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Synthesis of dimethyl adipate from cyclopentanone and dimethyl carbonate over solid base catalysts

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A facile route for the synthesis of dimethyl adipate (DAP) from cyclopentanone and dimethyl carbonate (DMC) in the presence of solid base catalysts has been developed. It was found that the intermediate carbomethoxycyclopentanone (CMCP) was produced from cyclopentanone with DMC in the first step, and then CMCP was further converted to DAP by reacting with a methoxide group. The role of the basic catalysts can be mainly ascribed to the activation of cyclopentanone via the abstraction of a proton in the α -position by base sites, and solid bases with moderate strength, such as MgO, favor the formation of DAP.

dimethyl adipate, cyclopentanone, dimethyl carbonate, solid base catalysts

1 Introduction

Dimethyl adipate (DAP) is a fine chemical that is widely used as an industrial solvent for pharmaceuticals, perfumes, plastics and other organic compounds [1]. It is usually obtained by esterification of adipic acid with methanol [2]. However, this process has several limitations, such as harsh reaction conditions, lack of chemoselectivity, and significant corrosion and separation problems. In particular, a stoichiometric amount of water is produced in this esterification process, which required tedious procedures for disposal [3].

Recently, much attention has been given to dimethyl carbonate (DMC) due to its versatile chemical properties and low toxicity. It is believed to be an ideal additive for gasoline, because of its high oxygen content (53%) and good blending properties with octane [4]. As an environmentally benign building block, it is mainly used in methylation and carbonylation reactions as a safe substitute for methyl halides, dimethyl sulfate and phosgene [5, 6]. In the

presence of a base, it can also react with a number of nucleophilic anions generated from different substrates such as ketones, amines, oximes, indoles, and phenols to give the corresponding methoxycarbonylation products [7–12].

The synthetic route for DAP from cyclopentanone with DMC is an eco-friendly alternative to esterification due to the safe and clean chemical process involved. In the 1970s, Ruest *et al.* [13] first reported a route for the synthesis of carbomethoxycyclopentanone (CMCP), which might be the intermediate to DAP, from the reaction of cyclopentanone with organic carbonates over NaH. Later, others reported that DMC reacted with cyclopentanone to produce DAP in the presence of homogenous catalysts such as Cs_2CO_3 -crown ether, CH₃OK, and organic amines [14–17]. However, homogenous reactions give rise to problems with separation of the products and catalyst reuse.

Over the past decade, research on the synthesis of fine chemicals using solid bases as catalysts has become an important topic [18]. The replacement of homogeneous bases by solid base catalysts has the advantages of decreasing corrosion and environmental problems, while allowing easier separation and recovery of the products, catalyst and solvent [19]. However to the best of our knowledge, solid

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bases such as metallic oxides have seldom been used to carry out the synthesis of DAP from DMC with cyclopentanone. In this work, metallic oxides, which are easily prepared, have been used as catalysts for this reaction and the function of the catalysts has been investigated in detail.

2 Materials and methods

2.1 Preparation of catalysts

CaO, MgO and ZrO₂ were prepared by thermal decomposition of calcium carbonate (CaCO₃, Tianjin Kermel Chemical Reagent Co. Ltd., A.R. grade) at 800 °C for 2 h, magnesium hydroxide (Mg(OH)₂, Tianjin Kermel Chemical Reagent Co. Ltd., A.R. grade) at 500 °C for 5 h, and zirconium hydroxide (Zr(OH)₄, Tianjin Kermel Chemical Reagent Co. Ltd., A.R. grade) at 500 °C for 5 h, respectively, under a nitrogen atmosphere. Lanthana (La2O3, Tianjin Kermel Chemical Reagent Co. Ltd., A.R. grade) and alumina (Al₂O₃, Tianjin Kermel Chemical Reagent Co. Ltd., A.R. grade) were calcined at 700 and 500 °C respectively for 5 h in N2 before use. A series of Al/MgO catalysts with molar ratios of 0.01-0.3 were also prepared using the impregnation method. The desired amount of aluminum isopropoxide was dissolved in benzene before adding to Mg(OH)₂ to form the impregnated samples. The samples were dried at 100 °C overnight and then thermally decomposed at 500 °C for 5 h to afford Al/MgO catalysts.

The specific surface area and pore volume of the samples were obtained by the BET method. The samples were degassed at 350 °C for 5 h under vacuum (10^{-6} Torr) prior to the measurements, and nitrogen adsorption/desorption isotherms were obtained at -196 °C on a Micromeritics ASAP-2000 instrument (Norcross, GA).

