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Reaction Pathway in Vapour Phase Hydrogenation of Maleic Anhydride and Its Esters to γ-Butyrolactone

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The catalytic reactivity of maleic anhydride (MA), succinic anhydride (SA) and their dimethyl esters (dimethyl maleate and dimethyl succinate) in the vapour phase hydrogenation to γ-butyrolacetone (GBL) was investigated. In order to obtain general data, both a multicomponent catalyst (CAT 1: Cu/Zn/Mg/Cr = 40 : 5 : 5 : 50, atomic ratio %), obtained by reduction of a nonstoichiometric spinel-type precursor, and a commercial catalyst (CAT 2: Cu/Mn/Ba/Cr = 44 : 8 : 1 : 47, atomic ratio %) were used. The MA/GBL solution exhibited the highest GBL production, while the SA/GBL solution was converted only partially due to a competitive adsorption of GBL on the active sites, as evidenced by the similar reactivities observed with pure anhydrides. The best carbon balances were observed with the esters, probably the result of lowest light hydrocarbon synthesis and tar formation. With all the feedstocks, the activity of CAT 2 is higher than that of CAT 1, which, however, gives the best yield in GBL due its lower activity in the overhydrogenation and hydrogenolysis reaction. It was found that *n*-butanol (BuOH) and butyric acid (BuA) derived mainly from GBL. On this basis, the reactivities of the main products observed were investigated separately, confirming the stability of tetrahydrofuran (THF), which reacted only at high temperature with low conversions to ethanol. On the other hand, GBL gave rise to overhydrogenation and/or hydrogenolysis, with high conversion (mainly with CAT 2), confirming its key role in both reactions. Furthermore, the formation in the catalytic tests with BuA and BuOH of *n*-butanal, notwithstanding the high H_2/organic ratio, implies that it is the main intermediate in the hydrogenolysis reactions. A new reaction scheme is proposed, pointing out the key role of GBL as the "intersection" of two possible reaction pathways, giving rise to THF or overhydrogenation and hydrogenolysis products, respectively. © 1994 Academic Press, Inc.

1. INTRODUCTION

γ-Butyrolactone (GBL), tetrahydrofuran (THF), and 1,4-butanediol (BDO) are three examples of small volume commodities of considerable industrial interest, as indicated by both the present market and the growth prospects (1–5). GBL is used as a solvent and for the production of intermediates which find application in the pharmaceutical industry (2). THF is used mainly as a raw material for spandex fibers and polyurethane elastomers and, like GBL, also finds application as a solvent (it is a strong dissolving agent for both synthetic and natural resins). The main use of BDO is in the production of engineering plastics (polyurethanes and polybutylene terephthalates); the world demand for BDO is currently growing at 6 to 10% per year and almost all major producers have announced plant expansions (3). Furthermore, it should be noted that the production of these compounds provides good examples of how industrial plants that make interdependent products operate, taking into account that GBL, THF, and BDO may be produced in different amounts as a function of the reaction conditions (5–7).

There are basically four processes for the production of these compounds (5): (i) Reppe (based on acetylene and formaldehyde condensation); (ii) Arco (isomerization of propylene oxide to allyl alcohol and subsequent hydroformylation); (iii) Mitsubishi Kasei (MKC) (based on 1,3-butadiene diacetoxylation); (iv) Davy McKee (hydrogenation of diethyl or dimethyl maleates). This last process seems to be particularly interesting because its variable costs (i.e., the costs directly related to the amount produced) are the lowest (3,5). Likewise for the Davy McKee process, the hydrogenation of maleic anhydride (MA) is the most direct way to produce GBL (for instance, as compared to butadiene diacetoxylation) and does not require the use of hazardous materials (such as acetylene). Furthermore, MA may nowadays, be considered a feedstock because of its availability and lower price made possible by the construction of large fluid-bed MA plants (about 50,000 tons/year), based on Alusuisse-Lummus Crest and British Petroleum-Union Chimique Belge technologies (3, 5, 8, 9).

