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Catalytic Conversion of Cyclopentanone into Dimethyl Adipate over Solid Basic Catalysts with Dimethyl Carbonate

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Abstract: The synthesis of dimethyl adipate (DAP), a stable configuration of adipic acid, from biomass-derived cyclopentanone (CPO) and dimethyl carbonate (DMC) constitutes an attractive greener route than petroleum-based industrial processes. Solid basic catalysts such as MgO, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, $KOCH_3$ and $Ca(OCH_3)_2$ have been used achieving a DAP yield up to 30% at 533 K. In addition to the type of catalyst, other operating conditions such as the substrate, reaction time, temperature and CPO concentration have been studied. The methylation of DAP and CPO and the self-aldol condensation of CPO to form dimers and oligomers are reactions that occur in parallel with the production of DAP. It has been established that the main challenge is the self-aldol condensation of CPO. It has been identified that at short reaction times, to prevent methylation, and at dilute concentrations, to avoid CPO self-condensation, the DAP formation rate is much higher than these other competitive reactions. Finally, it should be noted that a DAP productivity up to 3.45 $g \cdot gcat^{-1} \cdot h^{-1}$ has been achieved under mild conditions.

Keywords: cyclopentanone; dimethyl carbonate; dimethyl adipate; solid basic catalysts

1. Introduction

Adipic acid (AdA) is an essential building block used to manufacture nylon 6-6, adipic esters and polyurethanes. Among its many applications, its uses in the pharmaceutical, cosmetic and food industries stand out [1,2]. Currently, adipic acid is mainly produced from petroleum-based feedstock. Benzene is hydrogenated to cyclohexane and further treated to synthesize ketone/alcohol oil (KA-oil), a mixture of cyclohexanone and cyclohexanol, which is oxidized with nitric acid to obtain AdA [3]. Given that this process is not sustainable due to its several steps and the nitrous emissions produced [4], a number of greener routes have been proposed over the last decade [5,6]. Lignocellulose biomass, made up of cellulose, hemicellulose and lignin, presents itself as a renewable carbon source, from which the conversion to valuable chemical products has attracted interest over the last years [7–9]. Among the processes to obtain AdA from biomass, an attractive process is the synthesis of dimethyl adipate (DAP) from cyclopentanone (CPO) and dimethyl carbonate (DMC). CPO is an interesting compound used in the synthesis of fungicides, pharmaceuticals, flavors, fragrances and rubber chemicals. Currently, it is obtained through petrochemical routes [10,11]; however, recently, its synthesis from biomass has been thoroughly studied via the hydrogenation of furfural [12–15]. DMC is an attractive solvent and reactant due to its chemical properties and low toxicity. It is used in methylation and carboxymethylation reactions as an eco-friendly substitute to phosgene, dimethylsulfate and metal halides [16,17]. Furthermore, its origin is also green, since it can be obtained from the reaction between CO_2 and CH_3OH [18]. Given that CO_2 is one of the compounds responsible for the greenhouse effect, its capture and use in the synthesis of carbonates is highly interesting. By choosing the DAP synthesis from CPO and DMC, we combine biomass and CO_2 to synthesize biopolymers (Scheme 1).
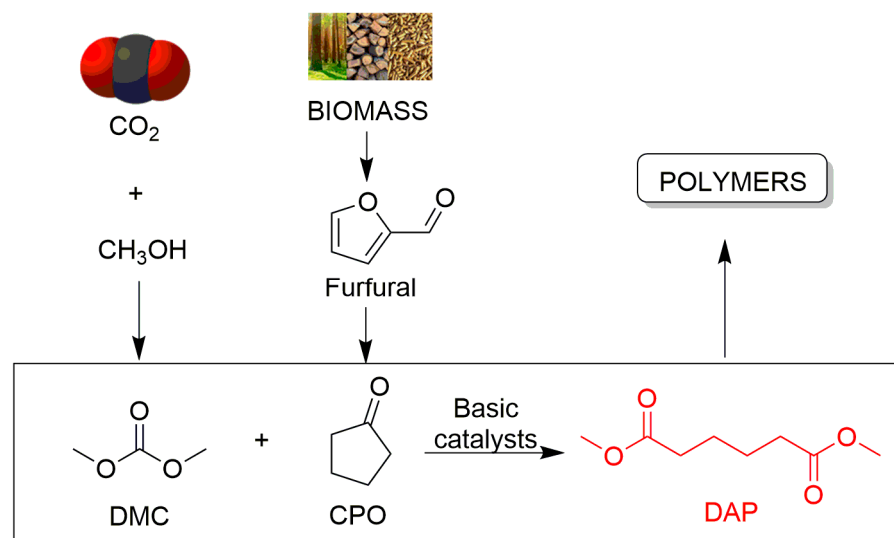
Scheme 1. Combination of CO_2 and biomass to synthesize polymers.

