

Guerbet condensation of methanol with *n*-propanol to isobutyl alcohol over heterogeneous copper chromite/Mg–Al mixed oxides catalysts

Carlo Carlini^{a,*}, Cristina Flego^b, Mario Marchionna^b, Marilena Noviello^{a,c},
Anna Maria Raspolti Galletti^a, Glauco Sbrana^a, Francesco Basile^d, Angelo Vaccari^d

^a Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

^b EniTecnologie S.p.A., Via Maritano 26, 20097 San Donato Milanese MI, Italy

^c Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy

^d Dipartimento di Chimica Industriale e dei Materiali, ALMA MATER STUDIORUM, University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

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Abstract

The synthesis of isobutyl alcohol (*i*BuOH) from methanol (MeOH) and *n*-propanol (PrOH) through the Guerbet condensation has been studied at 200 °C and under inert atmosphere (3.0 MPa of N₂), using a two-component heterogeneous catalytic system based on pre-activated copper chromite and Mg–Al mixed oxides deriving from hydrotalcite-type (HT) precursors with different Mg/Al ratios. All the investigated catalysts displayed a significant activity, with an almost complete selectivity to *i*BuOH. Unlike the copper chromite/soluble sodium methoxide system, the catalysts were tolerant of the co-produced water and did not display any appreciable deactivation during the course of the reaction. The catalyst productivity was found to increase by reducing the Mg/Al ratio in the heterogeneous base, according to the increase of the fraction of medium–strong and strong basic sites which favour the aldol condensation between the aldehydes derived from MeOH and PrOH.

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1. Introduction

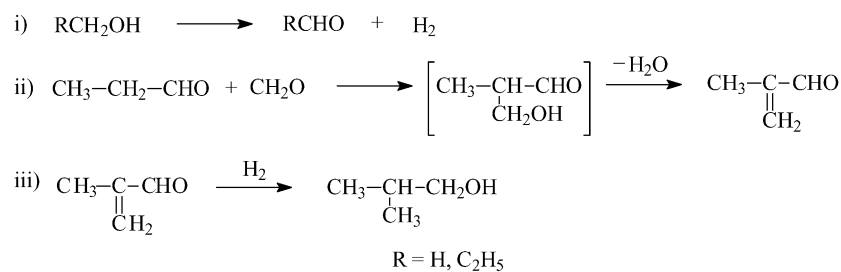
The selective synthesis of isobutyl alcohol (*i*BuOH) has recently gained an increasing interest because this substrate is a potential precursor of gasoline additives such as methyl-*tert*-butyl-ether or isooctane. *i*BuOH may be directly synthesized from syngas through the higher-molecular-weight alcohols synthesis (HAS) carried out at high temperature and pressure over heterogeneous catalysts. However, this process is characterized by rather low selectivity and productivity [1]. An alternative route would be represented by a two-step process [2,3] where in the first stage methanol (MeOH) and higher alcohols are obtained at low temperature from syngas adopting modified low-temperature-methanol catalysts and in the second stage they are converted to an *i*BuOH-rich product using

high-temperature-methanol catalysts [4–6]. However, the latter step has several drawbacks, particularly in terms of selectivity to *i*BuOH and retroconversion of MeOH to syngas. In this context, taking into account that from the first step of the above mentioned process a MeOH/ethanol (EtOH)/*n*-propanol (PrOH) mixture with a large excess of MeOH was generally obtained [2], it appeared convenient to transform this mixture in an *i*BuOH-rich product through the Guerbet reaction. Indeed, the Guerbet reaction consists of a condensation between alcohols, promoted by a bifunctional catalytic system based on a basic component and a metal species with dehydrogenating/hydrogenating properties. Moreover, it has to be underlined that *i*BuOH does not yield subsequent condensation products, probably due to its steric hindrance and to the presence of only one hydrogen on the carbon atom in α -position to the methylol group [7].

In particular, it is well established that the Guerbet reaction may be split into the following three steps: (1) dehydrogenation of alcohols to the corresponding aldehydes, (2) aldol condensation of the resulting aldehydes, and (3) hydro-

* Corresponding author. Tel.: +39 050 2219222; fax: +39 050 2219260.

E-mail address: carlini@ccci.unipi.it (C. Carlini).



Scheme 1.

genation of the unsaturated condensation products to give the higher alcohols [8,9]. In Scheme 1 the reaction pathway is reported for the MeOH/PrOH condensation.