As mentioned above, GBL can be easily hydrogenated to THF or BDO; however, many different less valuable by-products may also be easily obtained (such as linear alcohols, acids, acetone, and esters). For this reason to develop new catalysts it is necessary to take into account the appropriate requirements of activity, selectivity, and

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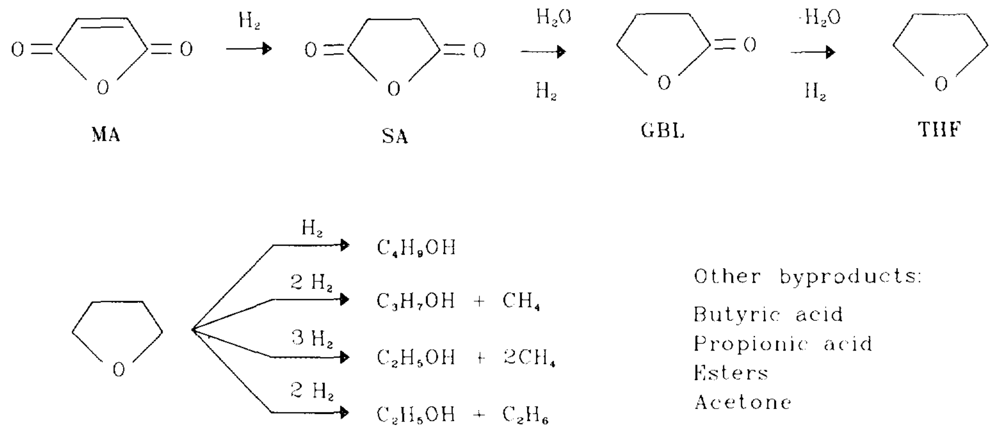

FIG. 1. Reaction pathway proposed in the literature for maleic anhydride hydrogenation (1, 4, 24).

life. In fact, deactivation phenomena are very important in the production of GBL by MA hydrogenation. It is reported in the patent literature, for instance, that the addition of water to the organic feed extends catalyst life, by suppressing the formation of coke and tar (10). The patent literature is rich in data regarding the nature and the composition of catalysts as well as the operating conditions for the hydrogenation reaction (11–23). On the other hand, very little data are reported in the open literature concerning the vapour phase hydrogenation of MA and, especially, on the reaction pathway. In addition, the behaviour of the main intermediates identified in GBL catalytic production has not been investigated. Figure 1 illustrates the reaction mechanism generally proposed for vapour phase hydrogenation of MA, involving only consecutive reactions (1, 4, 24).

In previous papers (25, 26) it was shown that catalysts obtained by reduction of cubic spinel-type phases containing excess copper ions can be usefully employed in the vapour phase hydrogenation of MA to GBL. These cubic spinel-type phases may be obtained by controlled thermal decomposition of homogeneous precipitates, as a function of the composition, heating atmosphere and temperature (27–31). In the samples calcined at $T \leq 753$ K quantitative XRD analysis showed amounts of CuO significantly lower than those expected on the basis of a phase composition CuO + stoichiometric spinel (29, 31), thus suggesting the existence of a consistent fraction of Cu^{2+} ions which escape XRD detection, probably present inside the cubic spinel-type phase or strongly interacting with it. It is worth noting that the presence of a well-dispersed and stable copper fraction, not detectable by XRD analysis, has already been reported in the literature on catalysts for methanol synthesis (32, 33).

On the other hand, it must be pointed out that in these catalysts part of the copper ions may be replaced by other divalent cations, with corresponding changes in physical and catalytic properties (25, 26, 29, 30). In particular, high GBL productivities can be achieved by partial substitution of copper ions by zinc ions (which increases the activity in the hydrogenation of SA) and by magnesium ions (which inhibits the overhydrogenation and/or hydrogenolysis reactions) (25, 26). Based on this information, a Cu/Zn/Mg/Cr catalyst was investigated and catalytic performances better than those of a widely employed commercial catalyst were found. Furthermore, the Cu/Zn/Mg/Cr catalyst investigated in reaction conditions of industrial interest did not show any scale-up problems or deactivation phenomena with increasing time-on-stream (34).

The aim of this study was to shed light on the mechanism of vapour phase hydrogenation of MA or its methyl ester, a fundamental step for the design of new catalytic formulations. To this end, in a first step the hydrogenation of MA and succinic anhydride (SA) and the corresponding methyl esters was compared, in order to clarify the role of the feedstock, taking into account the industrial relevance of the ester hydrogenation (3, 5, 17, 35, 36). On the basis of the results obtained, the subsequent step was to investigate the behaviour in the same conditions of the main reaction intermediates. In order to have general data, the behaviour of a multicomponent catalyst, obtained by reduction of a spinel-type precursor, and a commercial catalyst, of widespread industrial use, was investigated.

