Journal of Catalysis 275 (2010) 257–269

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Methylation of cyclopentadiene on solid base catalysts with different surface acid–base properties

Dongxue Lan, Li Ma, Yuan Chun *, Chen Wu, Linbing Sun, Jianhua Zhu

Key Laboratory of Mesoscopic Chemistry of the Ministry of Education, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 21 June 2010
Revised 9 August 2010
Accepted 12 August 2010
Available online 16 September 2010

Keywords:
Cyclopentadiene
Methylation
Solid base
Magnesium oxide
Potassium hydroxide
Alumina
Reaction mechanism
Deactivation
Methanol
Formaldehyde

ABSTRACT

The methylation of cyclopentadiene with methanol has been studied over Al_2O_3 and KOH promoted MgO and unpromoted MgO. The dehydrogenation of methanol to formaldehyde was found to be a key-step in the generation of the active methylating species on these solid bases. The modification with Al_2O_3 or KOH favors the formation of methylcyclopentadienes and elevates the activity of MgO based on different reasons: introduction of acidic sites for Al_2O_3/MgO and superbasic effect for KOH/MgO. These catalysts present different deactivation behaviors due to the different surface acid–base properties. The heavy coking of cyclopentadiene on basic sites is responsible for the rapid deactivation of KOH/MgO along the catalytic test at 773 K. However, the coking can be well suppressed at 723 K, and KOH/MgO exhibits the catalytic performance apparently superior to MgO and Al_2O_3/MgO.

1. Introduction

The gasoline with high quality is extremely demanded with the development of transportation vehicles manufacturing and stricter regulations on environmental protection. The leaded antiknock additive, which used to be an important component in gasoline, should be replaced by unleaded antiknock additive. Methylcyclopentadienyl manganese tricarbonyl (MMT), as one of the alternate antiknock additives, has the advantage of low cost, improving the octane number and combustion efficiency of gasoline as well as reducing emission pollution [1]. As the precursor of MMT, methylcyclopentadienes (MCPD) can be formed from the petroleum cracking, however, the yield is quite limited. Contrarily, cyclopentadiene (CPD) is a more abundant product, and thus many researchers have endeavored to produce MCPD from the methylation of CPD.

In the earlier studies, the methylation of CPD is realized through the following procedure: CPD reacts first with alkali metal sodium, and the formed cyclopentadienyl sodium then reacts with methyl halides to produce MCPD [2,3]. This method has the advantages of high yield (76–85%) and relative simple post-treatment procedure. It has been used for producing commercial MCPD [4]. However, this process concerns the expensive reactants, such as metal sodium and methyl halides (usually methyl iodide), and must be carried out in liquid ammonia in order to disperse and stabilize sodium. Some researchers attempt to prepare alkylcyclopentadiene with alcohol in the presence of a liquid strong basic catalyst such as potassium or sodium hydroxide or alkoxide [5]. It should be noted that this reaction is still carried out in liquid-phase and only a tarry product can be obtained when methanol is involved. Yoshida et al. [6] report a vapor-phase reaction of CPD with an aliphatic lower alcohol in the presence of a catalyst containing oxides such as an alkaline earth metal oxide or alkali metal oxide. They also utilize the basic zeolites in this process but mainly for producing the multi-alkylated CPD derivatives [7]. Compared with liquid base, the use of solid base has apparent advantages in many aspects, e.g. noncorrosive and environmentally benign. The replacement of liquid-phase catalysis with vapor-phase catalysis allows easier separation of the products as well as the possibility of catalysts regeneration and reuse. Therefore, the vapor-phase methylation of CPD is a very attractive route to prepare MCPD.

Although the catalysts concerned in the patent [6] cover most of the conventional oxide or mixed oxide solid bases, little work has focused on the reaction process. In the previous work, we found

---

* Corresponding author. Fax: +86 25 83317761.
E-mail address: ychun@nju.edu.cn (Y. Chun).

0021-9517/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2010.08.008

that the base strength of catalysts plays a key role in vapor-phase methylation of CPD with methanol [8,9]. In the present work, we have investigated the catalytic behaviors and the deactivation of unpromoted, KOH and Al_2O_3 promoted magnesium oxides in the vapor-phase methylation of CPD with methanol. Our aim is to correlate the catalytic performance in CPD methylation with the nature of catalysts and explore the possible reaction and deactivation mechanisms.

2. Experimental

2.1. Catalyst preparation

KOH and Al_2O_3 promoted MgO catalysts were prepared by impregnation of potassium hydroxide and aluminum nitrate from their aqueous solution, respectively. Typically, a calculated amount of potassium hydroxide or aluminum nitrate was dissolved in 20 mL of distilled water, and then 2 g commercial MgO (Shanghai Chemical Reagent, China, ⩾97.0%) was added into this solution. After stirring at room temperature for 24 h, the mixture was evaporated to remove most of the water in a water bath and then dried at 373 K overnight. The resulting solid was further calcined at 873 K for 2 h to form KOH- or Al_2O_3-modified MgO. These prepared solid bases were denoted as x%KOH/MgO and x%Al_2O_3/MgO, respectively, where x% indicated the mass percentage of KOH or Al_2O_3 in the whole catalysts. For comparison, pure Al_2O_3 was prepared by calcining aluminum nitrate at 873 K for 2 h, and portions of these prepared Al_2O_3 powders were mechanically mixed with MgO powders according to the mass ratio of 10%Al_2O_3 in the whole catalyst, which was denoted as 10%Al_2O_3/MgO(mix).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku, D/max-RA diffractometer with Cu Kα radiation in the 2θ range from 10° to 80°. N_2 adsorption at 77 K was measured using a Micromeritics ASAP 2020 system. Sample was evacuated at 573 K for 4 h prior to testing. Specific surface area of MgO was determined using the Brunauer–Emmett–Teller (BET) equation with adsorption data in the relative pressure range from 0.04 to 0.2. The base strength (H–) of samples was determined using Hammett indicators [10], and sample was activated at 873 K for 1 h in the flow of N_2 (30 mL/min) before contacting with the indicators. Acidity of sample was determined by using temperature-programmed desorption (TPD) of NH_3. Sample (100 mg) was treated in He (50 ml/min) at 873 K for 1 h and 40 ml of NH_3 was injected at room temperature. Weakly adsorbed NH_3 was removed by flowing He at 30 ml/min for 1 h. Temperature was then increased to 873 K at 8 K/min, and the liberated NH_3 was detected by an on-line gas chromatograph with a thermal conductivity detector (TCD) and quantitatively measured by the external standard method. CO_2-TPD measurements were performed in the manner similar to NH_3-TPD measurements, except that CO_2 was injected instead of NH_3. Inductively coupled plasma-optical emission spectrometric (ICP-OES) analysis was performed in JA1100 ICP instrument. X-ray photoelectron spectra (XPS) were acquired from Thermo Fisher scientific K-Alpha spectrometer using a nonmonochromatized Al Kα X-ray source (1486.6 eV). Base pressure in the analysis chamber was maintained in the range of 10^{-9} mbar. Energy resolution of the spectrometer was set at 0.9 eV. The error in the reported binding energy (BE) values is ±0.1 eV. Solid-state ^{13}C MAS nuclear magnetic resonance (NMR) spectrum of spent catalyst was performed on a Bruker advance III NMR spectrometer, operating at a frequency of 100.62 MHz for ^{13}C. To obtain quantitative data, single pulse excitements (SPEs) were used with a 90° pulse length $p_1 = 3.5$ s and a delay time $d_1 = 5.0$ s. The sample was spun in a 7-mm zircon rotor at 6 kHz and 4200 scans. Adamantane was used as external reference for the chemical shift.

2.3. Catalytic testing

The catalytic decomposition of isopropanol or methanol was measured in a conventional flow reactor at atmospheric pressure. The sample (50 mg, 20–40 mesh) was activated at 873 K in the flow of N_2 (30 mL/min) for 1 h and then was cooled to the reaction temperature. The reactant isopropanol (Nanjing Chemical Reagent, China, ⩾99.7%) or methanol (Nanjing Chemical Reagent, China, ⩾99.7%) was introduced using a syringe pump with the space velocity of 1.9 or 0.9 h^{-1} in the flow of N_2 (20 mL/min). The reaction mixture was analyzed by on-line gas chromatography, using a Varian 3700 instrument equipped with a flame ionization detector (FID) and a Propark-T column or a thermal conductivity detector and a TDX-01 column. Conversion was defined as C_i = (moles of substrate reacted per mole of reactant in the feed); yields of H_2, dimethylether (DME) and other product i were defined as Y_{H2} = (-moles of product H_2 formed per 2 moles of reactant in the feed), Y_{DME} = (moles of product DME formed per 0.5 moles of reactant in the feed), Y_i = (moles of product i formed per mole of reactant in the feed), respectively; selectivity was defined as S_i = (moles of product i formed per mole of reactant reacted).

The vapor-phase methylation of CPD with methanol was carried out in a conventional flow reactor at atmospheric pressure [11]. The catalyst (50 mg, 20–40 mesh) was thermally activated at 873 K for 1 h in N_2 and then was cooled to the reaction temperature. CPD was obtained by thermal depolymerization of dicyclopentadiene (Aldrich) at 873 K, and the reactants CPD and methanol (Nanjing Chemical Reagent, China, ⩾99.7%) were introduced by syringe pumps with a molar ratio of 0.9 or 1.8 (space velocity of 1.6 or 2.5 h^{-1}) in the flow of N_2 (20 mL/min). The reaction was carried out in two modes: (1) the reaction was performed at various temperatures with the same reaction time of 10 min, in order to study the effect of temperature on the catalytic activity and (2) the reaction was performed at various times with the same reaction temperature, in order to compare the deactivation rate on different catalysts. The reaction mixture was analyzed by on-line GC (Varian 3700). In situ poisoning experiments were carried out by doping methanol with a certain amount of acetic acid or pyridine, and were ended by repumping pure methanol for reaction. In order to study the regeneration of the deactivated catalyst, the catalyst after reaction was calcined at 873 K for 1 h in the flow of air, and then cooled to the reaction temperature for further reaction. The coking was observed on these catalysts at higher reaction temperatures, and the coking amount varied with the difference in catalysts, temperatures and even the time. In order to better compare the activity of these catalysts in CPD methylation, the calculations of the conversion and product selectivity were irrespective of the contribution of the coking. Thus conversion and selectivity in this reaction were defined as C_i = (moles of substrate reacted per mole of CPD in the feed except what was transformed to the coke deposit) and S_i = (moles of product i formed per mole of CPD reacted), respectively. Carbon balance measurement indicated that this treatment has little effect on the calculated values of conversions in the temperature range of 673–723 K; however, the calculated value is lower than that including the contribution of the coking in the temperature range of 773–823 K, especially for KOH/MgO at a lower reaction time. For example, when the reaction was carried out at 773 K for 10 min on 10%KOH/MgO, 41% of conversion was calculated irrespective of the contribution of the coking, while 68% of conversion was obtained including the contribution of the coking.

