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The balance of acid, basic and redox sites in Mg/Me-mixed oxides: The effect on catalytic performance in the gas-phase alkylation of *m*-cresol with methanol

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ABSTRACT

The reactivity of Mg/Me-mixed oxides (Me = Fe, Cr, Al) in *m*-cresol gas-phase methylation with methanol was studied, with the aim of finding relationships between catalytic performance and surface/bulk features. All systems exhibit similar surface properties (basically due to the presence of basic and Lewis-type acid sites), but the presence of extra cations in the MgO framework affects greatly the products obtained in the mentioned catalytic reaction, depending on the possible co-presence of redox capacity.

In particular, (i) the Mg/Al/O system, characterized by no redox capacity, shows catalytic behaviour quite similar to that of conventional Brønsted-type acid catalysts, though with the advantage of exhibiting almost no deactivation during use (a rather common problem *for acid catalysts activating methanol for phenol attack*); (ii) the Mg/Cr/O catalyst shows a reactivity typical of a basic catalyst, with high chemo- and regio-selectivity and the favoured formation of 2,5-dimethylphenol; (iii) the Mg/Fe/O system presents a catalytic behaviour closer to that of Mg/Cr/O, if referred to the distribution of phenolic products, but it also exhibits a better activity in methanol dehydrogenation to formaldehyde (that is the true electrophilic reactant for *m*-cresol ring methylation), and in the decomposition of formaldehyde into light compounds. This behaviour causes a poor selectivity to dimethylphenols with respect to converted methanol, whereas the selectivity with respect to converted *m*-cresol is not different from that shown by Mg/Cr/O system.

1. Introduction

The methylation of phenol and phenol derivatives has a high industrial relevance. For instance, 2,6-xylenol is the monomer for the production of poly-(2,6-dimethyl)phenylene oxide resins, 2-methylphenol (*o*-cresol) is the monomer for the synthesis of epoxycresol paints, 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 synthesis of vitamin E [1]. The products of phenol or anisole and diphenols methylation reaction are intermediates in the production of skin-protecting agents and food additives. Starting from *m*-cresol, and using 2-propanol as the alkylating agent, thymol is produced, which is a commercially interesting intermediate for the synthesis of menthol.

The C-alkylation of phenol derivatives is carried out either in the liquid-phase, using alkyl halides as alkylating agents, or in the gas-phase, with alcohols over acid or basic catalysts. The latter may be (supported) alkali and alkaline-earth metal oxides, (mixed) transition metal oxides, or combinations of both [2–19].

Previous reactivity experiments, carried out in liquid-phase in mild conditions, showed that this reaction may provide useful information about chemo- and regio-selectivity; they are driven by catalyst properties [35–39]. However, these kinds of tests achieved very low *m*-cresol conversion, so limiting the possibility of examining catalyst deactivation and the role of methanol decomposition. And in this respect, we decided to study the gas-phase methylation of *m*-cresol.

When methanol is the co-reactant, the ring methylation of phenolic compounds is carried out in the gas-phase, typically at temperatures higher than 300 °C, and one of the major problems of the industrial process is the decomposition of methanol occurring in these conditions. Consequently, a large excess of methanol is usually fed in order to reach an acceptable per-pass conversion of phenol.

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When the ring alkylation is carried out with solid acid catalysts, the main drawback is a rapid catalyst deactivation, due to the parallel transformation of methanol into olefins and aromatics, both precursors of coke formation. Moreover, the use of basic or acid catalysts can select the type of products obtained [22–26]. With acid catalysts, the reaction is scarcely regio- and chemo-selective, as the products of both O- and C-methylation are formed (O/C-selectivity ratio is a function of the reaction temperature and of the conversion degree). Furthermore, the regio-selectivity is low since all possible isomers for C-methylation are formed, although a predominance of the ortho-isomer can be observed. On the contrary, basic catalysts show very high chemo-selectivity, producing only minor amounts of the O-methylation product, as well as high regio-selectivity, being the ortho-isomer by far favoured.

In previous works [23,24], we reported that basic catalysts of moderate strength, *e.g.*, MgO-based systems, act first on the dehydrogenation of methanol to formaldehyde. Then, the latter acts as the active species in C-alkylation of the aromatic ring. A good catalyst for this kind of reactions needs to reach a proper balance between (i) the generation of adsorbed phenolate, *via* deprotonation of phenolic –OH groups; (ii) methanol dehydrogenation, to generate the highly reactive electrophilic formaldehyde; (iii) the decomposition of formaldehyde into waste light compounds [23,24]. Basic catalysts can guarantee all these features. Among them, MgO-based systems, and specifically Mg/Me-mixed oxides prepared by incorporation of guest ions into the MgO lattice, can provide a flexible tool for a proper tuning of the material reactivity properties.

Mixed oxides of the cited family can be prepared by various procedures, including decomposition of hydrotalcite precursors and sol–gel methods [27–34]. In the present work, we will compare the physico-chemical features and the catalytic properties of Mg^{2+}/Me^{3+}-mixed oxides (Me = Al, Fe, Cr), with the aim of finding general rules for the control of catalytic performance in the gas-phase methylation of phenol derivatives.

A fixed Mg/Me atomic ratio equal to 2 was chosen in order to (i) allow the synthesis of the proper mixed oxides starting from hydrotalcite-like precursors; (ii) guarantee a good dispersion of the elements; (iii) tune the strong basic properties of MgO by adding in the MgO structure a small amount of the hetero-element.

The role of methanol during the catalytic reaction and its decomposition during alkylation of phenolic compounds have not been sufficiently studied [5,17,20,21] so far. For this reason, final aim of the present contribution is to examine all these factors in order to explain the alkylation reaction mechanism.

2. Experimental

Mg/Me-mixed oxides were prepared by thermal treatment of hydrotalcite-like precursors. The latter were synthesized by a conventional procedure that was described elsewhere [35,40–42]. Precursors were synthesized using a Mg^{2+}/Me^{3+} ratio equal to 2, which is inside the interval of values at which the corresponding hydrotalcite-like material is formed. X-ray diffraction (XRD) pattern of precursors showed the presence of crystalline-layered mixed hydroxyl-carbonates in the case of Mg/Fe/O and Mg/Al/O systems, whereas an amorphous pattern was observed in the case of the Mg/Cr/O precursor. All samples were calcined in air at 450 °C for 8 h in a muffle, and then in N_2 for 3 h inside the reactor. Reference oxides, such as MgO and γ-Al_2O_3, were prepared following the same procedure as for the mixed oxides. The USY zeolite is a commercial sample, supplied by Tosoh (code: HSZ-330HUA).

XRD powder patterns of the catalysts were recorded with Ni-filtered Cu Kα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyser and a secondary curved graphite-crystal monochromator. Specific surface areas (SSA) were 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.

Laser Raman spectra were recorded at room temperature using a Renishaw 1000 spectrometer equipped with a Leica DMLM microscope. Samples were excited with an Argon laser beam (514 nm).

In situ FTIR spectra were obtained at 4 cm^{-1} resolution on a Bruker IFS113v spectrophotometer equipped with a MCT cryodetector. All samples were examined in the form of self-supporting pellets ($\sim$20 mg cm^{-2}). The spectra of adsorbed probe molecules were obtained with the solid sample contained in a homemade quartz cell, equipped with KBr windows, connected to a conventional high vacuum line (UHV) that allows samples activation and vibrational spectral analysis of the materials in a strictly *in situ* situation. Prior to probe-molecules adsorption/desorption and spectroscopic analyses, all catalysts were preliminarily thermally activated *in vacuo* at 500 °C. In the case of the Mg/Fe/O system, thermal activations were carried out either *in vacuo* (reduced "*red*" samples) or in oxidizing conditions in the presence of O_2 (oxidized "*ox*" samples). The surface characterization has been performed using: (i) carbon monoxide to check strong Lewis acidity and redox capacity; (ii) 2,6-dimethylpyridine (family of lutidine, Lu in the text) to test both total and Brønsted acidity. Lu was first adsorbed/desorbed at BT (the temperature of the sample in the IR beam), and then desorbed at 100 °C.

