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A novel route for the synthesis of methyl acetoacetate from dimethyl carbonate and acetone over solid base

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Abstract

A novel route for the synthesis of methyl acetoacetate by the methoxycarbonylation of acetone with dimethyl carbonate was developed in the presence of solid base catalysts. Solid bases with moderate strength (such as MgO) facilitated the formation of methyl acetoacetate, and the yield of methyl acetoacetate could be linearly correlated with the amount of moderate base sites. The in situ FTIR indicated that the reaction was mainly attributed to the activation of acetone via the abstraction of H^{α} by basic sites.

Keywords: Methyl acetoacetate; Acetone; Dimethyl carbonate; Solid bases

1. Introduction

Methyl acetoacetate (MAA), as a model of β-ketoesters is widely used for synthesis of a number of complex products [1]. However, traditional methods, including the esterification of diketene and CH_3OH, Claisen condensation of methyl acetate or carbonylation of chloroacetone with CH_3OH, suffered from some drawbacks such as the use of toxic reagents and the generation of corrosive by-products [2–4]. Thus, a clean and safe chemical process needs to solve such problems.

Dimethyl carbonate (DMC), as an environmentally benign building block, led to an eco-friendly alternative to both methyl halide and phosgene for methylation and carbonylation process, respectively [5–8]. In the presence of a base, it can also react with a number of nucleophilic anions containing compounds such as ketones, amines, oximes, indoles, phenols [9–16]. Selva et al. reported that dimethyl carbonate reacted with alicyclic ketones to produce dimethyl esters in the presence of homogeneous base catalysts (usually K_2CO_3) [17–19]. However, the homogeneous catalysts had the drawbacks of separation, liquid waste treatment and corrosion problems. Thus, we developed a novel and facile one-pot approach to the production of methyl acetoacetate from dimethyl carbonate and acetone over solid bases, which could be an eco-friendly alternative because of both gentle reaction conditions and environmentally benign feedstocks.

2. Experimental

2.1. Catalyst preparation and characterization

CaO, MgO and ZrO_2 were prepared by thermal decomposition of calcium carbonate at 800 °C for 2 h, magnesium hydroxide at 500 °C for 5 h, zirconium hydroxide at 500 °C for 5 h under nitrogen atmosphere, respectively. Lanthana (La_2O_3, Tianjin Kermel Chemical Reagent Co. Ltd.) and alumina (Al_2O_3, Tianjin Kermel Chemical Reagent Co. Ltd.) were purchased and treated in N_2 at 700 and 500 °C for 5 h before used, respectively. Hβ was obtained by calcining NH_4-beta zeolite (Shanghai Chemical Reagent Co., China) in the air at 550 °C for 3 h. A series of Al/MgO samples with the molar ratios of 0.01–0.3 were prepared using the impregnation method. A certain amount of aluminum isopropoxide were dissolved in benzene and then added into $Mg(OH)_2$ to form the impregnated samples. The samples were first dried at 100 °C overnight and then thermally decomposed in N_2 at 500 °C for 5 h. Alkali-promoted A/MgO samples (A = Li, Na) were also prepared using the impregnation. The alkali metal A was added

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to MgO using a hydroxide aqueous solution that contained the required A concentration to obtain an A/Mg = 0.01 (molar ratio). After impregnation, the sample was dried at 100 °C for 12 h and finally treated under N_2 flowing at 500 °C for 5 h.

Nitrogen adsorption/desorption isotherms were obtained at −196 °C on a Micromeritics ASAP-2000 instrument (Norcross, GA), using static adsorption procedures. Samples were degassed at 350 °C for a minimum of 5 h under vacuum (10^{-6} Torr) prior to the measurement. Surface areas were measured using the BET method. Basic properties of those samples were measured by temperature programmed desorption of CO_2 (CO_2-TPD). Catalysts (0.10 g, 40–60 mesh) were placed in the quartz reactor bed. After 2 h pretreatment under Ar flowing at 500 °C, the catalysts were cooled to room temperature. CO_2 was pulsed to the reactor using a six-way valve till reaching saturation. Once the physically adsorbed CO_2 was purged off, the CO_2-TPD experiments were started from 20 to 500 °C with a heating rate of 10 °C/min under Ar flow (50 mL/min), and the effluent was detected by a Balzers Omnistar mass spectrometer.

