Catalysis Today 75 (2002) 103–111

www.elsevier.com/locate/cattod

Heterogeneous basic catalysts as alternatives to homogeneous catalysts: reactivity of Mg/Al mixed oxides in the alkylation of *m*-cresol with methanol

M. Bolognini [a], F. Cavani [a,*], D. Scagliarini [a], C. Flego [b], C. Perego [b], M. Saba [b]

[a] *Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy*
[b] *EniTecnologie SpA, Via Maritano 26, 20097 S. Donato Milanese (MI), Italy*

Abstract

Mg/Al mixed oxides, obtained by decomposition of hydrotalcite-like precursors, represent interesting heterogeneous catalytic systems for basic-catalyzed reactions, as an alternative to environmentally unfriendly homogeneous catalysts. The reactivity of these oxides was evaluated using the methylation of *m*-cresol as a test reaction and relationships between catalytic performance and chemical–physical features were established. The basicity of the samples was evaluated by CO_2 adsorption and thermal-programmed-desorption. The presence of Al in the mixed oxides considerably affected the density and the strength of the basic sites with respect to MgO. These basic properties in turn influenced the catalytic performance of the materials. Under the reaction conditions used in the present work, medium strength basic sites played the major role in the reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous basic catalysts; Alkylation of *m*-cresol; Hydrotalcites; Magnesium/aluminum mixed oxide

1. Introduction

In recent years attention has been focused on the development of heterogeneous materials with basic properties, which can efficiently catalyze reactions of industrial interest (alkylation, condensation, isomerization), and for which homogeneous bases are currently employed [1,2]. Heterogeneous basic systems would make it possible to decrease or avoid effluents containing inorganic salts and thus considerably lower the negative environmental impact of these processes. Among the different types of materials studied, Mg/Al mixed oxides, prepared starting from hydrotalcite precursors, have shown the best basic features, and indeed in recent years these materials have been reported as catalysts for many different reactions, such as the Claisen–Schmidt condensation [3], the Knoevenagel condensation [4], the Claisen condensation, and many others [5–7]. The reactions examined are of industrial interest for the synthesis of intermediates for pharmaceuticals or in general for the fine-chemicals industry.

In order to study the acid–base properties of Mg/Al mixed oxides, we chose the liquid-phase alkylation of *m*-cresol with methanol [8,9] as a test reaction. The catalytic performances in *m*-cresol methylation of Mg/Al mixed oxides prepared by decomposition of HT precursors were compared with results of surface characterization determined using CO_2 adsorption and thermal-programmed-desorption (TPD), in order to find relationships between surface characteristics and basicity as inferred from the reactivity tests. Understanding these relationships may be useful to

---

[*] Corresponding author. Tel.: +39-51-2093680.
E-mail address: cavani@ms.fci.unibo.it (F. Cavani).

PII: S0920-5861(02)00050-0

develop heterogeneous catalytic materials with a basicity tailored for specific industrial applications.

2. Experimental

Mg/Al hydrotalcite (HT) precursors were prepared following the conventional procedure as described elsewhere [10]. The so-obtained precursors were calcined at 450 °C for 8 h. Activation of the catalysts before reaction was carried out at 450 °C for 3 h in a gas-chromatographic N_2 flow. Reference MgO and Al_2O_3 were prepared following the same procedure as for the preparation of the HT precursors, in the absence of the second element.

The catalysts were characterized by means of: (i) X-ray diffraction analysis (Philips PW 1050/81), (ii) surface area measurements (single point BET, Sorpty 1700 Carlo Erba), (iii) adsorption and TPD of CO_2 (PulseChemisorb 2705, Micromeritics), and (iv) atomic absorption spectroscopy (Philips PU 9100).

The overall density (μmol/g) of the basic sites was evaluated from the adsorption of CO_2 at 21 °C. The presence of physisorbed CO_2 was avoided by carrying out the adsorption under helium flow. The basic strength distribution was evaluated from the capacity of the material to retain the probe during desorption at increasing temperature. A deconvolution procedure was applied to the experimental TPD profiles; curve fit quality was measured by the correlation coefficient (R^2), standard deviation (σ) and the Levenberg–Marquardt algorithm (χ^2). The quality of the deconvolution was high in all experiments: $R^2 > 0.996$, $\delta < 0.004$ and $\chi^2 < 1.133$.