Catalytic tests were carried out by vapourization of a methanol/*m*-cresol liquid mixture (methanol/*m*-cresol molar ratio 5/1; *m*-cresol supplied by Sigma Aldrich; methanol supplied by Carlo Erba Reagenti) in a N_2 stream (gas flow 60 N mL/min, with a N_2/reactants molar ratio equal to 5). The composition of the feed gas was the following (in molar fractions): methanol 0.139, *m*-cresol 0.028, nitrogen 0.833. Overall gas reciprocal flow was 50 g_{cat} h mol^{-1}. Total pressure was atmospheric. For tests made in the absence of *m*-cresol, the inlet stream of methanol and carrier was maintained the same as the one used in *m*-cresol methylation tests. The gas/vapours stream was fed to a stainless steel reactor (length 30 cm, internal diameter 3/4″), containing 1.5 g of catalyst shaped in 30–60 mesh particles. 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 analysed 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 °C to 250 °C, with a heating rate of 10 °C/min. Non-condensable gases (CO, CO_2, H_2, CH_4) were analysed 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 °C to 220 °C, with a heating rate of 10 °C/min.

3. Results

3.1. Bulk features of the catalysts

Table 1 reports some results concerning morphology and structure (relevant XRD patterns are shown in Fig. 1) of the calcined Mg/Me samples. XRD patterns well agree with those reported in the literature [34,43,44] for the formation of microcrystalline-mixed Mg/Me oxides, in which the incorporation of the trivalent Me^{3+} cation in the periclase lattice generates cationic defects and produces a low crystallinity degree. In the case of the Mg/Cr/O sample, reflexes consistent with the presence of $MgCrO_4$ (JCPDS file 21-1255) are also observed (in the forthcoming section, the presence of

Table 1
Nature and specific surface area of the catalysts.

Catalyst	Surface area (m^2/g)	Crystalline phases (XRD)	Composition (atomic ratio, by AAS)
MgO	206	Periclase	–
Fe_2O_3	32	Haematite	–
Al_2O_3	203	γ-Alumina	–
Mg/Al/O	185	MgO-like mixed oxide	Mg/(Mg + Al) = 0.64
Mg/Fe/O	149	MgO-like mixed oxide	Mg/(Mg + Fe) = 0.67
Mg/Cr/O	62	MgO-like mixed oxide + $MgCrO_4$	Mg/(Mg + Cr) = 0.65

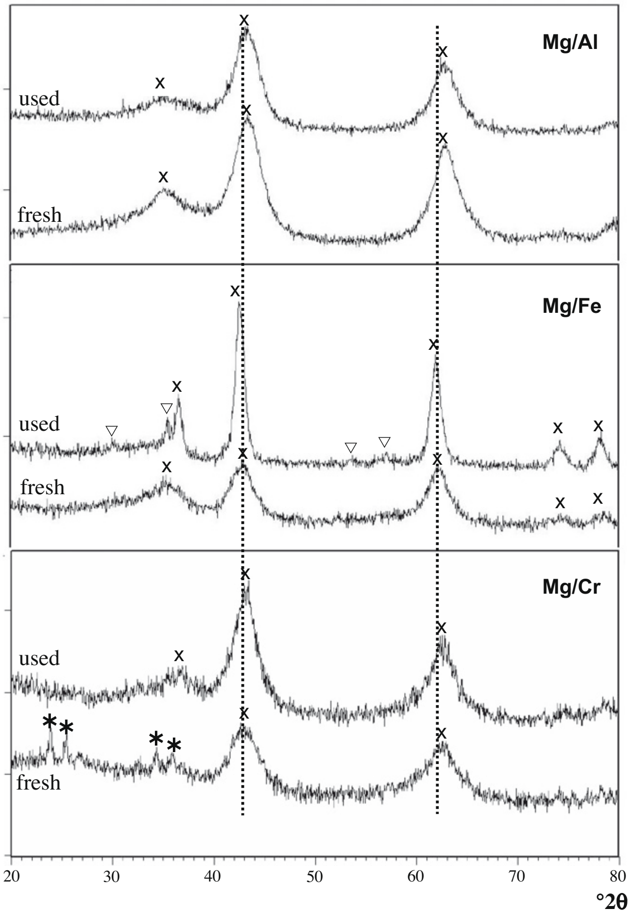


Fig. 1. XRD patterns of calcined (fresh) and used mixed oxides. All fresh samples were calcined at 450 °C. ×, MgO-like oxide; ∗, $MgCrO_4$; ∇, $MgFe_2O_4$. Dotted lines: main reflections of reference MgO (periclase).

chromates will be confirmed by IR spectroscopy). The formation of the latter compound, which crystallizes in larger particles (as suggested by the sharp peaks present in the XRD curves), may be considered to explain the low surface area obtained for this sample (actually, much smaller than that of the other mixed oxides).

Fig. 1 shows the XRD patterns of both as-calcined and used samples. All samples present low crystallinity (broad peaks). For all of them, the observed patterns are fairly similar to that of the starting MgO phase, but for Mg/Al/O where a shift of the reflexes towards greater 2 theta values (with respect to those of the reference MgO) is indicative of the partial substitution in the lattice of Mg^{2+} cations with Al^{3+} ones (ionic radii: Mg^{2+} 0.65 Å *vs.* Al^{3+} 0.50 Å). In the case of either Mg/Fe/O or Mg/Cr/O, no appreciable shifts of XRD reflexes were observed, because the ionic radii of guest cations (Fe^{3+} 0.69 Å; Cr^{3+} 0.615 Å) are very similar to the radius of Mg^{2+} (0.65 Å).

In the case of Mg/Al/O, the pattern of the used sample is quite similar to that of the corresponding fresh catalyst. Conversely, the patterns of both used Mg/Fe/O and Mg/Cr/O systems exhibit appreciable differences with respect to the corresponding calcined samples. Used Mg/Fe/O is more crystalline than the fresh one, as indicated by the full width at half maximum (FWHM) of the XRD signals, and components due to the most intense reflexes of the $MgFe_2O_4$ spinel phase (JCPDS 88-1943) appear. (Still, we cannot exclude the partial reduction of Fe^{3+} species during the reaction, with formation of magnetite (Fe_3O_4), because $MgFe_2O_4$ and Fe_3O_4 spinel phases possess similar XRD patterns.) In the case of the used Mg/Cr/O system, reflexes attributed to Mg chromate disappear. This suggests that the catalytic reaction generates a strongly reducing environment [23–25], which may cause the reduction of Cr^{6+} and either the segregation of amorphous Cr_2O_3 or the incorporation of Cr^{3+} within the MgO lattice. FTIR spectroscopic measurements are expected to better clarify this point.

Laser Raman spectra relative to the calcined samples (not reported for the sake of brevity) confirmed the presence of $MgCrO_4$ in the as-calcined (fresh) Mg/Cr/O system, whereas no bands ascribable to this compound were present anymore in the spectrum of the used sample. No Raman spectroscopic evidence was either found for the formation of Cr_2O_3 in the used Mg/Cr/O catalyst, and this seems to support the hypothesis of an incorporation of Cr^{3+} into the MgO lattice. In the case of used Mg/Fe/O, no Raman bands ascribable to magnetite were observed, and this confirms the segregation of the $MgFe_2O_4$ spinel compound. However, a preliminary calcination of the used sample was carried out before Raman investigation in order to remove organic contaminants responsible for a strong fluorescence, and this treatment could have modified the used catalyst, causing the oxidation of reduced Fe^{n+}-containing species, if present. Bands ascribable to coke were evident in the spectra of used Mg/Fe/O, but they did not appear in the spectra of both used Mg/Cr/O and Mg/Al/O catalysts.