2. EXPERIMENTAL

The atomic compositions of the home-made multicomponent catalyst (CAT 1) and of the commercial catalyst (CAT 2) were Cu/Zn/Mg/Cr = 40 : 5 : 5 : 50 and Cu/Mn/Ba/Cr = 44 : 8 : 1 : 47 (atomic ratio percent), respectively. CAT 1 was prepared by coprecipitation at pH = 8 of a solution of nitrates of the elements with a slight excess

TABLE 1

Feedstock Conditions Employed in the Catalytic Tests

Feedstock	Composition (w/w%)	Total organic feed (10^{-3} mol/h)	H_2/organic ratio (mol/mol)
DMM	100	2.0	103 : 1
DMS	100	1.9	108 : 1
MA/GBL	60 : 40	3.0	69 : 1
SA/GBL	20 : 80	3.2	64 : 1
GBL	100	1.3	158 : 1
THF	100	1.2	172 : 1
BuA	100	1.0	206 : 1
BuOH	100	1.1	187 : 1
PrA	100	1.3	158 : 1

Note. DMM = dimethyl maleate; DMS = dimethyl succinate; MA = maleic anhydride; SA = succinic anhydride; GBL = γ-butyrolactone; THF = tetrahydrofuran; BuA = butyric acid; BuOH = *n*-butanol; PrA = propionic acid.

of $NaHCO_3$. The resulting precipitate was washed until the sodium concentration was lower than 0.1% (as Na_2O), dried at 363 K and calcined in air at 653 K for 24 h.

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 catalytic tests were carried out using about 2 g of catalyst in a tubular fixed-bed microreactor (i.d. 2 mm, length 520 mm), operating at atmospheric pressure in the 485-548 K range. The reactor was fed with a stream of organic substance in hydrogen (total flow 5.0 liter/h), the organic feedstock being introduced by an Infors Precidor 5003 infusion pump. The data relative to the feedstock conditions are reported in Table 1. MA and SA were introduced as solution because of the difficulties involved in maintaining heated pumps to feed melted MA or SA in a very low flow range. GBL was used as the solvent considering that most of the usual solvents react preferentially with MA.

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 Poropak QS.

3. RESULTS

3.1. Reactivity of the Different Feedstocks

It must first be pointed out that in the catalytic tests with the MA/GBL (60 : 40 w/w) and SA/GBL (20 : 80 w/w) solutions (as a function of the different solubilities of the anhydrides in GBL), a yield in GBL of 43.2 and 82.3%, respectively, corresponds to the amount introduced as the solvent, with theoretically complete absence of its conversion. For both the samples investigated, the tests carried out at $T < 473$ K show mainly surface adsorption and/or condensation, while at $T > 573$ K the reactions of hydrogenolysis and cracking predominated. Furthermore, it should be pointed out that the complement of the yield data in the tables and figures has to be attributed

TABLE 2

Catalytic Data for the Tests of MA and SA Hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40 : 5 : 5 : 50, Atomic Ratio %) and CAT 2 (Cu/Mn/Ba/Cr = 44 : 8 : 1 : 47, Atomic Ratio %)

Sample	Feed[a]	Temp. (K)	Conv.[b] (%)	Yield (%) GBL[c]	SA	THF	BuA	BuOH	Others
CAT 1	MA	485	100.0	58.3	5.7	—	—	0.5	—
		518	100.0	82.7	6.1	0.1	0.5	1.0	—
		548	100.0	74.3	7.9	0.9	0.7	1.4	0.8
CAT 2	MA	485	100.0	50.0	6.6	—	0.2	0.3	—
		518	100.0	64.3	10.1	0.3	0.3	0.8	—
		548	100.0	75.3	—	5.4	0.8	1.1	0.5
CAT 1	SA	485	46.6	85.0	—	—	0.1	—	—
		518	77.8	92.4	—	0.4	0.3	—	—
		548	100.0	89.1	—	1.8	3.1	0.6	—
CAT 2	SA	485	89.6	86.0	—	0.2	0.4	—	—
		518	100.0	71.7	—	3.8	0.1	—	1.6
		548	100.0	68.6	—	7.8	1.1	—	2.2

Note. $P = 0.1$ MPa; feedstock conditions as in Table 1.