The catalytic tests were carried out in a 300 ml Parr 4560 autoclave reactor loading 32 g of *m*-cresol, 19 g of methanol (molar ratio *m*-cresol/methanol 0.5) and 5.7 g of catalyst. The initial molar ratio between *m*-cresol and methanol at reaction conditions in the liquid phase was equal to 2.3 (in the gas-phase 0.31). The reaction temperature was 300 °C; the initial autogeneous pressure at 300 °C was 38 atm and the final pressure was around 35 atm. The reaction was carried out for 6 h and the stirring rate was 700 $\min^{-1}$. The testing procedure can be summarized as follows: the catalyst is loaded first, the reactor is sealed and evacuated, and the *m*-cresol/methanol mixture is then loaded. Heating up is started, and the beginning of the reaction time is taken as being when the temperature reaches 300 °C.

3. Results and discussion

3.1. Characterization of the oxides obtained by thermal treatment of HT precursors

The theoretical and experimentally determined Mg/Al atomic ratios for the samples prepared are reported in Table 1, together with the surface areas of the samples after calcination at 450 °C. The experimentally determined atomic ratios were systematically lower than the theoretical values, due either to incomplete precipitation or to partial re-dissolution of some components during the washing step. Throughout the text, however, the samples are referred to on the basis of the theoretical ratio, i.e., the ratio used for the preparation of the starting solutions.

Fig. 1 reports the X-ray diffraction patterns of the calcined samples. In all samples, the patterns correspond to that of a poorly crystallized MgO. The progressive increase in Al content (i.e., a decrease in the Mg/Al ratio) causes a shift in the reflections towards higher 2θ values. This implies a decrease in the volume of the crystallographic cell of MgO (periclase), in agreement with progressive isomorphic replacement of Mg^{2+} cations with the smaller Al^{3+} cations ($Mg^{2+} = 0.65$ Å; $Al^{3+} = 0.50$ Å) [5]. Only in the Mg/Al = 4.0 mixed oxide, having the lowest Al content, are additional reflections present, which can be attributed to the presence of the spinel-like

Table 1
Main characteristics of the Mg/Al samples obtained by thermal decomposition of HT precursors, and of reference MgO and γ-Al_2O_3

Theoretical Mg/Al atomic ratio[a]	Surface area (m^2/g)	Experimental Mg/Al atomic ratio[b]
∞ (MgO)	206	∞
4.0	209	3.7
3.5	204	3.0
3.0	223	2.6
2.5	224	2.2
2.0	185	1.8
0 (γ-Al_2O_3)	203	0

[a] Ratio used in the starting solution for preparation of HT precursors.

[b] As determined by atomic absorption spectroscopy.

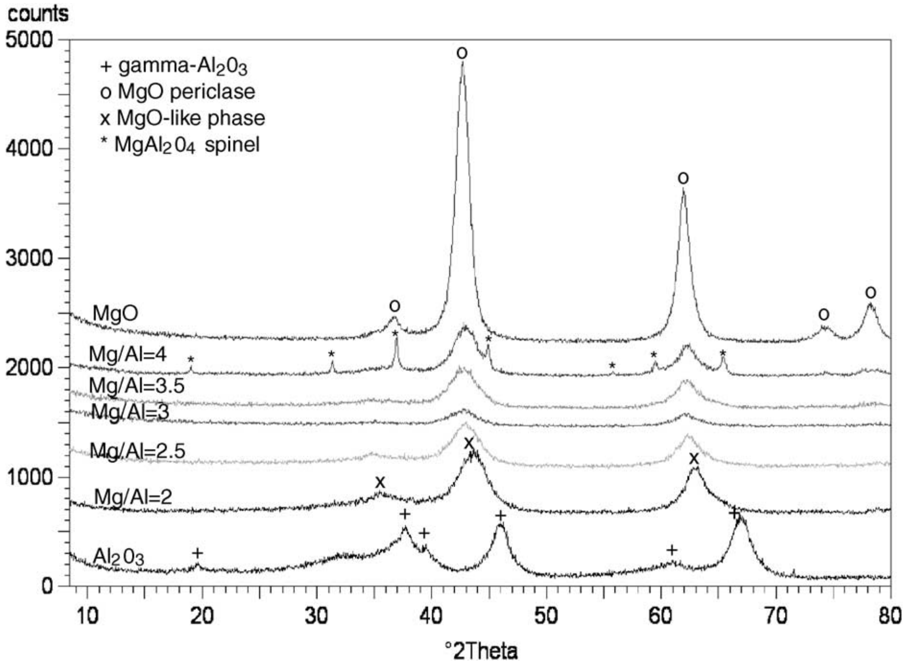

Fig. 1. X-ray diffraction patterns of Mg/Al mixed oxides having different Mg/Al ratios and the pure oxides MgO and Al_2O_3.

phase $MgAl_2O_4$. It is known that non-stoichiometric spinel-like phases may be formed, together with the poorly crystallized MgO, by decomposition of the HT precursor when a large excess of the divalent metal ion is present; for lower Mg/Al ratios instead a random distribution of Al^{3+} in the MgO lattice develops [10 and references therein]. The same sample is also characterized by a crystal size slightly higher than that of samples having an Mg/Al ratio lower than 4, i.e., 40 Å against 30 Å, supporting the hypothesis of MgO segregation. The sample prepared in the absence of magnesium corresponds to γ-Al_2O_3.