3. Results

3.1. The characterization of catalysts

Commercial MgO was used for solid base catalyst, which possesses a BET-specific surface area of 163 m^2/g. The surface acidity and basicity of MgO were modified by introducing various amounts of Al_2O_3 and KOH. Fig. 1 compares the XRD patterns of these catalysts. In the case of the unpromoted MgO, reflections corresponding to both periclase MgO [JCPDS database, entry file: 45-0496] and brucite $Mg(OH)_2$ [JCPDS database, entry file: 07-0239] are present. The appearance of $Mg(OH)_2$ derives from the hydration of MgO during storage. After impregnation of KOH, the catalysts were hydrated, and reflections attributed to periclase MgO disappeared. In fact, the existence of KOH is unnecessary for the hydration of MgO, $Mg(OH)_2$ can also be formed by treating MgO with pure water, as indicated in Fig. 1A. Nevertheless, the XRD patterns of calcined samples correspond overwhelmingly to periclase MgO, indicating that $Mg(OH)_2$ can be completely converted to MgO by the thermal decomposition. The existence of peak at 32.3° with very weak intensity indicates that a small amount of KOH was converted to K_2CO_3 with CO_2 in the air [12,13]. Similarly, the XRD patterns of $Al(NO_3)_3/MgO$ (uncalcined) and Al_2O_3/MgO (calcined) correspond to those of brucite $Mg(OH)_2$ and periclase MgO, respectively, as shown in Fig. 1B. It should be pointed out that no alumina phase can be distinguished from the XRD patterns of these Al_2O_3/MgO samples. One possible reason is that Al_2O_3 is well dispersed on the surfaces of MgO, which possesses relatively larger specific surface area.

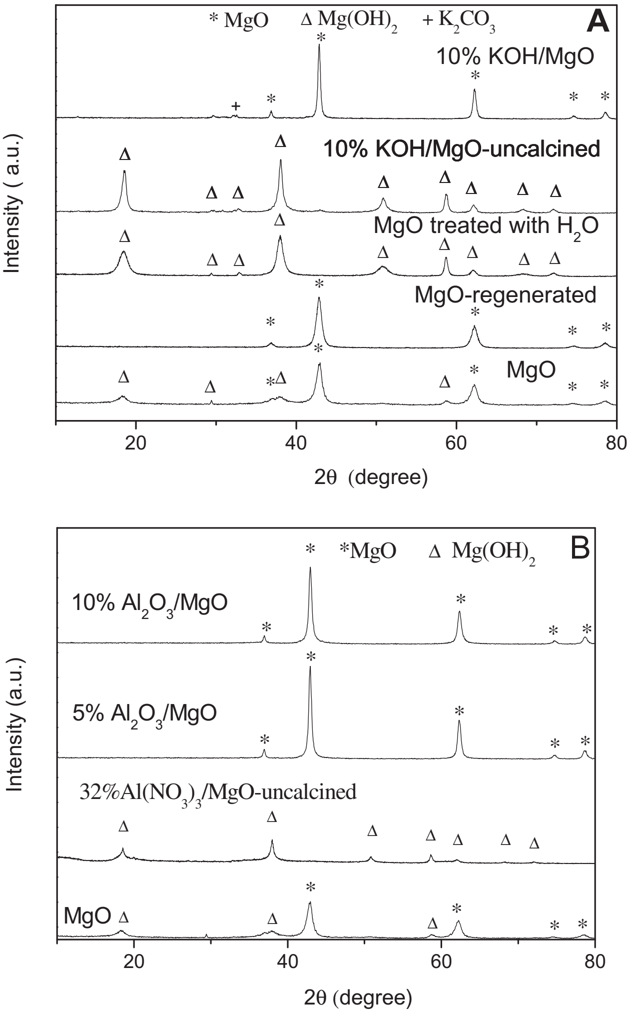


Fig. 1. XRD patterns of MgO and MgO promoted with Al_2O_3 or KOH with various loading amounts under different treatments.

Table 1
Base strength of selected catalysts detected by Hammett indicator.

Catalyst	Base strength (H−)
MgO	18.4
1%KOH/MgO	~26.5
5%KOH/MgO	26.5
10%KOH/MgO	26.5
10%Al_2O_3/MgO	17.2

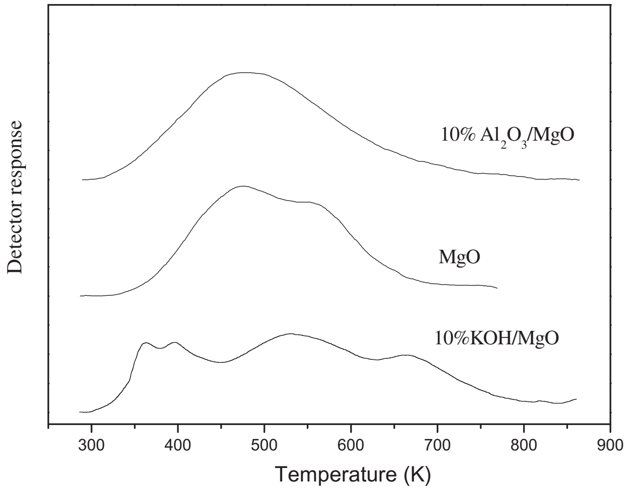


Fig. 2. TPD profiles of CO_2 on MgO, 10%Al_2O_3/MgO and 10%KOH/MgO. CO_2 adsorption at 303 K, 8 K/min heating rate.

Table 1 lists the base strength of selected catalysts. The unpromoted MgO shows a base strength (H−) of 18.4, similar to the result reported in [14]. The base strength (H−) of catalyst increases from 18.4 to 26.5 after loading 5% of KOH, similar to our previous result on KNO_3-loaded MgO [8] and Al_2O_3 [15]. According to Tanabe's definition [16], these KOH/MgO catalysts possess superbasic sites. Contrarily, loading 10% of Al_2O_3 results in the decrease of base strength (H−) from 18.4 to 17.2.

The TPD profiles of CO_2 preadsorbed at room temperature on selected catalysts are presented in Fig. 2. The TPD profile of CO_2 on the unpromoted MgO can be deconvoluted in three desorption peaks with the peak temperature around 390, 470 and 555 K, which are attributed to bicarbonates formed on Brønsted OH groups, bidentate carbonates desorbed from metal–oxygen pairs and unidentate carbonates released from low coordination oxygen anions, respectively [17]. Among them, the desorption peaks around 470 and 555 K are dominant, indicating that its basicity derives mainly from the metal–oxygen pair and low coordination oxygen anion. Few Brønsted OH groups are present on this MgO activated at 873 K. The relative contribution of peaks at 470 and 555 K decreases after loading of 10%Al_2O_3, demonstrating that 10%Al_2O_3/MgO has weaker basicity than the unpromoted MgO. Contrarily, a new desorption peak around 665 K appeared on the TPD profile of CO_2 on 10%KOH/MgO, indicating that this catalyst shows stronger basicity than MgO, in agreement with the result determined using Hammett indicators.

Acidity of MgO, 10%KOH/MgO and 10%Al_2O_3/MgO was investigated by TPD of NH_3 preadsorbed at room temperature, and the result is presented in Fig. 3. The TPD profile of NH_3 on MgO can be

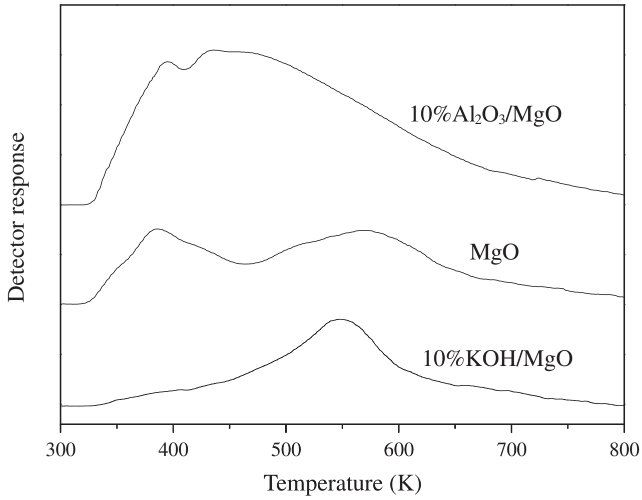


Fig. 3. TPD profiles of NH_3 on MgO, 10%Al_2O_3/MgO and 10%KOH/MgO. NH_3 adsorption at 303 K, 8 K/min heating rate.

Table 2
The catalytic performances in the decomposition of isopropanol and the contents of carbon on catalysts before and after the methylation of CPD at 773 K for 300 min.

Catalyst	On clean surface (%)		On spent surface (%)		
	Y_P[a]	Y_A[b]	Y_P	Y_A	C_C[c]
MgO	2	26	2	26	2.9
10%Al_2O_3/MgO	12	30	16	24	4.7
10%KOH/MgO	2	26	0.1	13	28

[a] Yield of propylene.
[b] Yield of acetone (T = 673 K, p = 101 kPa, space velocity = 1.9 h^{-1}).
[c] Content of carbon determined by elemental analysis.

deconvoluted in two desorption peaks, similar to the report in [17]. The lower temperature peak around 385 K may be attributed to the reversible H-bond adsorption on Brønsted acidic sites, and the higher temperature peak around 570 K may result not only from the irreversible coordinated NH_3 adsorption on Mg^{2+} cations but also from the heterolytic dissociative adsorption leading to NH_2^-–H^+ species on Mg^{2+}–O^{2-} pairs [17,18]. The desorption amount of NH_3 has an apparent decrease after loading of 10%KOH, especially for those preadsorbed on the Brønsted acidic sites. It indicates that the acidity of 10%KOH/MgO is weaker than the unpromoted MgO. While the desorption amount of NH_3 has an apparent increase after loading of 10%Al_2O_3, which mainly results from the contribution of the Brønsted acidic sites on Al_2O_3 [17].