CO₂-Temperature programmed desorption (CO₂-TPD) measurements were performed using Ar as a carrier gas. Catalyst samples (0.10 g, 40–60 mesh) were pretreated in Ar at 500 °C for 2 h. After the samples were cooled down to room temperature, CO₂ was pulsed into the reactor until saturation was reached. Once physically adsorbed CO₂ was purged by the carrier gas, the CO₂-TPD experiments were carried out from 20 to 800 °C with a heating rate of 10 °C/min under Ar flow (50 mL/min), and the effluent was analyzed with a gas chromatograph that employed a thermal conductivity detector. The amount of basic sites was quantified through calculating the areas of desorption peaks in the CO₂-TPD profiles using K_2CO_3 as primary standard.

2.2 Experimental setup and procedure

The reaction was carried out in an autoclave reactor, which was composed of a 150 mL stainless-steel autoclave and a magnetic stirrer (revolving at a rate of 1000 r/min). Cyclopentanone (5.00 g), DMC (35.97 g) and the catalyst (0.68 g) were charged into the autoclave and then the resulting mix-

ture was heated to 260 °C within 30 min. After running at 260 °C for 5 h under autogenous pressure (about 1–3 MPa in the temperature region from 200 to 280 °C), the reactor was cooled *in situ* to room temperature. The catalyst was removed by rapid filtration and the liquid products were analyzed by a gas chromatograph (GC-920, Shanghai Haixin Chromatograph Instrument Co. Ltd.) with a flame ionization detector and a HP-5 column. The selectivity is defined as $m_A/\Sigma m_A \times 100\%$, where m_A is the weight of product A, and Σm_A is the total weight of the products.

3 Results and discussion

3.1 Catalyst characterization

Figure 1 depicts the TPD profiles of CO₂ desorbed from ZrO_2 , MgO, La_2O_3 and CaO. CaO exhibited strong basic sites with a sharp desorption peak at 550 °C. La₂O₃ showed relatively strong base strength with a CO₂ desorption peak at 450 °C. For MgO, there were three desorption peaks at 100, 200 and 300 °C, suggesting that MgO had both weak and moderate strength basic sites, but for ZrO₂ a single CO₂ desorption peak at 150 °C was observed, indicating that only weak basic sites were present. The base strength follows the order: $CaO > La_2O_3 > MgO > ZrO_2$, but the basic numbers of the catalysts (the amount of basic sites per unit area of catalysts) decreased in the order: CaO > MgO > $La_2O_3 > ZrO_2$ (see Table 1). After addition of alumina into MgO, three desorption peaks were also found, around at 120, 200 and 300 °C for the resulting Al/MgO samples, which suggested that the addition of alumina did not change the basic strength of MgO (see Figure 2), but the basic number decreased with increasing Al content (see Table 1).

3.2 Catalytic performance

The reaction was carried out within the temperature range from 200 to 280 °C and the main products were DAP and CMCP. The self-condensation products of cyclopentanone



Figure 1 CO₂-TPD profiles of solid bases.

Table 1 CO2 uptake of solid bases

Catalyst	BET surface	CO ₂ uptake		
	area $(m^2 g^{-1})$	$(\text{mmol g}^{-1}) (\times 10^3)$	$(\text{mmol m}^{-2}) (\times 10^5)$	
ZrO_2	144.1	5.68	3.94	
La_2O_3	6.9	0.306	4.43	
CaO	10.5	78.5	748	
MgO	142.5	9.89	6.94	
Al/MgO(0.01)	110.5	7.39	6.69	
Al/MgO(0.05)	95.3	6.04	6.34	
Al/MgO(0.1)	96.7	5.24	5.42	
Al/MgO(0.2)	79.6	4.67	5.87	
Al/MgO(0.3)	68.2	3.71	5.44	



Figure 2 CO₂-TPD profiles of MgO with different Al contents.

(2-cyclopentylidenecyclopentanone), (2-methylcyclopentanone, dimethyl 2-methyladipate), and attendant methylation products (methanol and carbon dioxide) were also detected. Table 2 gives the catalytic performance of the different solid catalysts in the synthesis of DAP from cyclopentanone with DMC. In the absence of catalysts, no products were detected (Entry 1). Over solid acids such as zeolite H β and Al₂O₃, only the aldol condensation products of cyclopenta-

