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Synthesis of methyl acetoacetate from acetone and dimethyl carbonate with alkali-promoted MgO catalysts

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The synthesis of methyl acetoacetate (MAA) by methoxycarbonylation of acetone with dimethyl carbonate (DMC) was carried out in the presence of MgO and alkali-promoted MgO catalysts. From among Li, Na, K, and Cs, potassium was found to be the most effective promoter to improve the activity of MgO. The effect of K/MgO with variable content of K was also investigated, and the individual catalysts were characterised by the XRD, BET, SEM, CO₂-TPD, and in situ CO₂ IR techniques. The results showed that the addition of a small amount of K (1.97 mass %) could promote MAA formation, but a higher K loading caused a decrease in the yield of MAA, which might result from particle agglomeration and the presence of stable potassium carbonates. In situ FTIR experiments of co-adsorbed reactants indicated that the reaction probably proceeded via abstraction of H_{α} from acetone by base sites.

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Keywords: methyl acetoacetate, acetone, dimethyl carbonate, MgO, alkali metals

Introduction

Methyl acetoacetate (MAA) is widely used in the production of valuable synthetic intermediates (Yadav & Lathi, 2004). Methods for the synthesis of MAA in current use are the esterification of diketene with methanol, Claisen condensation of methyl acetate, and carbonylation of chloroacetone with methanol. However, these methods suffer from undesirable sideeffects such as corrosion, pollution and separation problems (Pohl & Schmidt, 1944; Lapidus et al., 2001). Therefore, a clean and safe chemical process should be developed to eliminate the negative environmental impact.

In recent years, dimethyl carbonate (DMC), as an environmentally benign building block, has attracted attention due to its versatile chemical properties and low toxicity (Fu et al., 1998; Jyothi et al., 2001; Shivarkar et al., 2005). In the presence of alkali metal compounds, it can react with a number of nucleophilic substances, such as ketones, amines, oximes, indoles, and phenols to produce methoxycarbonylation products (Tundo et al., 1988, 1989; Tundo & Selva, 2002; Marques et al., 1993; Vauthey et al., 2000; Shieh et al., 2003; Fuming et al., 2004). Ruest et al. (1976) were the first to report the reaction of cyclohexanone and DMC in the presence of NaH by which a methoxycarbonylation product (carbomethoxycyclohexanone) was formed. Later, the reaction of alicyclic ketones with DMC in the presence of homogenous catalysts such as Cs₂CO₃-crown ether, CH₃ONa, and organic amines (Fischer, 1995; Köhler, 1995; Koehler & Metz 1998; Tundo & Selva, 2002) yielded dimethyl esters. However, only a few works have been devoted to the reaction of aliphatic ketones with DMC (Selva et al., 1993). To the best of our knowledge, the reaction of acetone with DMC, which might be an attractive method for the production of MAA due to the moderate reaction conditions and environmentally benign reactants, has not previously been investigated.

Our preliminary research revealed that acidic catalysts were unfavourable to this reaction, and this

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process was a base-catalysed reaction. A solid base of moderate strength, such as MgO, facilitated the formation of MAA (Wu et al., 2008). However, the role of the requirements on the base site which promoted this reaction in terms of density and strength was yet to be elucidated. In the present work, a set of alkali metal–MgO catalysts with different base site and base density was prepared by the conventional impregnation method, and these were used to study the reaction of acetone with DMC. In our experiments, we focused on K-promoted MgO which showed a high activity in this reaction. Furthermore, a plausible reaction mechanism was proposed on the basis of in situ FTIR results.

Experimental

Catalysts preparation and characterisation

Magnesium oxide was prepared by thermal decomposition of magnesium hydroxide at 500 °C for 5 h in a nitrogen atmosphere. A series of samples of alkalidoped A/MgO (A = Li, Na, K, Cs) was prepared using the incipient impregnation. An aqueous solution of alkali metal hydroxide with the required amount of A was added to MgO to obtain the sample with an A/Mg mole ratio of 0.01. In addition, K/MgO catalysts with 0.66 mass %, 1.32 mass %, 1.97 mass %, 3.23 mass %, and 6.27 mass % of potassium, corresponding to the mole ratios of 0.01, 0.02, 0.03, 0.05, and 0.10 (K/Mg), were also prepared. After impregnation, all the samples were dried at 100 °C for 12 h and finally treated in the stream of N₂ at 500 °C for 5 h. The K-doped MgO samples were denoted as K/MgO-x.