[a] MA = MA/GBL solution (60 : 40 w/w %); SA = SA/GBL solution (20 : 80 w/w %).

[b] Referred to the anhydride.

[c] GBL = γ-butyrolactone; SA = succinic anhydride; THF = tetrahydrofuran; BuA = butyric acid; BuOH = *n*-butanol; Others = hydrogenolysis products [ethanol; *n*-propanol and acetone (traces)].

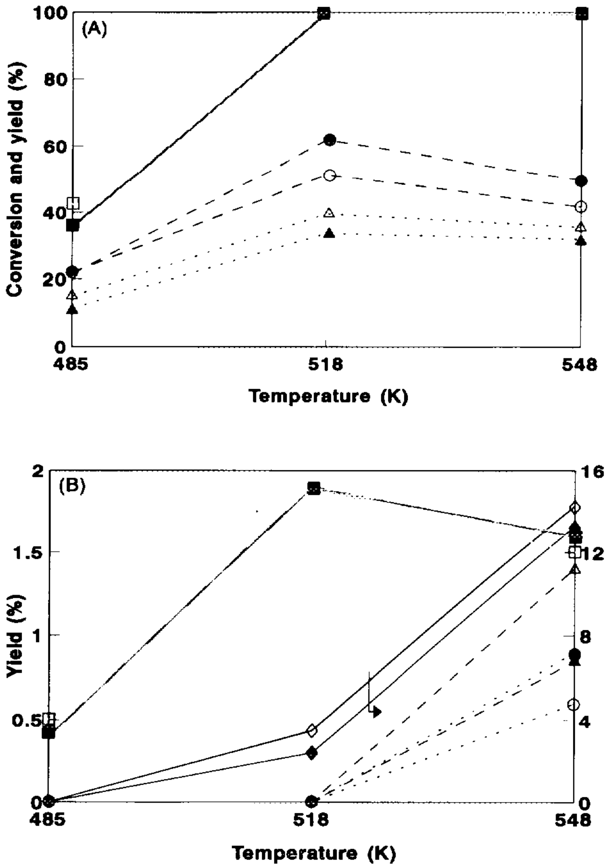

FIG. 2. Catalytic data for the tests of dimethyl maleate (DMM) or dimethyl succinate (DMS) hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40 : 5 : 5 : 50, atomic ratio %) (P = 0.1 MPa; feedstock conditions as in Table 1). (DMM = dimethyl maleate; DMS = dimethyl succinate; GBL = γ-butyrolactone; MeOH = methanol; THF = tetrahydrofuran; BuA = butyric acid; BuOH = n-butanol; MeBu = methyl butyrate). [(A): ■ DMM conversion; □ DMS conversion; ● GBL yield (DMM); ○ GBL yield (DMS); ▲ MeOH yield (DMM); △ MeOH yield (DMS)] [(B): ■ THF yield (DMM); □ THF yield (DMS); ● BuA yield (DMM); ○ BuA yield (DMS); ▲ BuOH yield (DMM); △ BuOH yield (DMS); ◆ MeBu yield (DMM); ◇ MeBu yield (DMS)].

to both light products (mainly hydrocarbons) and irreversible surface adsorption with tar formation.

The catalytic tests with the MA/GBL solution (Table 2) show that both catalysts are very active in the hydrogenation of MA, exhibiting a complete conversion at all temperatures investigated. In all conditions the production of GBL is observed (yields higher than 43.2%), with a maximum for CAT 1 at 518 K. On the contrary, with the SA/GBL solution (Table 2), complete conversion is achieved only at 548 K for CAT 1 and at 518 K for CAT 2, respectively. The GBL yield is higher than 82.3% at all the temperatures for CAT 1 and only at 485 K for CAT 2, indicating both a higher activity of this latter catalyst at all the temperatures studied and a higher reactivity of MA in comparison to SA. However, it is worth noting that during catalytic tests on a large bench-scale fixed-bed tubular reactor, in which the feed consisted of melted MA or SA, no significant differences were observed in the reactivity of the two anhydrides (37).