The acid–base properties of unpromoted MgO and MgO promoted with KOH or Al_2O_3 were further investigated by the catalytic decomposition of isopropanol, and the results are listed in Table 2. It is well known that propylene and water are generated on acidic sites, while acetone and hydrogen are formed on basic sites in this probe reaction [11,19]. The conversion of isopropanol and the selectivity to acetone on MgO at 773 K are 28% and 93%, respectively. The high selectivity to acetone indicates that few acidic sites exist on this solid base, similar to the report in [20]. After loading 10% of Al_2O_3, the conversion of isopropanol increases but selectivity to acetone decreases. It indicates that 10%Al_2O_3/MgO sample possesses more acidity compared with MgO, in agreement with the result from TPD of NH_3. The conversion of isopropanol and the selectivity to acetone on 10%KOH/MgO are close to those on unpromoted MgO. This result is surprising since it is well known that KOH has much stronger basicity than MgO. One of the possible reasons is that the dehydrogenation of isopropanol requires weaker basicity [19], acetone is largely formed on the intermediate strong basic sites on this unpromoted MgO, and thus the effect of KOH is not pronounced in this reaction. Another possible reason is the formation of enolate under such strong basic condition, which may react with acetone and finally transform the oligomer species over the catalyst surface. Therefore, actually the KOH/MgO would be, intrinsically, more active, as expected, but the higher activity is quickly suppressed by these parallel reactions, with the final effect to balance each other and to leave a final apparent activity like MgO only.

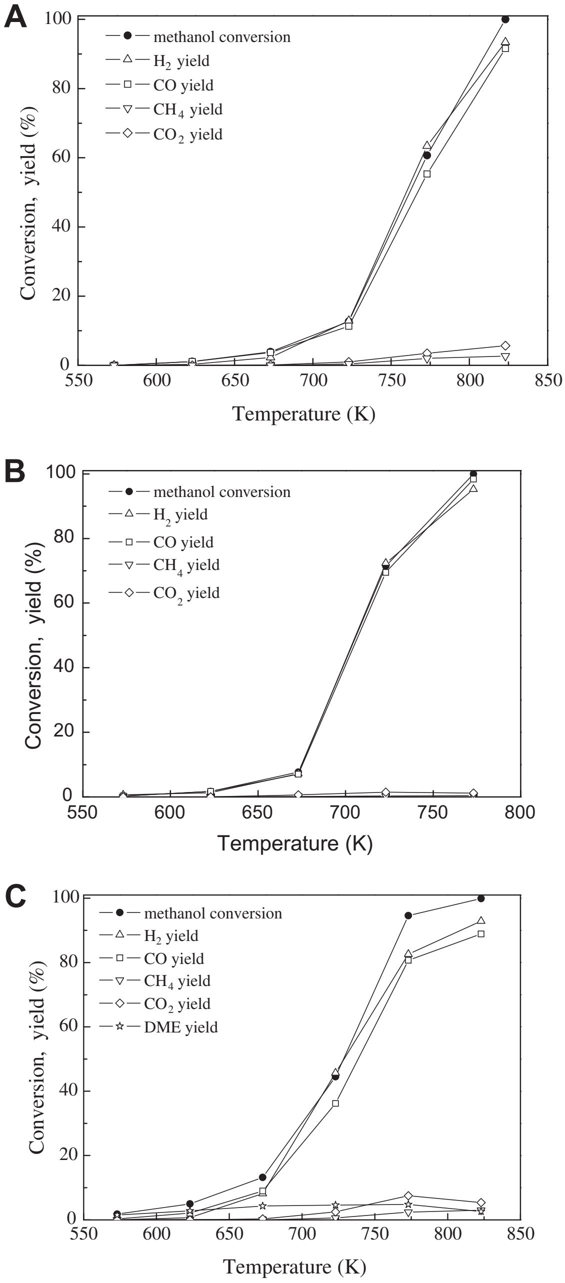


Fig. 4. Conversion of methanol, yields of H_2, CO, CH_4, CO_2 and DME as functions of temperature on (A) MgO, (B) 10%KOH/MgO and (C) 10%Al_2O_3/MgO (space velocity = 0.9 h^{-1}, p = 101 kPa).

3.2. Catalytic decomposition of methanol

The catalytic performances of MgO, 10%Al_2O_3/MgO and 10%KOH/MgO in methanol decomposition are shown in Fig. 4, in which the conversion of methanol and the yields of H_2, CO, CH_4, CO_2 and even DME are reported as functions of reaction temperature.

It can be found that these solid base catalysts exhibit different catalytic activities in methanol decomposition. The decomposition of methanol starts at 623 K on unpromoted MgO; however, the conversion of methanol is lower than 4% at 673 K. An appreciable conversion can be observed at 723 K, which is similar to the report in [21]. The conversion of methanol reaches 100% at 823 K on this catalyst. Apparent increase in conversion is observed on MgO modified with either Al_2O_3 or KOH. It can be found that the conversions reach 95% and 100% at 773 K on 10%Al_2O_3/MgO and 10%KOH/MgO, respectively, which are much higher than 61% on unpromoted MgO. The higher activity of 10%KOH/MgO should be attributed to its stronger basicity compared with MgO, which exhibits stronger dehydrogenating ability. While on 10%Al_2O_3/MgO, the formation of DME and its further transformation may have a certain contribution to the higher conversion of methanol.

As shown in Fig. 4A and B, CO and H_2 are the major products on MgO and 10%KOH/MgO, and the yields of all products increase with temperature. It is well known that H_2 is obtained as a co-product in the formation of C-containing compounds, and several routes of the methanol transformations and the intermediates decomposition have been reported to produce H_2 [21]. The yield of H_2 approximately corresponds to the sum of yields of CO + 1/2CH_4 + 1/2CO_2 at high temperature, indicating that the intermediates, i.e. formaldehyde, formic acid and methylformate, from methanol transformation quickly decompose to the final products. It should be pointed out that the selectivity to CO is over 88% among the C-containing products under the conditions used for catalytic tests, and the formation of CH_4 is almost ignorable. This result seems to suggest that most of the formaldehyde, which derives from methanol dehydrogenation, directly decomposes to CO and H_2. Less formic acid and methylformate are formed on these catalysts since the decomposition of these intermediates would produce CO_2 and/or CH_4 [21].

Due to the existence of a certain amount of the acidic sites, dehydration of methanol also occurs on 10%Al_2O_3/MgO, and the products DME may further transform to alkylbenzenes [21,22]. It is reported that alkylaromatics are the prevailing compounds on H-mordenite in the temperature range comprised between 523 and 623 K [21]. However, less alkylaromatics are formed on 10%Al_2O_3/MgO, since the acidity of this catalyst is apparently weaker than that of acidic zeolites. As shown in Fig. 4C, DME is the prevailing product on 10%Al_2O_3/MgO at 573 K. The yield of CO dramatically increases with temperature, and CO becomes the main product at a temperature higher than 623 K. Similar to the result on MgO and 10%KOH/MgO, the yield of H_2 approximately corresponds to the sum of yields of CO + 1/2CH_4 + 1/2CO_2 at high temperature on 10%Al_2O_3/MgO, and yield of CO is much higher than those of CH_4 and CO_2. It indicates that the formation of the light compounds undergoes a similar reaction process on these solid base catalysts.

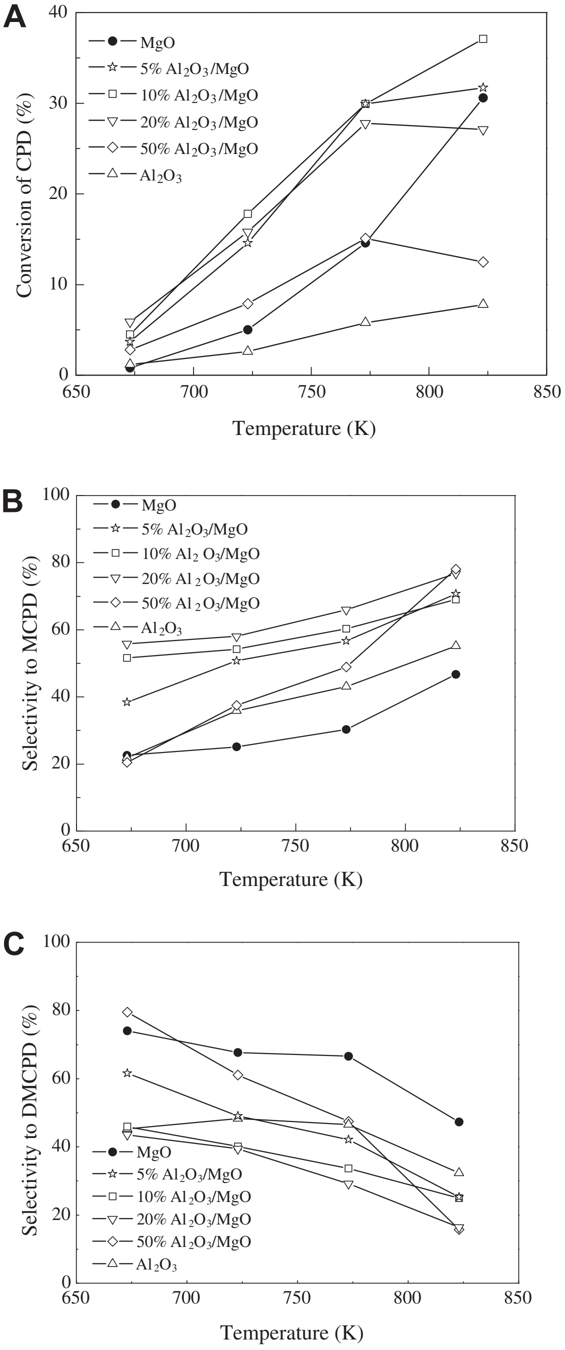


Fig. 5. (A) Conversion of CPD, (B and C) selectivity to MCPD and DMCPD, respectively, with methanol/CPD ratio of 1.8 (space velocity = 2.5 h^{-1}) as functions of temperature on MgO promoted with various amounts of Al_2O_3 (p = 101 kPa).