DAP has been obtained from CPO with $PdCl_2$, methanol and CO instead of DMC [19,20]. However, the use of DMC as a solvent and reactant makes the reaction greener. To carry out the desired synthesis, temperatures between 473 and 533 K and basic catalysts are required. The use of solid catalysts instead of homogeneous ones has several advantages. The ease with which the catalyst can be separated from the reaction mixture and later reused, the reduction in the waste produced during the reaction as a result of the elimination of the catalyst neutralization step, the capacity to run continuous processes and the ability to work at higher temperatures are just a few of them [21]. DAP has been obtained using organic carbonates as catalysts [22,23]. Its synthesis was also reported using a nanostructured CeO_2, giving an 84% DAP yield; however, a large amount of catalyst (catalyst/CPO wt% = 42) and highly diluted solutions (CPO/DMC wt% = 2.2) were used [24]. These authors have also tested MgO as a catalyst, giving a 47% yield of DAP. This catalyst was also studied by Wu et al. [25] under milder conditions (CPO/DMC wt% = 14.0 and catalyst/CPO wt% = 14.0), obtaining a 44% yield of DAP. Other cyclic ketones have been reported to react with DMC in a similar reaction using MgO and $NaOCH_3$ as catalysts, giving moderate yields [26].

Regarding the reaction mechanism, DMC facilitates both methylation and carboxymethylation reactions, as mentioned above. Therefore, the methylation of reagents, intermediates and products can represent a competitive route of the selective pathway towards DAP. Scheme 2 shows a plausible mechanism. The basic catalyst abstracts a proton from the CPO, forming an enolate that attacks the carbonyl group of DMC, possibly obtaining the intermediate 2-carbomethoxy-cyclopentanone (CMCP). Later, the previously leaving methoxide anion attacks CMCP, giving DAP (route a). The desired product can be further methylated in the reaction media to synthesize dimethyl 2-methyladipate (DMAP). This compound can also come from the carboxymethylation of 2-methyl cyclopentanone (MCP), which is obtained by CPO methylation (route b). Furthermore, the self-aldol condensation of CPO can occur, giving 2-cyclopentylidene-cyclopentanone (CPCP) (route c).

This study aims to analyze the different routes proposed in the mechanism to understand the selectivity of each of the products. It has been confirmed that the main challenge is to achieve a high selectivity towards DAP, since the methylation of the reactants and products and the self-aldol condensation of CPO to form dimers occurs at the same time. A study of the operation conditions has been conducted to understand the different reaction pathways' relevance.
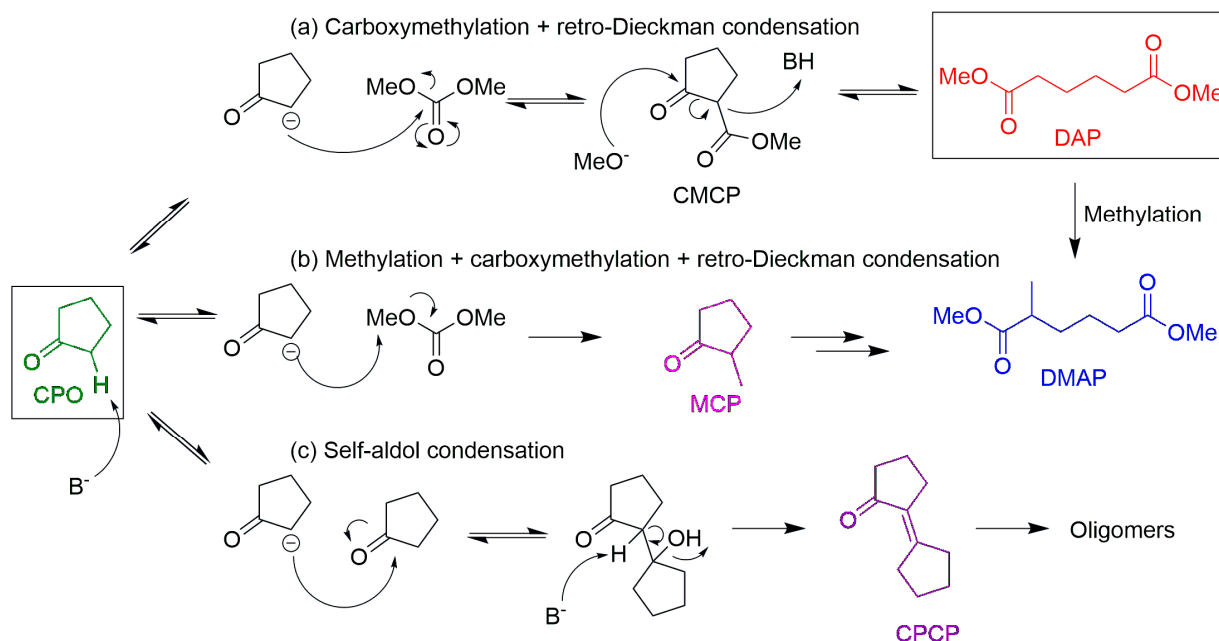
Scheme 2. Reaction pathways for the catalytic conversion of cyclopentanone and dimethyl carbonate (adapted from [25]).