XRD was carried out using Rigaku D/max-A with a Ni filter (Rigaku Corporation, Japan). Diffraction patterns were obtained with the X-ray gun operated at 50 kV and 30 mA, using a scan rate of 5° min⁻¹ from 20° to 80°.

The specific surface area and pore volume of the samples were obtained by the BET (Brunauer, Emmett, and Teller) method. Prior to measurement, the samples were degassed in a vacuum $(1.33 \times 10^{-4} \text{ Pa})$ at 350 °C for 5 h and nitrogen adsorption/desorption isotherms were obtained with an ASAP-2000 instrument (Micromeritics, Norcross, GA, USA) at -196 °C.

Scanning electron micrographs (SEM) were obtained from powdered carbon-coated samples with a Philips SEM 505 microscope (Philips/FEI, The Netherlands) with a LaB₆ filament and low voltage anode operating at 4 keV.

CO₂ temperature-programmed desorption (CO₂-TPD) measurement was performed using Ar as a carrier gas. Catalyst samples (0.10 g, 40–60 mesh) were pre-treated in the Ar atmosphere at 500 °C for 2 h. After the samples were cooled to room temperature, CO₂ was introduced into the reactor until saturation was attained. Once the physically-adsorbed CO₂ had been purged by the carrier gas, the CO₂-TPD measurements were carried out from 20 °C to 800 °C at a heating rate of 10 °C min⁻¹ in the stream of Ar at a flow-rate of 50 mL min⁻¹, and the effluent was detected with a GC-950 gas chromatograph (Shangai Haixin Chromatograph Company, China) equipped with a thermal conductivity detector.

The chemical nature of CO_2 species adsorbed on the surface was determined by IR spectroscopy following CO_2 adsorption at room temperature, and at increased temperatures under reduced pressure. Prior to the experiments, the samples were pre-treated in a vacuum at 500 °C for 5 h. The IR spectrum of the pre-treated catalysts was obtained after the samples were cooled to room temperature. Experiments were performed on self-supporting wafers (15 mg) in an inverted T-shaped cell with CaF₂ windows. Following introduction of 13 kPa of CO_2 into the cell at room temperature for 1 h, the samples were evaluated at a temperature of 25 °C, 100 °C, 200 °C, and 300° , respectively, and the resulting spectrum was recorded. Data were collected using a Nicolet Magna 550 Fourier-transform infrared spectrometer (at a resolution of 4 $\rm cm^{-1}$). The spectra of the species adsorbed were obtained by subtracting the spectrum of a catalyst. In situ FTIR experiments of co-adsorbed reactants were also carried out following the above procedures. All the samples were pre-treated in a vacuum at 500 $^{\circ}$ C for 5 h, and then cooled to room temperature to obtain the spectrum of the pre-treated catalysts. After the temperature was increased to 250°C, the adsorbates (DMC and acetone) were introduced into the cell for 5 h, and the resulting spectrum was recorded after the samples were cooled to room temperature by removing the gas phase by evacuation.

Testing methods

The synthesis of MAA from DMC and acetone was performed in a 150 mL batch CGF-150 reactor (Shanxi Taikang Instrument Company, China). DMC (35.97 g), acetone (5.00 g), and the catalyst (0.68 g)were transferred to the reactor and the mixture was heated to 240 °C for 5 h with stirring (1000 min⁻¹). After the reaction was completed, the reactor was cooled to room temperature. The reaction products were separated from the catalyst by vacuum filtration with 100 mm sand core Büchner funnel (Chubo Instrument Company, China) and analysed in a gas chromatograph equipped with a HP-5 column and a flame-ionisation detector. The main reaction products were MAA and 2-methoxypropene (MOP). The aldol condensation products of acetone (ACA), such as diacetone alcohol, mesityl oxide, and isophorone, were also detected. The selectivity was defined as $m_{\rm A}/\sum m_{\rm A}$ \times 100, where $m_{\rm A}$ is the mass of the promoter A, and $\sum m_{\rm A}$ is the total mass of the products.