Recently, the Guerbet reaction of MeOH with PrOH [7] or with an EtOH/PrOH mixture [10] has been investigated by some of us adopting copper-based/sodium methoxide (MeONa) catalytic systems. In particular, when MeOH/PrOH mixtures were reacted in the presence of copper chromite/MeONa, an almost complete selectivity to *i*BuOH was observed, the yield increasing with a temperature enhancement from 180 to 220 °C [7]. The productivity was also found to improve on increasing the relative amount of MeONa with respect to the copper component. When the reaction was carried out under N₂ atmosphere, better catalytic performances were obtained than under H₂ atmosphere, thus indirectly confirming that the dehydrogenation of the alcohols to the corresponding aldehydes is the rate limiting step of the reaction. In addition, the recycle tests of both the solid copper component and the liquid reaction mixture allowed to conclude that copper chromite essentially works in heterogeneous phase, unlike that observed for Pd-, Rh- or Ru-based catalysts [11,12].

However, the main drawback of the process was the use of MeONa as homogeneous basic component, due to its progressive hydrolysis to MeOH and inactive NaOH by the H₂O co-produced in the condensation step [7–10]. Therefore, in the present work for the first time a fully heterogeneous system was adopted, i.e. combining a solid base with the copper chromite component. The replacement of a soluble base with an insoluble one would facilitate the separation and recovery of the catalyst from reaction products and would strongly decrease corrosion phenomena and environmental constraints [13–15]. Moreover, the use of solid base catalytic components in the reaction of MeOH with PrOH could allow an easier integration of the condensation step with the subsequent hydrogenation reaction [16], whenever needed.

In this context, among the different types of heterogeneous basic catalysts reported in the literature Mg/Al mixed oxides prepared by controlled calcination of hydrotalcite-type (HT) precursors have shown the best basic features and, in the recent years, these materials have been applied as catalysts for many reactions [17–19]. Hydrotalcite is a layered mineral having the formula Mg₆Al₂(OH)₁₆CO₃·4H₂O,

which can also be easily and cheaply synthesized [20–22]. The properties may be easily tailored by varying the amount of the cations (or their mixtures) and/or the anions, giving rise to a wide range of HT compounds having the general formula [(M_{1-x}²⁺M_x³⁺(OH)₂)^{x+}(A_{x/m}^{m-})·nH₂O], where M²⁺ and M³⁺ are cations and A^{m-} is an interlayer anion [20–22]. When HT precursors are calcined at temperatures lower than ca. 650 °C, the resulting mixed oxides display (i) high surface area, (ii) basic properties, (iii) memory effect, since they may recover the original HT structure when in contact with water solution containing various anions [20–22].

Therefore, HT precursors with various Mg/Al ratios were prepared, calcined and tested in combination with copper chromite in the Guerbet condensation of MeOH with PrOH to obtain *i*BuOH with high yield and selectivity in a completely heterogeneous process. In this particular case, the heterogeneous bases derived from HT precursors appeared very promising, since the basic properties are not only retained, but very probably enhanced in the presence of the co-produced water [23,24].

2. Experimental

2.1. Materials

MeOH (Prolabo) and PrOH (Carlo Erba) were dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide, according to the Lund and Bjerrum method [25].

MeONa (Aldrich) was used as received and stored under dry argon.

Copper chromite catalyst (Cu 1955-P, Engelhard), with the following composition: Cu (36.0 wt.%), Cr (33.0 wt.%), Mn (3.0 wt.%), was dried under vacuum at room temperature and then activated before the use in a mechanically stirred Parr reactor in the presence of methanol at 180 °C, for 4 h and under 8.0 MPa of H₂.

HT precursors with different Mg/Al atomic ratios were prepared by co-precipitation of magnesium and aluminium nitrates by Na₂CO₃, maintaining the pH = 10.0 ± 0.1 by dropwise addition of a concentrated solution of NaOH [20,22,26]. The main characteristics of the prepared Mg/Al

Table 1
Composition and surface area of the heterogeneous basic catalysts obtained by calcination at 500 °C for 5 h of the HT precursors

Catalyst	Mg/Al (atomic ratio) ^a	Weight composition (%)		BET surface area (m ² /g)
		MgO	Al ₂ O ₃	
Cat1	80/20	76.0	24.0	208
Cat2	71/29	65.9	34.5	232
Cat3	66/34	60.5	39.5	214

^a Ratio between aluminium and magnesium nitrates in the starting solution used for the preparation of the HT precursors.

samples, after calcination at 500 °C for 5 h, crushing and sieving to 125–250 µm particle size and finally storage under argon, are reported in Table 1.