Figures 2 and 3 show the results of the catalytic tests in the ester hydrogenation with CAT 1 and CAT 2, respectively. For CAT 1 the qualitative trends are substantially the same for both esters dimethyl maleate (DMM) and dimethyl succinate (DMS), with only a little higher conversion with DMS. The yield in GBL as well as those in methanol (MeOH) and THF present a maximum value at the intermediate temperature (with higher values for DMM). The decrease in GBL and THF production observed at 548 K corresponds to the formation of unwanted and lower cost overhydrogenation products, such as n-

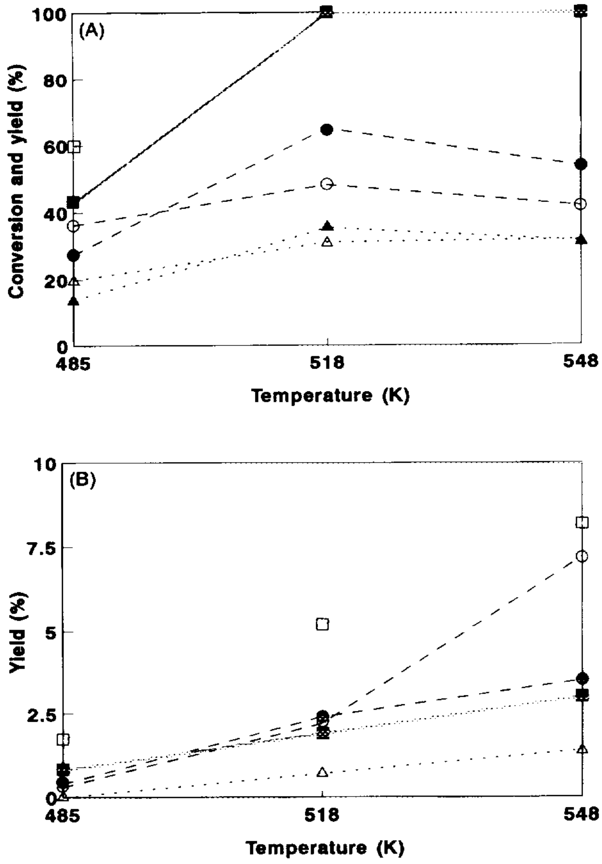

FIG. 3. Catalytic data for the tests of dimethyl maleate (DMM) or dimethyl succinate (DMS) hydrogenation with CAT 2 (Cu/Mn/Ba/Cr = 44 : 8 : 1 : 47, atomic ratio %) (P = 0.1 MPa; feedstock conditions as in Table 1). (DMM = dimethyl maleate; DMS = dimethyl succinate; GBL = γ-butyrolactone; MeOH = methanol; THF = tetrahydrofuran; BuA = butyric acid; BuOH = n-butanol; MeBu = methyl butyrate). [(A): ■ DMM conversion; □ DMS conversion; ● GBL yield (DMM); ○ GBL yield (DMS); ▲ MeOh yield (DMM); △ MeOh yield (DMS)] [(B): ■ THF yield (DMM); □ THF yield (DMS); ● MeBu yield (DMM); ○ MeBu yield (DMS); △ BuA yield (DMS)].

TABLE 3

Catalytic Data for the Tests of γ-Butyrolactone Hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40:5:5:50, Atomic Ratio %), and CAT 2 (Cu/Mn/Ba/Cr = 44:8:1:47, Atomic Ratio %)

Sample	Temp. (K)	Conv. (%)	Yield (%)				
			THF[a]	BuA	BuOH	Esters	Others
CAT 1	518	32.1	17.2	9.3	—	0.6	1.5
	548	74.7	14.1	16.6	23.5	6.2	9.8
CAT 2	518	92.6	53.5	—	17.1	3.5	6.0
	548	99.1	34.8	—	—	13.0	49.7

Note. P = 0.1 MPa; feedstock conditions as in Table 1.

[a] THF = tetrahydrofuran; BuA = butyric acid; BuOH = *n*-butanol; Esters = ethyl and butyl butyrate; others = hydrogenolysis products (ethanol ≫ methanol and acetone).

butanol (BuOH), butyric acid (BuA), and methyl butyrate (MeBu). The formation of the ester explains the decrease in the yield in MeOH, also observed at this temperature. The ratio BuOH/BuA (and its ester) is higher when DMS is the feed instead of DMM, in agreement with its higher reactivity. These results suggest that BuA and BuOH derive from both GBL and THF and not only from the latter as reported in the reaction pathway of Fig. 1.