	Metal A						Selectivity		
$Catalyst^a$	Loading	Ionic radius ^{b}	Surface area	Pore volume	$\rm CO_2$ uptake	Acetone conversion	%		
	mole %	Å	$\mathrm{m}^2~\mathrm{g}^{-1}$	mL g^{-1}	$mmol m^{-2}$	%	MAA	ACA	MOP
MgO	_	0.66^{c}	122.5	0.34	5.02×10^{-4}	27.4	50.6	22.0	27.4
Li/MgO	0.01	0.68	112.8	0.30	5.50×10^{-4}	33.8	48.0	18.5	33.5
Na/MgO	0.01	0.97	86.2	0.27	6.86×10^{-4}	36.2	50.8	16.9	32.3
K/MgO	0.01	1.33	84.8	0.28	7.69×10^{-4}	41.2	50.3	18.4	31.3
Cs/MgO	0.01	1.67	67.9	0.18	9.21×10^{-4}	34.5	41.0	26.5	32.5

Table 1. Physical and chemical properties and catalytic effect of A/MgO and MgO catalysts

a) Reaction conditions: T = 240 °C, acetone/DMC ($\varphi_r = 1:4$), time = 5 h, catalyst = 1.7 mass %; b) from (Lide, 1990); c) Mg²⁺.



Fig. 1. X-ray diffraction patterns of MgO and K/MgO-x catalysts: (■) MgO, (●) K₂CO₃; upward curves for: MgO, K/MgO-1, K/MgO-2, K/MgO-3, K/MgO-4, K/MgO-5.

Results and discussion

Selection of the alkali metal promoter

Table 1 gives the catalytic performance of MgO and alkali-promoted MgO in the synthesis of MAA from acetone with DMC. The addition of alkali metal promoters improved the conversion of acetone and MAA selectivity in comparison with pure MgO. The yield of MAA increased in the following order: Li/MgO, Na/MgO, K/MgO. However, acetone conversion on Cs/MgO was slightly lower than that of K/MgO, and the selectivity of MAA was also the lowest from among all the catalysts.

The increase in basic character of MgO was ascribed to the formation of A_2O by the addition of a promoter A (Di Cosimo et al., 1996). The differing basicity of the individual alkali-promoted MgO samples was attributed to the different electron-donating properties of the alkali metal oxides: the stronger the electron donor properties of the promoter (in increasing order: Li, Na, K), the greater the number of surface base sites. As a result, K/MgO showed a higher yield of MAA than Li/MgO, Na/MgO, and pure MgO catalyst (Table 1). In addition, because the alkali metal cations have a larger ionic radius than Mg^{2+} (with the exception of Li⁺ where the difference in ionic radius is minimum) (Table 1), the alkali metal could not exchange with Mg^{2+} ions of MgO and be effectively incorporated into the MgO lattice. As a result, A₂O remained attached to the surface, thereby decreasing the solid surface area due to blockage of the catalyst pores (Table 1). Although the basic character increased from Li₂O to Cs₂O, the presence of the bulky Cs₂O on the MgO surface hindered the formation of MAA. As a consequence, we selected K to promote MgO and we prepared a series of K/MgO samples with different K loadings in order to investigate the influence of the loading of K on the methoxycarbonylation of acetone with DMC.

Textural and structural characterisation of Kpromoted MgO catalysts

The physical and chemical properties, such as BET surface area, pore volume and, XRD results for pure MgO and K-promoted MgO, are given in Table 2. It was found that BET surface area and pore volume decreased with the increase of K content in K/MgO-*x* catalysts.