3.2. Surface features of the catalysts

The surface basicity of our Mg/Me/O samples, determined by means of CO_2-TPD and reported in previous papers [37,39], showed that in mixed systems the hosting of a cation having high electronegativity decreases the basicity of the bridging O^{2-} ion when compared to pure MgO, in agreement with literature findings [34,43,44]. On the other hand, O^{2-} ions are sites characterized by strong basic strength, in particular when O^{2-} ions are paired with cationic vacancies. Mg/Me-mixed oxides showed a predominance of medium strength sites, in that all of them were considerably less basic than MgO, which showed a predominance of strongly basic sites [37,39].

In order to integrate the data obtained with different techniques and to correlate the surface behaviour of the materials with catalytic reactivity, FTIR spectroscopy of adsorbed probe molecules has been resorted to.

First of all, the ambient temperature adsorption of CO_2 on the various Mg/Me-mixed oxides (no IR spectra are reported here for brevity) has been examined in a recent study [45] and indicated that redox systems, like Mg/Fe/O and Mg/Cr/O, result less basic than the non-redox one (Mg/Al/O).

As for strong Lewis acidity, carbon monoxide (CO) adsorption/desorption at BT has been carried out. In fact: (i) CO acts as a weak Lewis base and, in these experimental conditions, can reveal only the strongest fraction of surface Lewis acid sites [46]. Moreover, (ii) CO adsorption is expected to evidence the redox capacity of the samples, when present.

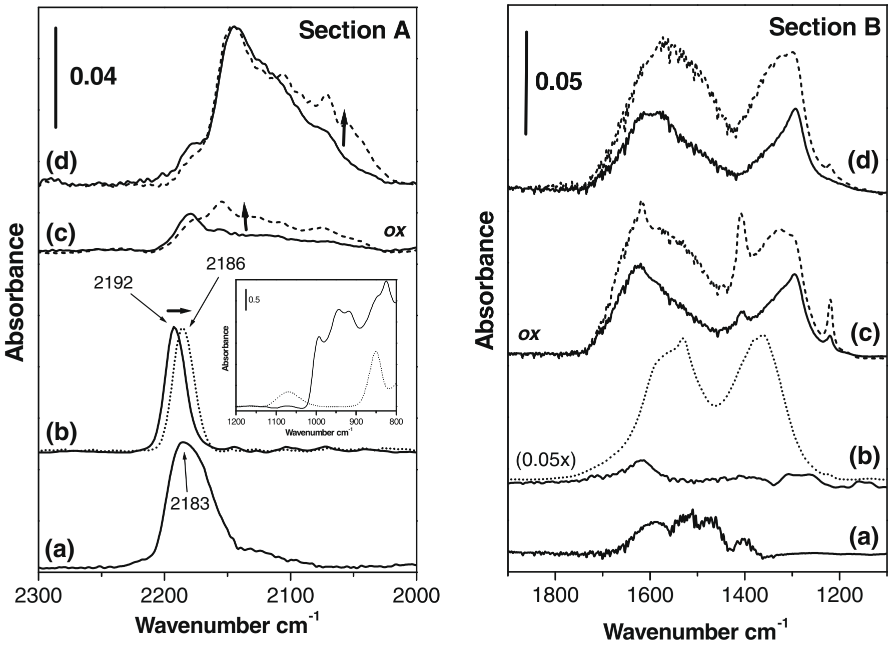


Fig. 2. Absorbance differential spectra, normalized against the background spectrum of the starting samples activated at 500 °C of Mg/Al/O (spectral set a), Mg/Cr/O (spectral set b), and *ox* and *red* Mg/Fe/O (spectral set c and d), obtained in the ν_{CO} (Section A) and in the ν_{OCO} (Section B) vibrational regions, after adsorption of 100 Torr CO at BT (solid lines), after up to 150 min of contact with CO (broken lines), and after prolonged contact with CO at 350 °C (dotted lines). Where the symbol *ox* is reported, within the activation process also a contact (for 30 min) with O_2 at the activation temperature was performed, to guarantee the oxidation of the sample. In Section B, spectra relative to the Mg/Cr/O sample (curves b) are 0.05-fold magnified. Inset to Section A: absorbance spectra obtained in the 1200–900 cm^{-1} region of Mg/Cr/O sample after CO adsorption at BT (solid lines) and after contact with CO at 350 °C (dotted lines).

Fig. 2 reports the spectra of CO contacted with Mg/Al/O (curves a), Mg/Cr/O (curves b), (reduced) "*red*" Mg/Fe/O and (oxidized) "*ox*" Mg/Fe/O samples (curves c and d, respectively), vacuum-activated at 500 °C. Two interesting "analytical" spectral regions are considered: Section A is relative to ν_{CO} signals (carbonyl-like species), whereas Section B is relative to ν_{OCO} vibrations (carbonate-like species). Upon BT contact with CO, all samples present Lewis acidity, characterized by the formation of Lewis acid/base surface CO-complexes, absorbing in the high-ν spectral range of Section A.

In the case of Mg/Al/O, CO adsorption indicates the presence of only σ-coordinated adspecies (solid line a). In fact, a single broad band is observed, located at ~2183 cm^{-1} and ascribable to coordinatively unsaturated (cus) Al^{3+} ions in tetrahedral coordination [47]. This signal is not modified for prolonged contact with CO at BT.

Curve b (solid line) in the same figure reports the spectrum relative to the interaction of CO with Mg/Cr/O. A single band located at ~2192 cm^{-1}, sharp and symmetrical (FWHM ≈ 25 cm^{-1}), witnesses the homogeneity of the adsorbing sites, which can be identified as cus Cr^{3+} cations, on the basis of the spectral behaviour and what reported in the literature [48].

The behaviour of Mg/Fe/O is completely different in that CO admitted on "*ox*" and "*red*" samples produces very different spectra: CO adsorbed on "*ox*" sample yields a principal absorption at ~2190 cm^{-1} (ascribable to the interaction with cus Fe^{3+} ions [45]) and (almost) negligible absorptions at lower wavenumbers, whereas CO contacted with "*red*" sample yields a very strong and heterogeneous absorption in the 2190–2000 cm^{-1} range (indicating carbonyl complexes characterized by the presence of π-back-donation), most likely due to the presence of Fe^{n+} species in which $n \leqslant 3$. Prolonged contact with CO at BT (up to 2 h) with both samples produces an increase in the spectral components at low wavenumbers (broken-line curves c and d), indicating the ability of BT–CO adsorbed in increasing the reduction state of the samples. As a consequence of samples reduction, CO is oxidized and forms surface carbonate-like species, characterized by typical absorptions in the 2000–1000 cm^{-1} spectral range [49]. Section B of Fig. 2 schematizes the evolution of low-ν spectra with CO contact. It is clear that virtually no reactivity towards BT–CO adsorbed is evidenced for both Mg/Al/O and Mg/Cr/O samples (very weak solid line components and no increase upon prolonged contact are observed in curves a and b, respectively), whereas strong bands due to bidentate carbonates (ν_{OCO} bands at ~1600 and ~1350 cm^{-1}) and bicarbonates (ν_{OCO} bands at ~1650, ~1400 cm^{-1}, and a δ_{OH} signal at 1230 cm^{-1}) are formed on both "*ox*" and "*red*" Mg/Fe/O samples in the presence of CO (solid line curves c and d). All these components increase upon BT–CO contact, confirming the capacity of CO in increasing the reduction state of the samples (broken-line curves c and d). The redox behaviour of Fe^{n+} species is well known and explains well the experimental results just reported, but one would expect that Cr^{n+} species could exert the same redox behaviour. To ascertain this possibility, some IR spectroscopic measurements have been carried out after heating a just activated Cr-containing sample at 350 °C in the presence of CO. The results are reported in Fig. 2A, dotted line curve b (for the high-ν region), and in the inset (relative to the spectral region below 1200 cm^{-1}). A very large signal centred at ~900 cm^{-1} is present in the background spectrum of the Mg/Cr/O sample and is due to the presence of chromate groups [50,51], as already evidenced by XRD data (Fig. 1). The strong absorption disappears upon heating the sample in the presence of CO (dotted line spectrum in the inset), and simultaneously the sharp ~2190 cm^{-1} band, ascribed above to CO/Cr^{3+} carbonyl-like species, shifts down to 2186 cm^{-1}, indicating the presence of Cr^{2+} species, that are known from literature data [48] to be formed only if very dry conditions are reached. This redox mechanism is confirmed by spectra in the low-ν region (Section B, dotted line curve b), where very large absorptions appear, most likely due to the formation of a huge amount of carbonate species of the bidentate type and representing the oxidation products. This is a clear indication that a redox activity can indeed be exerted by chromium species, although this activity needs to be activated by a treatment at relatively high temperatures. The overall redox behaviour of the Cr-containing system is reversible, as the back-formation of Cr^{3+} species occurs when some water is present in the reactor, and the re-formation of chromate species is easily induced by oxidation in air.