In situ FTIR measurement was carried out using an inverted T-shaped cell containing the sample pellet and fitted with CaF_2 windows. The samples were normalized to 15 mg pellets and pretreated in vacuum at 500 °C for 5 h. After the temperature was increased up to 250 °C, the adsorbates (dimethyl carbonate and acetone) were introduced into the cell for 5 h, and the resulting spectrum was recorded at room temperature by removing the gas phase in evacuation. The FTIR spectra were collected using a Nicolet Magna 550 Fourier-transform infrared spectrometer (at a resolution of 4 cm^{-1}).

2.2. Catalytic test

The one-pot synthesis of methyl acetoacetate from dimethyl carbonate and acetone was carried out in 150 mL batch reactor under autogenous pressure (about 1–3 MPa in the temperature region from 200 to 260 °C). Dimethyl carbonate (35.97 g), acetone (5.00 g) and the catalyst (0.68 g) were charged in the reactor and the mixture was heated to 240 °C for 5 h with stirring. Afterwards, the reactor was cooled down to room temperature, and the 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 after filtration from the catalyst. The selectivity was defined as $m_i/\sum m_i \times 100$, where m_i was the weight of product of i, and $\sum m_i$ was the total weight of the products.

3. Results and discussion

3.1. Basicity

Fig. 1 depicts the CO_2 desorption profiles on ZrO_2, MgO, La_2O_3 and CaO. CaO exhibited the strong basic sites with a sharp desorption peak at 550 °C. La_2O_3 showed relatively strong basic strength with CO_2 desorption peak at 450 °C. As for MgO, there were three desorption peaks at 150, 210 and 310 °C, respectively, suggesting that MgO had weak and moderate strength basic sites, but for ZrO_2, only weak basic sites with CO_2 desorption peak at 170 °C was observed. Their basicity (i.e. the basic sites amount per unit area of catalysts) followed the order: $CaO > MgO > La_2O_3 > ZrO_2$ (see Table 1). The addition of alumina did not change the basic character of MgO (see Fig. 2), but the basicity decreased with the increase of the Al contents. In contrast, the addition of alkali metals increased the basicity, and the Na/MgO showed the relative higher basicity.

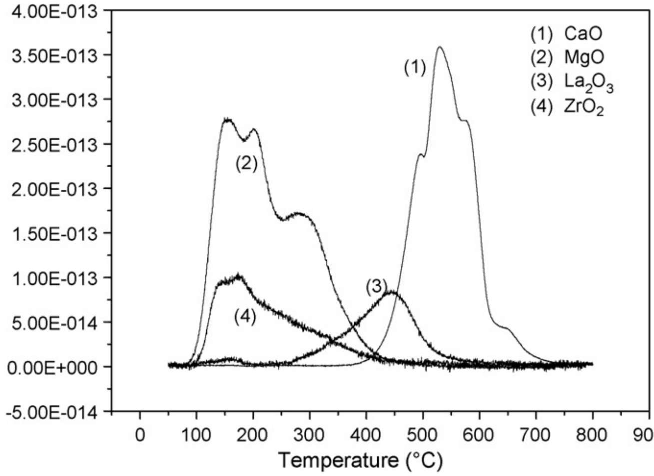


Fig. 1. CO_2-TPD profiles of solid bases.

3.2. Catalytic performance

Table 1 gives the catalytic performance of solid catalysts in synthesis of methyl acetoacetate from the reaction of acetone with dimethyl carbonate. In the absence of catalyst, no products were detected. Over solid acids such as Hβ and Al_2O_3, the catalyst hardly appeared active towards the formation of methyl acetoacetate, indicating that solid acids were inactive towards the reaction. However, the reaction was highly catalyzed by solid bases. Among those bases, MgO, which possessed the

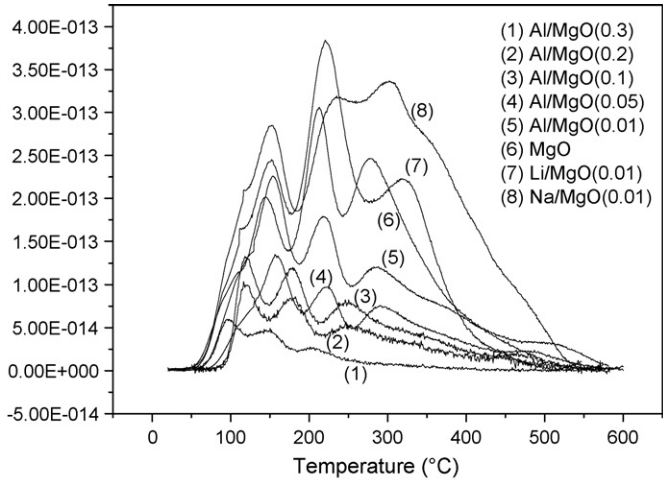


Fig. 2. CO_2-TPD profiles of MgO with different Al contents and alkali-promoted MgO.