CO_2–TPD profiles for MgO and for two Mg/Al mixed oxides ($Mg/Al = 2.0$ and 4.0) are shown in Fig. 2. The complex desorption profiles are clearly related to the presence of basic sites with different strengths. For all samples the profiles consist of: (i) a low temperature peak, with a maximum of desorption at temperatures lower than 100 °C, and attributed to the interaction with sites having weak basic strength, (ii) a desorption peak with a maximum in the range 140–170 °C, related to desorption of CO_2 from sites at medium basic strength, and (iii) a broad desorption area which covers the temperature range from 200 to 450 °C, attributed to CO_2 desorption from sites with strong basicity. A deconvolution procedure was applied to discriminate the different components. The results of this analysis are summarized in Table 2, which also reports the overall amount of ammonia adsorbed at 21 °C, and the overall amount of desorbed ammonia, the latter value having been determined by integration of the desorption profile. The good correspondence between the two values indicates that no ammonia was retained by the samples at the end of the desorption experiment.

The following considerations can be drawn from the data of Table 2:

(a) The pure oxides (MgO, Al_2O_3) have a large number of strong basic sites and a small amount of basic sites with weak or medium strength. Furthermore, MgO shows the highest total basic density compared to the other materials.
(b) Within the series of Mg/Al mixed oxides, the distribution of the basic strength is quite different from that of the pure oxides. The Mg/Al atomic ratio does not seem to have much influence

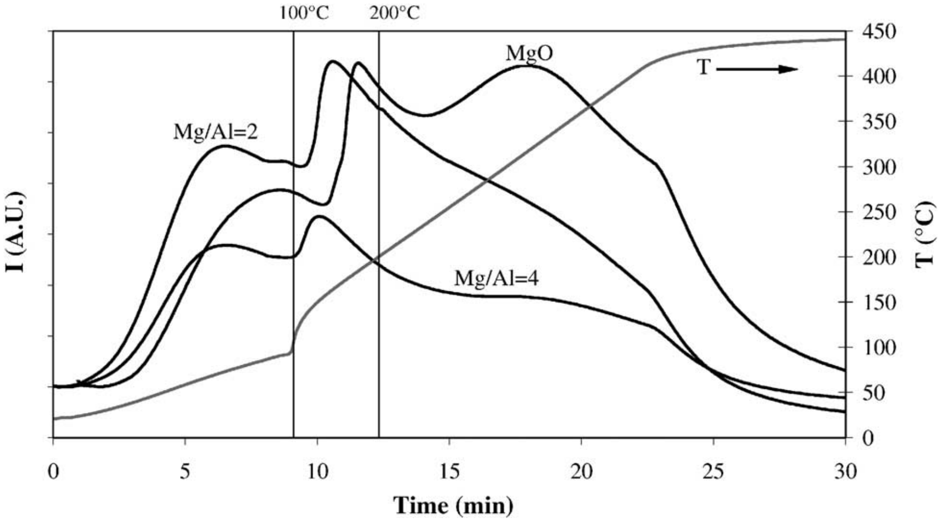

Fig. 2. TPD profiles of MgO and of Mg/Al mixed oxides ($Mg/Al = 2.0$; $Mg/Al = 4.0$).

on the basicity of the calcined hydrotalcites in the range $2.0 < Mg/Al < 3.5$. The amount of the medium strength sites is predominant (125–145 μmol/g), followed by lower amounts of strong (50–105 μmol/g) and weak basic sites (30–50 μmol/g).

(c) The sample with an Mg/Al atomic ratio of 4.0 is clearly the least basic, with both a low density and a reduced strength of the basic sites.