2. Results and Discussion

Initially, a study on the performance of different basic solid catalysts was conducted to determine the most promising catalyst to synthetize DAP (see Table S1 in the Supporting Information). It has been mentioned in the Introduction section that basic catalysts based on Ce have shown good behavior [24]. However, the tested cerium catalysts did not achieve a CPO conversion higher than 10% under our operation conditions, even after 2 and 4 h at 533 K (entries 1 to 3 in Table S1). CaO and Ca(OH)$_2$ gave higher CPO conversions; however, the selectivity for DAP did not reach satisfactory values (entries 6 and 7 in Table S1). Carbonates such as CaCO$_3$, (NH$_4$)$_2$CO$_3$ and Na$_2$CO$_3$ went up to a 30% conversion of CPO (entries 8 to 10 Table S1), but also, the selectivity for DAP was considerably low and even negligible. The catalysts that showed a higher CPO conversion, over 80%, were KOCH$_3$, Ca(OCH$_3$)$_2$, MgCO$_3$ (HC), Mg(NO$_3$)$_2$·6H$_2$O and MgO (entries 4, 5, 11, 14 and 15 in Table S1), with the magnesium catalysts being the ones showing the highest DAP yields. Mg(NO$_3$)$_2$·6H$_2$O did not prove to be a heterogeneous catalyst, since it melted at the high temperatures employed in the reaction; therefore, it was ruled out. Finally, Ca(OCH$_3$)$_2$ showed a high DMAP yield, compared to the other catalysts, which could be due to the methylation of DAP in the reaction media, suggesting that shorter reaction times would be more appropriate. The KOCH$_3$ catalyst did not show a high DAP or DMAP yield in the tested conditions; however, a new compound was found, which will be discussed later on. An interesting fact is that in some of the entries, we observe high conversions of CPO and relatively low yields of identified products. This study aims to explain the low carbon balance of this reaction.

2.1. A Kinetic Study of the Reaction Using MgO and MgCO$_3$ (HC)

Based on the DAP yield data, the chosen basic catalysts for this kinetic study were MgO and MgCO$_3$ (HC). Accordingly, the selectivity has been displayed versus the conversion of CPO for both basic solid catalysts (Figure 1 and Figure S1 in the Supporting Information). Although there are some quantitative differences between both basic catalysts, their behaviors are similar from a qualitative point of view. The products identified are the same, and their evolution over the conversion of CPO is similar. The CPCP dimer selectivity is the highest (over 40%) at a lower conversion of CPO. Since the self-aldol condensation reaction is not reversible, the decrease in the selectivity observed at a higher

conversion means that this compound is transformed into other side products, likely via the successive aldol condensation of CPCP into heavier oligomers. The DAP selectivity reaches a maximum at higher conversions (between 2 and 3 h of reaction) and then drops. Another product is DMAP, for which the yield increases with the conversion, suggesting the methylation of DAP occurs in the presence of DMC. It would explain, at least partially, the drop in the DAP selectivity at a higher conversion of CPO, indicating that DAP, once formed, further reacts in the reaction medium. Traces of MCP are also identified as a reaction product without a clear trend.
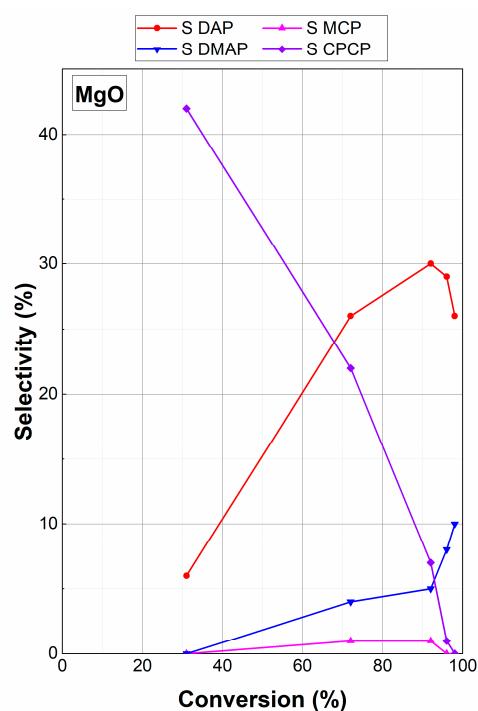

Figure 1. Product selectivity versus conversion using MgO as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC, 0.05 g catalyst and 533 K.

Here, it should be noted that all the products identified after the reaction can be explained considering the reaction pathways shown in Scheme 2. It suggests that under our operation conditions, in the presence of basic solid catalysts, the reaction of CPO with DMC follows the three proposed pathways. Moreover, a further transformation of DAP in the reaction medium with DMC can also occur. Therefore, to increase the selectivity and consequently, the yield of DAP, route (a) in Scheme 2 should be promoted, whereas the other nonselective routes (b and c) must be inhibited. The main challenge here is the self-aldol condensation reaction of CPO to form the CPCP dimer and other oligomers, since its maximum selectivity is higher than the DAP selectivity. In an attempt to inhibit the undesired side products, the three routes mentioned above will be studied more in detail.