2.1.1. Catalytic experiments for the condensation of methanol with *n*-propanol

A 300 ml Parr reactor, equipped with a mechanical stirrer, a heating system and a control device assisted by a J thermocouple inserted into the reactor, a sampling valve for liquids, an inlet valve for gas introduction and an outlet sampling valve for gaseous products, was used in the catalytic batch experiments. The copper chromite catalyst was introduced in the reactor, then this latter was evacuated and MeOH was added through the sampling valve. The reactor was subsequently pressurized with H₂ up to 8.0 MPa and heated at 180 °C for 4 h. After the activation step, the reactor was cooled to room temperature and degassed. The reactor was evacuated and MeOH removed under vacuum, then it was opened and the alcohols mixture and the heterogeneous basic catalyst were introduced under argon atmosphere. Finally, the reactor was pressurized with N₂. The reaction was followed by collecting at different times portions of the reaction mixture, quickly cooled to 0 °C, through the sampling valve. At the end of each test, the reactor was rapidly cooled to room temperature, slowly degassed through a trap maintained at –30 °C, in order to condense any liquid products present in the gas phase, and finally the liquid reaction mixture was analyzed by gas-chromatography (GC) after the addition of a known amount of benzene as internal standard.

2.1.2. Analytical procedures

The analysis of the reaction products was performed by GC using a Perkin-Elmer Sigma 3B chromatograph equipped with a thermal conductivity detector, a CE Instruments DP 700 integrator and a (3 mm × 2 m) Poropak PS packed column with a stationary phase based on ethylvinylbenzene/divinylbenzene resin. Helium was used as carrier gas with a 25 ml/min flow rate. The following temperature program was adopted for the oven: 80 °C for 5 min, then the temperature was increased by a 8 °C/min heating until 210 °C was reached, maintaining this value constant for further 15 min. For the quantitative determination of the reaction mixtures, the chromatographic response factor for each individual component was determined using mixtures

of pure compounds of known composition, with benzene as internal standard.

In all the experiments an almost total selectivity to ⁱBuOH was observed. Indeed, only traces (<0.5 mol%) of methyl and propyl formate were detected by GC/MS analysis carried out employing a HP5973 Mass Selective Detector and a HP6890 Series GC System, equipped with a HP5-MS crosslinked 5% phenylmethylsiloxane column (30 m × 0.25 mm × 0.25 µm).

2.1.3. Catalysts characterization

The adsorption and temperature programmed desorption (TPD) of CO₂, as probe-molecule for determining the basic properties of the Mg/Al mixed oxides, was carried out on a Pulse Chemisorb 2705 Micromeritics instrument. Each sample (almost 0.5 g) was pre-treated under He at 500 °C for 2 h in order to eliminate water and gas impurities eventually present. After cooling the sample, the adsorption of CO₂ at 21 °C was carried out until surface saturation was reached; the presence of physically adsorbed CO₂ was avoided by performing the adsorption under He flow. The temperature was then increased with a linear rate from room temperature up to 500 °C and the CO₂ evolution was monitored by mass spectrometry. The basic strength distribution of the sites was evaluated from the capability of the material to retain the probe molecule during the desorption. The TPD profiles were analyzed by a deconvolution program (Galactic Peaksolve) in order to determine the signal number and position. The quality of the elaboration obtained by the Levenberg–Marquadt algorithm was evaluated on the basis of the correlation coefficient ($R^2 > 0.97$).

BET surface area values were obtained using a single point ThermoQuest Surface Area Analyzer Qsurf S1.

3. Results and discussion

A preliminary test (entry 1, Table 2) was carried out using copper chromite as dehydrogenating/hydrogenating catalyst and a solid basic component having an intermediate Mg/Al atomic ratio (71/29) as well as a BET surface area equal to 232 g/m² (Cat2), to check if a fully heterogeneous two-component catalyst may be active in the Guerbet condensation of MeOH with PrOH to give ⁱBuOH. The reaction was performed at 200 °C and under N₂ atmosphere (3.0 MPa) as these conditions were previously proved to give the best catalytic performances when the copper chromite/MeONa system was employed [7,10]; moreover copper chromite was pre-activated (see Section 2), this procedure allowing to significantly improve the activity of the metal-containing component. By comparison, a test under the same conditions (entry 2, Table 2) was performed using a pre-activated copper chromite/MeONa system. The obtained results clearly indicate that the Cat2/copper chromite system was active in the Guerbet reaction, the ⁱBuOH yield being 26.3 mol% after 12 h. These data suggest that the ac-