These general findings are in agreement with the literature data [10–13]. It has been proposed that the weak basic sites in calcined hydrotalcites are the surface OH^- groups; in agreement with this hypothesis the density of these OH^- groups is roughly comparable in all our materials characterized by a similar surface area. The medium strength sites are related to the oxygen in both Mg^{2+}–O^{2-} and Al^{3+}–O^{2-} pairs. The presence of these sites is favored in Mg/Al mixed oxides due to the higher electronegativity of Al^{3+} as compared to Mg^{2+}, which decreases the electron density and thus the nucleophilicity of the neighboring oxygen anions. Correspondingly, a higher density of medium strength basic sites is found in our Mg/Al mixed oxides. Isolated O^{2-} anions are responsible for the strong basic sites in single oxides; in calcined hydrotalcites, strong basic sites consist predominantly of low-coordination O^{2-} ions associated with cationic vacancies which are generated as a consequence of the introduction of Al^{3+} in the MgO lattice [14,15]. Therefore, the density of the strong basic sites decreases compared to that of MgO.

Table 2
Basicity distribution from CO_2 adsorption/TPD experiments

Sample Mg/Al	Overall amount adsorbed (μmol/g)	Overall amount desorbed (μmol/g)	Weak sites (μmol/g)	Medium sites (μmol/g)	Strong sites (μmol/g)
∞ (MgO)	356	346	56	25	265
4.0	144	146	25	68	52
3.5	270	275	44	126	105
3.0	262	272	36	139	96
2.5	212	221	32	135	54
2.0	263	274	50	148	77
0 (γ-Al_2O_3)	264	286	37	20	229

The addition of a small amount of Al (i.e., the amount of Al in the Mg/Al = 4.0 sample) decreases drastically the overall density of the basic sites in MgO, probably due to the partial coverage of the sites at the surface of MgO by segregation of the spinel phase, as indicated by XRD analysis, or by AlO_x clusters, in agreement with Di Cosimo et al. [14]. Further additions of Al (i.e., Mg/Al ratios lower than 4) lead to a better dispersion of Al ions in MgO with development of the Mg/Al mixed oxide, and consequently to an improvement in the basic character.

In regard to the presence of acid sites, it is known that the introduction of Al also generates weak Lewis acid sites [15]. Pyridine adsorption at 21 °C on our samples indicates the presence of coordinatively unsaturated Al^{3+}(Td) in the lower Mg/Al atomic ratios and coordinatively unsaturated Al^{3+}(Oh) in the sample Mg/Al = 4.0. These Lewis acid sites are very weak and thus they are likely unable to interact with molecules such as *m*-cresol and methanol, whose basicity is lower that that of pyridine.

3.2. Reactivity in m-cresol methylation

Preliminary tests were carried out to determine the absence of external diffusional limitations. Specifically, tests made by varying the stirring rate demonstrated that for values between 400 and 700 rpm the rate of reaction was not affected by this parameter.

The absence of deactivation phenomena was verified by re-loading a catalyst (Mg/Al = 2.0), previously discharged after 6 h reaction, washed with methanol to remove the adsorbed compounds, and checking again the catalytic performance. The recycled sample gave a *m*-cresol conversion of 9.3%, lower than that of the corresponding fresh catalyst (12.9%). However, it has to be considered that each fresh catalyst is usually activated in flowing nitrogen at high temperature; this pretreatment could not be applied for the unloaded catalyst. Therefore, we can assume that no heavy deactivation phenomenon occurred during the catalytic tests. This validates both the experimental conditions chosen and the comparison among the catalytic performances after 6 h reaction.

In order to check the reaction scheme, tests were made using different reaction times, with the Mg/Al = 2.0 mixed oxide as the catalyst. The results of this series of experiments are shown in Fig. 3. The conversion of *m*-cresol increased with increasing reaction time. Apparently, no short-term deactivation phenomena of the active sites occurred, confirming the results of the previous experiments on deactivation.

The scheme of reaction is depicted in Fig. 4. The reaction products were: 3-methylanisole (3-MA, the product of O-alkylation), 2,3-dimethylphenol and 2,5-dimethylphenol (2,3-DMP and 2,5-DMP, the products of ortho C-alkylation), 3,4-dimethylphenol (3,4-DMP,