It is so preliminarily concluded that an order of redox capability can be set for the MgO-based samples under study, in that: (i) as expected, the Mg/Al/O system shows no redox capacity; (ii) the Mg/Cr/O system exhibits weak redox capacity, because chromates reduction is an activated process; (iii) the Mg/Fe/O system is characterized by a very vigorous redox capacity, evidenced even at low temperatures and with mild reducing agents (like vacuum activation and BT contact with CO).

In order to find out whether the samples under study exhibit also weak Lewis and/or Brønsted acidity, a strong base like Lu has been employed. Fig. 3 reports the spectra relative to the adsorption/desorption of Lu at BT (solid line curves), and Lu desorption at 100 °C (dotted line curves), on the various Mg/Me-mixed oxides. It is known from the literature [52] that in the 1680–1540 cm^{-1} spectral range are located the “analytical” 8a and 8b vibrational modes of both neutral or ionic (lutidinium) adsorbed species. For this reason, we focussed our attention only on this spectral region.

Lu vapour pressure admitted/evacuated at BT on the mixed oxides leads, on all systems, to the formation of three spectral components at $\nu < 1615\ cm^{-1}$: (i) the 8b mode band of all species, and thus related to the total amount of Lu adsorbed on the samples, is located at $\sim$1580 cm^{-1}; (ii) the 8a mode relative to very weak interactions (*i.e.*, H-bonding between Lu and surface OH groups and/or non-specific liquid-like physisorption) lies at $\sim$1595 cm^{-1}; (iii) the 8a mode relative to stronger interactions (*i.e.*, specific coordinative chemisorption onto surface cus Me^{n+} and/or Mg^{2+} cations) is located in the $\sim$1600–1610 cm^{-1} range. It is so deduced that, as far as Lewis acidity is concerned, all mixed oxide systems exhibit a similar behaviour, as witnessed by the common presence of an absorption of variable complexity at $1600\ cm^{-1} < \nu < 1615\ cm^{-1}$. When the base excess is evacuated at 100 °C (dotted line curves in Fig. 3), on all systems only part of the higher-ν Lewis coordinated component remains, whereas for the sole non-reduced Mg/Cr/O sample (dotted line curve c) a complex absorption at $\nu > 1620\ cm^{-1}$ evidences, far more clearly than in the presence of Lu excess, the presence of Brønsted acidity. The presence of Brønsted acid sites turns out to be related to the surface presence of chromate groups, as Brønsted Lu activity totally disappears when chromates are reduced by carbon monoxide (see curves set d). The phenomenon is reversible also in this case, and when chromates are formed again by oxidation in air, Brønsted Lu activity shows up again and the spectral set c is reproduced.

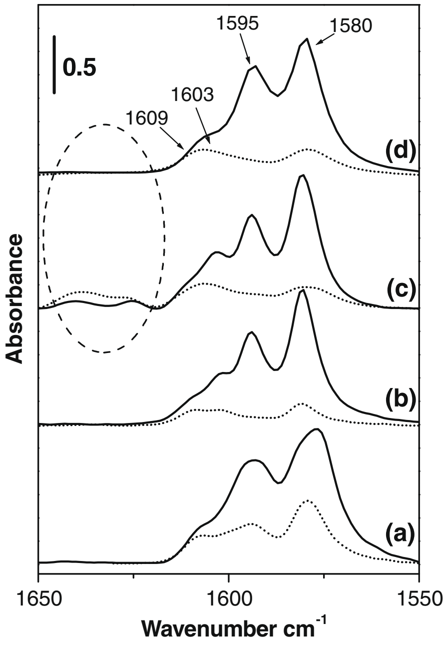


Fig. 3. Absorbance differential spectra, normalized against the background spectrum of the starting samples activated at 500 °C of Mg/Al/O (curves a), Mg/Fe/O (curves b) and Mg/Cr/O before and after the reduction with CO (curves c and d, respectively), obtained in the vibrational region of Lu 8a and 8b modes after (i) contact at BT with the vapour pressure of Lu, and subsequent BT vacuum removal of the Lu excess (solid lines); (ii) outgassing at 100 °C for 10 min (dotted lines).

In summary, characterization measurements indicate the following:

(1) All samples show basic features [45], but also Lewis-type acidity associated to the presence of guest trivalent metal cations.
(2) In Mg/Al/O, Al^{3+} species are exclusively present in the form of cus Al^{3+} cations in either octahedral and/or tetrahedral coordination, but only the latter species exhibit strong Lewis acidity.
(3) In Mg/Cr/O, part of Cr is present as Cr^{3+} species incorporated in the MgO lattice, and part of it forms crystalline Mg chromates. Brønsted acid sites are attributed to OH groups linked to chromate groups. The latter species are reduced to Cr^{2+}/Cr^{3+} species by CO at high temperature (and also during the catalytic reaction), becoming (reversibly) incorporated in the MgO lattice.
(4) In Mg/Fe/O, Fe^{3+} ions are incorporated in the MgO framework and are easily reduced by CO, also in mild conditions. Under catalytic conditions, a partial segregation of either Fe_3O_4 or $MgFe_2O_4$ occurs. The main feature of this sample is the pronounced redox behaviour, associated with the couple Fe^{3+}/Fe^{n+} with $n < 3$.

3.3. The reactivity in gas-phase methylation of *m*-cresol: acid and basic behaviour

Fig. 4 reports, for the Mg/Al/O catalyst, the conversion of *m*-cresol and the selectivity to the products, as a function of the reaction temperature. Products were 3-methylanisole (3-MA, the product of O-methylation), 2,3-dimethylphenol and 2,5-dimethylphenol (2,3-DMP and 2,5-DMP, the products of ortho-C-methylation), 3,4-dimethylphenol (3,4-DMP, the product of para-C-methylation), and polyalkylated phenols. Products formed in minor amount were dimethylanisoles (DMA), toluene and benzene. At low temperature, the prevailing product was 3-MA. Its selectivity rapidly declined when the temperature was increased, with a concomitant increase in the selectivity first to DMPs and then to polyalkylated compounds. Above 350 °C, the selectivity to 3-MA became nil, and also that to DMPs decreased in favour of the formation of polyalkylates.