Fig. 1 illustrates the XRD patterns of MgO and K/MgO-x catalysts. Typical peaks of MgO are observed at 2θ values of around 36.7° , 42.7° , 62.2° , 74.5° , 78.5° (ASTM 4-0829). With K loadings up to 0.05 mole %, all the XRD peaks remained unchanged and just a single phase of MgO, periclase, was observed. However in the K/MgO-5 catalyst with the highest K loading tested, some peaks located at 2θ values of 12.8° , 25.9° , 32.7° , and 38.6° , which were assigned to the K₂CO₃ phase (ASTM 27-1348), were observed. The formation of the K₂CO₃ phase was probably due to exposure to ambient CO₂ during sample preparation.

The unit cell parameter values of a for the MgO (face-centred cubic structure) and K/MgO-x catalysts were calculated from the XRD patterns depicted in Fig. 1 and the results were included in Table 2. The a values in Table 2 are almost constant, which indicates that the addition of K does not markedly modify the

	$\rm K^+$ loading	Surface areas	Pore volume	XRD analysis		
Catalyst	mole %	$\mathrm{m}^2~\mathrm{g}^{-1}$	mL g^{-1}	Lattice parameter, $a/Å$	Crystallite size/Å	
MgO	_	122.5	0.34	4.219	109	
K/MgO-1	0.01	84.8	0.28	4.223	144	
K/MgO-2	0.02	76.4	0.25	4.232	151	
K/MgO-3	0.03	75.6	0.24	4.233	159	
K/MgO-4	0.05	45.4	0.20	4.228	231	
K/MgO-5	0.10	35.3	0.17	4.241	241	

Table 2. Textural and structural characterisation of MgO and K/MgO-x catalysts

Table 3. Surface base site properties and catalytic performance of MgO and K/MgO-x catalysts

	TPD of CO_2 adsorbed					Selectivity		
Catalyst	$\rm CO_2$ uptake	Desorption peaks/(area %) ^{a}		Acetone conversion ^{b}	%			
	$\mathrm{mmol}\;\mathrm{m}^{-2}$	L	М	Н	%	MAA	ACA	MOP
MgO	5.02×10^{-4}	21.9	21.0	57.1	27.4	50.6	22.0	27.4
K/MgO-1	7.69×10^{-4}	18.7	19.9	63.4	41.2	50.3	18.4	31.3
K/MgO-2	8.87×10^{-4}	10.5	19.8	69.7	46.9	48.7	19.5	31.8
K/MgO-3	9.12×10^{-4}	5.94	17.3	76.8	51.8	49.5	18.0	32.5
K/MgO-4	8.04×10^{-4}	2.47	9.93	87.6	57.2	41.1	17.1	41.8
K/MgO-5	7.23×10^{-4}	2.62	7.18	90.2	60.9	35.2	13.7	51.0
K_2CO_3	_	-	—	—	66.9	27.2	6.50	66.3

a) Peak at 550 °C is not considered; b) reaction conditions: T = 240 °C, acetone/DMC ($\varphi_r = 1 : 4$), time = 5 h, catalyst = 1.7 mass %.

structure of MgO, and that the K promoter is located on the surface of MgO rather than in the MgO matrix. The crystallite size was also determined from XRD patterns using the Scherrer equation for the reflection at $2\theta = 42.7^{\circ}$. It is apparent from Table 2 that the crystallite size of K/MgO-*x* increased with increasing K concentration ($c_{\rm K}$). This was also confirmed by the SEM (Fig. 2).

As shown in Fig. 2, MgO has a typical flake-like structure. However, the addition of K caused this structure to be covered with layers of melted compounds, probably due to the formation of K₂O. Furthermore, at high levels of K doped ($c_{\rm K} > 1.97$ mass %, samples K/MgO-4 and K/MgO-5), the particles tend to agglomerate, which can be ascribed to the formation of K₂CO₃ and three-dimensional carbonates (Díez et al., 2006), as discussed below.