Table 2
Synthesis of *i*BuOH by condensation of MeOH with PrOH using the Cat2/pre-activated copper chromite catalytic system^a

Entry	Cu-chromite (mmol)	Basic component			<i>i</i> BuOH yield (mol%) ^b			TN ^c (h ⁻¹)
		Type	Mg/Al (atomic ratio)	MgO (mmol)	1 h	6 h	12 h	
1	2.5	Cat2	71/29	20	6.8	18.3	26.3	1.22
2	2.5	MeONa ^d	–	–	13.3	20.8	24.2	1.33
3	2.5	Cat2	71/29	45	5.2	17.0	25.6	1.13
4	2.5	Cat2	71/29	90	4.3	18.4	30.5	1.23
5	5.4	Cat2	71/29	20	7.8	24.3	31.5	0.75
6	11.0	Cat2	71/29	45	5.1	14.6	18.5	0.22
7	11.0	Cat2	71/29	90	5.0	15.9	–	0.24

^a Reaction conditions: MeOH = 1250 mmol; PrOH = 100 mmol; P_{N_2} = 3.0 MPa; T = 200 °C.

^b Referred to the amount of PrOH feed.

^c Productivity expressed as mole of *i*BuOH/(mol Cu h) and calculated at 6 h of reaction.

^d 20 mmol were used.

tivity of this system is of the same order of magnitude as that of the copper chromite/MeONa system, for which a conversion up to 24.2 mol% was obtained. However, the trend of the conversion with the reaction time in the two experiments (Fig. 1) clearly indicates that the former system is much less sensitive to the effect of co-produced water, since the *i*BuOH yield increased monotonically with the reaction time for the copper chromite/Cat2 system, whereas it substantially reached a plateau after few hours of reaction in the case of the copper chromite/MeONa system, showing a subsequent substantial deactivation.

On progressively increasing the amount of the basic component Cat2 (from 20 up to 90 mmol), still retaining constant that of the copper chromite (entries 3 and 4, Table 2), the *i*BuOH yield did not significantly change, unlike what was previously observed for the copper chromite/MeONa system [7,10]. Moreover, the increase of the relative amount of the copper chromite, still maintaining constant the amount of the basic component, gave rise to a decrease in the catalytic performances in terms of productivity (TN) to *i*BuOH (compare entries 1, 3 and 4 with entries 5, 6 and 7 of Table 2, respectively).

To investigate the effect of the nature of the heterogeneous basic component on the catalytic performances, heterogeneous bases having different Mg/Al atomic ratios with respect to Cat2 (Cat1 and Cat3) were employed in combination with pre-activated copper chromite. Indeed, the above samples, having substantially the same specific surface area, would be characterized by different number and strength of basic sites [27–29].

When the entries 1 and 3 of Table 2 were repeated using Cat1, characterized by a higher Mg/Al atomic ratio (80/20) (entries 8 and 9 in Table 3, respectively) a significant reduction in both yield and productivity to *i*BuOH was observed. In the case of Cat1, the increase of the relative amount of the basic component, still retaining constant the other reaction parameters, lowered the catalytic productivity (compare entries 8–10 in Table 3). When Cat3 (Mg/Al atomic ratio = 66/34), was used in the lowest amount (entry 11, Table 3) the best performance was obtained in comparison with the analogous tests carried out using Cat1 (entry 8, Table 3) and Cat2 (entry 1, Table 2). An increase in the amount of the basic component with respect to copper chromite from 20 to 60 mmol (entries 12 and 13, Table 3)

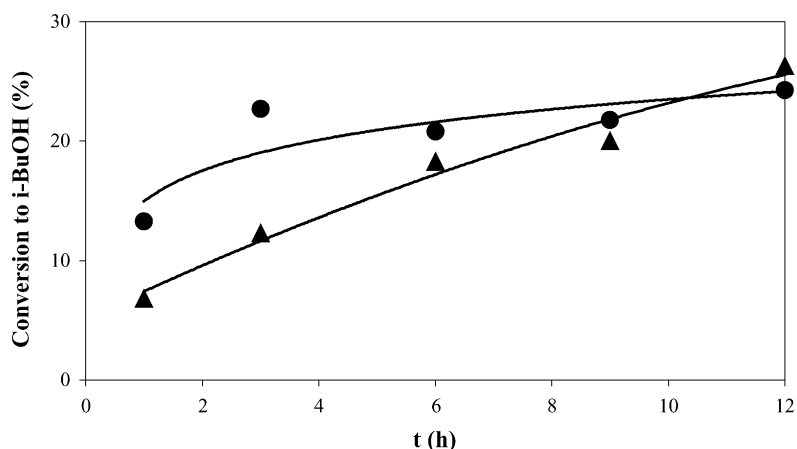


Fig. 1. Conversion to *i*BuOH as a function of the reaction time for the Guerbet condensation of MeOH with PrOH in the presence of: (▲) pre-activated copper chromite/Cat2 or (●) pre-activated copper chromite/MeONa systems.