Table 1
Synthesis of methyl acetoacetate from dimethyl carbonate and acetone over solid catalysts and CO_2 uptake of solid bases

Run[a]	Catalyst	BET surface area (m^2/g)	CO_2 uptake		Acetone conversion (%)	Selectivity (%)[b]		
			mmol/g	mmol/m^2		MAA	ACA	MOP
1	–	–	–	–	–	–	–	–
2	Al_2O_3	–	–	–	10.2	Traces	92.7	7.26
3	Hβ	–	–	–	61.6	Traces	57.0	43.0
4	ZrO_2	33.4	3.22E−03	9.64E−05	18.4	6.98	75.6	15.4
5	MgO	10.1	1.78E−02	1.76E−03	32.3	52.8	15.3	31.9
6	La_2O_3	4.8	1.69E−03	3.52E−04	6.47	62.6	14.1	23.3
7	CaO	9.1	6.37E−02	7.00E−03	21.2	65.1	4.52	30.4

[a] Reaction conditions: $T = 260$ °C, acetone:DMC = 1:4, time = 5 h, catalyst wt% = 1.7%.

[b] MAA: methyl acetoacetate; ACA: diacetone alcohol + mesity oxide + isophorone; MOP: 2-methoxypropene.

moderate basic strength, exhibited the high performance. ZrO_2 and La_2O_3 showed lower methyl acetoacetate yields, which might be due to their relative weak basicity than MgO. As far as CaO was concerned, it provided slightly lower acetone conversion and methyl acetoacetate selectivity despite its high basicity. This could be attributed to that the acid strength of Ca cation was too weak to stabilize the carbanion species [20]. Therefore, both basic basicity and basic strength played the important role in the reaction, and the basic sites with moderate strength were effective for the synthesis of methyl acetoacetate by the methoxycarbonylation of acetone with dimethyl carbonate.

In order to further clarify the effect of moderate basic strength on catalytic performance, a series of MgO with different Al contents and alkali-promoted MgO were prepared to supply the different amount of moderate base sites (see Fig. 2). It was found that the addition of metal ions did not change the basic character of MgO, but influenced the basicity of MgO. The Na/MgO showed the relative higher basicity, and the increasing Al content decreased the density of basic sites. For MgO-based catalysts, a good linear correlation was observed between the methyl acetoacetate yield and the amount of moderate base sites (see Fig. 3). Thus, the synthesis of methyl acetoacetate over solid base should be closely related to the moderate base sites.

3.3. Effects of the reaction parameters

The reaction was carried out in the temperature region from 200 to 280 °C. The main reaction product was methyl acetoacetate, and the etherification products (such as 2-methoxypropene (MOP)), and the aldol condensation products of acetone (ACA) (such as diacetone alcohol, mesity oxide and isophorone) were also detected, which were dependent on the reaction conditions. As shown in Fig. 4, the conversion of acetone increased sharply with the temperature, suggesting that the high temperature favored the acetone conversion. With the temperature at 260 °C, the selectivity of MAA reached the maximum of 52.8%. This could be attributed to the production of aldol condensation products and 2-methoxypropene at high temperature. Furthermore, both acetone conversion and selectivity changed a little after 5 h (see Fig. 5), indicating that the reaction almost reached the equilibrium. Moreover, when the molar ratio of DMC to acetone was over 4, both acetone conversion and ACA selectivity remained unchanged (see Fig. 6), but the MOP selectivity increased. It was reasonable that the excessive