These data can be interpreted by considering the following: (i) the different activation energy for the reactions of O- and C-methylation, the former being favoured at low temperature and the latter at high temperature; (ii) the effect of *m*-cresol conversion on the distribution of products, since an increasing conversion favours consecutive reactions occurring on 3-MA, that may act as an alkylating agent. This is shown in Fig. 5, which reports the results of tests carried out by feeding 3-MA (*i.e.*, without methanol) at increasing temperatures over the Mg/Al/O catalyst. The almost equimolar amount of *m*-cresol and DMAs produced at low temper-

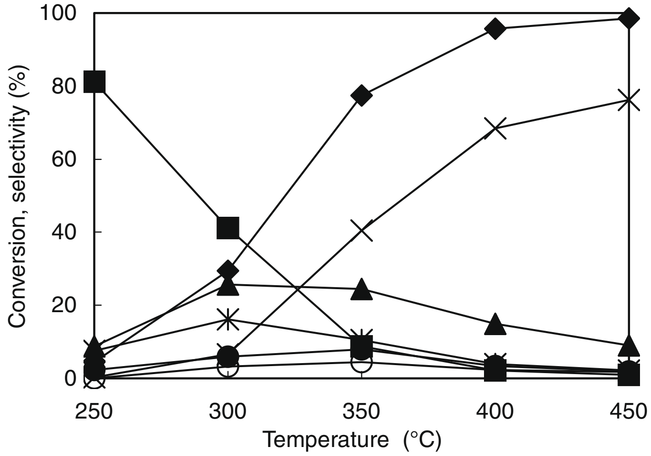
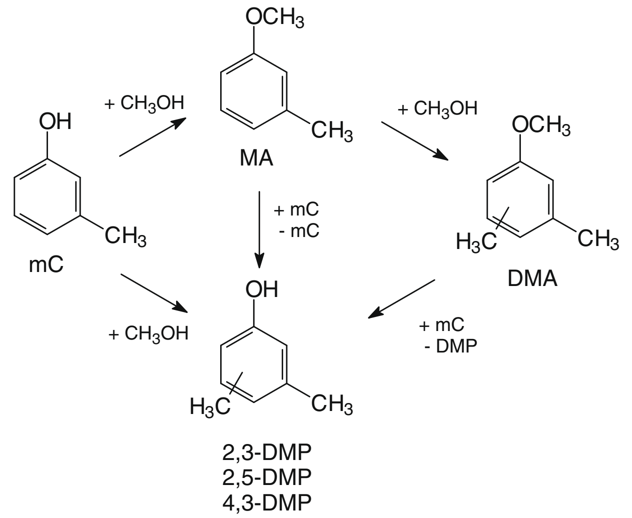


Fig. 4. *m*-Cresol conversion (♦) and selectivity to: 3-MA (■), 2,3-DMP (∗), 2,5-DMP (▲), 3,4-DMP (●), DMA (○), polyalkylates (×), as a function of the reaction temperature. Catalyst: Mg/Al/O. Feed composition (molar fractions): methanol, 0.139; *m*-cresol, 0.028; nitrogen, 0.833.

ature indicates an intermolecular reaction between two 3-MA molecules. Also, minor amounts of DMPs formed. When the reaction temperature was increased, the selectivity to DMAs decreased, with a concomitant increase in the selectivity to DMPs and polyalkylates. DMPs formed either by reaction between 3-MA and *m*-cresol, with the co-formation again of *m*-cresol (this explains why the selectivity to *m*-cresol was substantially not affected by temperature), or by reaction between DMAs and *m*-cresol (in this case two molecules of DMPs are produced). These data suggest that consecutive reactions occurring on 3-MA may contribute to the decrease in selectivity to the latter compound during *m*-cresol methylation, when the temperature is increased. However, the very high selectivity to polyalkylated phenols observed at high temperature during *m*-cresol methylation suggests that the direct attack on the aromatic ring by the electrophilic species is the preferred reaction.

Scheme 1 summarizes the reaction network, showing the main reactions occurring with the Mg/Al/O catalyst. It is worth noting that the nature of products obtained with this catalytic system is similar to that obtained with acid catalysts and different from that obtained with MgO. For comparison purposes, the behaviour of a USY zeolite is shown in Fig. 6. It is noted that, at low temperature, 3-MA was the major product, with also an appreciable formation of DMAs. The selectivity to the latter compounds was similar to the overall selectivity to monoalkylated cresols (DMPs) plus polyalkylated phenols, showing that the consecutive methylation on 3-MA (to yield DMAs) was kinetically favoured as much as the direct methylation on *m*-cresol, likely because the counter-diffusion path of 3-MA inside the zeolite porous network increased the effective residence time of the molecule and the probability of consecutive reactions. Another difference of USY with respect to Mg/Al/O was a remarkable deactivation effect, which was the reason for the conversion decrease experimentally observed when the temperature was raised. The deactivation was due to the formation of coke [23,26]. As a consequence of the decreased conversion, the selectivity to 3-MA did not change even when reaction temperatures higher than 350 °C were used. But, at this point, it is important to note that, despite the similar conversion exhibited at low temperature and the similar distribution of products obtained with Mg/Al/O and USY catalysts, the former system did not show any



Scheme 1. Reaction network for the gas-phase methylation of *m*-cresol with methanol, catalysed by Mg/Al/O.

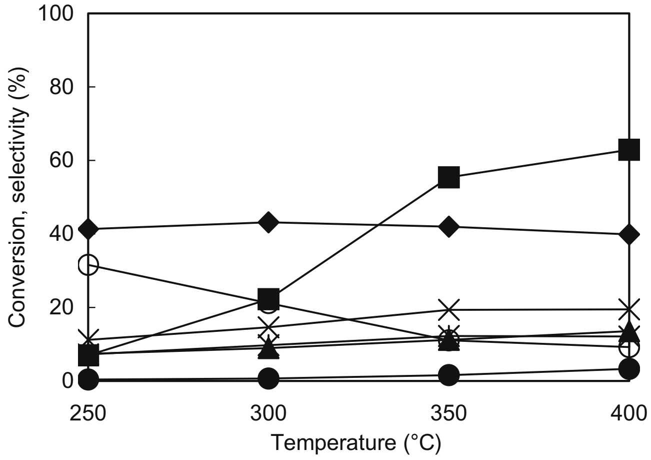


Fig. 5. 3-Methylanisole (3-MA) conversion (■) and selectivity to: *m*-cresol (♦), 2,3-DMP (∗), 2,5-DMP (▲), 3,4-DMP (●), DMA (○), polyalkylates (×), as a function of the reaction temperature. Catalyst: Mg/Al/O. Feed composition (molar fractions): 3-MA, 0.01; nitrogen, 0.99.

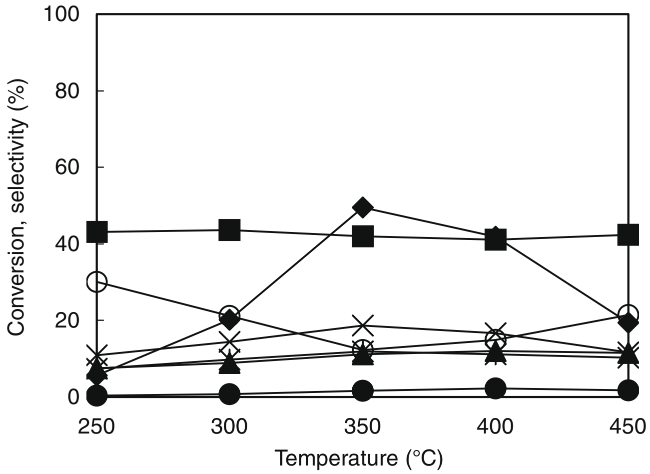


Fig. 6. *m*-Cresol conversion (♦) and selectivity to: 3-MA (■), 2,3-DMP (∗), 2,5-DMP (▲), 3,4-DMP (●), DMA (○), polyalkylates (×), as a function of the reaction temperature. Catalyst: USY zeolite. Feed composition (molar fractions): methanol, 0.139; *m*-cresol, 0.028; nitrogen, 0.833.

noticeable deactivation effect (as also confirmed by repeated tests on the used catalysts).

MgO was found to be much less active than Mg/Al/O [23]. This is because strongly basic sites, typical of MgO, are poisoned by the almost irreversible adsorption of acid molecules like, for instance, of carbon dioxide or even *m*-cresol itself. Also with the MgO used in the present work, the conversion at 400 °C was only 6%, notwithstanding the high surface area of the sample used. The prevailing products were 2,3- and 2,5-DMP (overall selectivity 75%), with a lesser formation of the product of para-alkylation (3,4-DMP, selectivity 20%) and of 3-MA (selectivity 5%).

