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Chromium-free catalysts for selective vapor phase hydrogenation of maleic anhydride to γ-butyrolactone

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Abstract

The replacement of chromite catalysts in the selective vapor phase hydrogenation of maleic anhydride (MA) to γ-butyrolactone (GBL), useful intermediate in the production of chlorine-free solvents, was investigated. In order to avoid the interferences related to physical dishomogeneity of the precursors, Cu/Zn/M catalysts (38:38:24, atomic ratio percent, where M = Cr, Al or Ga) obtained by thermal decomposition of hydrotalcite-type anionic clays were used. The Al-containing catalyst exhibited better performances than the Cr-containing catalyst, while with gallium no significant differences in comparison to aluminum were observed, capable of justifying the significantly higher cost. Cu/Zn/Al catalysts showed complete MA conversion and high yields in GBL, with maximum values when the Al-content was about 17% (as atomic ratio) and the Cu/Zn ratio fell between 0.5 and 1.0. Furthermore, better carbon balances were observed for these last catalysts, which may be attributed to lower light hydrocarbon synthesis and tar formation.

Keywords: Chromium-free catalysts; Maleic anhydride; γ-Butyrolactone; Selective vapour phase hydrogenation

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1. Introduction

γ-Butyrolactone (GBL) is currently one of the most useful intermediates in the production of new solvents for use as alternatives to chlorine-based solvents [1], the use of which will be subjected to increasing restrictions related to their negative environmental impact. Vapor phase hydrogenation of maleic anhydride (MA) or its esters is the most direct way to produce GBL (for instance, in comparison to the Mitsubishi Kasei process) and does not require the use of hazardous materials (such as in the Reppe process) [2,3]. However, when maleates are used as feedstocks, it is necessary to take into account the additional costs related to the processes of esterification and alcohol recovery. MA may actually be considered a feedstock because of its availability and lower price made possible by the construction of large fluid-bed plants (about 50 000 ton/year), based on Alusuisse-Lummus and British Petroleum-Union Chimique Belge technologies [2–5].

Reduced copper chromite catalysts, sometimes containing physical and chemical promoters, are currently used as catalysts in the vapor phase hydrogenation of MA or its esters [6–11]. However, Cr-containing catalysts are becoming increasingly difficult to use because of the toxic

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nature of the spent catalysts, related to the chromium and barium contents. A partial solution may be the use of catalysts obtained by the reduction of cubic spinel-type phases, containing excess copper ions, which exhibit good catalytic performances, also in conditions of industrial interest, and do not require any promoter [9–11]. On the basis of some recent patents, aluminum containing catalysts may represent an interesting and promising alternative to the chromite catalysts [12–14].

In the present study the possible replacement of the chromium containing catalysts was investigated, with attention focused on the role of the catalyst composition in order to define the best catalyst composition for the selective vapor phase hydrogenation of MA. In all cases, to favor synergetic effects between the elements and reduce the interferences related to physical dishomogeneity and/or phase segregation in the precursor, all the samples were obtained starting from hydrotalcite-type (HT) precipitates, pure or with side phases.

2. Experimental

All catalysts (Table 1) were prepared by coprecipitation at pH 8.0 of a solution of nitrates of the elements with a slight excess of $NaHCO_3$. The resulting precipitates were washed until the sodium concentration was lower than 0.1% w/w (as Na_2O), dried overnight at 363 K and calcined at 653 K for 24 h. The XRD powder patterns were recorded using a Philips PW 1050/81 diffractometer controlled by a PW 1710 unit and Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The data were processed using an Olivetti M240 computer. Quantitative XRD determinations were carried out according to the method of Klug and Alexander [15]. A Carlo Erba Sorpty 1750 apparatus with nitrogen adsorption was used to measure the surface area of the samples.

