe sites. It is worth noting that also with Mg/Fe/O a competition effect between phenol and methanol caused a decrease of methanol conversion to light products as compared to that achieved in the absence of phenol (Fig. 2, bottom). The distribution of the phenolic products was also similar to that one obtained with Fe/O. The main product at low temperature was $o$-cresol, but its selectivity decreased in favor of 2,6-xylenol when the reaction temperature was increased.

Tests were carried out with the Mg/Fe/O catalyst and with a methanol/phenol feed ratio equal to 5/1, by keeping the partial pressure of methanol the same as for tests reported in Fig. 8, while the phenol partial pressure was increased. At 390 °C, the conversion of phenol decreased from 28% (obtained with a feed ratio of 10/1), to 15% (feed ratio 5/1); the rate of phe-
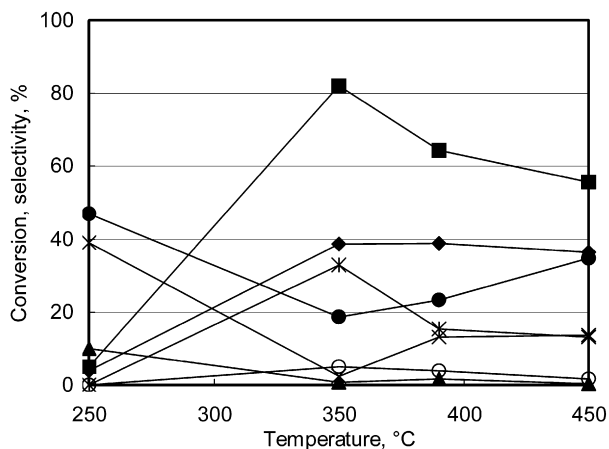
Fig. 9. Conversion of phenol (■), selectivity to *o*-cresol (●), 2,6-xylenol (◆), *p*-cresol (▲), anisole (×), 2,4-xylenol (○) and polyalkylated phenols (✳) as functions of temperature. Feed composition (molar fractions): methanol 0.108, phenol 0.011, nitrogen 0.881. Catalyst: H-mordenite.



Fig. 10. Conversion of anisole (■), selectivity to *o*-cresol (●), 2,6-xylenol (◆), *p*-cresol (▲), phenol (×) and 2,4-xylenol (○) as functions of temperature. Feed composition (molar fractions): anisole 0.01, nitrogen 0.99. Catalyst: H-mordenite.

nol transformation remained the same in the two series of tests. Therefore, the reaction rate order for the partial pressure of phenol was close to zero, possibly indicating a saturation of surface sites devoted to phenol adsorption and activation. On the other hand, the conversion of methanol to yield methylated phenols and light compounds was not affected by the variation of phenol partial pressure.

### 3.6. The methylation of phenol with the acid catalyst

The catalytic performance in phenol methylation of the H-mordenite is illustrated in Fig. 9. The catalyst was very active; at 350 °C the conversion of phenol was 80%. A further increase of temperature led to a decrease of conversion. This can be attributed to two concomitant phenomena, (i) a progressive deactivation of the catalyst, due to the formation of condensed aromatics (coke precursors) by transformation of methanol [61–66], and (ii) a considerable increase in the parallel reactions of methanol decomposition to light compounds. Indeed, the spent catalyst was coked, and its surface area was considerably lower than that one of the fresh catalyst (Table 1). The *in situ* regeneration of the catalyst by treatment in nitrogen-diluted air increased the activity. For instance, the conversion of phenol at 390 °C after the regeneration treatment was 87% (before regeneration, 64%); in correspondence, the selectivity to anisole decreased from 12% to less than 1%. The structural integrity of the spent catalyst was checked by means of X-ray diffraction.

The main products at low temperature were *o*-cresol and anisole, but also 2,6-xylenol and *p*-cresol formed in relevant amounts. The increase of temperature led to a lower selectivity to all mono-alkylated compounds, in favor of the formation of xylenols and polyalkylated compounds. However, above 350 °C the decrease of phenol conversion caused an increase of the selectivity to *o*-cresol and anisole.