2.2. Study of the Selective Pathway (Route a) Using MgO and MgCO₃ (HC) Catalysts

The DAP yield using these two catalysts is approximately 30% at high conversions (Table S1). It has already been proven that route (c) in Scheme 2 is responsible for most of the selectivity loss. Nonetheless, there are other factors to take into account when route (a) in Scheme 2 is followed. Other side products could be formed before the synthesis of DAP, and additionally, DAP could further react in the reaction media to give other products, such as DMAP (Scheme 2). These two possibilities have been studied in more detail.

The selective pathway describes the synthesis of our target monomer DAP, where CMCP (Scheme 2) is possibly the intermediate compound in this route. This intermediate is highly reactive because of its acid proton located between the two carbonyl groups

(Scheme 3a). It is possible that, instead of following the selective route, the base catalyst abstracts this proton, synthesizing a different active intermediate that could end up giving other unidentified products at the expense of the DAP yield (Scheme 3a). To evaluate this hypothesis, a reaction using MCP as the substrate instead of CPO and MgCO₃ (HC) as the catalyst was conducted. In this case, due to the methyl group of the substrate, two possible enolates can be formed once the MCP is deprotonated: the kinetic and thermodynamic enolate. Given the use of high temperatures and low amounts of catalyst, the thermodynamic enolate is favored (Scheme 3b) [27–29]. This means that the produced intermediate lacks that acid proton found in CMCP. Since this proton is absent, this intermediate can only synthesize DMAP through a ring-opening reaction (Scheme 3b). If the acid proton in CMCP was responsible for the low DAP yields, in this second reaction (Scheme 3b), the DMAP yield would be higher. However, the DMAP yield was 30%, comparable with the 29% of DAP obtained using CPO as the substrate (Table 1, entries 1 and 2). Consequently, the consumption of the intermediate CMCP to form new compounds other than DAP can be ruled out as a source of DAP selectivity loss.

(a) Possible side reaction

(b) Testing of hypothesis
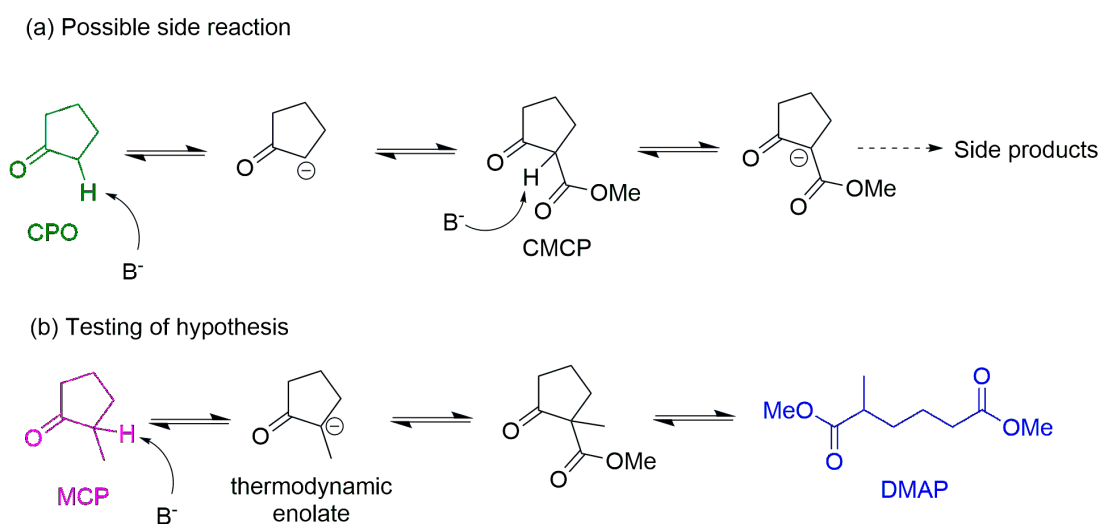
Scheme 3. Mechanism for the synthesis of DMAP from MCP via thermodynamic enolate.

Table 1. Product distributions for MgCO₃ (HC) and MgO catalysts using different substrates.

#	Catalyst	Substrate	Catalytic Results (%)				
			X_{Subs}	Y_{DAP} Route a	Y_{MCP} Route b	Y_{DMAP} Route b/Further a	Y_{CPCP} Route c
1	MgCO₃ (HC)	CPO [a]	85	29	0	3	10
2	MgCO₃ (HC)	MCP [a]	80	0	–	30	0
3	MgCO₃ (HC)	DAP [b]	32	–	–	5	–
4	MgO	DAP [b]	32	–	–	5	–

[a] Reaction conditions: 0.5 g of substrate, 5.4 g DMC and 0.05 g catalyst at 533 K during 2 h of reaction; [b] 1 g of substrate.

Another challenge to this route is the transformation of the formed DAP into DMAP and other side products. To evaluate this possibility, DAP was exposed to each catalyst under the same reaction conditions (Table 1, entries 3 and 4). In both cases, quite similar results were obtained: a DAP conversion of 32% and a DMAP yield of 5%. Along with DMAP formation, DAP transforms into another four unknown products detected using GC (see chromatograms in Figures S2 and S3 of the Supporting Information). Therefore, it can be concluded that, at least partially, the observed DMAP is formed by the methylation of DAP and that part of the lack of carbon balance in the CPO transformation to DAP is due to the transformation of DAP to compounds that cannot be quantified using GC.