The catalytic tests were carried out using about 2 g of catalyst (0.420–0.841 mm particle size) in a copper tubular fixed-bed microreactor (internal diameter 2 mm, length 520 mm), operating at atmospheric pressure in the 485–548 K temperature range. The U-shaped reactor was fully immersed in a carborundum-bath in order to ensure an isothermal axial temperature profile during the catalytic tests. Before the catalytic tests, the samples were activated in situ at atmospheric pressure in a flowing H_2–N_2 (5:95 v/v) stream, while the temperature was progressively increased from 298 to 603 K. The reactor was fed with a stream of MA/GBL solution (60:40 w/w) in hydrogen (total flow 5.0 l h^{-1}, H_2/C_4 molar ratio

Table 1
Physico-chemical characterization of the catalysts investigated

Sample	Cu	Zn	Al	Cr	Ga	XRD characterization		BET surface area (m^2 g^{-1})	
	atomic ratio (%)					A[a]	B[b]	(A)	(B)
Cat 1	38.0	38.0	0.0	24.0	0.0	HT	NSS, CuO, ZnO	64	90
Cat 2	38.0	38.0	24.0	0.0	0.0	HT	NSS, CuO, ZnO	50	65
Cat 3	38.0	38.0	0.0	0.0	24.0	HT>M	NSS, CuO, ZnO	64	93
Cat 4	25.0	25.0	50.0	0.0	0.0	HT	NSS, CuO, ZnO	82	144
Cat 5	41.5	41.5	17.0	0.0	0.0	HT>M	NSS, CuO, ZnO	60	84
Cat 6	45.0	45.0	10.0	0.0	0.0	M>HT	NSS, CuO, ZnO	71	66
Cat 7	25.3	50.7	24.0	0.0	0.0	HT>HZ	NSS, CuO, ZnO	53	81
Cat 8	27.6	55.4	17.0	0.0	0.0	HT, HZ	NSS, CuO, ZnO	62	54

[a] Precipitates dried at 363 K.

[b] Samples calcined at 623 K for 24 h.

HT = Hydrotalcite-type phase (ICDD 22-700); NSS = Cubic non-stoichiometric spinel-type phase (ICDD 33-448 and 26-509); M = Malachite- or rosasite-type phase (ICDD 10-399 or 18-1095); CuO (ICDD 5-661); ZnO (ICDD 5-664); HZ = Hydrozincite- or auricalcite-type phase (ICDD 19-1458 or 17-743).

equal to 170). Preliminary catalytic tests with GBL (H_2/GBL molar ratio equal to 173) were also carried out, taking into account both that GBL is an intermediate in the hydrogenation of MA and that it is also the solvent employed to feed MA, because most of the usual solvents react preferentially with MA. The organic feedstock was introduced by an Infors Precidor model 5003 infusion pump. The reaction products were analyzed on-line without condensation using a Carlo Erba 4300 gas chromatograph, equipped with FID and two columns (3.2 mm×2.0 m) filled with Porapak QS.

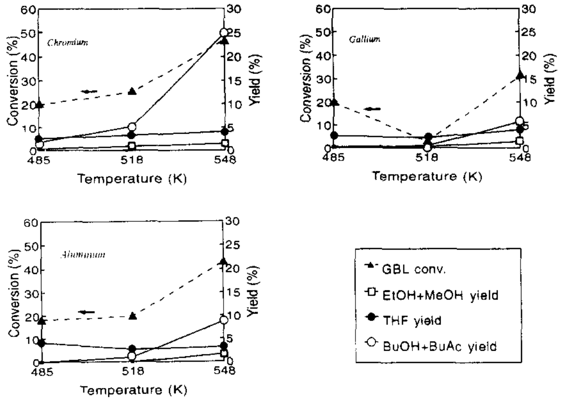

Fig. 1. Catalytic activity of Cu/Zn/M (38:38:24, atomic ratio %) catalysts in the hydrogenation of γ-butyrolactone, as a function of the nature of the trivalent ions present ($P = 0.1$ MPa; H_2/GBL = 173 mol/mol).