CAT 2 exhibits conversion trends similar to those of CAT 1. CAT 2 is more active towards DMS than DMM. Also in these cases the yield in GBL is a maximum at 518 K and decreases with increasing temperature. On the contrary, the yield in THF increases linearly with increasing temperature. BuA and BuOH are not detected with DMM as the feed and with DMS as the feed, only BuA is produced at the two higher temperatures. These data are in agreement with the higher activity of CAT 2 and confirm the main role of GBL in the overhydrogenation reactions.

3.2. Reactivity of Some Intermediates

In all the catalytic tests, GBL (Table 3) gave rise to THF and overhydrogenation and/or hydrogenolysis products (in agreement with the role of GBL previously reported), with high conversion values, mainly with CAT 2. At the higher temperatures, the formation of THF decreases, while the formation of overhydrogenation (CAT 1) or hydrogenolysis products (CAT 2) increases. Furthermore, these results suggest that BuOH forms via BuA and may be the possible intermediate in the hydrogenolysis reactions to form ethanol (EtOH) or other lower molecular weight products.

With both catalysts, the hydrogenation of THF (Table 4) is characterized by low conversion values, with the formation mainly of EtOH, while BuOH was never detected. The formation with CAT 2 of ethane together with EtOH confirmed the higher hydrogenating capacity of this catalyst. On this basis, it may be hypothesized that THF does not undergo hydrogenation reactions with formation of BuOH, but only hydrogenolysis reactions, which take place with very low conversion, suggesting a high stability of THF in the reaction conditions investigated.

On the contrary, with both CAT 1 and CAT 2, BuA undergoes mainly hydrogenation with formation of BuOH and *n*-butanal (Table 5). Also in this case, CAT 2 exhibits higher conversion, with, furthermore, formation of EtOH, especially at the higher temperature. It is worth noting that the catalytic tests with BuOH (Table 5) lead to the formation of *n*-butanal, due to its dehydrogenation reaction, which takes place notwithstanding the large excess of hydrogen present. Furthermore, with both catalysts, BuOH exhibits lower conversion than BuA, while higher amounts of lower molecular weight alcohols [EtOH and MeOH (CAT 1)] are formed. On this basis, it may be hypothesized that *n*-butanal is the main intermediate in the hydrogenolysis reactions, in agreement with its higher reactivity in comparison to BuOH (38).

Finally, Table 6 reports the catalytic data of the tests with propionic acid (PrA), which shows a higher reactivity than BuA, forming mainly *n*-propanol (PrOH), with higher conversion values for the commercial catalyst. Also in this case for both catalysts *n*-propanal was present notwithstanding the large excess of hydrogen.

4. DISCUSSION

Both catalysts are more active in MA than in SA hydrogenation, which is converted with greater difficulty notwithstanding the lower amount introduced in comparison to that in the MA/GBL solution. On the basis of the similar behaviours of MA and SA in the bench-scale tests,

TABLE 4

Catalytic Data for the Tests of Tetrahydrofuran Hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40:5:5:50, Atomic Ratio %), and CAT 2 (Cu/Mn/Ba/Cr = 44:8:1:47, Atomic Ratio %)

Sample	Temp. (K)	Conv. (%)	Yield (%)	
			Ethanol	Ethane
CAT 1	518	2.7	—	—
	548	5.7	2.4	—
CAT 2	518	1.4	1.0	0.3
	548	17.5	11.9	0.6

Note. P = 0.1 MPa; feedstock conditions as in Table 1.

in which melted anhydrides were used as feedstock, this lower reactivity may be attributed mainly to the competitive adsorption of GBL on the active sites, in agreement with the lower concentration of the SA/GBL solution. However, according to the literature, a possible contribution of double bonds to the adsorption/desorption properties on MA cannot be excluded (39, 40).

On the contrary, it must be noted that in the test with the two esters, DMS was more reactive than DMM, in agreement with the presence in MA of a double bond which requires a further hydrogenation step. Therefore, as previously hypothesized, the competitive adsorption on the catalytic sites between solvent and anhydride can actually be a key factor in the vapour phase hydrogenation of MA/GBL and SA/GBL solutions. However, different adsorption mechanisms may operate with anhydride solutions or their esters, making difficult a direct comparison between the different feedstocks. In all cases, the complete conversion achieved at all the temperatures for the MA/GBL solution, unlike that observed with DMM [notwithstanding the lower H_2/organic ratio (Table 1)], indicates a higher reactivity of MA. Therefore, the MA vapour phase hydrogenation can be considered as an actual alternative to the hydrogenation of ethyl or methyl maleates (3, 5, 17, 35, 36).