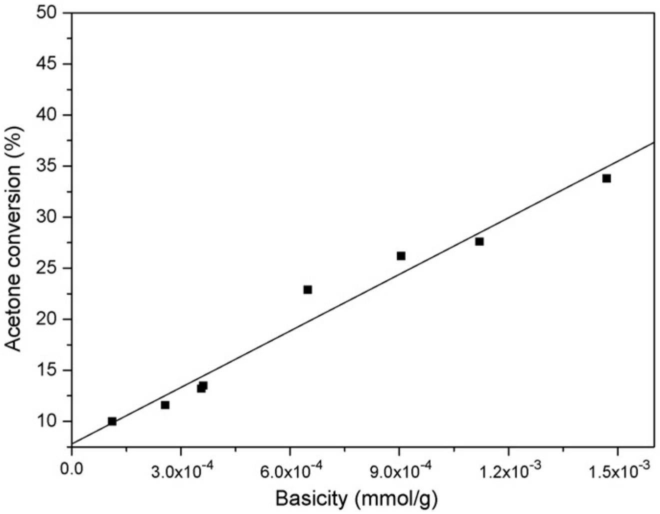


Fig. 3. The relationship between the yield of methyl acetoacetate and moderate basicity.

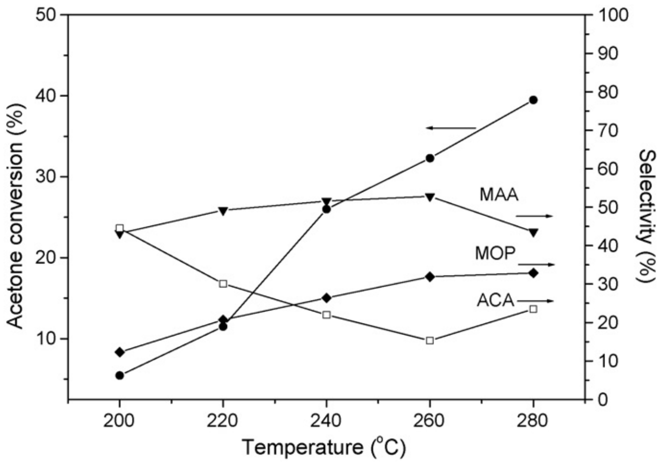


Fig. 4. Effect of temperature on the conversion of acetone and selectivity of products. Reaction conditions: acetone:DMC = 1:4, time = 5 h, catalyst wt% = 1.7%.

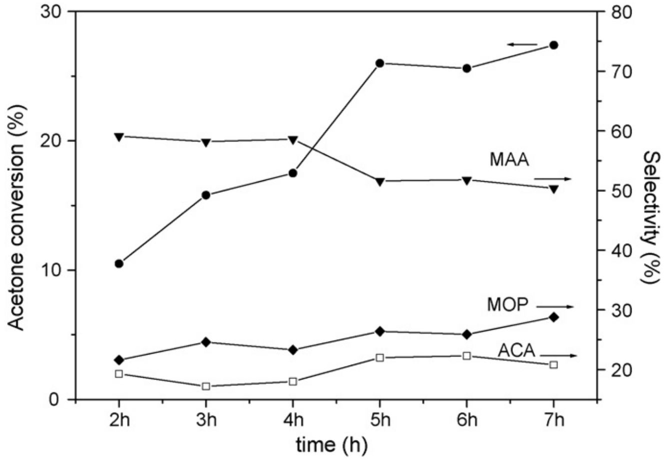


Fig. 5. Effect of reaction time on the conversion of acetone and selectivity of products. Reaction conditions: acetone:DMC = 1:4, $T = 240\ ^\circ C$, catalyst wt% = 1.7%.

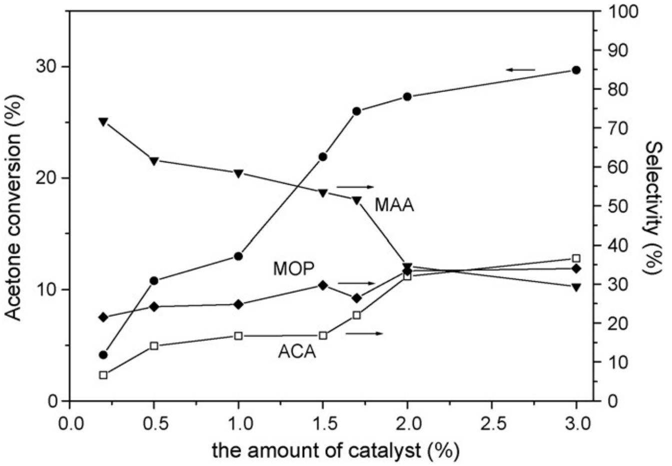


Fig. 7. Effect of amount of catalyst on the conversion of acetone and selectivity of products. Reaction conditions: acetone:DMC = 1:4, $T = 240\ ^\circ C$, time = 5 h.