3. Results and discussion

To minimize the effects related to physical dishomogeneity of the precursors, the possibility of substituting chromium ions with aluminum or gallium ions was investigated for samples obtained by thermal decomposition of HT precursors, in which all cations are randomly distributed inside brucite-type sheets, thus, favoring interactions and synergetic effects between the elements [16]. Gallium was chosen on the basis of its good catalytic performances recently reported in the hydrogenation of CO_2 [17] and was the only element for which small amounts of a malachite-type phase was also detected in the precursor (Table 1). In the studies to define the best Cu/Zn/Al composition, once again the catalyst samples were all obtained starting mainly from HT precursors; in fact, with the exception of the sample with the lowest aluminum content (Cat 6), all the dried precipitates show the presence mainly of a well crystallized HT phase, pure or with side phases as a function of the aluminum content and Cu/Zn atomic ratio (Table 1), in agreement to that reported in previous papers [18–20].

After calcination (Table 1), the XRD powder patterns showed the presence of a poorly crystalline cubic spinel-type phase together with different amounts of CuO and/or ZnO as a function of the catalyst composition [18,20,21]. However, the quantitative XRD analyses show, mainly for the higher aluminum contents, amounts of oxide lower than those expected on the basis of a phase composition oxides + stoichiometric spinel, indicative of the existence of a consistent fraction of divalent ions which escapes XRD detection, present inside the cubic spinel-type phase or strongly interacting with it [21,22].

For all the samples investigated the catalytic tests carried out at $T < 473$ K showed mainly surface adsorption and/or condensation phenomena, while at $T > 573$ K hydrogenolysis and cracking predominated. In the tests carried out using MA/GBL solution as the feedstock, a GBL yield of 43% corresponds to the amount introduced as solvent, with theoretically absence of conversion and production. The accuracy of the conversion and yield values reported in the figures and tables is ± 1. Finally, it should be pointed out that the complement of the yield data has to be attributed to both light products (mainly hydrocarbons) and irreversible surface adsorption with tar formation.

In the tests carried out with GBL (Fig. 1), the chromium containing sample (Cat 1) showed higher GBL conversions than the samples containing aluminum or gallium (Cat 2 and 3, respectively), with formation at 548 K of significant amounts of by-products, due to overhydrogenation reactions [butyric acid (BuAc) and n-butanol (BuOH)] [23]. On the contrary, no significant differences in the yield in THF or ethanol (EtOH), this last formed by hydrogenolysis reactions, were

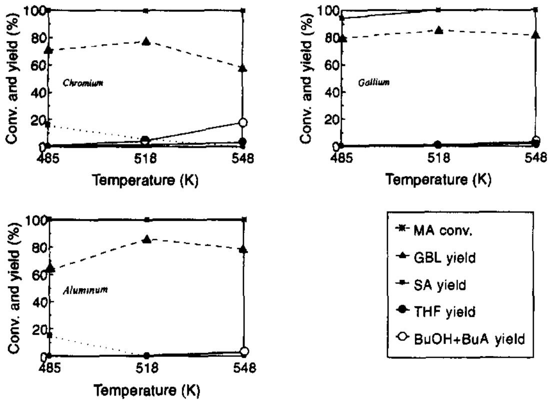

Fig. 2. Catalytic activity of Cu/Zn/M (38:38:24, atomic ratio %) catalysts in the hydrogenation of a solution of maleic anhydride in γ-butyrolactone (60/40 w/w), as a function of the nature of the trivalent ions present ($P = 0.1$ MPa; $H_2/C_4 = 170$ mol/mol).

observed as a function of the trivalent ions present.