 Table 2
 Synthesis of DAP from DMC and cyclopentanone over solid bases

none and a trace amount of DAP and CMCP were detected
(Entries 4 and 5), indicating that solid acids are ineffective
catalysts for the methoxycarbonylation reaction. However,
when solid bases were employed as the catalysts, the meth-
oxycarbonylation products were obtained (Entries 6-10),
which is consistent with the literature [13-17]. In 1993,
Selva and coworkers reported that the yield of DAP reached
14% when using aqueous K_2CO_3 as the catalyst [14], and a
similar result was observed when we repeated this experi-
ment (Entry 2). When MgO-which possesses moderate
basic strength-was used as the catalyst, the major meth-
oxycarbonylation product at lower temperatures was CMCP
(Entry 7). However, with increasing reaction temperature,
higher yields of DAP were obtained over MgO (Entry 8),
even higher than that with K_2CO_3 (the major product was
dimethyl 2-methyladipate at 260 °C) (Entries 3 and 8). This
suggests that solid bases with moderate strength, such as
MgO, show better catalytic performances than a simple
homogeneous base such as K_2CO_3 . As for the other solid
bases, ZrO ₂ and La ₂ O ₃ gave lower DAP yields, which might
be due to the relatively low basic numbers compared with
that for MgO. CaO also gave lower cyclohexanone conver-
sion and DAP selectivity despite its high basic number. This
could be attributed to the fact that the acid strength of the
Ca^{2+} cation is too weak to stabilize the carbanion species
[20]. As a result, the catalytic performance is strongly de-
pendent on both basic number and basic strength, and basic
sites with moderate strength are most effective for the syn-
thesis of DAP from cyclopentanone with DMC.

In order to further study the effect of moderate basic strength on catalytic performance, a series of MgO catalysts with different Al contents were prepared in order to provide materials with different amounts of moderate basic sites (see Figure 2). It can be seen that the DAP yield was linearly correlated with the amount of moderate basic sites (see Figure 3). Moreover, a similar tendency was also observed when changing the amount of pure MgO catalyst (see Fig-

Entry	Catalant	Temperature (°C)		Selectivity (%)		
	Catalyst		Cyclopentanone conversion (%)	DAP	CMCP	Other products ^{c)}
1 ^{a)}	-	260	_	-	_	-
2 ^{b)}	K ₂ CO ₃	200	32.8	48.2	10.9	40.9
3 ^{a)}	K ₂ CO ₃	260	67.8	25.1	2.02	72.9 ^{d)}
4 ^{a)}	Нβ	260	33.9	Traces	Traces	100
5 ^{a)}	Al_2O_3	260	39.4	Traces	Traces	100
6 ^{b)}	ZrO_2	260	50.1	10.5	9.82	79.7
7 ^{a)}	MgO	200	15.6	5.61	43.7	50.7
8 ^{a)}	MgO	260	85.5	50.9	11.0	38.1
9 ^{a)}	La_2O_3	260	30.3	45.6	13.2	41.2
10 ^{a)}	CaO	260	76.5	52.3	3.07	44.6

a) Reaction conditions : cyclopentanone: DMC = 1 : 4, time = 5 h, catalyst wt.% = 1.5%; b) reaction conditions : cyclopentanone : DMC : cat (molar ratio) = 1 : 20 : 2, time = 4 h; c) other products = 2-methylcyclopentanone + dimethyl 2-methyladipate + 2-cyclopentylidenecyclopentanone; d) selectivity of dimethyl 2-methyladipate was 42.1%.



Figure 3 The relationship between the amount of basic sites and DAP yield.



Figure 4 The relationship between the amount of MgO catalyst and DAP yield.

Table 3 The recycling of MgO in the reaction of DMC and cyclopentanone

ure 4). Thus, these results confirm that base sites with moderate strength favor the formation of DAP.

The effect of recycling the MgO catalyst in the reaction of DMC with cyclopentanone is shown in Table 3. It was found that cyclopentanone conversion decreased by 39.1% and DAP selectivity decreased by 21.7% after the catalysts were used five times. Meanwhile, the selectivity of dimethyl 2-methyladipate reached 40.3%, which is comparable with that of K_2CO_3 (see Table 2). In addition, it was found that the there was little leaching of Mg²⁺ from the catalyst into the reaction medium. These results therefore suggest that the generation of Mg carbonate salts, due to the formation of carbon dioxide in the methylation reaction, was the reason for deactivation of the catalyst. Fortunately, the used catalysts could be regenerated by calcination even after having been used several times (see Table 3).

3.3 Plausible reaction mechanism

Figures 5 and 6 show the influence of reaction time on the reaction of DMC with cyclopentanone over MgO. As can be seen, the conversion of cyclopentanone gradually increased with reaction time, and then reached a stable value after 5 h (see Figure 5). After that time, the conversion of cyclopentanone and yield of products remained essentially unchanged (see Figure 6). Interestingly, the selectivity of DAP increased with prolonged reaction time, whereas the opposite change was observed for the selectivity of CMCP, whilst the selectivity of the other products remained almost unchanged. Similar trends were also observed for the effect of varying reaction temperature (see Figure 7). These results suggest that the reaction proceeds via CMCP as the intermediate. Our group has previously reported that DMC is hardly activated on solid bases [21]. Thus, a plausible reaction mechanism for the synthesis of DAP can be proposed