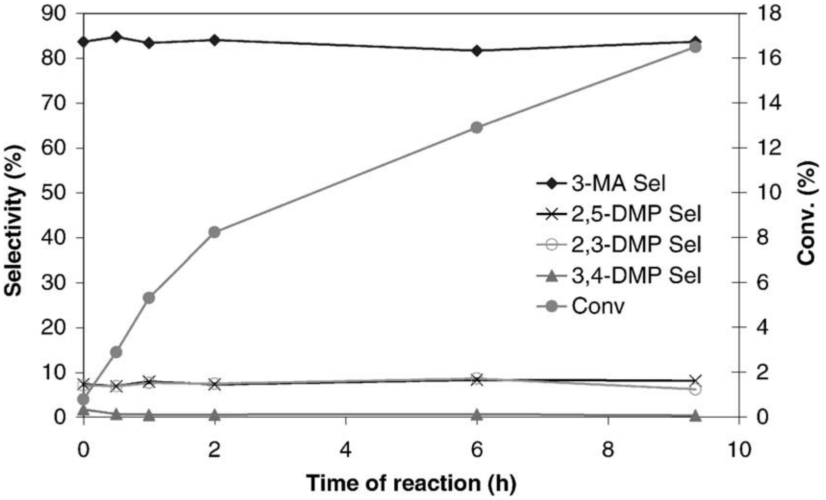

Fig. 3. *m*-Cresol conversion and selectivity to the main products as functions of the reaction time. Catalyst with Mg/Al = 2.0. Reaction conditions described in Section 2.

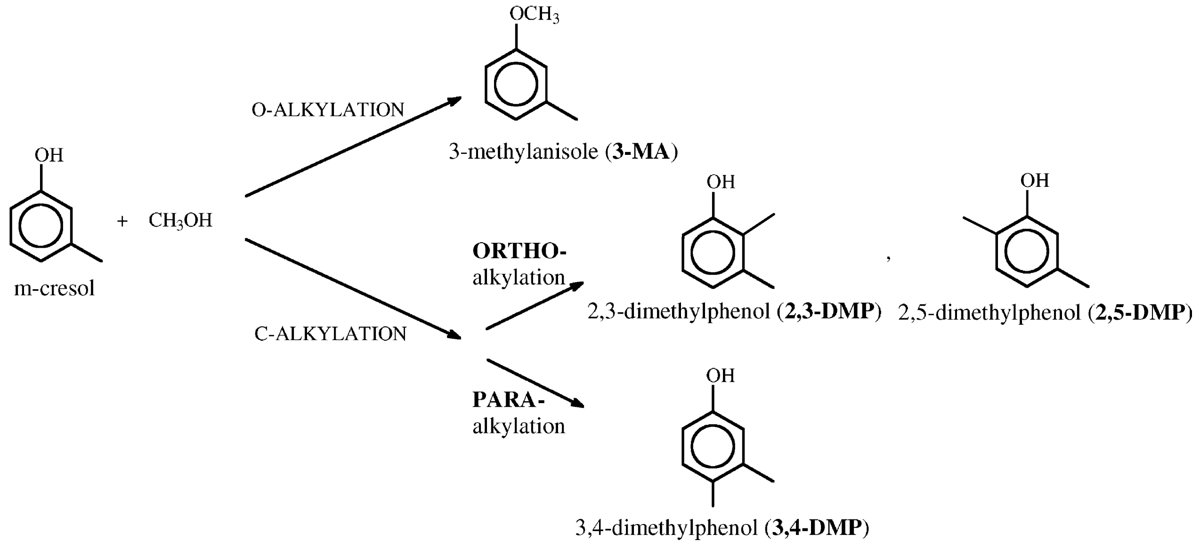

Fig. 4. Reaction scheme for the methylation of *m*-cresol.

the product of para C-alkylation), side-chain alkylation products, 2,3,6-trimethylphenol (2,3,6-TMP, the product of ortho C-dialkylation), and 2,3-dimethylanisole and 2,5-dimethylanisole (2,3-DMA, 2,5-DMA). In our catalytic tests, the prevailing product was 3-MA, with a selectivity around 80%, while the remaining products were mainly DMPs. The amounts of DMAs and TMPs, as well as the amounts of side-chain alkylated products and of other polyalkylated and heavier products were in all cases very low (selectivity far lower than 0.5%).

As shown in Fig. 3, the reaction proceeds through the parallel formation of the main products, none of which underwent consecutive transformations. This may be due to the relatively low *m*-cresol conversion achieved under these conditions (maximum 16%). The absence of consecutive reactions makes it possible to use the values of selectivity to specific products as parameters for the characterization of the surface properties. These parameters include: (i) the conversion of *m*-cresol (since the surface areas of all samples are very close, the specific activity shows the same trend as the absolute conversion), (ii) the ratio between the selectivity of products of ortho C-alkylation and those of para C-alkylation (ortho/para ratio), and (iii) the ratio between the selectivity to 3-MA and the selectivity of the products of C-alkylation (O/C ratio).