Consequently, the reaction time is an important variable, since the longer the reaction time, the higher the yield of DAP, but the further transformation to DMAP and other products is also favored; thus, a balance is required.

2.3. Cyclopentanone Methylation (Route b) Using KOCH₃ Catalyst

We have also studied the methylation of CPO to form MCP and its further conversion to DMAP (route b in Scheme 2). Since we found out that the potassium methoxide (KOCH₃) catalyst showed preference to the methylated products compared to other catalysts, we have considered it more appropriate to use this basic catalyst in the study of this nonselective route.

Figure 2 shows the conversion and yields at different temperatures using KOCH₃ as the catalyst. The yields of DMAP at all temperatures are higher than those of DAP. This could mean that the transformation of DAP to DMAP occurs faster using this catalyst. However, when the reaction was conducted at 473 K, the conversion of CPO is considerably low, whereas the DMAP yield is almost double to that of DAP, indicating clearly that the KOCH₃ catalyst is more selective to route b. Furthermore, a new compound was observed when the reaction was conducted at higher temperatures (503 and 533 K). Using GC–MS, this product was identified as dimethyl 2,5-dimethyl adipate, a DAP with two methyl groups labeled as DMMAP, a compound that comes from the further methylation of DMAP with DMC under the operating conditions.
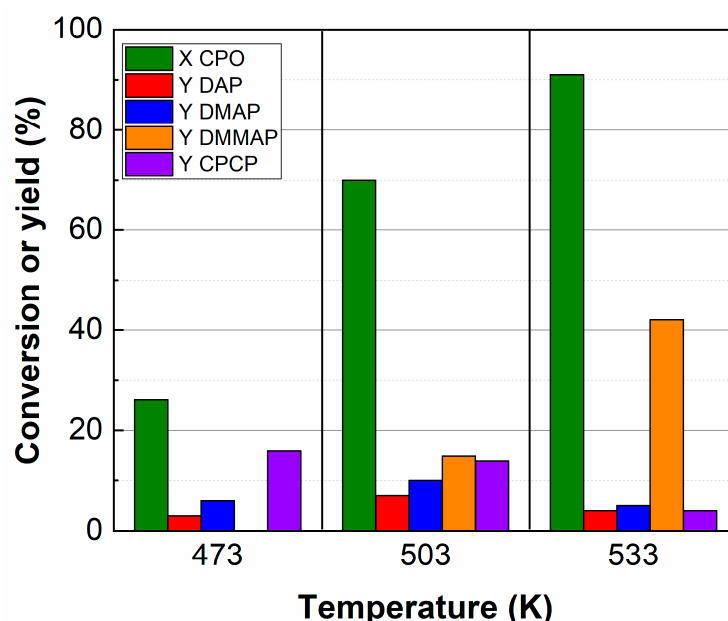

Figure 2. CPO conversion and product yields at different temperatures using KOCH₃ as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC and 0.05 g catalyst for 2 h.

2.4. The Self-Aldol Condensation of CPO (Route c) Using MgCO₃ (HC), MgO and Ca(OCH₃)₂ Catalysts

The other nonselective and therefore competitive reaction for the synthesis of DAP is the self-aldol condensation of CPO (route c in Scheme 2). The relevance of this route can be previously observed in Figure 2, where a high CPCP yield at 473 K is reached, comparable to the other product yields. However, this value decreases with the increase in temperature. It suggests that temperature is an important variable in the selectivity towards the different routes. In this case, and since route c required to be compared to the selective synthesis of DAP (route a), the chosen basic catalysts were MgO and Ca(OCH₃).

Figure 3 shows the use of MgO as the catalyst at 503 K and 533 K. In both cases, the CPCP yield at a shorter reaction time is higher than the DAP yield. While the CPCP yield goes up to 24% at 503 K before further reacting, with the increase in temperature