In fact, the decrease in surface area and pore volume, the increase in crystallite size, as well as the smoother appearance as the $c_{\rm K}$ increased, could be the result of the agglomeration of particles on the surface. These surface species comprised mainly K₂O/MgO solids, which were formed in the course of thermal decomposition of incipient impregnation samples and probably a small amount of potassium carbonate.

Basic properties of K/MgO-x catalysts

The surface basic properties of MgO and K/MgO-

x catalysts were investigated by CO₂-TPD and in situ CO₂ IR measurement. The number of accessible base sites on the surface of these catalysts was estimated from the amount of CO₂ molecules chemisorbed by the integration of TPD curves. The results from these measurements are summarised in Table 3. It can be seen that the total amount of base sites was 5.02×10^{-4} mmol m⁻² for MgO, and the base site density increased with the increase in K doped, which indicated that the introduction of K could promote the concentration of base sites on the surface.

The CO_2 -TPD profiles of K/MgO-*x* catalysts are shown in Fig. 3. It was found that MgO showed three desorption peaks at 170 °C, 230 °C, and 330 °C, respectively, which suggested that three different base sites species were disclosed by CO_2 adsorption (Díez et al., 2006). The low temperature peak at $170 \,^{\circ}C$ (L) was assigned to OH groups; the peak at $230 \,^{\circ}\text{C}$ (M) was ascribed to $Mg^{2+}-O^{2-}$ pairs with probably a small contribution of K^+-O^{2-} pairs and the high temperature peak at $330 \,^{\circ}$ C (H) was attributed to isolated surface O^{2-} ions (low coordination anions in corners or edges). As for K/MgO-x catalysts, the addition of K did not change the basic character of MgO at low K loadings, but high desorption peaks at 550 °C appeared at K loadings exceeding 1.97 mass % (samples K/MgO-4 and K/MgO-5). This observation can be explained by the formation of three-dimensional carbonate. In order to quantify the contribution of the different sur-



Fig. 2. SEM micrographs of: (a) MgO; (b) 0.66 mass % K/MgO; (c) 3.23 mass % K/MgO; (d) 6.27 mass % K/MgO.



Fig. 3. CO₂-TPD profiles of MgO and K/MgO-*x* catalysts: (a) MgO, (b) K/MgO-1, (c) K/MgO-2, (d) K/MgO-3, (e) K/MgO-4, (f) K/MgO-5; L – low temperature peak, M – medium temperature peak, H – high temperature peak.

face species to the total basicity, de-convolution of the CO₂-TPD profiles was performed (the peak at 550 °C was not taken into consideration), and the results are given in Table 3. The isolated surface O^{2-} ions predominated in the above catalysts and their concentration increased with the increase in $c_{\rm K}$, whereas the concentration surface OH groups and Mg²⁺–O²⁻ pairs decreased.

Further, in situ CO₂ IR measurement was carried out in order to investigate the basic types and strengths of MgO and K/MgO-x catalysts. Fig. 4 shows the IR spectra of the catalysts under investigation after CO_2 adsorption at room temperature and at temperatures of 100 °C, 200 °C, and 300 °C, respectively, under reduced pressure. Three different CO₂adsorption species were detected in the catalysts: bicarbonate, bidentate carbonate, and unidentate carbonate, which presumably were related to the three different types of surface base sites. The three CO₂adsorption species on MgO are depicted in Fig. 5 (Díez et al., 2006). The formation of bicarbonate species involved surface hydroxyl groups and showed C—OH stretching at 1220 cm⁻¹. Bidentate carbonate formed on Mg^{2+} (A⁺)-O²⁻ pairs, and exhibited symmetric O—C—O bands at 1320–1360 $\rm cm^{-1}$ and asymmetric O—C—O bands at 1620–1640 cm⁻¹. Unidentate carbonate, which was associated with isolated surface O^{2-} ions, showed symmetric O—C—O bands at 1400– 1420 cm^{-1} and asymmetric O—C—O bands at 1560–1600 cm⁻¹ (Díez et al., 2000).