Anisole itself may act as an alkylating agent, favoring the formation of cresols and polyalkylates. This possibility has
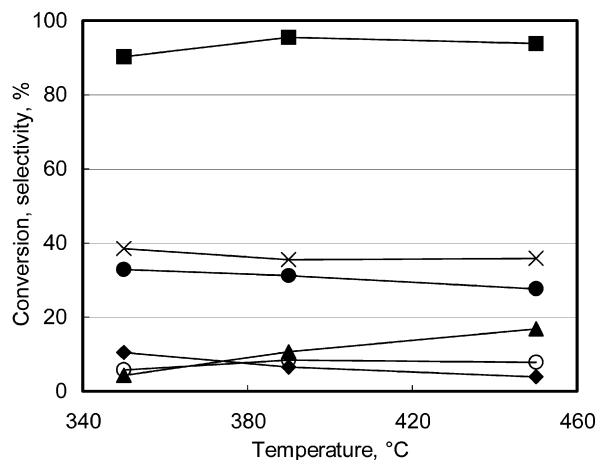
been investigated by feeding vapors of anisole in the absence of methanol. The results plotted in Fig. 10 show that anisole is very reactive at temperatures higher than 300 °C. Therefore, the anisole formed in phenol methylation may actually be an intermediate in the formation of *C*-alkylated compounds, especially for high phenol conversion. In fact, data in Fig. 9 show that in phenol methylation the selectivity to anisole was the lowest (3%) at 350 °C, in correspondence of the highest phenol conversion, while at 400 and 450 °C it was higher than 10%, due to the decrease of phenol conversion.

In tests made by feeding anisole (Fig. 10), comparable amounts of phenol and *o*-cresol were obtained, and minor amounts of *p*-cresol (which formation increased with temperature), of 2,4- and 2,6-xylenols and of polyalkylated phenols. Since methylanisoles were not formed at all, it is possible to exclude the intermolecular methylation:

2 anisole → phenol + methylanisole.
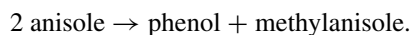
Therefore the formation of *o*-cresol mainly occurred by intramolecular rearrangement of anisole. The formation of phenol is not to be attributed to the hydrolysis of anisole, since water was not present. However, it is known that alkylarylethers may decompose at high temperature, to form alkylphenols (*ortho > para*) and phenols [67]. Noteworthy, we detected the formation of ethylene and of minor amounts of light alkanes (methane, ethane and propane); this suggests that the transformation of anisole to phenol indeed occurred through a high-temperature, radical-like bimolecular mechanism with generation of two molecules of phenol and one of ethylene.

One further aspect of tests made by feeding anisole is the absence of any evident deactivation phenomena at high temperature, in contrast with what observed in the case of phenol methylation. This was due to the absence of methanol in the reaction feed, reactant for the formation of coke precursors; in fact, polyalkylated aromatics were not produced at all.

## 4. Discussion

### 4.1. The transformation of methanol over basic (dehydrogenating) catalysts

It is worth making a short overview of the properties of metal oxides in methanol transformation, as inferred from the wide literature available in this field. Higher alcohols dehydrate to olefins on acidic catalysts, while they dehydrogenate to aldehydes or ketones on catalysts having basic features; these reactions have often been used as test reactions to estimate the surface properties of catalysts [68]. The alcohol typically used is 2-propanol, due to the stability of the cation that develops by protonation and elimination of water, and to the easy detection of the corresponding ketone, i.e. acetone.

For what specifically concerns methanol, even in the 60's infrared studies have demonstrated that the chemisorption of methanol on alumina leads to the formation of methoxide in the 35–170 °C range; its transformation at higher temperatures into formate-like surface compound [69,70] is accompanied by evolution of $H_2$, with the possible intermediate formation of formaldehyde [71].