Table 3

Synthesis of *i*BuOH by condensation of MeOH with PrOH using pre-activated copper chromite in combination with different heterogeneous basic components (Cat1 and Cat3)^a

Entry	Cu-chromite (mmol)	Basic component			<i>i</i> BuOH yield (mol%) ^b			TN ^c (h ⁻¹)
		Type	Mg/Al (atomic ratio)	MgO (mmol)	1 h	6 h	12 h	
8	2.5	Cat1	80/20	20	1.2	9.5	13.5	0.63
9	2.5	Cat1	80/20	45	1.6	8.3	15.2	0.55
10	2.5	Cat1	80/20	60	0.2	2.6	4.6	0.17
11	2.5	Cat3	66/34	20	3.4	19.3	29.5	1.29
12	2.5	Cat3	66/34	45	2.3	8.9	14.2	0.59
13	2.5	Cat3	66/34	60	1.7	7.0	13.7	0.47

^a Reaction conditions: MeOH = 1250 mmol; PrOH = 100 mmol; P_{N_2} = 3.0 MPa; T = 200 °C.

^b Referred to the amount of PrOH feed.

^c Productivity expressed as mol of *i*BuOH/(mol Cu h) and calculated at 6 h of reaction.

Table 4

Distribution of the basic sites evaluated by CO₂ adsorption in the TPD experiments

Basic catalyst (Mg/Al atomic ratio, %)	Overall amount of desorbed CO ₂ (μmol/g)	Weak basic sites (μmol/g)	Medium basic sites (μmol/g)	Medium–strong basic sites (μmol/g)	Strong basic sites (μmol/g)
Cat1 (80/20)	282	36	112	108	25
Cat2 (71/29)	249	17	59	135	38
Cat3 (66/34)	270	39	10	117	118

caused a detrimental effect on the yield and productivity to *i*BuOH.

Thus, an excess of the heterogeneous base must be avoided considering both catalytic activity and application perspectives.

In order to have a deeper insight into the relations between activity and number and strength of basic sites in the catalysts, TPD of CO₂ was used. The results obtained are reported in Table 4.

The low temperature CO₂ evolution peak corresponds to species adsorbed on weakly basic OH⁻ groups, whereas the medium strength basic sites, related to intermediate temperature peaks, are connected with the oxygen in Mg²⁺–O²⁻ site pairs and, finally, the strong basic sites, corresponding to the high temperature peaks, are the isolated O²⁻ anions [30].

Although the overall number of basic sites is not appreciably influenced by the Mg/Al atomic ratio value, the fraction of medium–strong and strong basic sites however increases when this parameter decreases, accordingly to what was previously reported by Corma et al. which also evidenced that the aldol condensation reaction requires strong basic sites [27]. Analogous results were obtained by Tichit et al. in their study about the effect of the Mg/Al ratio on the initial condensation rate of benzaldehyde with acetone [31]. Therefore, we have to conclude that the increase of catalyst activity observed when moving from Cat1 to Cat3, i.e. decreasing the Mg/Al atomic ratio, has to be addressed to the enhancement of the fraction of medium–strong and strong basic sites which favour the aldol condensation of the aldehydes formed by dehydrogenation of PrOH and MeOH on pre-activated copper chromite.

4. Conclusions

On the basis of the obtained results the following concluding remarks can be drawn:

- (1) For the first time fully heterogeneous two-component catalysts, based on pre-activated copper chromite and Mg/Al mixed oxides derived from HT precursors, have been proved to be active in the synthesis of *i*BuOH starting from MeOH/PrOH mixtures through the Guerbet condensation. In all cases an almost complete selectivity to *i*BuOH was found to occur.
- (2) The activity of these systems was not affected by the co-produced water, unlike that detected for the corresponding catalysts containing sodium methoxide as basic component, without any evidence of inhibition during the course of the reaction.
- (3) The activity was found to be influenced by the Mg/Al atomic ratio in the HT precursor, according to the variation of the relative amount of medium–strong and strong basic sites. The heterogeneous base with the lowest Mg/Al atomic ratio showed the maximum of productivity in *i*BuOH when employed in the lowest amount, thus opening interesting application perspectives.