Catalyst ^{a)}	Cyclopentanone – conversion (%)	Selectivity (%)				Contents of Mg in	
		DAP	CMCP	dimethyl 2-methyl adipate	2-methyl- cyclopentanone	2-cyclopentylidene cyclopentanone	filter liquor $(\%)^{d}$
MgO ^{a)}	85.5	50.9	11.0	11.3	5.67	21.1	0.06
MgO $(r1)^{b)}$	73.6	42.7	5.97	25.5	6.58	19.2	0.17
MgO $(r2)^{b)}$	65.5	38.1	4.40	30.7	7.03	19.8	0.28
MgO (r3) ^{b)}	60.7	33.3	3.98	36.4	8.51	17.8	0.31
MgO (r5) ^{b)}	56.4	29.2	2.68	40.3	11.4	16.4	0.84
MgO (r1)* ^{c)}	83.7	51.2	9.80	10.8	6.29	21.9	-
MgO (r2)* c)	82.6	50.1	8.67	10.9	7.51	22.8	-
MgO (r3)* c)	84.2	49.6	7.79	11.9	7.99	22.7	-
MgO (r5)* c)	79.6	48.8	7.68	13.6	8.54	21.4	-

a) Reaction conditions: cyclopentanone: T = 260 °C, DMC = 1 : 4, time = 5 h, catalyst wt.% = 1.5%; b) the used catalysts were separated by filtration and washed with 20 mL of methanol three times, and then used for the next run; c) the used catalysts obtained by calcination at 500 °C for 5 h under nitrogen atmosphere after filtration from the reaction mixture; d) the contents of Mg in the filtrate were determined by complexometric titration in ammonia–ammonium chloride buffer solution (pH = 10), using EDTA as titrant and Eriochrome Black T as indicator. The results were calculated using Mg(%) = Mg (l)/ Mg (s), where Mg(l) is the content of Mg in the filtrate, and Mg(s) is the total content of Mg in the original solid base.



Figure 5 Effect of reaction time on the conversion of cyclopentanone and selectivity of products over MgO. Reaction conditions: T = 260 °C, cyclopentanone : DMC = 1 : 4, catalyst wt.% = 1.5%. Other products = 2-meth-ylcyclopentanone + dimethyl 2-methyladipate + 2-cyclopenty-lidenecy-clopentanone.

as follows (see Scheme 1(a)): initially, a proton is abstracted from cyclopentanone to form a carbanion of cyclopentanone (1⁻), and then 1⁻ and the proton were absorbed on acidic sites (M^{n+}) and basic sites (O^{2-}) of the solid base surface, respectively. Afterwards, 1⁻ attacked the carbonyl group of a DMC molecule, which produced CMCP as the primary product. After that, the resulting intermediate reacted with a methoxide anion to yield the corresponding carbanion, which was subjected to ring-opening giving DAP as the final product.

A similar anionic mechanism has also been proposed for the condensation of cyclopentanone (to give 2-cyclopentylidenecyclopentanone) and the products of methylation of cyclopentanone with DMC (2-methylcyclopentanone and dimethyl 2-methyladipate). As shown in Scheme 1(b), $1^$ could attack a second cyclopentanone molecule to produce



Figure 6 The relationship between conversion of cyclopentanone and yield of products. Reaction conditions: T = 260 °C, cyclopentanone : DMC = 1 : 4, catalyst wt.% = 1.5%. Other products = 2-methylcyclopentanone + dimethyl 2-methyladipate + 2-cyclopentylidenecyclopentanone.



Scheme 1 A plausible mechanism for the reaction of DMC with cyclopentanone.



Figure 7 Effect of reaction temperature on the conversion of cyclopentanone and selectivity of products over MgO. Reaction conditions: time = 5 h, cyclopentanone : DMC = 1 : 4, catalyst wt.% = 1.5%. Other products = 2-methylcyclopentanone + dimethyl 2-methyladipate + 2-cyclopentylidenecyclopentanone.

2-cyclopentylidenecyclopentanone and water. Likewise, 1^- can abstract the methyl group of DMC to produce the methylation product 2-methylcyclopentanone, which formed methanol and carbon dioxide at the same time (see Scheme 1(c)). Afterwards, the anion of 2-methylcyclopentanone can react with another molecule of DMC to give dimethyl 2-methyladipate as a further product (see Scheme 1(c)).

4 Conclusions

The synthesis of DAP from cyclopentanone with DMC can be carried out over solid base catalysts. The results revealed that MgO, which possesses moderate basic strength, showed the best performance among the solid bases investigated. The role of the basic catalysts was mainly attributed to activation of the cyclopentanone via abstraction of a proton in the α -position by base sites, and a possible reaction pathway, which includes CMCP as an intermediate was proposed. Under the optimal conditions, using MgO as a catalyst, the cyclopentanone conversion and the DAP selectivity reached 85.5% and 50.9%, respectively.

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