With the MA/GBL solution as feedstock (Fig. 2), the chromium containing sample (Cat 1) showed low yields in GBL due, up to 518 K, to reduced hydrogenation activity towards succinic anhydride (SA) and, at higher temperature, to the overhydrogenation and hydrogenolysis of GBL, with formation of unwanted and lower price by-products. On the contrary, aluminum (Cat 2) has to be considered an interesting alternative to chromium; indeed, the presence of aluminum favored high yields in GBL, with a maximum value observed at 518 K, although SA was not fully hydrogenated at the lowest temperature. Gallium favored the hydrogenation of SA at 485 K (although at this temperature MA was not fully converted), while at higher temperatures no significant differences were observed in comparison to aluminum, capable of justifying the significantly higher cost of the gallium containing samples.

On the basis of the previous data, attention was focused on the aluminum containing catalysts. Initially, the role of the aluminum content was investigated for the catalysts with a Cu/Zn atomic ratio equal to one, which shows an increase in the amounts of oxides detected and a linear decrease (with the exception of Cat 2) in the surface area with decreasing aluminum content (Table 1). With GBL as the feedstock, a decrease in activity is observed as aluminum content decreases (Table 2), with, furthermore, a change in selectivity in the different by-products. In fact, it is worth noting that a high aluminum content favored the formation of THF, and as the amount of aluminum decreased there was a corresponding significant increase in the by-products attributable to overhydrogenation and hydrogenolysis reactions [23].

Table 2
Catalytic activity in the hydrogenation of γ-butyrolactone (GBL) of the catalysts with atomic ratio Cu/Zn = 1.0 and different aluminum content (as atomic ratio %)

	50.0		24.0		17.0		10.0	
Temperature (K)	518	548	518	548	518	548	518	548
GBL conversion (%)	43	59	20	43	3	25	10	22
THF yield (%)	17	17	3	3	1	1	1	2
BuOH + BuAc yield (%)	6	18	1	9	0	10	2	17
PrOH + Acetone (%)	0	0	0	0	0	0	0	0
EtOH + MeOH yield (%)	0	2	0	2	0	1	0	4

$P = 0.1$ MPa; H_2/GBL = 173 mol/mol.
GBL = γ-butyrolactone; THF = tetrahydrofuran; BuOH = n-butanol; BuAc = butyric acid; PrOH = propanol; EtOH = ethanol; MeOH = methanol.

Table 3
Catalytic activity in the hydrogenation of the solution of maleic anhydride in γ-butyrolactone (60/40% w/w) of the catalysts having Cu/Zn = 1.0 ratio and different aluminum content (as atomic ratio %)

	50.0		24.0		17.0		10.0	
	518 K	548 K	518 K	548 K	518 K	548 K	518 K	548 K
MA conversion (%)	100	100	100	100	100	100	100	100
GBL yield (%)	80	73	86	78	91	88	88	77
SA yield (%)	17	0	0	0	0	0	0	0
THF yield (%)	1	7	0	3	1	1	1	2
Other yield (%)	< 1	3	0	2	0	1	3	10

$P = 0.1$ MPa; $H_2/C_4 = 170$ mol/mol.
MA = maleic anhydride; GBL = γ-butyrolactone; SA = succinic anhydride; THF = tetrahydrofuran; Others = by-products, mainly n-butanol and butyric acid.

Table 4
Catalytic activity of the catalysts with atomic ratio Cu/Zn = 0.5 and different aluminum content (as atomic ratio %) in the hydrogenation of γ-butyrolactone (GBL)

	24.0		17.0	
Temperature (K)	518	548	518	548
GBL conversion (%)	5	10	9	28
THF yield (%)	2	3	1	2
BuOH + BuAc yield (%)	0	6	0	18
PrOH + Acetone (%)	0	0	0	0
EtOH + MeOH yield (%)	0	1	0	3

$P = 0.1$ MPa; H_2/GBL = 173 mol/mol.
GBL = γ-butyrolactone; THF = tetrahydrofuran; BuOH = n-butanol; BuAc = butyric acid; PrOH = propanol; EtOH = ethanol; MeOH = methanol.