Several reviews have examined the nature of the species that develop by interaction between methanol and redox-type solid oxides [54,55]. The interaction with cations having Lewis-type acid properties yields an undissociated $CH_3OH_{ads}$, bonded species [72]. Dissociated methoxy species are preferentially formed over basic (ionic) oxides ($Bi_2O_3$, $Fe_2O_3$, NiO, ZnO, $ZrO_2$). The covalent and Lewis-type acid oxides ($WO_3$, $SiO_2$, $V_2O_5$, $Nb_2O_5$, $MoO_3$) and the amphoteric ones ($CeO_2$, $TiO_2$) produce both undissociated and dissociated terminal methoxy. Bridging methoxy, the intermediate for the formate species, can also form, e.g., on ZnO [73].

The interaction of methanol with non-reducible metal oxides has been the object of several investigations as well. MgO is known to catalyze the dehydrogenation of methanol to formaldehyde [74]. Methanol gives rise to physisorption, chemisorption or heterolytic dissociation [75] via acid–base mechanism, with formation of the $CH_3O^-$ species [76]. The development of the adsorbed formate species occurs through a Cannizzaro-type reaction with intermolecular disproportionation; a nucleophilic attack of the $O^{2-}$ surface species to the carbonyl (with development of the formate), is accompanied by a hydride transfer to a second molecule of adsorbed formaldehyde, which is converted to a methoxy species [73,77]. The formate may finally decompose to CO and $H_2$, without any supply of $O^{2-}$ from the solid. The disproportionation mechanism may also occur on metal oxides such as ZnO, through intermediate dioxymethylene species; finally, carbonate and bicarbonate species develop, with evolution of $CO_2$. Alternatively, the adsorbed methoxy and formate species may yield methylformate; however, the latter also forms by the direct dimerization of adsorbed formaldehyde (Tischenko reaction).

An overview of the interactions that formaldehyde may develop with metal oxides has been reported in the review of Barteau [13, and references therein]. Over redox-type oxides (ZnO, CuO, etc.), formaldehyde gives rise to adsorbed for-

mates, with incorporation of the $O^{2-}$ species. The nucleophilic attack on the carbonyl moiety occurs with the concomitant abstraction of an $H^+$ by a second $O^{2-}$ species. The attack at the carbonyl produces a dioxymethylene complex, further evolved to the formate species. The desorption of HCOOH, or its decomposition, leads to the reduction of the metal ion.

Formic acid on alumina may decompose either through a dehydrative route to $H_2O + CO$, or through a dehydrogenative route to $H_2 + CO_2$ [78–80], via intermediate surface formate species [81]. The formation of methylformate from methanol may occur through different mechanisms, depending on the nature of the oxide (either easily reducible or non reducible), the conditions (temperature, pressure, presence of $H_2O$), and the surface concentration of formaldehyde, the latter being primarily a function of the dehydrogenative properties of the oxide. Methylformate decomposes to yield either $CH_4 + CO_2$ or $CH_3OH + CO$, or gives back formaldehyde through a reverse Tischenko reaction [82]. In the presence of water, methylformate decomposes to formic acid and methanol.

In conclusion, several examples exist in literature showing that methanol undergoes different transformations on metal oxides, depending on redox properties of the cation and on the "basicity" of the oxygen anion. It is worth underlying that in our tests the formation of light products (CO, $CH_4$, $CO_2$ and $H_2$) is indicative of the dehydrogenation of methanol to formaldehyde and of the further transformation of the latter. Other mechanisms that might lead to the formation of the same compounds, e.g., a Fischer–Tropsch or methanation leading to the formation of $CH_4$ and $H_2O$ from $CO + H_2$, possibly catalyzed by Fe in Mg/Fe/O and Fe/O catalysts, can be excluded due to the following reasons: (i) the same light products also formed with Mg/O, although in lower amount, and (ii) no metallic Fe was found in spent samples.

The catalysts investigated possessed different activity in the dehydrogenation of methanol to formaldehyde and in the consecutive transformation of formaldehyde. The preferred pathway for the transformation of formaldehyde was a function of the catalyst type. With Mg/O, formaldehyde dimerized to yield methylformate; however, due to the relatively high temperature at which methanol dehydrogenated, the ester readily decomposed to $CO_2 + CH_4$. The overall conversion of methanol over Mg/O was not remarkably affected by the presence of phenol; therefore, the adsorption of the aromatic compound was not favored over that of methanol.