3.3. Methylation of CPD with methanol

The catalytic performances of MgO and Al_2O_3 or KOH promoted MgO in CPD methylation are shown in Figs. 5–7, in which the conversion of CPD and the selectivity to MCPD and dimethylcyclopentadienes (DMCPD) are reported as functions of reaction temperature.

The target product of this reaction is MCPD, and by-products consist mainly of DMCPD, accompanied with small amount of hydrogenated products (i.e. cyclopentene, cyclopentane, methylcyclopentene, and dimethylcyclopentene). The sum of yields of these hydrogenated products on these catalysts is lower than 1% in the temperature range of 673–773 K and may reach 1–2% at 823 K. Some light compounds, e.g. CO, CH_4, CO_2 and H_2, can also be produced by the decomposition of methanol. The conversion of CPD is only 1.4% at 673 K on the unpromoted MgO, as shown in Fig. 5A. With the increase in reaction temperature, the conversion of CPD increases and reaches 24% at 823 K. This unpromoted MgO shows poor selectivity to MCPD and higher selectivity to DMCPD at lower temperature, e.g. the selectivity to MCPD and DMCPD are 23% and 74%, respectively, at 673 K. Higher temperature favors the formation of MCPD, and the selectivity to MCPD reaches 47% at 823 K.

The catalytic performances on Al_2O_3 promoted MgO are shown in Fig. 5, which are plotted as functions of reaction temperature. Generally, the conversion curves on these solid bases present the similar tendency to that on the unpromoted MgO. Modification

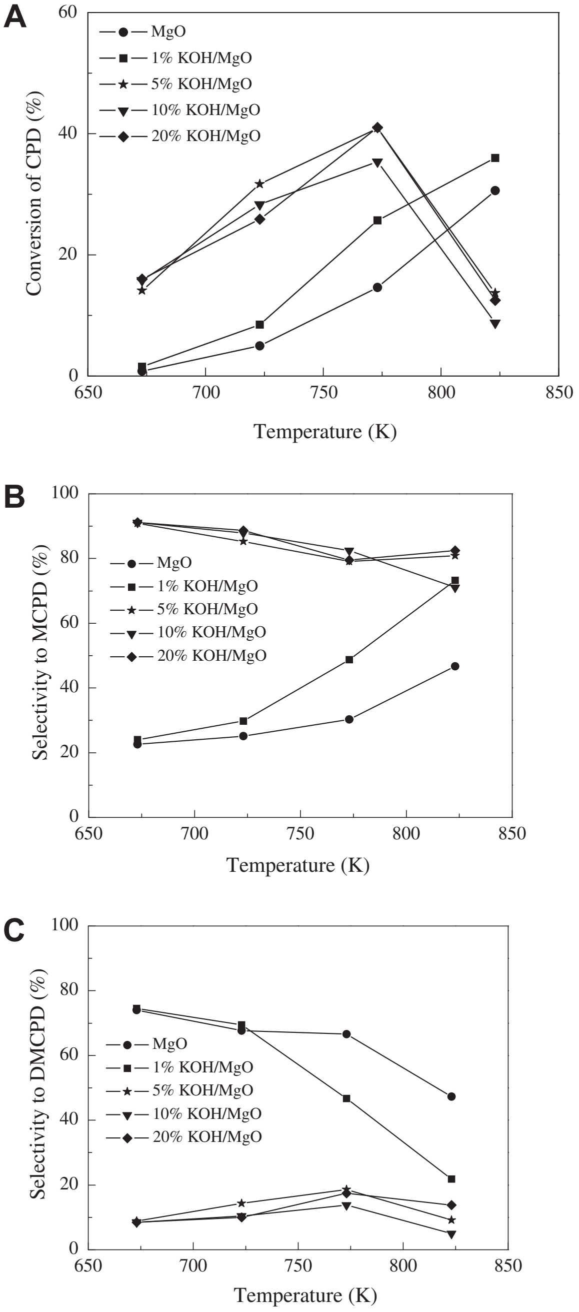


Fig. 6. (A) Conversion of CPD, (B and C) selectivity to MCPD and DMCPD, respectively, with methanol/CPD ratio of 1.8 (space velocity = 2.5 h^{-1}) as functions of temperature on MgO promoted with various amounts of KOH (p = 101 kPa).

with Al_2O_3 can enhance the conversion at lower temperature, however, the conversion decreases apparently when loading amount exceeds 20%, as indicated in Fig. 5A. On the other hand, the selectivity to MCPD almost linearly increases and the selectivity to DMCPD decreases accordingly, when the loading amount of Al_2O_3 increases from 5% to 20% (Fig. 5B and C). It is reasonable to suggest that the introduction of Al_2O_3 can suppress the deep methylation of MCPD. The selectivity to MCPD decreases dramatically when the loading amount of Al_2O_3 exceeds 20%, demonstrating that overloading Al_2O_3 is disadvantageous for the formation of MCPD. Therefore, the appropriate loading amount of Al_2O_3 is between 10% and 20% in order to obtain the optimal catalytic performance.

The catalytic performances on KOH promoted MgO are shown in Fig. 6, which are plotted as functions of reaction temperature.

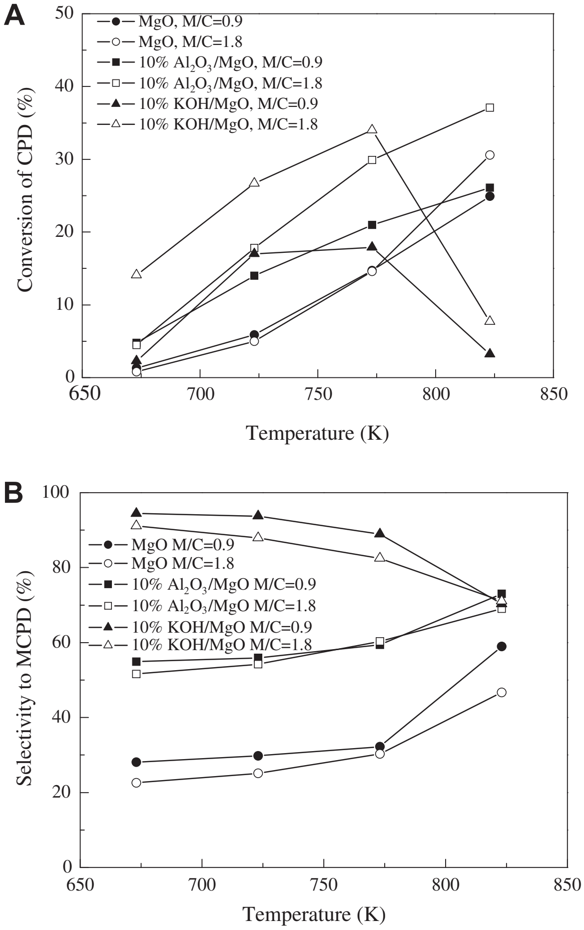


Fig. 7. (A) Conversion of CPD and (B) selectivity to MCPD with methanol/CPD ratio of 0.9 and 1.8 (space velocity was 1.6 and 2.5 h^{-1}, respectively) as functions of temperature on unpromoted MgO, 10%Al_2O_3/MgO and 10%KOH/MgO (p = 101 kPa).

The highest conversion appears at 823 K on 1%KOH/MgO. However, when the loading amount of KOH reaches 5%, the conversion of CPD declines at temperature higher than 773 K. Catalysts containing 5–20%KOH exhibit the similar activity at the same reaction condition and 80–90% of products are MCPD, while prevailing product on the unpromoted MgO is DMCPD at a temperature lower than 823 K. The existence of KOH greatly enhances the selectivity to MCPD, i.e. suppresses the deep methylation of MCPD. These results seem to suggest that the methylation of CPD is dominated by KOH species when its loading amount reaches 5%.

Fig. 7A and B shows the effect of the dosage ratio of methanol and CPD on the catalytic performance of these solid bases. Higher dosage of methanol favors the methylation of CPD, especially for KOH promoted MgO. The conversion is doubled (e.g. from 16% to 34% at 773 K) on 10%KOH/MgO when the dosage ratio of methanol and CPD increases from 0.9 to 1.8. On the other hand, lower dosage of methanol favors the formation of MCPD. However, the effect of the dosage ratio of methanol and CPD on selectivity is not as pronounced as on conversion. The selectivity curves present a similar tendency on each catalyst when different dosage ratios of the two reactants are fed.

3.4. Deactivation of catalysts

Fig. 8 illustrates the time-on-stream behaviors of these promoted and unpromoted MgO catalysts during the methylation of CPD. Generally, different deactivation behaviors can be observed on these solid bases. As shown in Fig. 8A, the activity of MgO increases slightly along the catalytic test, while the activities of Al_2O_3/MgO and KOH/MgO decrease apparently. It can be found that the conversion of CPD on 10%Al_2O_3/MgO drops gradually from 25% to 18% in 300-min run at 773 K. The deactivation of 10%KOH/MgO is more serious than that of 10%Al_2O_3/MgO at 773 K. About 80% of the initial activity is lost on 10%KOH/MgO in 120-min run, and the conversion of CPD is only 4% in 300-min run. The final conversion follows the order MgO > 10%Al_2O_3/MgO > 10%KOH/MgO, which is just the reverse of the order for the initial conversion. As shown in Fig. 8B and C, the change is not pronounced for the selectivity to MCPD and DMCPD as a function of time at 773 K on 10%Al_2O_3/MgO or 10%KOH/MgO. However, the selectivity to MCPD on unpromoted MgO increases progressively along the catalytic test and is doubled in 300-min run, and the selectivity to DMCPD decreases accordingly. This is obviously different from most of the base catalytic processes [23,24]. Fig. 8 also depicts the time-on-stream behavior of 10%Al_2O_3/MgO(mix), which was prepared by mechanically mixing MgO with 10%Al_2O_3. It clearly shows that both the activity of this mixed sample and the selectivity to MCPD increase along the catalytic test, which is like the result on the unpromoted MgO rather than on 10%Al_2O_3/MgO (prepared by impregnation of aluminum nitrate). Therefore, the preparation method has the apparent effect on the catalytic performance of Al_2O_3/MgO.