3.4. The reactivity in gas-phase methylation of m-cresol: the role of Me in Mg/Me-mixed oxides

Figs. 7 and 8 show the results obtained with Mg/Fe/O and Mg/Cr/O catalysts, respectively. It is evident that the two samples behaved quite similarly: the conversion was very similar, though the surface area of Mg/Cr/O is half that of Mg/Fe/O. Moreover, with the latter catalyst the conversion decreased at 450 °C, because of a deactivation effect. In fact, when catalytic measurements were carried out again at 400 and 350 °C, the conversion measured was lower than that originally recorded for these temperatures. Deactivation arose because of the reduction of Fe^{3+} to Fe^{2+}, the latter species being produced by the dehydrogenation of methanol and oxidation of the hydrogen formed to water [23,24,53,54] (see the description on the transformations occurring on methanol). Unlike that, no high-temperature deactivation occurred in the case of the Mg/Cr/O catalyst.

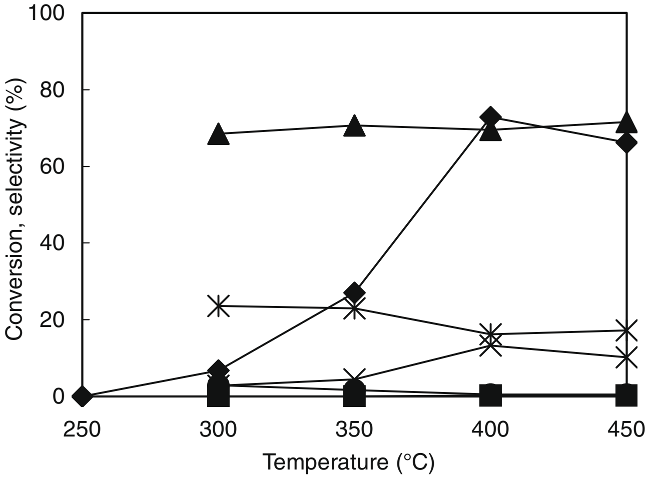


Fig. 7. *m*-Cresol conversion (♦) and selectivity to: 3-MA (■), 2,3-DMP (∗), 2,5-DMP (▲), 3,4-DMP (●), DMA (○), polyalkylates (×), as a function of the reaction temperature. Catalyst: Mg/Fe/O. Feed composition (molar fractions): methanol, 0.139; *m*-cresol, 0.028; nitrogen 0.833.

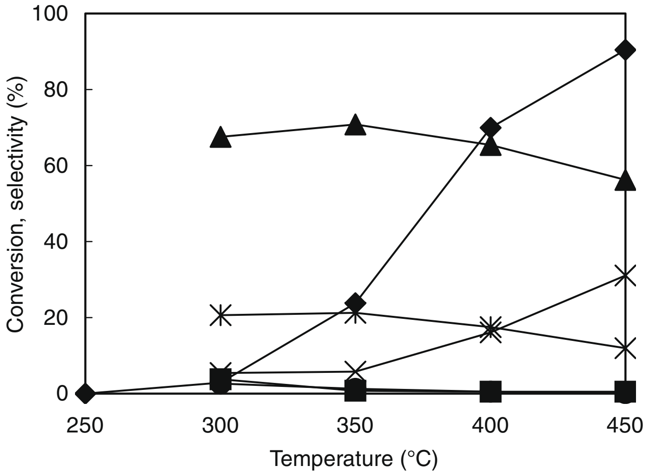


Fig. 8. *m*-Cresol conversion (♦) and selectivity to: 3-MA (■), 2,3-DMP (∗), 2,5-DMP (▲), 3,4-DMP (●), DMA (○), polyalkylates (×), as a function of the reaction temperature. Catalyst: Mg/Cr/O. Feed composition (molar fractions): methanol, 0.139; *m*-cresol, 0.028; nitrogen, 0.833.

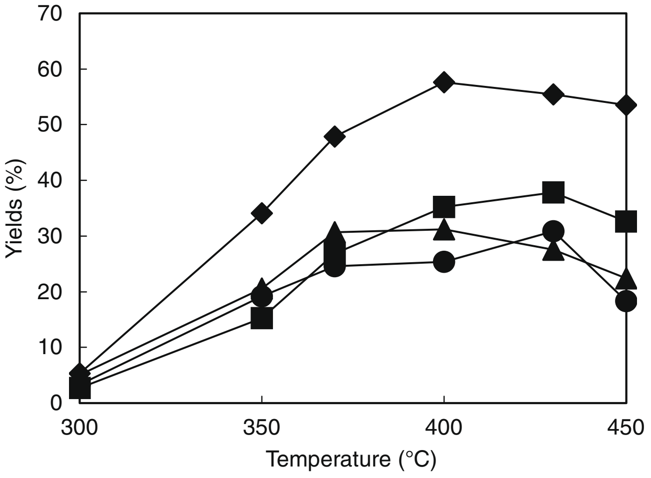


Fig. 9. Yield to: CO (■), CO_2 (▲), CH_4 (●), H_2 (♦) as a function of temperature. Catalyst: Mg/Fe/O. Feed composition (molar fractions): methanol, 0.14; nitrogen, 0.86.

For what concerns the distribution of products, both samples exhibited a behaviour which should be that typical of basic systems [23–26], with predominance of the products of ortho-methylation (2,3- and 2,5-DMP), and very low selectivity to 3,4-DMP. The prevailing polyalkylated phenol was the 2,3,6-trimethylphenol, the product of *m*-cresol ortho-dialkylation. The selectivity to 3-MA was very low with Mg/Cr/O and nil with Mg/Fe/O.

3.5. The reactivity in gas-phase methylation of m-cresol: the transformations occurring on methanol

In previous works, we demonstrated that catalysts possessing basic reactivity cause the dehydrogenation of methanol to formaldehyde [23,24]. The latter is a highly electrophilic reagent and acts as the real methylating agent for ring substitution in phenol, likely *via* the intermediate hydroxymethyl group. On the other hand, formaldehyde may rapidly dehydrogenate to CO or dimerize to yield methylformate (Tishchenko reaction), which also may eventually decompose to CO_2 and CH_4. In order to highlight a possible different behaviour of the catalysts in regard to methanol dehydrogenation and decomposition, tests were carried out by feeding only methanol.

Mg/Al/O showed a negligible activity in methanol dehydrogenation to formaldehyde and decomposition into light compounds. In fact, the formation of CO, CO_2 and CH_4 was very low up to 400 °C (yield to light compounds less than 5%). The main product of methanol transformation was dimethylether (with the co-production of water), yield to this latter compound being comprised between 20% and 35% below 400 °C. Noteworthy, no aliphatic and aromatic compounds were formed, whereas they are produced in the zeolite-catalysed transformation of methanol and are precursors of coke formation. However, at 450 °C, the dehydrogenation of meth-

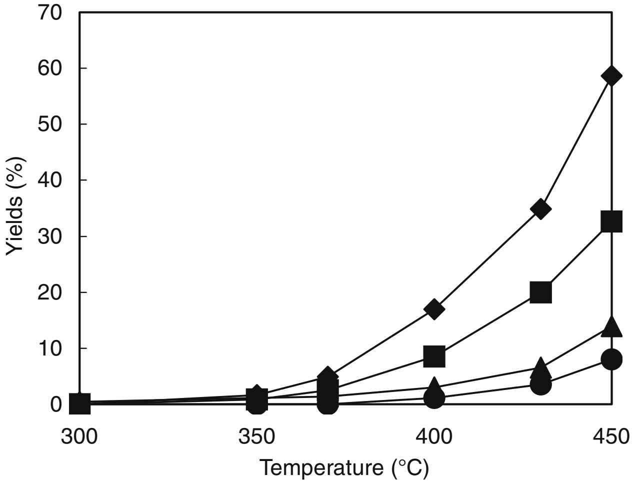


Fig. 10. Yield to: CO (■), CO_2 (▲), CH_4 (●), H_2 (♦) as a function of temperature. Catalyst: Mg/Cr/O. Feed composition (molar fractions): methanol, 0.14; nitrogen 0.86.

anol to formaldehyde and to CO became appreciable: the yield to CO was 15%, whereas the yield to CO_2 was even lower than at 400 °C.