DMC could produce more CH_3^- group, which would react with acetone to produce MOP. The conversion increased a little after the amount of catalyst was up to 1.7 wt% (see Fig. 7). However, the selectivity of MAA decreased with the increase of the amount of catalyst, showing that the high catalyst loadings were favorable to the side-reaction, i.e. aldol condensation.

3.4. Plausible reaction mechanism

Fig. 8 presents the FTIR spectra of Na/MgO catalyst after the adsorption of reactants. The adsorption bands at 2960 and 1261 cm^{-1} were detected after the sample was pretreated in vacuum at 500 °C (see Fig. 8(a)), which were due to the evaporation of high vacuum silicone grease in the T-shaped cell. No more adsorption bands were detected after dimethyl carbonate was adsorbed on Na/MgO at 250 °C (see Fig. 8(b)), indicating that dimethyl carbonate was hardly anchored on solid base surface. However, when acetone was admitted to the cell, the bands were detected at 3584, 1715 and 1220 cm^{-1} (see Fig. 8(c)). The broad band around 3584 cm^{-1} belonged to the OH stretching vibration originated from the hydrogen bonding of acetone to the oxygen atoms of MgO. The C=O stretching vibration at 1715 cm^{-1} band and the C–C:–C stretching vibration at 1220 cm^{-1} band illustrated that acetone remained its framework after adsorbed onto solid base. These suggested that acetone was mainly bonded by its H^{α} to MgO oxygen atoms, which led to the formation of acetonyl species over solid base. FTIR spectra of co-adsorbed reactants showed bands at 1721 and 1771 cm^{-1}, which were ascribed to C=O stretching vibration of ketoesters, and bands at 1179 and 1193 cm^{-1} due to C–O–C stretching vibration of ester groups (see Fig. 8(d)). Because dimethyl carbonate was hardly adsorbed on solid base after the evacuation (see Fig. 8(b)), these new bands should be attributed to methyl acetoacetate. Based on the above results, the mechanism of methyl acetoacetate formation was proposed as follows (see Scheme 1), a acetonyl anion was generated due

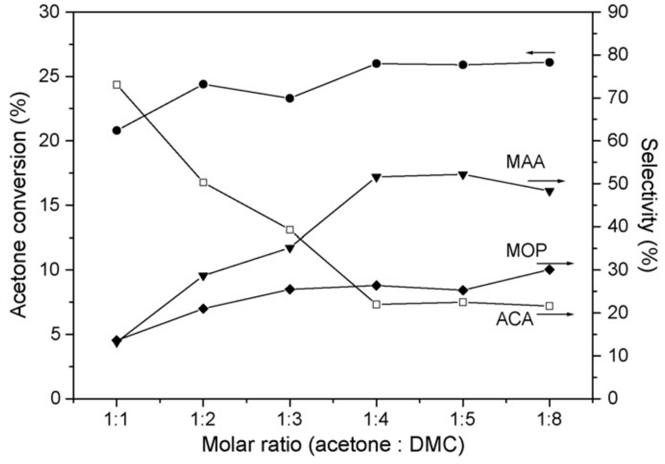


Fig. 6. Effect of molar ratio on the conversion of acetone and selectivity of products. Reaction conditions: $T = 240\ ^\circ C$, time = 5 h, catalyst wt% = 1.7%.