(533 K), this maximum yield is only 16%. Regarding the behavior of Ca(OCH$_3$)$_2$ catalysts, the difference between the CPCP yield is not so easily appreciated. While the maximum at 503 K is 16%, at 533 K, it is 12% (see Figure 3). This finding shows a lower selectivity for route c at higher temperatures. Nonetheless, the maximum DAP yield in all cases is approximately 30%, which could be due to the competitive nature of the aldol condensation reaction. The self-aldol condensation of CPO has proven to be one of the main challenges of this reaction regardless of the temperature. While the selectivity for CPCP is higher than that for DAP at shorter reaction times, a decrease in the yield of CPCP has been observed as the reaction time increases, possibly due to its ability to continue to react with more CPO to form oligomers [30].
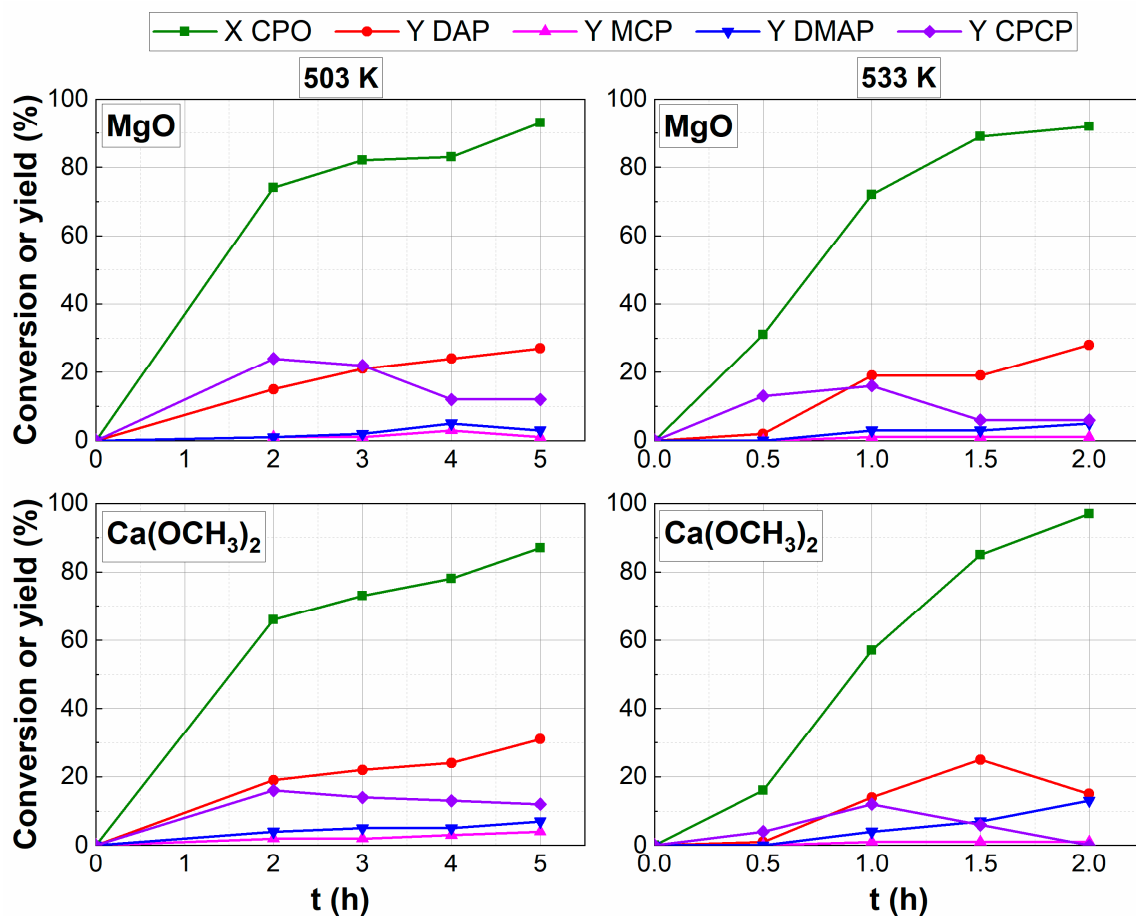

Figure 3. Kinetic experiments using MgO and Ca(OCH$_3$)$_2$ as catalysts at 503 K and 533 K temperatures. Reaction conditions: 0.5 g CPO, 5.4 g DMC and 0.05 g catalyst.

An approach to obtain a higher selectivity for DAP by eliminating the self-aldol condensation reaction is to use lower concentrations of CPO. Therefore, the CPO concentration was decreased, while the amount of catalyst, MgCO$_3$ (HC), was kept unchanged. In this case, the most appropriate way is to represent the formation rate of the main products, such as DAP and CPCP, against the concentration of CPO, which is shown in Figure 4 for 1 h of reaction.

At 1 h of reaction, the formation rate of DAP raises from 21.6 to 212.4 mmol h^{-1}·g^{-1}, while the CPO concentration decreases from 9.3 to 2.3 wt%, since both the CPO conversion and DAP selectivity increase (Figure S4). On the other hand, the formation rate of CPCP is low (ca. 65 mmol h^{-1}·g^{-1}) and remains practically constant regarding the concentration of the starting solution. These values result from the fact that the conversion of CPO and the CPCP selectivity decrease (Figure S4).
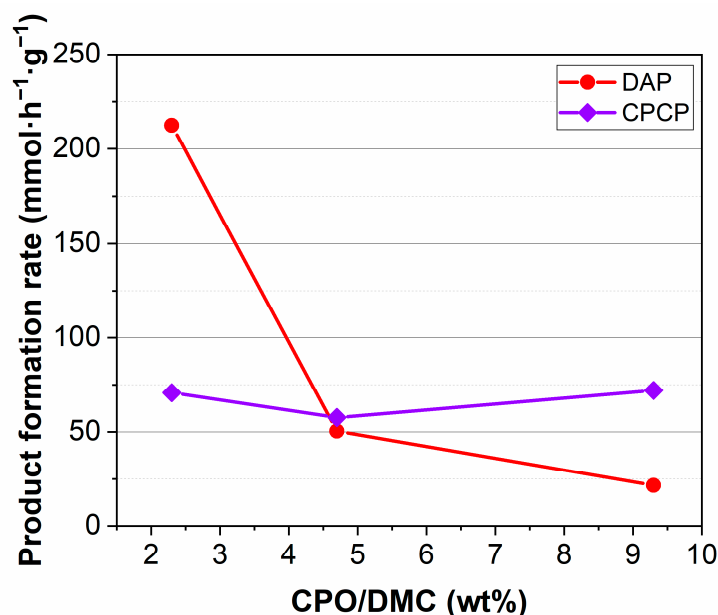
Figure 4. Product formation rate versus the CPO concentration at 1 h of reaction for $MgCO_3$ (HC) catalyst. Reaction conditions: 5.4 g of DMC and 0.05 g catalyst at 533 K.