Bicarbonate was noted as the most labile species and disappeared after evacuation at a temperature of $100 \,^{\circ}C$ (MgO and K/MgO-*x* at low K loadings), which confirmed that OH groups were the weak base sites. By contrast, both unidentate and bidentate carbon-



Fig. 4. IR spectra of CO₂ adsorbed on MgO and K/MgO-x catalysts at room temperature and desorbed under reduced pressure at increasing temperatures: (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C.

ates remained stable at high temperature, whereas only unidentate was observed at higher temperatures under diminished pressure. These results suggested that the base strength of these surface oxygen species decreased in the following order: isolated surface O^{2-} ions, oxygen in Mg²⁺ (A⁺)–O²⁻ pairs, OH groups.

Díez et al. (2006) reported that the addition of Li could promote the strong base sites, and a similar effect of K on MgO catalysts was observed. These observations were confirmed by the results of in situ CO_2 IR measurement and the CO_2 -TPD results. The intensities of the unidentate bands in all samples were stronger than the bands of bidentate carbonate after evacuation at room temperature, which indicated a predominant contribution of the isolated surface O^{2-} ions to the total basicity (Fig. 4). In agreement with the IR results, the areas of high temperature peak (H) in the CO_2 -TPD patterns, which belonged to strong base sites, represented over 55 % of the total base site density in all samples.

It was also found that the intensities of bidentate decreased with the increase in K content (Fig. 4: MgO, K/MgO-2, K/MgO-3) suggesting that the more basic isolated oxygen ions and fewer OH groups and Mg²⁺– O^{2-} pairs appeared on the surface of the K/MgO-*x* catalysts with the increase of $c_{\rm K}$ (Fig. 4, Table 3). The increase in strong base site density in MgO resulting from the addition of K could be explained by the fact that the addition of K strengthened the C_{CO2}– $O_{\rm K/MgO}$ bond and weakened the O_{CO2}– $M_{\rm K/MgO}$ bond of the bidentate species, a condition which would favour the formation of unidentate without the partic-



Fig. 5. CO_2 species on the surface of MgO and K/MgO-x catalysts with low and high concentrations of K.

ipation of metal cations (Kanno & Kobayashi, 1994).

In the case of K/MgO catalysts with $c_{\rm K}$ higher than 1.97 mass %, the intensities of adsorption peaks of CO₂ were reduced substantially and remained almost unchanged even at a higher temperature under reduced pressure. This presumably resulted from the predominance of potassium carbonates (K₂CO₃ and three-dimensional carbonates) on the surface of K/MgO which, as a consequence, could not provide enough base sites for the adsorption of CO₂ molecules. In fact, the decrease in intensities of adsorption peaks at high K loadings was related to the decrease in base site density and the appearance of high desorption peaks at 550 °C in the TPD profiles. The surface species including potassium carbonates are also depicted in Fig. 5.

Catalytic performance on K/MgO-x catalysts

The effect of $c_{\rm K}$ on the methoxycarbonylation of acetone with DMC on K/MgO-x catalysts was also studied in this work and the results of the tests are given in Table 3. They show that acetone conversion increased with the increase in $c_{\rm K}$, but the selectivity of MAA remained almost unchanged for $c_{\rm K}$ up to 1.97 mass % and then it decreased. These results suggested that the addition of a small amount of K could improve MgO activity in the formation of MAA, but high $c_{\rm K}$ exceeding 1.97 mass % caused a decrease in the yield of MAA. In order to clarify the catalytic behaviour of the samples in terms of their surface basic properties, we compared the catalytic performance of the catalysts with the different densities of base sites at low K loadings. A good correlation (linear; correlation coefficient: 0.98677) between the MAA yield and



Fig. 6. The relationship between the yield of MAA and the density of strong base sites in K/MgO at low K loadings.