In the case of Fe-containing samples, more active than Mg/O, the presence of $Fe^{3+}$ in the fresh catalyst may favor oxidative mechanisms (the oxidehydrogenation of methanol to $H_2CO + H_2O$ and the oxidation of formaldehyde to formate). Formic acid decomposed to either $CO + H_2O$ or $CO_2 + H_2$ (the former reaction being preferred at low temperature), or yielded methylformate. Due to the high reactivity of these samples (especially of Mg/Fe/O), methylformate was obtained even at temperature lower than 400 °C. The decomposition of methylformate led to the formation of either $CH_3OH + CO$ or $CH_4 + CO_2$, the former reaction being preferred at low temperature, the latter at high temperature.
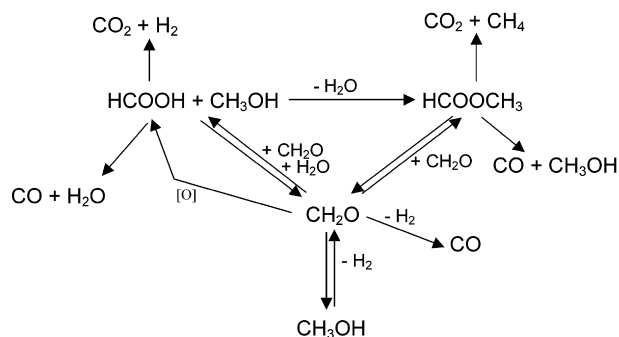
Fig. 11. Reaction network of methanol decomposition to light products.

The interaction of phenol with Mg/Fe/O was much stronger than with Mg/O, and the presence of phenol decreased the conversion of methanol, as inferred from the low yields of light compounds obtained during the reaction of phenol methylation. Therefore, an important contribution of the Lewis-acid characteristics of $Fe^{3+}$ [35,42] can be hypothesized. With both Fe/O and Mg/Fe/O, in the presence of phenol there was a decrease of the selectivity to CO and an increase of that to $CH_4$.

Furthermore, tests made with Mg/Fe/O and variation of the phenol partial pressure evidenced that an increase of the latter led to a decrease of phenol conversion, and that the reaction rate of phenol methylation was substantially independent from this reaction parameter. These data are consistent with a reaction mechanism in which the rate-limiting step is the activation of methanol, and with a Langmuir–Hinshelwood-type adsorption model in which, despite the large excess of methanol in the feed stream, phenol interacts strongly with Fe–O pairs and therefore competes with methanol for adsorption. This also confirms that the higher activity of the Fe-containing catalysts (Fe/O and Mg/Fe/O) as compared to Mg/O was due to the intrinsic dehydrogenating properties of the $Fe^{3+}$ cation.

Fig. 11 summarizes the different routes of methanol transformation over metal oxides having basic/dehydrogenating properties, as inferred from the analysis of the scientific literature. With our systems and under the conditions employed, the main reactions involved were different in function of the catalyst characteristics. Mg/O was poorly active in methanol dehydrogenation to formaldehyde; the latter then dimerized to methylformate, which finally decomposed to light products. With Fe-containing catalysts, an additional contribution to methylformate formation derived from the oxidation of formaldehyde to formate, at least in the fresh, oxidized catalyst. The intermediate compounds formed by methanol transformation (i.e., formaldehyde and formic acid) were identified in trace amounts only under non-steady-state conditions. This means that under the conditions used for catalytic tests these intermediates were very reactive, and were quickly transformed into the light compounds.

### 4.2. The transformation of methanol over zeolites

Over zeolites, the adsorption of methanol can generate framework-bonded methoxonium $CH_3OH_2^+$ and methoxy species that can co-exist at low temperature, but when the tem-