The importance of each one of the above mentioned parameters for the reaction of phenol alkylation has been widely discussed in the literature [16–23]. Even though there is not complete agreement on the proper use of these parameters for the characterization of surface sites, the following considerations can be done:

(a) With both acid and basic catalysts, C-alkylation becomes preferred with respect to O-alkylation as the strength of the site increases. It has been reported that it is possible to achieve very high (higher than 90%) selectivity to the product of O-alkylation when weakly acid [16] or weakly basic [17] catalysts are used, while formation of C-alkylated products is preferentially obtained with catalysts having strong acid sites [18,19]. Some authors have claimed that O-alkylation is preferred over basic sites [7,20].

(b) With basic sites, C-alkylation at the ortho position with respect to the hydroxy group is more preferred than the para position. In fact, the repulsion between the aromatic ring and the basic site favors phenol adsorption (through its hydroxyl group) perpendicular to the surface. This makes the adjacent ortho position closer to the surface and thus more available for electrophilic attack by activated methanol [21]. The product of *p*-methylation has been obtained only when the replacement of Mg by Cu in HT precursors led to more acidic mixed oxides [7,20]. On acidic sites the interaction with the aromatic ring brings it closer to the surface, and makes the reaction possible at both para and ortho positions.

(c) The product of O-alkylation may be an intermediate in the formation of C-alkylated products. For example, it has been found that in phenol methylation, anisole may act as an alkylating agent towards a second molecule of anisole, yielding phenol and 2-methylanisole, or towards a molecule of phenol, forming *o*-cresol, or may generate *o*-cresol with an intramolecular rearrangement [14,18]. Some authors [22,23] have reported that high selectivity to the product of O-alkylation of phenol (anisole) is found only for low conversions; anisole is then intermediate in the formation of *o*-cresol over Mg/Al mixed oxides [20], while with acid catalysts direct C-alkylation is preferred [7]. In *m*-cresol gas-phase methylation, 3-MA has been found to be intermediate in the formation of 2,3,6-TMP [8]. In our case, a possible reaction scheme involving 3-MA as a reaction intermediate was not operating (Fig. 3). However, it cannot be excluded that a consecutive contribution of 3-MA transformation to C-alkylated products might occur under conditions of *m*-cresol conversions higher than those achieved in our tests.

As a possible example of differences which occur between acid and basic catalysts, Table 3 compares the distribution of products for MgO, Mg/Al = 2.0, and an H-Y zeolite (Tosoh). The H-Y zeolite was considerably more active than the basic catalysts; after 6 h reaction time, a conversion of 67% was reached. The results reported in Table 3 are referred to 27% conversion, achieved in a few minutes of reaction. A lower amount of O-methylated product (3-MA) was obtained (implying a lower O/C ratio), as well as a greater selectivity to polyalkylated products (not only 2,3,6-TMP), and to heavier compounds. The selectivity to the para C-alkylated product (3,4-DMP) was considerably higher than for basic catalysts, and this led to a much lower ortho/para ratio.

The catalytic performances of the oxides having different Mg/Al atomic ratios (from pure Al_2O_3 to pure MgO) are summarized in Fig. 5. The following effects are observed:

(a) The pure oxides (MgO, Al_2O_3) showed a lower activity than the Mg/Al mixed oxides, and a lower ortho/para ratio, even though the total density of the basic sites was high.

(b) An increase in *m*-cresol conversion was observed in the Mg/Al mixed oxides as the Mg/Al ratio decreased. While the difference in activity between the Mg/Al = 4.0 and 3.5 samples was relevant, a further increase in Al content (from Mg/Al = 3.5 to 2.0) did not considerably affect the *m*-cresol conversion. The same behavior was also found for the ortho/para ratio, which exhibited minor changes for samples having Mg/Al ratios between 3.0 and 2.0.

(c) The O/C ratio decreased with decreasing Mg/Al ratio. On the basis of literature information, the C-alkylation might be favored by either an increase in the basic strength, or the contribution of the acid character, which develops with increasing Al content. The characterization of acidity could exclude the presence of acid sites playing a catalytic role in Mg/Al mixed oxides; furthermore the ortho/para ratio should decrease with increasing Al content (i.e., as the Mg/Al ratio decreases). On the contrary, the ortho/para ratio showed the opposite trend and, thus, the O/C ratio trend can be attributed to the increasing basic strength.