Fig. 7. FTIR spectra of the reactants adsorbed on K/MgO-1 catalyst: (a) K/MgO-1 pre-treated in vacuum; (b) adsorption of DMC on K/MgO-1 at 250 °C; (c) adsorption of acetone on K/MgO-1 at 250 °C; (d) co-adsorption of DMC and acetone on K/MgO-1 at 250 °C.

the density of strong base sites (a low number of coordination oxygen anions) was obtained (Fig. 6), in contrast to a poor correlation between the yield of MAA and the density of base sites of weak or mediumstrength, which indicated that the formation of MAA was promoted by strong base sites.

Moreover, the doping of MgO with K caused a marked increase in the yield of MOP, which involved O-methylation of acetone with DMC and should be accompanied by the co-generation of CO_2 . As the catalysts were CO_2 -sensitive, the formation of alkali carbonates was very likely, even when the alkali metal content was very low. In the light of the catalytic behaviour of K_2CO_3 (Table 3, last line), the formation of carbonates (which should be more important as the K-loading increased) may provide a rationale for the trend observed in Table 3 (i. e. progressive increase in acetone conversion, decrease in selectivity of MAA and ACA, increase in selectivity of MOP).

The plausible reaction mechanism

In situ FTIR measurement of acetone and DMC adsorbed on K/MgO-1 was carried out in order to investigate the plausible reaction mechanism of acetone with DMC (Fig. 7). The adsorption bands at 2961 cm^{-1} and 1260 cm^{-1} which were observed after the sample was pre-treated under diminished pressure at $500 \,^{\circ}$ C resulted from the evaporation of high vacuum silicone grease in the T-shaped cell. At 250 °C, no adsorption bands were detected with DMC adsorbed on MgO, indicating that DMC was scarcely activated by solid base. However, when acetone was admitted to the cell, bands were detected at 3600 cm⁻¹, 1718 cm⁻¹, and 1227 cm^{-1} , respectively. A broad band at 3600 $\rm cm^{-1}$ could be assigned to the OH stretching vibration due to the formation of acetone bound onto MgO oxygen atoms via H-bonds, while the C=O stretching vibration at 1718 cm^{-1} and the C—C—C stretching vibration at 1227 cm^{-1} indicated that acetone kept its original structure. This illustrated that acetone was activated via the abstraction of H_{α} by base sites, and then acetonyl species were formed on the K/MgO-1 catalyst. The FTIR spectra of co-adsorbed reactants showed the bands at 1726 cm^{-1} and 1765 cm^{-1} , which could be attributed to C=O stretching vibration of ketoesters. The bands at 1175 cm^{-1} and 1195 cm^{-1} , attributed to C—O—C stretching vibration of ester groups, were also detected (Beutel, 1998; Wu et al., 2008). Because DMC was strongly anchored onto K/MgO-1 after evacuation, these new bands suggested the formation of MAA. Therefore, a plausible mechanism for the reaction of acetone with DMC is proposed in Fig. 8. Acetonyl anion was generated by the abstraction of α -proton (H_{α}) from acetone by the base site. The acetonyl anion and proton generated were adsorbed on acidic sites (M^{n+}) and base sites (O^{2-}) on the solid base surface, respectively. Ultimately, the acetonyl anion reacted with the carbonyl group of the DMC molecule, leading to the formation of MAA and methanol.

Conclusions

The methoxycarbonylation of acetone with DMC was investigated with MgO and alkali-promoted MgO as catalysts. The results showed that the addition of alkali metal could improve the activity of MgO, and K was found to be the most efficient agent in promoting this reaction. The content of K up to 1.97 mass % could increase the density of strong base sites of the parent MgO, which played an important role in MAA synthesis, thereby promoting the formation of MAA. High K loadings caused particle agglomeration and the formation of potassium carbonates that blocked the active sites and decreased the yield of MAA. In situ FTIR experiments of reactants co-adsorbed showed that the formation of MAA presumably proceeded via



Fig. 8. Proposed mechanism for the methoxycarbonylation of acetone with DMC.

the abstraction of H_{α} from acetone by base sites. Under optimum conditions, the conversion of acetone and the selectivity of MAA with K/MgO catalyst ($c_{\rm K} = 1.97 \text{ mass \%}$) attained 51.8 % and 49.5 %, respectively.

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