The deactivation curves at 723 K as functions of time are given in Fig. 8D–F. The conversion of CPD diminishes gradually on 10%Al_2O_3/MgO and increases a little on the unpromoted MgO along the catalytic test. It is important to note that the deactivation of

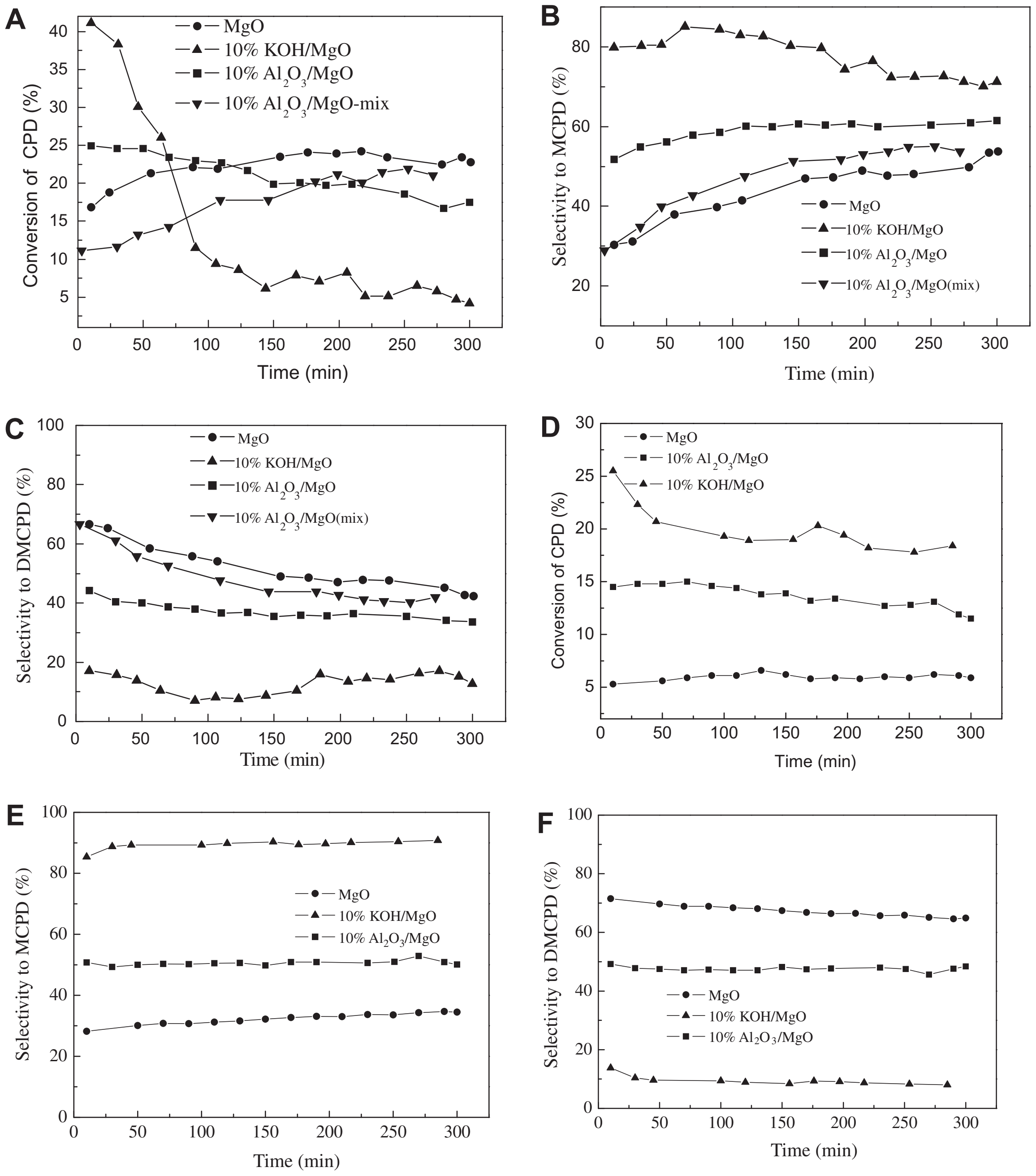


Fig. 8. (A–C) Conversion of CPD, selectivity to MCPD and DMCPD, respectively, at 773 K; (D–F) conversion of CPD, selectivity to MCPD and DMCPD, respectively, at 723 K as functions of time on unpromoted MgO, 10%Al_2O_3/MgO and 10%KOH/MgO (methanol/CPD = 1.8, space velocity = 2.5 h^{-1}, p = 101 kPa).

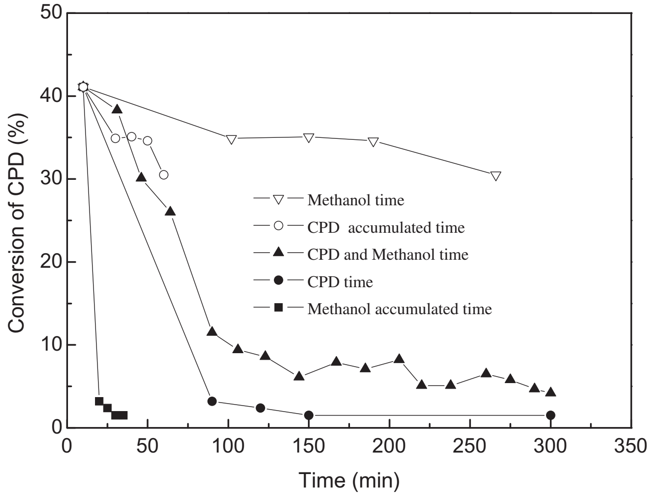


Fig. 9. Conversion of CPD as functions of contacting time of the reactants on 10%KOH/MgO based on various feeding modes: feeding methanol continuously and CPD intermittently (▽○), feeding CPD continuously and methanol intermittently(●■) and feeding both CPD and methanol continuously (▲) (T = 773 K, methanol/CPD = 1.8, space velocity = 2.5 h^{-1}, p = 101 kPa).

Table 3
Surface characterization (XPS) of the fresh and spent 10%KOH/MgO catalyst.

Catalyst	Binding Energy (eV)			K/Mg
	O 1s	Mg 2p	K $2p_{3/2}$	(Atomic ratio)
10%KOH/MgO-fresh	530.6	49.6	293.2	0.09
10%KOH/MgO-spent	531.4	49.9	293.5	2.6

10%KOH/MgO is suppressed apparently at this temperature, only 22% of its initial activity is lost in 300-min run; while at 773 K, over 90% is lost. Therefore, the final conversion of CPD follows the order of 10%KOH/MgO > 10%Al_2O_3/MgO > MgO, which is the same as the initial one. Furthermore, it can be found from Fig. 8E and F that the selectivities to MCPD and DMCPD on these catalysts keep nearly constant throughout the test at 723 K.

In order to distinguish the effects of methanol and CPD to the deactivation of catalyst, the methylation of CPD was carried out in two feeding modes: (1) methanol was continuously fed into reaction system while CPD was introduced at long intervals and (2) CPD was continuously fed into reaction system while methanol was introduced at long intervals. Fig. 9 depicts the time-on-stream behavior of 10%KOH/MgO based on these two feeding modes at 773 K. It shows that the conversion of CPD is still close to 30% after feeding methanol continually for 266 min in the first feeding mode, which is far higher than that of 4% detected at the same reaction time when methanol and CPD are co-fed. In fact, even the decrease in conversion in the first feeding mode can be ascribed to the effect of CPD, since the conversion trend based on CPD accumulated time in this feeding mode is very similar to that in ordinary co-feeding mode. Contrarily, the conversion of CPD drops more rapidly via both CPD time and methanol accumulated time, if the second feeding mode is used. It indicates that the deactivation rate of KOH/MgO is faster if feeding CPD only. Therefore, the deactivation of 10%KOH/MgO derives from the CPD transformation.

Table 3 gives the BE values and the surface atomic ratios of the fresh and spent 10%KOH/MgO catalyst. The BE value associated with O 1s for the spent catalyst is apparently lower than that of the fresh one (530.6 vs 531.4 eV), while the shift of the BE value of Mg 2p or K $2p_{3/2}$ is not pronounced. On the other hand, the spent 10%KOH/MgO possesses much higher surface atomic ratio of K/Mg than the fresh one (2.6 vs 0.09), indicating that the surface of catalyst is enriched with K after the methylation of CPD. This phenomenon has also been observed on KNO_3 promoted MgO for O-methylation of dihydroxybenzenes [25] and soot combustion [12].

The solid-state ^{13}C MAS-NMR spectrum of spent 10%KOH/MgO catalyst is shown in Fig. 10. The NMR spectrum of spent 10%KOH/MgO mainly exhibits two broad peaks in the chemical shift range 110–220 ppm centered at 134.2 and 170.7 ppm, respectively. It is well known that the broad peak in NMR indicates that the structures in the coke deposits are mainly condensed carbonaceous materials [26]. The peak centered at 134.2 ppm corresponds to the resonances of aromatics, which is possibly ascribed to carbon bridges between aromatic rings (130–140 ppm) or substituted aromatic carbons (135–150 ppm) [26–28]. The peak centered at 170.7 ppm corresponds to carboxyl [28]. Other peaks in the 10–100 ppm region might be distinguished from the NMR spectrum, which can be ascribed to aliphatics. Nevertheless, their intensities are very weak. Therefore, the coke deposit on spent 10%KOH/MgO comprises mainly of the polycyclic aromatic products.