Work is in progress to prepare and check bifunctional heterogeneous catalysts, i.e. characterized by both dehydrogenating/hydrogenating and basic sites present in the same matrix, to simplify the catalytic system and exploit potential synergistic effects in the Guerbet condensation.

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References

- [1] K.A.N. Verkerk, B. Jaegel, C.H. Finkeldei, W. Keim, *Appl. Catal. A: Gen.* 186 (1999) 407.
- [2] A. Beretta, Q. Sun, R.G. Herman, K. Klier, *Ind. Eng. Chem. Res.* 35 (1996) 1534.
- [3] R.G. Herman, *Catal. Today* 55 (2000) 233.
- [4] G. Natta, V. Colombo, I. Pasquon, in: P.H. Emmet (Ed.), *Catalysis*, vol. V, Reinhold, New York, 1957 (Chapter 3).
- [5] K. Klier, in: S. Kaliaguine, A. Mahay (Eds.), *Catalysis on the Energy Scene*, Elsevier, Amsterdam, 1984, p. 439.
- [6] X. Xiaoding, E.B.M. Doesburg, J.J.F. Scholten, *Catal. Today* 2 (1987) 125.
- [7] C. Carlini, M. Di Girolamo, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 184 (2002) 273.
- [8] S. Veibel, J.I. Nielsen, *Tetrahedron* 23 (1967) 1723.
- [9] R.E. Miller, G.E. Bennet, *Ind. Eng. Chem.* 53 (1961) 33.
- [10] C. Carlini, M. Di Girolamo, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 200 (2003) 137.
- [11] C. Carlini, M. Di Girolamo, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 204/205 (2003) 721.
- [12] C. Carlini, A. Macinai, M. Marchionna, M. Noviello, A.M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* 206 (2003) 409.
- [13] Y. Ono, T. Baba, *Catal. Today* 38 (1997) 321.
- [14] K. Tanabe, *Appl. Catal. A: Gen.* 181 (1999) 399.
- [15] W. Hölderich, *Catal. Today* 62 (2000) 115.
- [16] F. King, G.J. Kelly, *Catal. Today* 73 (2002) 75.
- [17] A. Vaccari, *Appl. Clay Sci.* 14 (1999) 161.
- [18] F. Basile, A. Vaccari, in: V. Rives (Ed.), *Layered Double Hydroxides—Present and Future* Nova Science, New York, 2001, p. 285.
- [19] M. Bolognini, F. Cavani, D. Scagliarini, C. Flego, C. Perego, M. Saba, *Catal. Today* 75 (2002) 103.
- [20] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* 11 (1991) 173.
- [21] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle (Eds.) *Comprehensive Supramolecular Chemistry*, vol. 7, Pergamon Press, Oxford, 1996, p. 251.
- [22] A. Vaccari, *Catal. Today* 41 (1998) 53.
- [23] K.K. Rao, M. Gravelle, J.S. Valente, F. Figueras, *J. Catal.* 173 (1998) 115.
- [24] J.C.A.A. Roelofs, D.J. Lensveld, A.J. van Dillen, K.P. de Jong, *J. Catal.* 203 (2001) 184.
- [25] A.I. Vogel, *Textbook of Practical Organic Chemistry*, 5th ed., Longman, London, 1989.
- [26] F. Basile, G. Fornasari, E. Poluzzi, A. Vaccari, *Appl. Clay Sci.* 13 (1998) 329.
- [27] A. Corma, V. Fornés, R.M. Martín-Aranda, F. Rey, *J. Catal.* 134 (1992) 58.
- [28] A.L. McKenzie, C.T. Fishel, R.J. Davis, *J. Catal.* 138 (1992) 547.
- [29] J. Shen, J.M. Kobe, Y. Chen, J.A. Dumesic, *Langmuir* 10 (1994) 3902.
- [30] J.I. Di Cosimo, V.K. Diez, M. Xu, E. Iglesia, C.R. Apesteguia, *J. Catal.* 178 (1998) 499.
- [31] D. Tichit, M. Lhouty, A. Guida, B. Chiche, F. Figueras, A. Aroux, D. Bartolini, E. Garrone, *J. Catal.* 151 (1995) 50.