The behaviour of Mg/Fe/O (Fig. 9) and Mg/Cr/O (Fig. 10) was quite different from that exhibited by Mg/Al/O. Both catalysts were very active in the dehydrogenation of methanol to formaldehyde and in the subsequent dehydrogenation of the aldehyde to CO. However, Mg/Fe/O was much more active than Mg/Cr/O. If we assume that there is no additional source of H_2, besides the H_2 derived from methanol (and, in fact, with both catalysts, there was no formation of dimethylether and water), 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 $CO + 1/2CH_4 + 1/2CO_2$. In fact, for mere calculation purposes, the following stoichiometries can be assumed:

$$CH_3OH \rightarrow CO + 2\ H_2$$
$$CH_3OH \rightarrow 1/2CO_2 + 1/2CH_4 + H_2$$

Where the first reaction corresponds to methanol decomposition and lumps together the dehydrogenation to formaldehyde and then to CO; the second reaction represents the overall stoichiometry for the transformation of methanol to formaldehyde, followed by formaldehyde dimerization to yield methylformate, and eventual decomposition of the latter into CH_4 and CO_2. Therefore, from the mass-balance point of view, all reactions that lead to the formation of H_2 starting from CH_3OH (and in the absence of any additional co-reactant) are actually included in these two reactions, when the assumption is made that there is no coke formation on the catalysts (the accumulation of which would lead to an additional formation of H_2). Indeed, used Mg/Fe/O contained approximately 5 wt.% of coke, whereas in used Mg/Cr/O the amount of coke was less than 1 wt.%.

Mg/Fe/O was much more active than Mg/Cr/O in the formation of light compounds. With the former catalyst, the conversion of methanol was almost total at 400 °C, whereas with Mg/Cr/O it was less than 40%. This confirms the result of spectroscopic measurements concerning the superior redox properties of Mg/Fe/O when compared to Mg/Cr/O. With both catalysts, the yield to H_2 did effectively correspond to the aforementioned sum of yields to light compounds. However, at temperatures higher than 400 °C, Mg/Fe/O did show a decline of light compounds. This is due to the reduction of Fe^{3+} and to the depletion of lattice O^{2-}, brought about by the oxidation of the H_2 generated to H_2O. This is also the reason for the decreased activity in *m*-cresol methylation (Fig. 7); a lower rate of generation of formaldehyde and a decreased rate of *m*-cresol activation (due to the removal of basic O^{2-}) cause the observed deactivation phenomenon. This did not occur with Mg/Cr/O and no deactivation effect was observed at high temperature in neither *m*-cresol or methanol transformation.

4. Discussion

The peculiar reactivity of Mg/Fe-mixed oxides in the gas-phase methylation of phenol was previously discussed by Velu and Swamy [33]. The authors hypothesized that the Lewis-type coordinative properties of Fe cations play an important role by orientating the introduction of the methyl group in the ortho position of adsorbed phenolate. This was assumed to be the reason for the high regio-selectivity observed with this catalyst when compared to Mg/Al/O. Still, this interpretation does not fit our experimental data. In fact, the same Lewis acidity is present in our Mg/Al/O and Mg/Fe/O systems that, however, gave quite a different catalytic performance in *m*-cresol methylation. Moreover, according to the widely accepted Tanabe's model for the adsorption of phenolic compounds on basic ionic oxides (the model predicts an orthogonal orientation of phenolate species with respect to the catalyst surface, due to the repulsion between the aromatic ring and nucleophilic surface (lattice) O^{2-} ions) [55], the presence of electrophilic surface sites should favour the interaction with the aromatic ring and bring the para position close to the surface, thus making easier the methylation at that position.

Characteristics and reactivity of Mg/Me/O systems described in the present work turned out to be greatly affected by the nature of host cation and by the type of mixed oxide formed. It is worth noting that all mixed oxide samples showed reactivity properties quite different from those typically observed with the corresponding single oxides (*i.e.*, in MgO and Me_2O_3). In general, MgO presents strongly basic features, arising from the high nucleophilicity of O^{2-} surface ions and from the ionicity of the MgO lattice [56,57]. γ-Al_2O_3 exhibits amphoteric behaviour [58–60], due to the presence of acidic cus Al^{3+} sites (besides, possibly, some Al–OH groups) going along with Al–O–Al moieties of pronounced basic character. However, the catalytic behaviour exhibited by alumina is a function of the characteristics of the reactants used; fairly acidic phenol and cresols undergo deprotonation by O^{2-} sites, whereas the electrophylic O atom in methanol undergoes protonation by Al–OH sites (possibly *via* methoxy or methylenoxy species). Fe_2O_3 shows a typically basic behaviour in regard to phenolic compounds, favouring the formation of phenolate species and leading to high chemo- and regio-selectivity in phenol [23] and 1-naphthol methylation [12]. On the other hand, it has been shown that in Fe_2O_3 and in Fe-rich Mg/Fe-mixed oxides, the pronounced redox activity favours methanol dehydrogenation to formaldehyde and its further decomposition into light compounds (CO_2, CO and CH_4) [24].

Acid catalysts drive the reaction preferentially towards ortho-isomer formation [23, and references therein], but they form also a not negligible amount of para-isomer. Moreover, the para-isomer becomes the prevailing species in the presence of some zeolitic catalysts [61]. On the contrary, heterogeneous systems showing some basic behaviour give rise only to ortho-mono and dimethylated phenol [23–24].

The reactivity behaviour of the Mg/Me-mixed oxides presented here can be summarized as follows.

Mg/Al/O does not present the basic reactivity typical of MgO. Still the interaction of CO_2 on this sample indicates a good basicity, if compared with that exhibited by the Mg/Fe/O and Mg/Cr/O systems [45]. Moreover, the Mg/Al/O catalyst exhibits a moderate Lewis acidity, deriving from cus Al^{3+} sites, whereas it has no surface

Brønsted acidity. This is likely because surface Mg–O–Al(OH)–O–Mg moieties are unstable at high temperatures, so that dehydration occurs easily during thermal treatments, with water release and generation of low coordinated Al^{3+} sites. In the reaction environment, the presence of water (derived from the transformation of methanol into dimethylether) may lead to the regeneration of Al–OH bonds and, possibly, to the hydrolysis of Mg–O–Al bonds. On the other hand, the presence of Al makes the bridging O less nucleophilic than in MgO. MgO is known to catalyse, though with very low activity, the dehydrogenation of methanol to formaldehyde [23]. But a lower nucleophilicity of the basic O site in Mg/Al/O, when compared to pure MgO, may limit the dehydrogenative property typical of high surface area MgO and, in the end, this can be the reason for the acid-type reactivity exhibited by Mg/Al/O (whose behaviour is, in fact, similar to that of conventional acid catalysts). However, one remarkable advantage of this system with respect to conventional solid acid materials is the large predominance of sites of medium acidic strength. Though strong enough to catalyse ring methylation, a moderate acidity is useful to limit the production of heavy compounds and the formation of coke, responsible for the rapid deactivation phenomena typically met with both Brønsted (*e.g.*, zeolites [26]) and Lewis (*e.g.*, AlF_3 [62]) strong acids during reactions in which methanol is one of the reactants.