3.5. Poisoning test of catalysts

In order to further investigate the catalytic behaviors of these solid bases in the methylation of CPD, acetic acid and pyridine were used to poison the basic sites and acidic sites during the reaction, respectively, and the results are plotted in Figs. 11 and 12. As shown in Fig. 11, the conversion of CPD maintains around 25% after co-feeding of pyridine on the unpromoted MgO, however, approximate 50% of the activity is lost during co-feeding of acetic acid. When acetic acid is removed from the feed stream, the conversion of CPD is recovered. On the other hand, co-feeding of pyridine elevates the selectivity to MCPD approximately from 45% to 60%. The selectivity to MCPD maintains about 64% when pyridine is removed from the feed stream, suggesting that the effect of pyridine is permanent. While the selectivity to MCPD decreases a little during co-feeding of acetic acid, it can be recovered by stopping acetic acid feeding, indicating that the effect of acetic acid is temporary. In the case of 10%Al_2O_3/MgO, both co-feeding of pyridine and acetic acid can decrease the activity of catalyst to a certain extent, and the effect of acetic acid is more pronounced. The conversion can be recovered in both cases by removing the poison from the feed stream. The selectivity to MCPD presents different variations in pyridine and acetic acid poisoning on this catalyst. Pyridine poisoning has little effect on the selectivity to MCPD, while acetic acid poisoning decreases the selectivity dramatically, and it can be

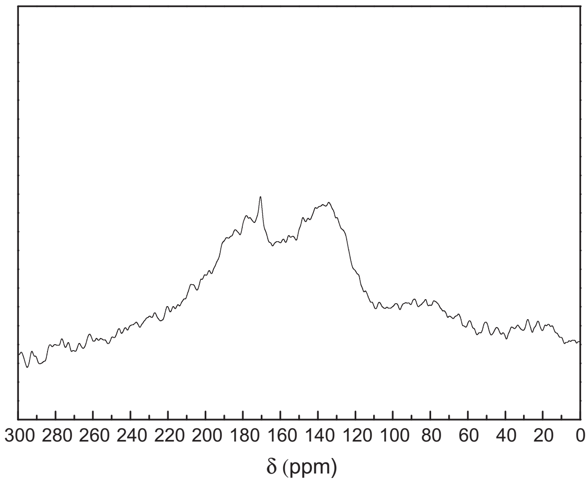


Fig. 10. Solid-state ^{13}C MAS NMR of spent 10%KOH/MgO catalyst.

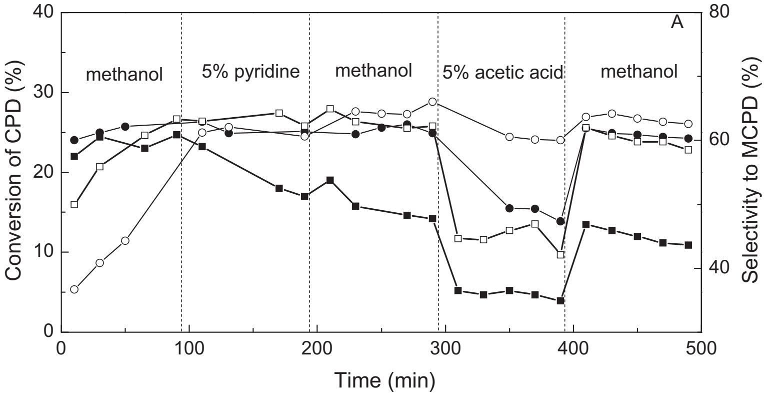


Fig. 11. Conversion of CPD (●■) and selectivity to MCPD (○□)as functions of time on unpromoted MgO (●○) and 10%Al_2O_3/MgO (■□). Effect of the addition of pyridine and acetic acid (T = 773 K, methanol/CPD = 1.8, space velocity = 2.5 h^{-1}, p = 101 kPa).

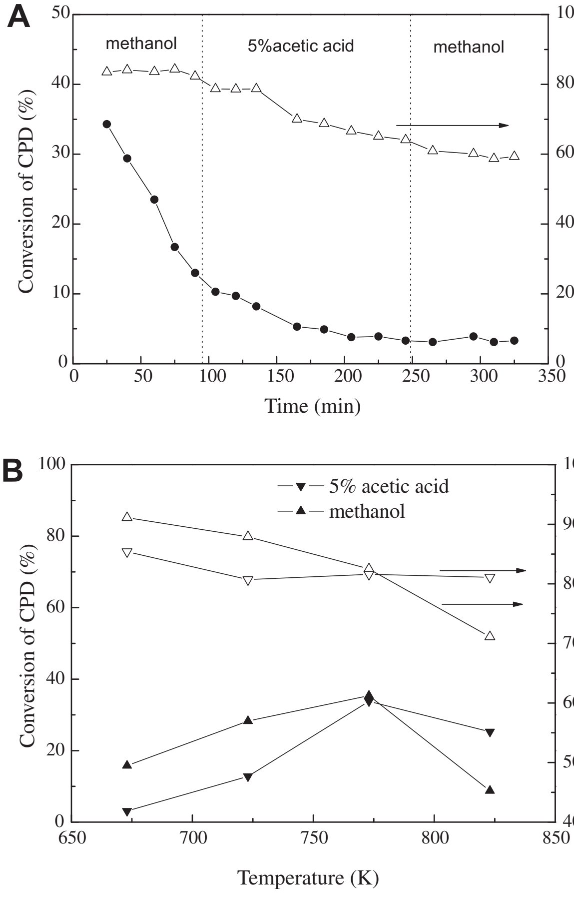


Fig. 12. Conversion of CPD and selectivity to MCPD (A) as functions of time at 773 K; (B) as functions of temperature in 10-min run on 10%KOH/MgO. Effect of the addition of acetic acid (methanol/CPD = 1.8, space velocity = 2.5 h^{-1}, p = 101 kPa).

recovered by removing acetic acid from the feed stream. Since 10%KOH/MgO possesses superbasicity, only the acid poisoning test was carried out. As shown in Fig. 12A, co-feeding of acetic acid does not alter the conversion curve tendency apparently, which is different from the forenamed results. Considering that the deactivation of this catalyst is too fast at this temperature before introducing acetic acid, the effect of acid poisoning may be enshrouded. Therefore, the conversions were further compared at different temperatures with or without co-feeding of acetic acid on this catalyst. As shown in Fig. 12B, the conversion of CPD and the selectivity to MCPD on 10%KOH/MgO diminish with co-feeding of acetic acid at temperature below 773 K, but it is surprising to find that when the temperature is higher than 773 K, both the activity and selectivity increase. It seems that introducing acetic acid is helpful in lowering the deactivation rate of KOH/MgO at high temperature.

3.6. Methylation of CPD with formaldehyde

The methylation of CPD with formaldehyde was also carried out on these solid bases. Due to the difficulty to handle pure formaldehyde, formalin, which contains ca. 38% of formaldehyde, was used for this reaction. Accordingly, 38% methanol aqueous solution was employed for the comparison. Fig. 13 depicts the catalytic performance of unpromoted MgO, 10%Al_2O_3/MgO and 10%KOH/MgO on this reaction.

It can be found that the conversion of CPD (e.g. 4.5% at 773 K) on unpromoted MgO with 38% of methanol is apparently lower than that with pure methanol (e.g. 14.6% at 773 K), which can be ascribed to the effect of water. Replacing 38% methanol with formalin (38% of formaldehyde) elevates the conversion of CPD on MgO to a great extent, e.g. the conversion of CPD increases dramatically from 0.3% to 13.1% at 673 K. It indicates that formaldehyde is a more active methylating agent in CPD methylation. A similar change can be observed on 10%Al_2O_3/MgO when formalin is used as methylating agent instead of 38% methanol. As for 10%KOH/MgO, the conversion of CPD with formalin has an apparent increase at lower temperature compared to that with 38% methanol. However, a dramatic decrease in conversion is observed at a temperature higher than 723 K, which can be ascribed to the rapid decomposition of formaldehyde at this higher temperature, since this catalyst exhibits superbasicity. The selectivity to MCPD also increases to a certain extent on unpromoted MgO and 10%Al_2O_3/MgO, while it decreases a little on 10%KOH/MgO, when formalin is used as methylating agent instead of 38% methanol. Nevertheless, the selectivity curves with temperature present the similar tendency using both of the methylating agents.

4. Discussion

4.1. The role of methanol in CPD methylation

A lot of work has been done on the transformation of methanol on basic catalysts [21,29–36]. Chemisorption of methanol occurs via heterolytic dissociation [37], involving the formation of hydroxyl groups and CH_3O^- anions [34]. Formate and methoxy species occur via a nucleophilic attack reaction with intermolecular dis-

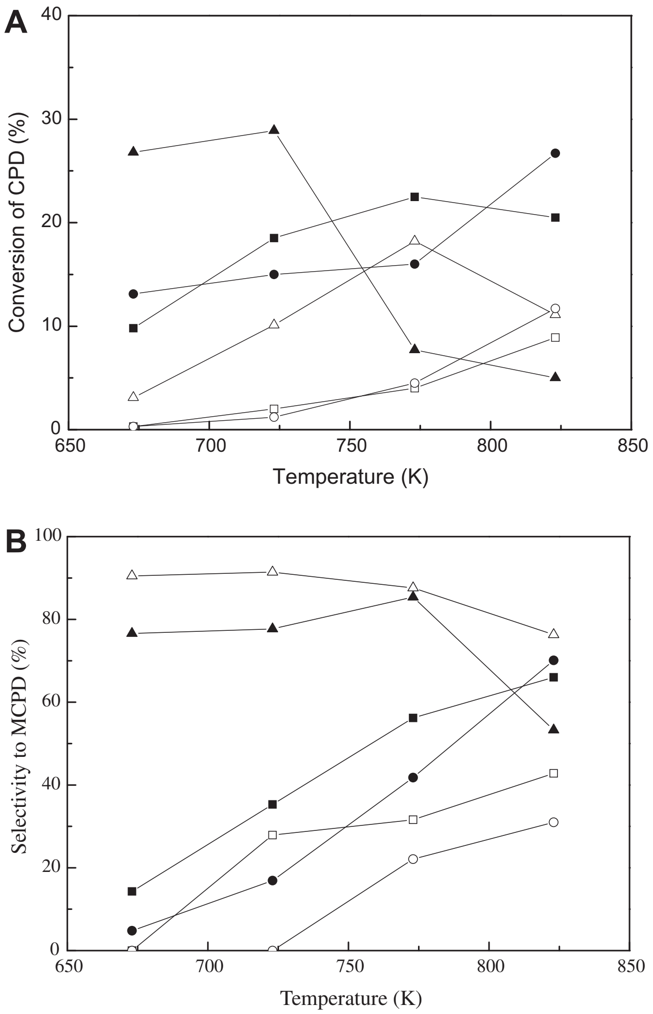


Fig. 13. (A) Conversion of CPD and (B) selectivity to MCPD, respectively, as functions of temperature on unpromoted MgO (●○), 10%Al_2O_3/MgO (■□) and 10%KOH/MgO (▲△) with 38% methanol solution (○□△) and formalin (●■▲) as the methylating agents, respectively (methylating agent/CPD = 1.8, space velocity = 2.5 h^{-1}, p = 101 kPa).