The self-aldol condensation of CPO is the most relevant competitive reaction in the synthesis of DAP, and more research will be required to fully understand how to suppress this side reaction and obtain high DAP yields. At short reaction times (1 h), it has been observed that the CPO concentration is key to slowing down the advance of this unwanted reaction.

2.5. DAP Productivity for Different Basic Solid Catalysts

The productivity of the desired product (DAP) was calculated and compared with the results from other authors and collected in Table 2. $MgCO_3$ (HC) and MgO obtained yields up to 30% at 533 K after 2 h (Table S1, entries 11 and 15), giving productivities of 3.00 and 2.90 $g \cdot g_{cat}^{-1} \cdot h^{-1}$, respectively (Table 2, entries 2 and 3). On the other hand, the reaction using $Ca(OCH_3)_2$ at 533 K proved to be faster, with a 25% yield after 1.5 h, and therefore, a productivity of 3.45 $g \cdot g_{cat}^{-1} \cdot h^{-1}$ (Table 2, entry 1). These values are higher than those previously reported on basic catalysts, where the productivities are below 1.5 $g \cdot g_{cat}^{-1} \cdot h^{-1}$ (Table 2, entries 4–6). The use of less catalyst and shorter reaction times allowed us to achieve a higher productivity, being relevant parameters to implement this process at the industrial scale [31].

Table 2. Productivities of the best catalysts in optimized conditions.

#	Catalyst	CPO/DMC (wt%)	Cat/CPO (wt%)	T (K)	t (h)	Prod $_{DAP}$ (g/g$_{cat}$·h)	Ref
1	$Ca(OCH_3)_2$	9.3	10	533	1.5	3.45	This work
2	$MgCO_3$ (HC)	9.3	10	533	2	3.00	This work
3	MgO	9.3	10	533	2	2.90	This work
4	MgO	14.0	14.0	533	5	1.09	[25]
5	MgO	2.2	42.0	533	3	0.65	[24]
6	CeO_2-nanorod	2.2	42.0	533	5	0.69	[24]

The data presented in this work confirm that the synthesis of DAP (selective pathway) is a challenge. The most relevant nonselective competitive pathways that we have demonstrated to occur are as follows: (i) the methylation with DMC towards DMAP, either by the reaction of MCP with DMC or the methylation of the product of interest (DAP) in the reaction medium and (ii) the self-aldol condensation of the CPO to its dimer CPCP. The

successive condensation to higher MW oligomers cannot be ruled out at a high temperature and long reaction times. The relevance of each one will depend on the catalyst used and the operating conditions. Nonetheless, the CPO self-aldol condensation route is the main barrier to reaching a high DAP selectivity. Unfortunately, the strategies followed by decreasing both the methylation and CPO self-aldol condensation in favor of the selective route have not been satisfactory at high CPO conversions, and more work needs to be performed in this direction.

In addition to looking for new compositions of basic catalysts that are more selective for the synthesis of DAP, another interesting approach would be to carry out this reaction in a continuous flow to study the DAP selectivity with the space velocity and catalyst deactivation. Lastly, the nature and strength of the basic sites of the catalyst could be interesting topics in future studies, since they could be important factors to control the reaction selectivity.

3. Materials and Methods

3.1. Reagents and Catalysts

The materials used as catalysts in the reactions were purchased from the following: (i) Alfa Aesar (Haverhill, Massachusetts, USA), $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ [labeled as $MgCO_3$ (HC)] and $Ca(OH)_2$, purity 95%; (ii) Panreac (Madrid, Spain), $MgCl_2 \cdot 6H_2O$; and (iii) Sigma Aldrich (St. Louis, MO, USA), MgO nanopowder, $KOCH_3$ 95%, $Ca(OCH_3)_2$ 97%, $Na_2CO_3 \cdot 10H_2O \geq 99.0\%$, $(NH_4)_2CO_3 \geq 30.0\%$ NH_3 basis, $CaCO_3$ 99.95–100.05% dry basis, CaO 99.9% trace metal basis, $MgSO_4$ anhydrous $\geq 99.5\%$, $Mg(NO_3)_2 \cdot 6H_2O \geq 98\%$, $Ce(OH)_4$, CeO_2/ZrO_2 nanopowder 99.0% and CeO_2 nanopowder.