Table 3
Catalytic performance of MgO, Mg/Al = 2.0 and H-Y zeolite in the methylation of *m*-cresol

Catalyst	Conversion percentage of *m*-cresol (%)	Selectivity percentage (%)							
		3-MA	2,3-DMP	2,5-DMP	DMA	3,4-DMP	Polyalkylates	3-EP	Heavies
MgO	2.9	87.2	4.4	5.2	0	2.4	0	0.5	0.3
Mg/Al = 2.0	12.9	81.7	8.6	8.3	0.2	0.7	0.1	0.3	0
HSZ-320HOA (H-Y, Tosoh)	26.6	44.4	13.5	11.8	6.5	17.0	4.6	0	2.1

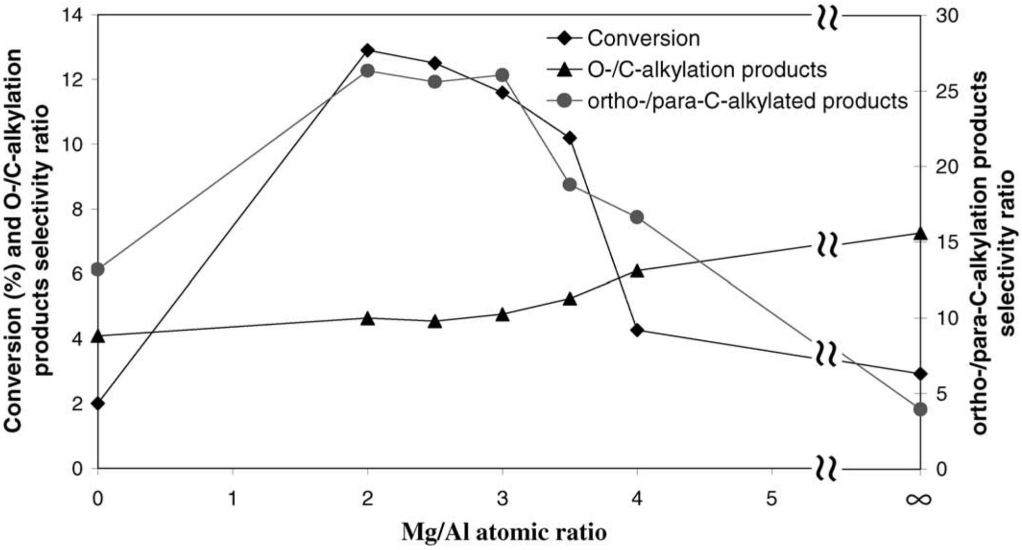

Fig. 5. Catalytic performance as function of the Mg/Al ratio.

These data can be explained by making the hypothesis that the strong basic sites (which are the prevailing sites in the two single oxides) do not take part in the reaction, because they immediately deactivate after interaction with the reagent molecules [14]. Under our reaction conditions (300 °C) it is likely that the strongest basic sites (those sites able to desorb CO_2 only at very high temperature) are not available, and this is even more important at high pressure, in the condensed phase. On the other hand, weakly basic sites probably do not play an important role in the reaction. Therefore, it can be hypothesized that sites having intermediate basic strength are the active sites for the alkylation of *m*-cresol under our reaction conditions. The increase in the number of these sites with decreasing Mg/Al ratio causes the enhancement of the ortho/para ratio and the decrease in the O/C ratio.

The catalytic behaviors of Mg/Al mixed oxides having Mg/Al ratios between 2.0 and 3.0 are similar, in agreement with the results of CO_2 characterization, which evidences a similar distribution of surface basic sites for these samples. Only for Mg/Al ratios higher than 3.0 are significant differences in the catalytic behavior observed, in correspondence with a decrease in the number of basic sites having medium strength.

Al_2O_3 represents a case on its own. CO_2 characterization indicates a predominance of strong basic sites, as observed for MgO, and correspondingly some reaction parameters are similar to those of MgO: *m*-cresol conversion and ortho/para ratio. On the other hand, the O/C ratio is lower than that of all the other samples. It is possible that the surface acidity of alumina may play a role in favoring C-alkylation rather than O-alkylation.

In the range examined in the present work no clear maximum in activity is observed in correspondence with an intermediate value of the Mg/Al ratio. A different behavior has been reported in the literature. A maximum has been observed for the dehydrogenation of isopropanol (maximum activity for the sample having $Mg/Al = 3$) [5], for Claisen–Schmidt condensation ($Mg/Al = 2.3$) [24], and for the gas-phase methylation of phenol ($Mg/Al = 4.0$) [25]. It has been proposed that intermediate Al contents might correspond to the highest basicity, due to the compromise between the large amount of low-coordination O sites (the concentration of which increases with decreasing Mg/Al ratio) and the low average electronic density of these O species (which decreases with increasing average electronegativity of the solid and thus the Al content) [5]. This discrepancy with our results may well be due to the different reaction conditions applied (i.e., reagents, temperature, pressure) and their influence on the reactivity of the sites playing a role in the mechanism. Under the conditions used in the present work, the strongest basic sites likely do not take part in the reaction, and good correspondence exists between the number of medium strength basic sites and the catalytic performance. If reaction conditions are chosen which allow participation of the strongest basic sites, a different trend in reactivity might be expected.