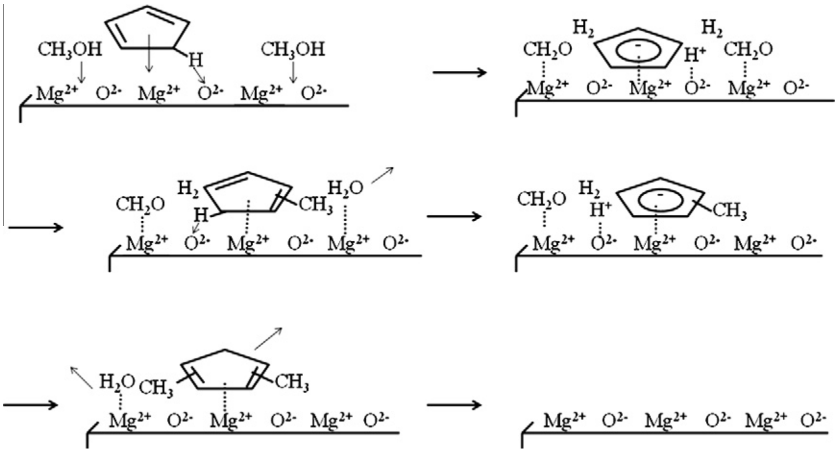
proportionation [38,39]. The formate may finally decompose to CO and H_2. The reactions between the adsorbed methoxy and formate species or by direct dimerization of adsorbed formaldehyde (Tischenko reaction) may yield methylformate, which finally decomposes at high temperatures to methane and CO_2 [40]. Therefore, several light products (CO, CH_4, CO_2 and H_2) can be detected via these reactions [21,41].

Formaldehyde plays an important role during the alkylation of toluene or ethylbenzene with methanol [20,42,43]. It is generally accepted that methanol is dehydrogenated to formaldehyde and it is formaldehyde that serves as the alkylation agent to form styrene [20,44]. Although the mechanism of reaction between phenol and methanol catalyzed by basic oxides is usually believed to occur by a direct electrophilic substitution on the aromatic ring, recent studies [21,41,45,46] indicate that the dehydrogenation of alcohol is also very important to the alkylation of phenol on MgO. Ballarini et al. [21,45] suggest that the true methylating agent is formaldehyde or some compound formed by transformation of formaldehyde itself rather than methanol in phenol methylation, based on their observation that the conversion of phenol begins exactly when the conversion of methanol to light compounds starts. Cavani et al. [41] take in situ IR technique combined with computational studies of sorbed molecules to further confirm this reaction mechanism. In the current reaction, CPD is slightly converted to the products at 673 K on MgO, and the conversion of CPD greatly increases along with the increase in reaction temperature. This variation is very similar to that in the formation of light compounds from methanol on MgO (Fig. 4A). The yield of H_2 is observed approximately corresponding to the sum of yields of CO + 1/2CH_4 + 1/2CO_2 (i.e. the amount of H_2 produced approximately corresponds to the sum of 2CO + CH_4 + CO_2), and the yield of CO is much higher than CH_4 and CO_2 on MgO, which indicates that formaldehyde is formed on this catalyst and further decomposes to light products. Therefore, it is reasonable to suggest that the dehydrogenation of methanol is also an important step in CPD methylation. The reaction result in CPD methylation with formaldehyde also supports this hypothesis. Replacing 38% methanol with formalin can elevate the conversion of CPD on MgO to a great extent, as indicated in Fig. 13. Therefore, the likely formation of formaldehyde could promote the methylation of CPD with methanol on MgO. This hypothesis is also supported by the comparison of the catalytic activities in CPD methylation and methanol decomposition on different catalysts. Compared with MgO, 10%KOH/MgO is more active in methanol decomposition (Fig. 4), and it also shows higher activity in CPD methylation (Fig. 6). Moreover, both 10%KOH/MgO and 10%Al_2O_3/MgO exhibit the catalytic performances in CPD methylation with formaldehyde superior to those with methanol in the temperature range of 673–723 K (Fig. 13), indicating that formaldehyde may play an important role in the conversion of CPD on all these solid base catalysts.

4.2. The role of acidic sites and basic sites in CPD methylation

In the methylation of CPD with methanol, loading Al_2O_3 or KOH can greatly elevate the catalytic performance of MgO in the temperature range of 673–773 K, as indicated in Figs. 5 and 6. However, their modifications bring totally different effects on the surface properties. MgO possesses moderately strong basicity (H– = 18.4) and weak acidity (see Tables 1 and 2 and Figs. 2 and 3). No Brønsted acidic sites exist on this conventional solid base [20]. Loading Al_2O_3 enhances the acidity of MgO apparently and decreases the base strength a little; while the modification of KOH generates some superbasic sites, so it is unreasonable to assume that they follow the same catalytic mechanism. It has been discussed above that CPD reacts more efficiently with formaldehyde, which is likely to be formed by the dehydrogenation of methanol on the basic sites. Due to relatively weaker basicity, few methanol molecules are dehydrogenated on MgO at lower temperature (e.g. 673 K), and accordingly, few products are formed. Spoto et al. [47] reported that CPD can be dissociated into cyclopentadienyl anions on MgO; however, this heterolytic dissociation of C–H bond preferentially occurs on the less frequent defective sites (e.g. sites located on or near the steps), the equivalent $Mg^{2+}O^{2-}$ pairs of the dominant {1 0 0} faces are inactive in CPD dissociation. As a result, few CPD molecules are dissociated on this catalyst at lower temperature. It might be another reason why MgO shows lower activity in CPD methylation.

Al_2O_3/MgO contains a certain amount of the basic and acidic sites, and both of them play the important roles in CPD methylation, as inferred from the higher activity on this catalyst compared with pure MgO and Al_2O_3, and the lower activity during acetic acid or pyridine poisoning (Fig. 11). It is well known that side chain alkylation of toluene with methanol follows a co-operative action of acid/base pairs [43,44,48]. Taking into account the similarity of both reactions, it is reasonable to assume that the methylation of CPD with methanol obeys a co-operative action of acid/base pairs on Al_2O_3/MgO. It is important to note that the mechanically mixed MgO with Al_2O_3 exhibits the catalytic behavior like unpromoted MgO rather than Al_2O_3/MgO prepared by impregnation of alumi-



Scheme 1. Proposed reaction mechanism for the methylation of CPD on MgO.

num nitrate, which should be ascribed to the different dispersion state of Al_2O_3 on MgO. It is well known that the interaction between Al_2O_3 and MgO on the mechanically mixed catalyst is far weaker than that prepared by impregnation method, and Al_2O_3 can be highly dispersed on the surface of MgO via the impregnation route [49]. Based on the reaction result in Fig. 8, highly dispersed acidic species around the basic sites on MgO are required for this reaction, not only by the simple makeup of MgO and Al_2O_3. In fact, 10%Al_2O_3/MgO(mix) shows the activity inferior to MgO due to the decrease in MgO content in catalyst. The highly dispersed acidic species can activate methanol or formaldehyde, and make it easier to react with CPD adsorbed even on {1 0 0} faces of MgO catalyst, and thus elevate the activity of catalyst. The surface nature of catalyst becomes more and more like the property of coating layer when the loading amount exceeds 20%, thus catalysts with high loading amount of Al_2O_3 show poor catalytic performance in CPD methylation.

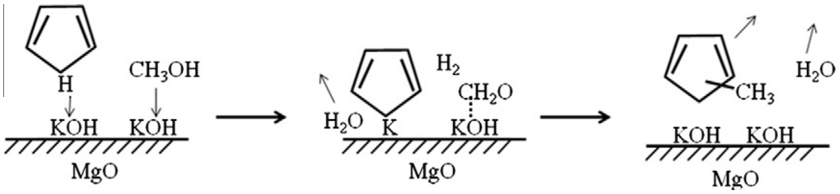
The acidity is very weak and some superbasic sites are formed on KOH/MgO. This catalyst exhibits stronger dehydrogenation ability, and more CPD and methanol are then converted to cyclopentadienyl potassium and formaldehyde, respectively, at lower temperature. It is helpful to the methylation of CPD. The XPS result supports this suggestion. As shown in Table 3, the surface K content on the spent 10%KOH/MgO catalyst is much higher than that on the fresh one. This significant surface segregation of K should be ascribed to the formation of cyclopentadienyl potassium, similar to the liquid-phase methylation of CPD with methylating agent, e.g. CH_3I, under the existence of strong base, e.g. $NaNH_2$ [2,3,50]. Although the basicity of KOH is weaker than that of $NaNH_2$ and methanol (or formaldehyde) is not as active as CH_3I, higher reaction temperature used in this vapor-phase catalysis enables the considerable conversion of CPD. These KOH/MgO samples exhibit the catalytic performance like KOH rather than MgO in CPD methylation except for 1%KOH/MgO, in which the surface of MgO is not fully covered by KOH and thus both the catalytic behaviors of MgO and KOH are observed (Fig. 6). When the whole surface of MgO is covered by KOH, the resulting KOH/MgO should have the similar catalytic performance. It can explain why the similar reaction results are observed on KOH/MgO with the loading amount between 5% and 20%, as indicated in Fig. 6.