The liquids used as solvents, reactants and products such as dimethyl carbonate 99%, cyclopentanone 99%, dimethyl adipate ≥99% and dimethyl 2-methyl adipate were supplied by Sigma Aldrich, and 2-methylcyclopentanone 99% by Acros Organics (Thermo Fisher Scientific: Waltham, Massachusetts, USA). Finally, decane ≥ 99% was used as the internal standard, and it was purchased from Sigma Aldrich. Mixtures at different concentrations of these products have been used for the chromatographic calibration.

3.2. Catalytic Activity Measurements

The reaction was carried out in a batch stainless steel reactor (20 mL volume) with an inner Teflon liner. The catalyst (0.05 g) was added first, followed by the CPO (0.5 g or 6 mmol) and the solvent, DMC (5.4 g or 60 mmol). The reactor was inserted in an aluminum block to maintain the temperature, and a thermocouple inserted in the block was used to control the reaction temperature. The mixture was heated at a temperature range between 473 and 533 K and stirred at 1200 rpm. The autogenous initial pressure was between 20 and 25 bars. After the reaction, the reactor was placed in an ice bath to stop the reaction. Afterward, an aliquot of the reaction (ca. 1.0 g) was taken from the mixture and decane (0.05 g) was added as the internal standard. The solution was analyzed using a gas chromatograph (6890N Agilent Technologies, Madrid, Spain) equipped with a flame ionization detector and an HP-5 column. The CPO conversion, the product yields and the productivities of the catalysts were calculated according to the following expressions:

$$CPO\ conversion(mol\%) = \frac{n^0_{CPO} - n_{CPO}}{n^0_{CPO}} \times 100 \tag{1}$$

$$Product\ yield(mol\%) = \frac{n_{prod}}{n^0_{CPO}} \times 100 \tag{2}$$

$$Productivity\left(g \cdot g_{cat}^{-1} \cdot h^{-1}\right) = \frac{Y_{DAP} \cdot MW_{DAP} / MW_{CPO}}{C/S \cdot t} \tag{3}$$

with n^0_{CPO} being the initial mole quantities introduced in the reactor, n_{CPO} and n_{prod} being the mole quantities of CPO and the product after the reaction, Y_{DAP} being the DAP yield in

%, MW_{DAP} and MW_{CPO} being the molecular weights of DAP and CPO, respectively, C/S being the catalyst to substrate weight ratio in % and t being the time in hours. For the yield calculation, the stoichiometric relationship was taken into account.

4. Conclusions

The main challenge in the synthesis of dimethyl adipate from cyclopentanone and dimethyl carbonate using basic solid catalysts is the inhibition of the self-aldol condensation of cyclopentanone. This reaction can further evolve by synthesizing heavy oligomers, consuming the cyclopentanone starting material, and therefore, limiting the yield of dimethyl adipate. Other undesirable reactions such as the methylation of dimethyl adipate and cyclopentanone occur under the reaction conditions. The extent of these competitive reactions will depend on the catalyst and operating conditions used such as the temperature, reaction time, and concentration of cyclopentanone. The methylation of the dimethyl adipate formed is favored with the reaction time, and the self-aldol condensation of cyclopentanone with its concentration. Despite this, it can be remarked that we have achieved a dimethyl adipate productivity up to $3.45 \text{ g·g}_{cat}^{-1}\text{·h}^{-1}$ under moderate reaction conditions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal14010086/s1, Figure S1: Product selectivity versus conversion using MgCO$_3$ (HC) as the catalyst. Reaction conditions: 0.5 g CPO, 5.4 g DMC, 0.05 g catalyst and 533 K. Figure S2: Chromatogram of DAP decomposition with MgCO$_3$ (HC) as the catalyst. Retention times (product assignation): 1.0 (DMC); 1.7 (CP); 3.99 (Decane, internal standard); 8.0 (DAP); 8.5 (DMAP); 1.2 (side product of DMC); *6.4, 8.3, 13.0 and 18.5 (side products of DAP). Figure S3: Chromatogram of DAP decomposition with MgO as the catalyst. Retention times and (product assignation) equal to Figure S2; Figure S4: Conversion and product selectivity with different amounts of CPO at 1 h (left) and 2 h (right). Reaction conditions: 5.4 g of DMC and 0.05 g catalyst MgCO$_3$ (HC) at 533 K; Table S1: Study of basic catalysts in the synthesis of DAP from CPO and DMC.

Author Contributions: Conceptualization, I.M.-S. and R.M.; methodology, I.M.-S. and R.M.; formal analysis, R.M.; investigation, I.M.-S. and A.O.-S.; data curation, I.M.-S.; writing—original draft preparation, I.M.-S. and R.M.; writing—review and editing, I.M.-S., A.O.-S., M.L.G. and R.M.; visualization, I.M.-S. and R.M.; supervision, M.L.G. and R.M.; project administration, R.M. and M.L.G.; funding acquisition, M.L.G. and R.M. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

List of Acronyms

2-Carbomethoxy-cyclopentanone	CMCP
2-Cyclopentylidene-cyclopentanone	CPCP
2-Methyl cyclopentanone	MCP
Adipic acid	AdA
Cyclopentanone	CPO
Dimethyl 2-methyladipate	DMAP
Dimethyl adipate	DAP
Dimethyl carbonate	DMC

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