perature is increased the equilibrium is shifted towards the methoxy species [83]; the latter acts as an electrophylic alkylating agent on alkylaromatics [84,85]. In the methanol-to-olefins process, the first step is the dehydration of methanol to dimethylether. Two mechanisms have been proposed: (a) an indirect pathway, in which the adsorbed methanol first reacts with methoxy species and then converts into dimethylether in the presence of another methanol molecule [86]; (b) a direct pathway, in which two methanol molecules react on an acid site with formation of dimethylether and $H_2O$ in one step [87]. Surface methoxy species $SiO(CH_3)Al$ play a role in the formation of dimethylether [88]. The conversion of the equilibrium mixture of methanol and dimethylether (and water as well) is dominated by a "hydrocarbon pool" route [89,90], in which methanol is directly added onto reactive organic compounds to form aliphatic and aromatic hydrocarbons. The methoxy species also plays a role in the kinetic "induction period," leading to the reactive hydrocarbon pool. Alternative "direct" mechanisms have been proposed, in which a carbenium ion $CH_3^+$ reacts with dimethylether to generate either a carbonium ion $CH_3–CH_3^+–OCH_3$, or a oxonium ylide species. Other mechanisms include a carbene species: $CH_2$, as the reaction intermediate (see the review [91], for an analysis of the several mechanisms proposed in the literature). The surface-stabilized ylide or the carbene species [92] are responsible for the methylation of aliphatic compounds and the formation of hydrocarbons, both aliphatics and aromatics (polymethylbenzenes) [93]. At $T > 420\,^\circ C$, relevant amounts of methane and formaldehyde were found, whose formation was attributed to a reaction between methanol and methoxy groups [94].

In the case of the H-BEA zeolite, the main products in methanol transformation at high temperature were light aliphatics, both saturated and unsaturated, hexamethylbenzene and pentamethylbenzene [61], while ZSM-5 gave mostly dimethyl and trimethylbenzenes [62]. These compounds were further converted to naphthalene derivatives that were finally responsible for the formation of coke precursors and the deactivation of the zeolite [63].

It is worth mentioning that hexamethylbenzene also formed by reaction between phenol and methanol over $\gamma$-$Al_2O_3$ at $T > 400\,^\circ C$ [64,65], while in benzene and toluene methylation the same compounds wee not formed [66]. Lower temperatures led to the formation of anisole and cresols. Therefore, the phenolic group was proposed to play an important role in the formation of hexamethylbenzene through oxygen-containing intermediates.

With our H-mordenite catalyst, the formation of polyalkylbenzenes occurred preferentially in the temperature range between 250 and 350 °C, while at higher temperature the decomposition to light compounds became the main reaction of methanol transformation (Fig. 5). A possible role of coke, deposited on zeolite surface, in the dehydrogenation of methanol and decomposition to light compounds can not be excluded.

A change of the main reaction occurring on methanol also corresponds to a variation in the distribution of products obtained in phenol methylation. In the low-temperature range, the prevailing compounds were anisole and cresols. The increase

of temperature and of phenol conversion caused an increase of the selectivity to xylenols and polyalkylated phenols. At temperature higher than 350 °C the selectivity to polyalkylated phenol decreased and that to anisole increased, because of the lower phenol conversion. Moreover, a relevant increase in the formation of *o*-cresol was observed, while the selectivity to 2,6-xylenol remained constant. The change in the type of mechanism involved in methanol activation and the generation of a different methylating species may contribute to a modification of the products obtained in phenol methylation.

### 4.3. The role of methanol transformation in the acid and basic-catalyzed methylation of phenol

The implications that methanol transformations may have on catalytic performance in phenol methylation are matter of discussion. Results indicate that differences between acid and basic catalysts concern both the nature of aromatic products obtained and the type of transformations occurring on methanol. Specifically, we can distinguish three different behaviors:

(1) Mg/O dehydrogenates methanol to formaldehyde, but possesses low activity in this reaction; in phenol methylation, it gives products of both *O*-methylation and *C*-alkylation, the latter being largely preferred, especially at high temperature. Amongst *C*-alkylated products, *o*-cresol is greatly favored over *p*-cresol (yielded in very low amount) and 2,6-xylenols.

(2) Fe/O and Mg/Fe/O are active in methanol dehydrogenation, even at relatively low temperature. The distribution of products in phenol methylation is similar to that obtained with Mg/O, except for the lower formation of anisole. These catalysts, especially Mg/Fe/O, are also more active than Mg/O in phenol methylation. In this case a competition between the reactions of methanol dehydrogenation and phenol methylation occurs, likely due to the strong adsorption of phenol on $Fe^{3+}$ sites having Lewis-type properties.