On the other hand, in the tests carried out using the MA/GBL solution (Table 3), for all catalysts the best yield in GBL was always observed at 518 K, while at 548 K consecutive reactions involving GBL took place. The catalyst containing 17% aluminum (as atomic ratio) (Cat 5) showed the maximum yield in GBL, while a high aluminum content (Cat 4) not only worsened the catalytic performances, but also increased the irreversible surface adsorption (with tar formation) and catalyst crush. However, as previously reported [24], these unwanted phenomena can be significantly reduced by pressing the catalyst powder without binders, with, furthermore, a positive effect on the catalytic properties. Also with the MA/GBL solution, higher contents of aluminum favored the formation of THF as a by-product (Cat 2 and 4), while for the other catalysts, low-cost by-products related to the GBL ring opening reaction were mainly obtained [23].

Table 5
Catalytic activity of the catalysts with atomic ratio Cu/Zn = 0.5 and different aluminum content (as atomic ratio %) in the hydrogenation of the solution of maleic anhydride in γ-butyrolactone (60/40% w/w)

	24.0		17.0	
Temperature (K)	518	548	518	548
MA conversion (%)	100	100	100	100
GBL yield (%)	81	96	79	88
SA yield (%)	6	0	0	0
THF yield (%)	< 1	2	1	2
Other yield (%)	5	2	2	9

$P = 0.1$ MPa; $H_2/C_4 = 170$ mol/mol.
MA = maleic anhydride; GBL = γ-butyrolactone; SA = succinic anhydride; THF = tetrahydrofuran; Others = by-products, mainly n-butanol and butyric acid.

On the basis of the above data, attention was then focused on the catalysts containing 17% and 24% aluminum (as atomic ratio), and the role of the Cu/Zn ratio was investigated. For both aluminum contents, an increase in the Cu/Zn ratio favored mainly the reactions of overhydrogenation and hydrogenolysis of GBL, with formation of unwanted and low-price by-products, according to that previously reported for catalysts with a high content of trivalent ions [25,26]. Therefore, in the tests carried out with the MA/GBL solution, a decrease in the yields in GBL was observed, attributable to the increase in the reactions involving GBL. On the contrary, a low Cu/Zn ratio showed different effects, as a function of the catalyst composition; however, the significant decrease in the GBL conversion observed for the catalysts with 24% aluminum (Cat 7) is worth noting (Table 4).

In the tests carried out using the MA/GBL solution (Table 5), for the catalyst with 24% aluminum (Cat 7), an increase in the zinc content favored the formation of GBL, which, at 548 K, reached the highest value ever observed (96%), with a very small formation of by-products. On the contrary, for the catalyst containing 17% aluminum (Cat 8), a higher zinc content gave rise to a worsening of the GBL yield at 518 K, attributable to the increase in activity observed using GBL as the feedstock, while no significant differences were observed at 548 K in comparison to Cat 5 (Cu/Zn ratio equal to one). However, it must be emphasized that for the highest zinc contents very good carbon balances were obtained for both catalysts investigated, proving the validity of the data obtained.

4. Conclusions

Aluminum containing catalysts represent a very interesting alternative to chromium containing catalysts in vapor phase hydrogenation of MA, due to increasing restrictions on the use of latter, in light of the toxicity of Cr^{6+} ions present in the spent catalysts. Cu/Zn/Al catalysts with the right composition give rise to complete MA conversion and high yields in GBL, with, furthermore, low light hydrocarbon synthesis and tar formation, as shown by good values of the carbon balance. On the other hand, it is worth noting that Cu/Zn/Al catalysts have been recently claimed also for the hydrogenation of coco methyl esters [13].

Therefore, vapor phase hydrogenation of MA using Cu/Zn/Al catalysts may actually be considered a significant example of a clean process, considering that it is the most direct and economic way to produce GBL, without using hazardous feedstocks and avoiding problems related to disposal of the catalyst. Furthermore, it must be pointed out that GBL is without doubt a useful intermediate in the production of new solvents on an industrial scale, which are more environmentally acceptable than the present chlorine-based solvents.

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