Furthermore, on the basis of the catalytic behaviour as a function of temperature (Table 2 and Figs. 2 and 3), the decrease in GBL yield at 548 K together with the formation of BuA and BuOH suggest that the overhydrogenation reactions (favoured at high temperatures) take place mainly from GBL and not from THF, as expected on the basis of the reaction scheme of Fig. 1. In fact, the trend of the THF yield with CAT 2, which always increases with increasing temperature, leads us to hypothesize that the overhydrogenation reaction does not take place essentially from THF. Therefore, it seems very interesting to investigate the reactivity of some of the observed intermediates in order to verify the hypothesis reported above.

The qualitative comparison between the two catalysts indicates similar behaviours, from the points of view of both products observed and trends with increasing temperature. The main difference is related to the catalytic activity, which is higher for CAT 2 for all the intermediates investigated, in agreement with the data previously obtained with the anhydride solutions and the esters. The largest differences in activity were observed in the tests with the acids (BuA and PrA), which were only partially hydrogenated with CAT 1, while complete conversion was achieved at 548 K with CAT 2. Therefore, the highest yield in GBL observed in the hydrogenation of MA/GBL solution with CAT 1 may be attributed to the capacity of this catalyst to minimise the reaction of overhydrogena-

TABLE 5

Catalytic Data for the Tests of Butyric Acid (BuA) and *n*-Butanol (BuOH) Hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40:5:5:50, Atomic Ratio %), and CAT 2 (Cu/Mn/Ba/Cr = 44:8:1:47, Atomic Ratio %)

Sample	Feed	Temp. (K)	Conv. (%)	Yield (%)			
				n-Butanol	*n*-Butanal	Ethanol	Methanol
CAT 1	BuA	518	2.4	—	2.4	—	—
		548	27.0	14.1	5.6	—	—
CAT 2		518	49.7	33.4	4.4	0.5	—
		548	100.0	70.4	9.3	19.4	—
CAT 1	BuOH	518	31.1	—	6.8	6.0	0.7
		548	56.3	—	4.7	22.6	2.3
CAT 2		518	20.3	—	7.0	14.7	—
		548	63.7	—	5.6	49.2	—

Note. P = 0.1 MPa; feedstock conditions as in Table 1.

TABLE 6

Catalytic Data for the Tests of Propionic Acid Hydrogenation with CAT 1 (Cu/Zn/Mg/Cr = 40:5:5:50, Atomic Ratio %), and CAT 2 (Cu/Mn/Ba/Cr = 44:8:1:47, Atomic Ratio %)

			Yield (%)			
Sample	Temp. (K)	Conv. (%)	*n*-Propanol	*n*-Propanal	Methanol	Propyl propionate
CAT 1	518	4.5	—	0.9	—	1.8
	548	19.5	14.5	2.5	—	1.9
CAT 2	518	66.8	31.7	2.8	—	17.0
	548	100.0	56.5	—	15.4	3.4

Note. $P = 0.1$ MPa; feedstock conditions as in Table 1.

tion and/or hydrogenolysis. In regard to this last point, it is worth noting that the hydrogenation of BuOH leads to the formation with good yields of *n*-butanal. The presence of the dehydrogenation product, notwithstanding the high H_2/organic ratio, suggests that in the MA hydrogenation *n*-butanal may be a key intermediate, because it can give rise to either BuOH (by hydrogenation) or lower molecular weight alcohols (by hydrogenolysis).

However, one of the most important results of the catalytic tests with the intermediates is that the hydrogenation reactions do not take place on THF, which undergoes only hydrogenolysis reactions, only at high temperatures and with low conversions. This high stability of THF indicates that the by-products observed in MA hydrogenation (Table 2) derive mainly from GBL, in contrast with the literature data. On the basis of our data, GBL may be seen as a central point in the reaction pathway, since it can react in two different ways, one with formation of THF and the second with ring opening and synthesis of BuA and BuOH and, successively, hydrogenolysis products.