(3) H-mordenite gives an acid-catalyzed activation of methanol and a wide distribution of products of phenol methylation, with relevant formation of both anisole and *C*-alkylated compounds. The prevailing reaction of methanol transformation at temperature lower than 350 °C is the formation of polymethylated benzenes, precursors of coke formation. In the high-temperature range, however, the prevailing mechanism of methanol activation is dehydrogenation; correspondingly, the distribution of products obtained in phenol methylation is slightly modified, with the prevailing formation of *o*-cresol over anisole.

With the three basic/dehydrogenating catalysts, the conversion of phenol began exactly when the conversion of methanol to light compounds also started. Therefore, these data support the hypothesis that the dehydrogenation of methanol is the necessary step for the generation of the active compound for phenol methylation. In other terms, it is possible that the true "methylating" agent is not methanol, but either formaldehyde or some compound formed by transformation of formaldehyde itself,

i.e., methylformate. Due to the presence of the carbonyl moiety, these compounds are more electrophylic than methanol, and hence are able to attack the aromatic ring even in the absence of an acid-catalyzed activation of the molecule. Moreover, the deprotonation of phenol and the generation of the phenolate species further activate the aromatic substrate.

This hypothesis is also supported by the comparison of the reactants conversion obtained with the three basic catalysts. In fact, Mg/O was clearly the least active catalyst in both methanol and phenol conversion. In Fe/O and Mg/Fe/O, the high activity has to be attributed to the dehydrogenating properties of $Fe^{3+}$; also, an oxidative mechanism may contribute to methanol activation, at least in the fresh catalyst Therefore, over Fe-containing catalysts the dehydrogenation of methanol represents the key-step for the generation of the active compound for the electrophylic attack to the aromatic ring.

The implications of methanol dehydrogenation on the mechanism of phenol methylation, in terms of regio- and chemoselectivity, is currently the object of our investigation. Several questions are still open, and specifically:

(1) If the dehydrogenation of methanol is the pre-requisite for the generation of the active compound in phenol methylation over metal oxides having basic/dehydrogenating properties, which is the true methylating species amongst those formed by methanol transformation, i.e., formaldehyde and methylformate? Are these compounds more reactive than methanol in phenol methylation?

(2) Which is the mechanism that leads to the formation of the methylated phenol, when the first step of the reaction is not a direct methylation by methanol?

(3) Is the generation of a reactive species different from methanol the reason for the high chemo- and regioselectivity experimentally observed in phenol methylation over metal oxides having basic/dehydrogenating properties? May the presence of metal cations having pronounced Lewis-acid characteristics also affect the selectivity?

## 5. Conclusions

This work compares the performance in phenol methylation of three catalysts having basic/dehydrogenation properties (Mg/O, Mg/Fe/O and Fe/O) with that of an acid catalyst, a H-mordenite. The main difference between the two classes of catalysts concerned the transformations occurring on methanol.

With basic catalysts the key-step was the dehydrogenation of methanol to formaldehyde, with generation of the active species for the methylation of phenol. In this case, the prevailing compounds obtained by reaction with phenol were *o*-cresol and 2,6-xylenol. Furthermore, formaldehyde underwent parallel transformations to methylformate and light products, i.e., $CO$, $CO_2$, $CH_4$ and $H_2$. The basic/dehydrogenating property of these catalysts played its main role in the activation of methanol and in the generation of an active species more electrophylic than methanol itself.

The acid-type activation of methanol led to the development of an electrophylic species and to the formation of anisole

and cresols. Methanol also underwent the parallel formation of alkylbenzenes, precursors of coke formation. At temperature higher than 350 °C methanol mainly decomposed to light products; under these conditions, the preferred products of phenol methylation were *o*-cresol and 2,6-xylenol.

It is proposed that the different nature of the methylating species generated by methanol activation may be the reason for the different type of products obtained in phenol methylation with acid and basic catalysts.

## Acknowledgments

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