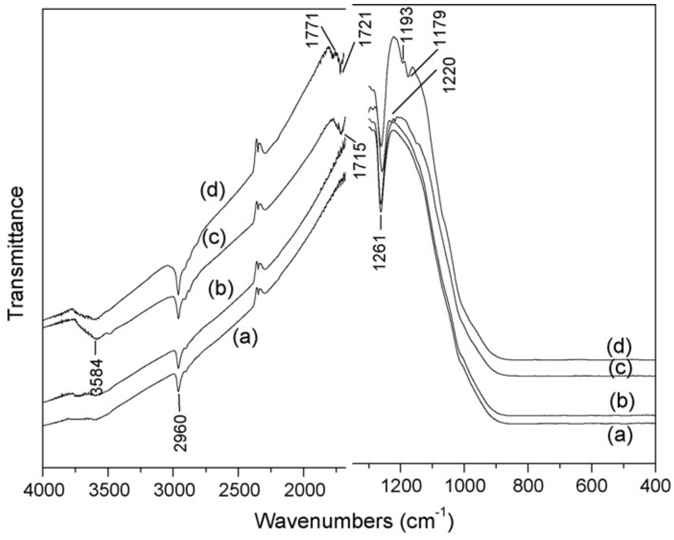
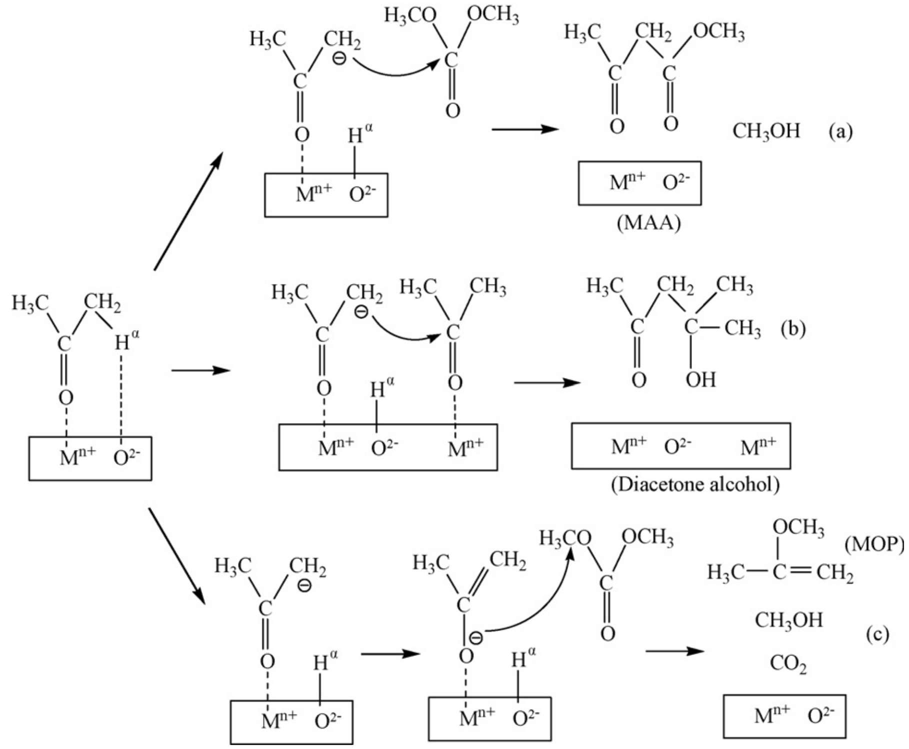


Fig. 8. FTIR spectra of the reactants adsorbed on Na/MgO catalyst. (a) Na/MgO catalyst pretreated in vacuum, (b) the adsorption of dimethyl carbonate on Na/MgO at 250 °C, (c) the adsorption of acetone on Na/MgO at 250 °C, and (d) the coadsorption of dimethyl carbonate and acetone on Na/MgO at 250 °C.



Scheme 1. The plausible mechanism of the reaction from acetone with DMC.

to the abstracting of the α-proton (H^α) from the acetone by the base site, and then the acetonyl anion and proton were absorbed on acidic sites (M^{n+}) and basic sites (O^{2-}) on the solid base surface, respectively. Afterwards, the carbanion reacted with the carbonyl group of DMC molecule to produce methyl acetoacetate and methanol (see Scheme 1(a)).

Because DMC was hardly activated by solid bases, the by-products such as the aldol condensation products (diacetone alcohol) and etherification product (2-methoxypropene) were also formed by the activation of ketones via the abstraction of H^α by basic sites. After the initial abstraction of the α-proton from acetone, the carbanion could attack a second acetone molecule to produce diacetone alcohol (see Scheme 1(b)). Similarly, the acetone carbanion, which was stabilized by the enolate resonance isomer, reacted with the methyl group of DMC to yield the final products of 2-methoxypropene, methanol and carbon dioxide (see Scheme 1(c)).

4. Conclusion

A novel benign route was developed for synthesis of methyl acetoacetate from the reaction of dimethyl carbonate and acetone. The synthesis of methyl acetoacetate was found to be closely related to the moderate base sites, and in situ FTIR indicated that the formation of methyl acetoacetate presumably was carried out via the abstraction of H^α from acetone by basic sites. Under the optimal conditions, the acetone conversion and the MAA selectivity reached 32.3 and 52.8% over the sample solid bases, respectively.

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