4. Conclusions

The reaction of *m*-cresol methylation can be used to check the reactivity of basic Mg/Al mixed oxides prepared by hydrotalcite decomposition. These materials are possible candidates for the preparation of heterogeneous systems alternative to the environmentally unfriendly homogeneous ones. Specific features such as: (i) the conversion of *m*-cresol, (ii) the ratio between the selectivity to the products of ortho C-alkylation and of para C-alkylation and (iii) the ratio between the selectivity to the products of O-alkylation and of C-alkylation, can give useful indications about the site strength.

In the present case, the total density of the basic sites was higher in MgO than in the other materials, while the number of the medium strength basic sites was higher in the Mg/Al mixed oxides than in the pure oxides, MgO and Al_2O_3. In correspondence, in Mg/Al mixed oxides the activity and the ortho-/para-C-alkylated products ratio increased, while the O-/C-alkylated products ratio decreased with decreasing Mg/Al atomic ratio. A relationship between the catalytic performance and the basicity distribution, as determined by adsorption/TPD of CO_2, is proposed. Under the reaction conditions used, the medium strength basic sites act as the active sites for the alkylation of *m*-cresol with methanol.

Acknowledgements

EniTecnologie SpA is acknowledged for financial support.

References

[1] H. Hattori, Chem. Rev. 95 (1995) 527.
[2] Y. Ono, T. Baba, Catal. Today 38 (1997) 321.
[3] A. Guida, M.-H. Lhouty, D. Tichit, F. Figueras, P. Geneste, Appl. Catal. A 164 (1997) 251.
[4] A. Corma, V. Fornés, R.M. Martin-Aranda, F. Rey, J. Catal. 134 (1992) 58.
[5] A. Corma, V. Fornés, F. Rey, J. Catal. 148 (1994) 205.
[6] R.J. Davis, E.G. Derouane, J. Catal. 132 (1991) 269.
[7] S. Velu, C.S. Swamy, Appl. Catal. A 162 (1997) 81.
[8] S. Velu, S. Sivasanker, Res. Chem. Intermed. 24 (6) (1998) 657.
[9] V. Durgakumari, S. Narayanan, J. Mol. Catal. 65 (1991) 385.
[10] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today 11 (2) (1991) 173.
[11] D. Tichit, F. Fajula, Stud. Surf. Sci. Catal. 125 (1999) 329.
[12] D. Tichit, M. Hassane Llhouty, A. Guida, B. Huong Chiche, F. Figueras, A. Auroux, D. Bartalini, E. Garrone, J. Catal. 151 (1995) 50.
[13] J. Shen, M. Tu, C. Hu, J. Solid State Chem. 137 (1998) 295.
[14] J. Di Cosimo, V.K. Diez, M. Xu, E. Iglesia, C.R. Apesteguia, J. Catal. 178 (1998) 499.
[15] T.M. Jyothi, T. Raja, M.B. Talawar, B.S. Rao, Appl. Catal. 211 (2001) 41.
[16] L. Calzolari, F. Cavani, T. Monti, CR Acad. Sci. Paris, Série IIc, Chimie 3 (2000) 533.
[17] S.C. Lee, S.W. Lee, K.S. Kim, T.J. Lee, D.H. Kim, J.C. Kim, Catal. Today 44 (1998) 253.
[18] M. Marczewski, J.P. Bodibo, G. Perof, M. Guisnet, J. Mol. Catal. 50 (1989) 211.
[19] S. Namba, T. Yashima, Y. Haba, N. Hara, Stud. Surf. Sci. Catal. 5 (1980) 105.
[20] S. Velu, C.S. Swamy, Appl. Catal. 145 (1996) 141.
[21] K. Tanabe, Stud. Surf. Sci. Catal. 20 (1985) 1.
[22] R. Tleimat-Manzalji, D. Bianchi, G.M. Pajonk, Appl. Catal. A 101 (1993) 339.
[23] M.C. Samolada, E. Grioriadou, Z. Kiparissides, I.A. Vasalos, J. Catal. 152 (1995) 52.
[24] M.J. Climent, A. Corma, S. Iborra, J. Primo, J. Catal. 151 (1995) 60.
[25] S. Velu, C.S. Swamy, Appl. Catal. A 119 (1994) 241.