The production of C_3 compounds (PrA, PrOH, and acetone) represents the most difficult point to explain, taking into account that these compounds form in very small and not fully reproducible amounts. However, C_3 compounds were observed mainly in the catalytic tests with MA and SA solutions, although acetone was also detected in some tests with GBL. In the bench-scale tests with melted MA and SA anhydrides, PrA and PrOH were obtained in amounts higher than those obtained with the solutions (however, also in this case the quantities remain very small and fluctuate with time-on-stream). Therefore, it may be hypothesized that the C_3 compounds are formed mainly from the anhydrides by CO and/or CO_2 elimination.

In a recent paper (41), we reported the results of catalytic tests carried out at different pressure, using CAT 2 and feeding BDO. By maintaining the same conditions adopted in GBL hydrogenation, the complete conversion of BDO was observed, with formation of GBL and the same products observed in the hydrogenation of GBL itself. The further catalytic tests under pressure were carried out in an autoclave (i.e., in static conditions) and showed a progressive decrease in the conversion of BDO with increasing hydrogen pressure, confirming the role of this last parameter on the BDO $\Leftrightarrow$ GBL equilibrium and the requirement to operate at 4.0–6.0 MPa to produce BDO (5, 21, 42, 43). Furthermore, the low amounts of overhydrogenation and/or hydrogenolysis products observed at the higher pressure, notwithstanding the increase in H_2/BDO ratio, was evidence for the high stability of BDO and showed that these low-cost by-products derived mainly from the GBL.

On the other hand, no significant change in the amounts of THF formed was observed as a function of the hydrogen pressure (and consequently of the BDO/GBL ratio), showing that THF may be formed from both BDO and GBL. This result is in contrast with the hypothesis reported recently of the formation of THF only via BDO (43), but is in agreement with the THF production by either dehydration of BDO or hydrogenation of GBL (24, 35) and, mainly, with the thermodynamic data of the reactions involved (15). Recently (44), we reported that aluminum-containing catalysts favoured the formation of THF in comparison to chromium-containing catalysts, reducing also the amounts of unwanted and low-cost by-products. Therefore, it may be hypothesized that the catalyst composition (for example, the nature of the trivalent element present) may influence the route by which the THF is formed, probably on account of the different adsorption mechanism of MA cited above (39, 40).

Therefore, on the basis of the data reported in this work and taking also into account the existing literature, a new reaction pathway may be proposed for selective vapour phase hydrogenation of MA to GBL and/or THF (Fig. 4).

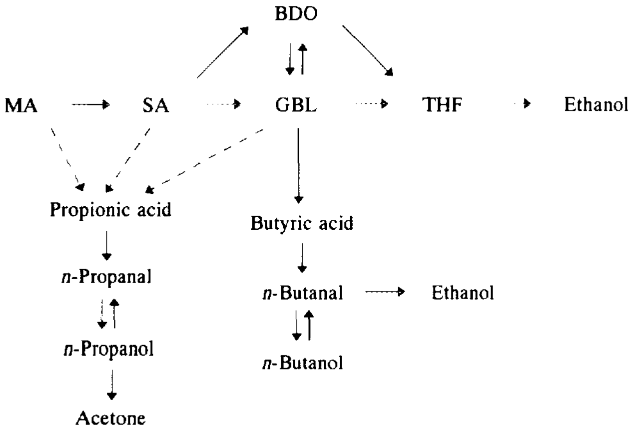

FIG. 4. New reaction pathway for the vapour phase hydrogenation of maleic anhydride. (MA = maleic anhydride; SA = succinic anhydride; GBL = γ-butyrolactone; BDO = 1,4-butanediol; THF = tetrahydrofuran).

5. CONCLUSIONS

Among the different feedstocks investigated, the highest GBL productions were obtained by hydrogenation of MA, which, therefore, may be considered an actual alternative to the methyl and ethyl maleates. However, with these latter feedstocks better carbon balances were observed, which may be attributed to lower light hydrocarbon synthesis and tar formation. Therefore, the use of maleates as feedstocks may probably be advantageous from the point of view of catalyst life, but it is necessary also to take into account the additional costs related to the processes of esterification and alcohol recovery.

A second key result of this work is the role that GBL plays as a point of "intersection" of two possible reaction pathways, giving rise to THF or overhydrogenation and hydrogenolysis products, respectively. Therefore, in new catalytic formulations it will be very important to control the capacity to favour the GBL ring opening, instead of the hydrogenation activity. Indeed, in the first case an increase in by-products results, while in the second case the GBL/THF ratio may be modified, with essentially no production of unwanted and lower cost products.

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