Also in the case of Mg/Cr/O, the main feature was a very homogeneous distribution of Lewis acid sites of medium strength, associated with Cr^{3+} ions. The presence of Brønsted acid sites resulted not so important in assessing the mechanism of catalytic reaction, as this feature is entirely due to chromate groups that reduce to Cr^{2+} (in reducing and very dry conditions) and/or to Cr^{3+} in the first reaction steps. The redox capability of the Mg/Cr/O system is evidenced only when the redox process is forced to occur, for instance by treatment at high temperatures. Mg/Cr/O was as active as Mg/Fe/O in the conversion of *m*-cresol, but it was remarkably less active in methanol transformation (as it should be, considering the different redox activity exhibited by the two systems). If the different SSA of the systems is taken into account, the aeral TOF for *m*-cresol methylation at 350 °C is, for Mg/Cr/O, twice as large as that of Mg/Fe/O, whereas the aeral TOF relative to methanol decomposition is approximately 1/10th of that of Mg/Fe/O. This means that the efficiency of Mg/Cr/O in the activation of *m*-cresol was similar to that of Mg/Fe/O, whereas the latter was far more efficient in the activation of methanol (*i.e.*, in the dehydrogenation of methanol to formaldehyde, which is the actual electrophilic reactant for the activated aromatic ring). However, Mg/Cr/O was much more selective than Mg/Fe/O in regard to transformations occurring on formaldehyde, as a major fraction of the aldehyde was incorporated in the aromatic ring, and only a minor part of it decomposed to light compounds. The opposite holds for Mg/Fe/O. Most of the aldehyde eventually decomposed, and only a very minor fraction of it reacted with the aromatics. Finally, Mg/Cr/O catalyst is expected to show also a limited reactivity due to its Brønsted acidity, at least in the first steps of the catalytic reaction, *i.e.*, when some surface chromate groups (responsible for Brønsted acidity) are not reduced yet. Actually, the formation of 3-MA, albeit very low, was not negligible. All these explain the catalytic behaviour experimentally observed, with a high regio-selectivity (typical of truly basic systems), and a very high (but not total) chemo-selectivity.

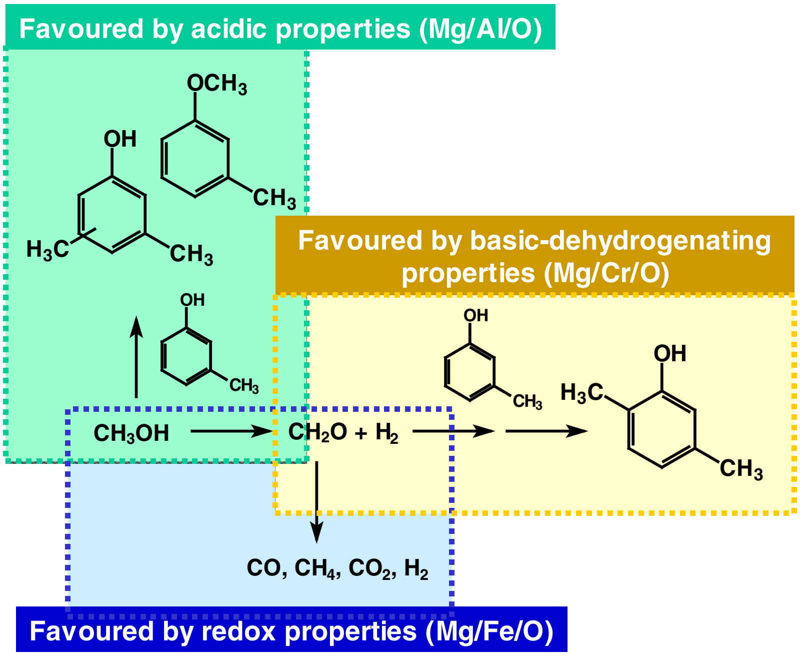
Mg/Fe/O has a surface acidity close to that of Mg/Al/O, with the predominance of Lewis sites of moderate strength. Therefore, one might expect also a similar catalytic behaviour. However, the main feature of the system was its pronounced redox behaviour, as shown by the reduction of Fe^{3+} cations by CO. During the reaction with methanol and *m*-cresol, reduction of Fe^{3+} by either H_2 or CO probably occurred in the entire range of temperatures examined, but reduction became relevant only above 400 °C. The catalyst was very active in the dehydrogenation of methanol to formaldehyde and in its decomposition to light compounds, in that formaldehyde is responsible for the electrophilic attack to the aromatic ring [24], but is also the precursor for the formation of light compounds. Therefore, despite the Lewis acidity experimentally observed, the dehydrogenation of methanol largely prevailed over its acid-type activation, and the behaviour observed was that typical of a basic/dehydrogenating reactivity, with both high regio- and chemo-selectivity. The selectivity to 3-MA was nil. This behaviour was not much different from that observed in the case of haematite [23], but in that case the dissolution of Fe inside MgO leads to a material of much higher SSA and, therefore, of much higher activity than bulky Fe_2O_3.

Our results indicate that the performance of the catalysts is mainly affected by the oxide capacity of generating the electrophilic reactant (formaldehyde) and of activating methanol with an acid-type mechanism. In the case of Mg/Cr/O and Mg/Fe/O systems, the dehydrogenating properties largely prevail over the acid/basic properties. Otherwise Mg/Al/O, which is a material characterized by good basicity (as revealed by the use of the probe molecule CO_2 [37,39,45]), shows a catalytic behaviour typical of acid/basic systems. And, in fact, it does not possess sites with dehydrogenating capacity.

Another peculiarity of the model proposed here is that methanol and formaldehyde give a different range of products in the reaction with *m*-cresol, regardless of the catalyst used. In other words, the catalyst affects the nature of the true electrophilic species, but the final type of phenol derivatives obtained is no longer a function of the catalyst type. This was previously demonstrated by tests carried out by feeding phenol and formaldehyde over a zeolitic material; in this case, the distribution of products obtained was quite different from that obtained by reacting phenol and methanol over the same zeolite, and similar to that obtained by reacting phenol and formaldehyde (or phenol and methanol) over MgO or Mg/Fe/O catalysts [24]. This also explains why no products of O-methylation were obtained using Mg/Fe/O or Mg/Cr/O as catalysts for the reaction between *m*-cresol and methanol: it is probable that the species ϕ-O–CH_2OH, which is the intermediate eventually formed by O-hydroxymethylation, is not stable enough to further react and give 3-MA. This will appear clearly in a forthcoming paper (still in preparation), where the whole reaction mechanism will be described in detail.

5. Conclusions

Mg/Al/O, Mg/Fe/O and Mg/Cr/O-mixed oxides have been thoroughly characterized and tested as catalysts for the gas-phase methylation of *m*-cresol with methanol. The incorporation of trivalent metal ions into the MgO lattice led to the generation of catalysts having pronounced basic features of medium strength as well as Lewis-type acidity. Despite these analogies, the catalytic behaviour (in *m*-cresol methylation) turned out to be completely different for the three systems under investigation. Mg/Cr/O showed a typical basic/dehydrogenating catalytic reactivity, with high chemo- and regio-selectivity and the favoured formation of 2,5-dimethylphenol. Mg/Al/O exhibited a catalytic behaviour quite similar to that shown by conventional Brønsted-type acid catalysts (*e.g.*, zeolites), but one remarkable advantage of Mg/Al/O systems consists in the absence of deactivation phenomena (typically observed with conventional acid catalysts in reactions employing methanol as reactant). With respect to the distribution of phenolic products, Mg/Fe/O presented a catalytic behaviour close to that of Mg/Cr/O, but showed a pronounced activity in both methanol-to-formaldehyde dehydrogenation and the decomposition of formaldehyde into light compounds.



Scheme 2. Summary of reactions occurring with Mg/Me/O systems.

The catalytic behaviour of the three mixed oxide systems followed the redox features of the hosted Me^{3+} species, as represented in Scheme 2. Only with Mg/Al/O, showing no capacity for methanol dehydrogenation, the performance was that typical of conventional acid-catalysed methylation of phenolic compounds. With Mg/Cr/O and Mg/Fe/O, methanol was activated and dehydrogenated to formaldehyde. Formaldehyde can either react with *m*-cresol or decompose into light compounds. The former reaction was the quickest one with Mg/Cr/O, whereas with Mg/Fe/O most of the formaldehyde generated kept reacting with continuity to yield light compounds. In the latter case, the selectivity to methylated phenolic compounds (with respect to converted methanol) was very low.

Acknowledgments

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