The difference of active sites also brings about the dramatic change of selectivities to MCPD and DMCPD on these catalysts. Scheme 1 explains the high selectivity to DMCPD on MgO at lower temperature, which is proposed according to the reports on the alkylation of aniline [51] and toluene [43,48] with methanol on MgO. During the reaction, formaldehyde is formed on the stronger basic sites, e.g. the O^{2-} sites on or near the steps, at lower temperature (e.g. 673 K). The heterolytic dissociation of CPD also occurs on these stronger basic sites and Mg^{2+} sites stabilize the formed cyclopentadienyl anions. Due to the stronger interaction between cyclopentadienyl and Mg^{2+}, the formed MCPD is readily dissociated on the nearby O^{2-} sites (as indicated in Scheme 1) and further converted to DMCPD. Therefore, MgO shows poor selectivity to MCPD and high selectivity to DMCPD at lower temperature. With the increase in reaction temperature, desorption of MCPD from the Mg^{2+} sites speeds up, thus the deep methylation of MCPD is weakened. Unlike MgO, KOH/MgO catalyzes the methylation of CPD via a mechanism more like the liquid-phase reaction (Scheme 2), and the actual active sites derive mainly from KOH. CPD first reacts with KOH and is converted to cyclopentadienyl potassium, and then reacts with formaldehyde (or methanol) to form MCPD. Because the formed intermediate is unbounded on Mg^{2+} and O^{2-} sites of MgO, product MCPD can be easily taken away with carrier gas and has little chance to take the further reaction. Therefore, high selectivity to MCPD is observed on KOH/MgO. As for Al_2O_3/MgO, introducing Al_2O_3 provides highly dispersed acidic species around the basic sites on MgO to activate formaldehyde (or methanol), which enables some weaker basic sites on {1 0 0} faces of MgO to take part in this reaction. Because only limited amount of methylating agents can be activated, the MCPD formed on {1 0 0} faces of MgO is relatively difficult to be converted into DMCPD, and thus Al_2O_3/MgO also exhibits higher selectivity to MCPD compared with MgO.

4.3. Deactivation of catalysts

Different deactivation behaviors are observed on MgO, Al_2O_3/MgO and KOH/MgO in vapor-phase methylation of CPD with methanol. In order to better understand the change of catalyst nature after this methylation reaction, the elemental analysis and catalytic decomposition of isopropanol were employed to detect the coking extent on spent catalysts and their acid–base properties, respectively, and the results are listed in Table 2.

It is unexpected that the selectivity to MCPD and the activity of MgO has a certain elevation during the reaction, which seems to suggest that the methylation of CPD contains an induction period on MgO. The result from elemental analysis (see Table 2) indicates that MgO contains small amount of carbonaceous species (2.9% of carbon) after 300-min run. However, this coking is not the reason for the elevation of activity and selectivity to MCPD. In fact, if calcining the spent catalyst at 873 K in the air, the activity of MgO can further increases to 33% (data not given in tables or



Scheme 2. Proposed reaction mechanism for the methylation of CPD on KOH/MgO.

figures), indicating that the coking is detrimental to the conversion of CPD. Therefore, the surface property of MgO must have been altered after CPD methylation. This change derives not from the formation of new component or phase after reaction, since the spent catalyst still presents the phase of periclase MgO (see Fig. 1). One possible reason is that more defective sites are formed during the methylation of CPD. It is known that some neutral oxygen vacancies could be formed on MgO during N_2 treatment at high temperature, which could enhance the catalytic activity. Moreover, CO_2 is one of the decomposition products of methanol, they could react with MgO during the methylation reaction, and the resulting carbonaceous or carbonated species could create distortions in the MgO lattice, which may have some effect on the final activity of catalyst. More work is still needed to interpret this change.

Al_2O_3/MgO possesses a higher initial activity than unpromoted MgO, however, the activity decreases to a lower value than that on MgO after a long run at 773 K. The result from elemental analysis (see Table 2) demonstrates that 10%Al_2O_3/MgO contains 4.7% of carbon after 300-min run due to the coke deposit, which is higher than that on the unpromoted MgO (2.9%). The result from the catalytic decomposition of isopropanol (see Table 2) indicates that the coking on 10%Al_2O_3/MgO mainly diminishes the yield of acetone, i.e. it decreases the basicity. Accordingly, the activity of Al_2O_3/MgO drops a little after this coking.

Fig. 8 shows that the deactivation of 10%KOH/MgO is serious at 773 K. Although it exhibits the highest initial activity, the conversion of CPD is only 6% after 300-min run. The result from elemental analysis (see Table 2) demonstrates that this spent catalyst contains 28% of carbon, which is about nine times of that on the unpromoted MgO. Obviously, this heavy coking should be responsible for the serious deactivation on KOH/MgO. This coke deposit comprises mainly of the polycyclic aromatic products, as indicated in Fig. 10. ICP-OES analysis indicates that 14% of K is lost after 300-min run (data not given in tables or figures), which may have a certain effect on the activity of catalyst. However, after calcining at 873 K in the air, the activity of KOH/MgO can be recovered (data not given in tables or figures) and the color of catalyst changes from black to original white, which gives further evidence that the deactivation is due to the coke deposition [52]. This spent catalyst shows apparent decrease in acetone yield in the catalytic decomposition of isopropanol (Table 2), indicating that the basicity on 10%KOH/MgO diminishes after the methylation of CPD. Furthermore, an apparent reduction in BE value associated with O 1s core level can be observed after the methylation of CPD from the XPS result (Table 3),which can be ascribed to electronic interaction between O^{2-} ions and reactants. Therefore, this coking occurs mainly on the basic sites and most possibly relates to KOH. The reaction result based on two feeding modes, i.e. feeding methanol continuously and CPD intermittently or feeding CPD continuously and methanol intermittently, indicates that the deactivation of catalyst and the coking derive from CPD transformation (Fig. 9). The deactivation mechanism on 10%KOH/MgO is different from that on acidic catalyst. As has been confirmed, the hexamethylbenzene and polynuclear aromatics formed by transformation of methanol on acidic sites are mainly responsible for the deactivation of catalyst in phenol methylation with methanol [21,22,53–55]. The heavy coking on KOH/MgO should be ascribed to the superbasicity of KOH/MgO, which possesses stronger electrodonating ability than MgO [24]. The superbasicity favors both the formation of cyclopentadienyl anion and the decomposition of methanol. The formed cyclopentadienyl anions can be converted to MCPD and polymers with methylating agent and CPD, respectively. At lower temperature, the cyclopentadienyl anions mainly react with methylating agent to form product MCPD. However, these cyclopentadienyl anions are more likely to polymerize due to the rapid decomposition of the methylating agent, and transform to polycyclic aromatic products (coking deposits) by further condensation and methylation. This deactivation mechanism can give a reasonable explanation for the abnormal phenomenon on 10%KOH/MgO during the acetic acid poisoning at higher temperature (Fig. 12B). Although the competitive adsorption of acetic acid would inhibit the transformation of CPD on basic sites, the existence of the superbasic sites induces heavy coking of CPD on 10%KOH/MgO at 773 K or higher temperature, which turns to be the overwhelming factor for the deactivation of catalyst. Co-feeding acetic acid decreases the basicity of catalyst, thus weakens both the coking of CPD and the decomposition of methanol, which are helpful to the formation of MCPD.

It should be pointed out that the deactivation rate on KOH/MgO decreases dramatically when temperature drops from 773 to 723 K, and accordingly, carbon content decreases from 28% to 4.8% (data not given in tables and figures) after 300-min run. Obviously, the coking on KOH/MgO can be well suppressed by lowering reaction temperature. One of the reasons is that the decomposition rate of methanol decreases remarkably as the reaction temperature drops to 723 K, as indicated in Fig. 4B. Thus, more methanol molecules are provided for the methylation reaction, and the polymerization of cyclopentadienyl anion is suppressed accordingly. Compared with other catalysts, KOH/MgO exhibits higher activity and selectivity to MCPD even after a long run at 723 K, and displays the potential as an effective catalyst in the methylation of CPD.

5. Conclusions

This work compares the catalytic performances of MgO and MgO promoted with Al_2O_3 or KOH in the methylation of CPD with methanol. The dehydrogenation of methanol is a key-step on these solid bases, with generation of the active species, e.g. formaldehyde, for the methylation of CPD. The modification with either Al_2O_3 or KOH can enhance the initial activity of MgO and the selectivity to MCPD at lower temperature; however, their catalytic mechanisms present apparent difference. As for Al_2O_3/MgO, both the acidic and basic sites play the important roles in CPD methylation; while for KOH/MgO, the existence of superbasic sites is responsible for the higher activity and selectivity to MCPD, and KOH rather than MgO catalyzes this reaction. Due to different active sites, these catalysts display different deactivation behaviors. The superbasicity of KOH/MgO makes it easy to deactivate at 773 K, due to the heavy coking of CPD on the basic sites. However, the coking effect can be greatly suppressed when the reaction temperature decreases to 723 K, and this catalyst exhibits much better performance than the unpromoted MgO even after a long run. Moreover, the activity of this spent catalyst can be recovered by calcining at 873 in the air.

Acknowledgments

We would like to thank the financial support from the NSF of China (20873061), the Ministry of Science and Technology of China (Grant 2008 AA06Z327 from the 863 Program), and the testing fund of Nanjing University.

References

[1] F.J. Wu, B.C. Berris, D.R. Bell, US Patent 4 946 975, to Ethyl Co., Ltd., 1990.
[2] S. Mclean, P. Haynes, Tetrahedron 21 (1965) 2313.
[3] V.A. Mironov, E.V. Sobolev, A.N. Elizarova, Tetrahedron 19 (1963) 1939.
[4] S.J. Rajan, US Patent 4 547 603, to Ethyl Co., Ltd., 1982.
[5] H.E. Fritz, D.W. Peck, US Patent 3 255 267, to Union Carbide Co., Ltd., 1966.
[6] Z. Yoshida, S. Kato, Y. Amemiya, K. Yanai, US Patent 4 567 308, to Asahi Chemical Co., Ltd., 1985.
[7] Z. Yoshida, S. Kato, Y. Amemiya, EP Patent 0 256 228, to Asahi Chemical Co., Ltd., 1987.
[8] L.B. Sun, Z.Y. Wu, J.H. Kou, Y. Chun, Y. Wang, J.H. Zhu, Z.G. Zou, Chin. J. Catal. 27 (2006) 725.
[9] L.B. Sun, L. Gong, X.Q. Liu, F.N. Gu, Y. Chun, J.H. Zhu, Catal. Lett. 132 (2009) 218.
[10] J.H. Zhu, Y. Chun, Y. Qin, Q.H. Xu, Micropor. Mesopor. Mater. 24 (1998) 19.
[11] R.Q. Sun, L.B. Sun, Y. Chun, Q.H. Xu, Carbon 46 (2008) 1757.
[12] R. Jimenez, X. Garcia, C. Cellier, P. Ruiz, A.L. Gordon, Appl. Catal. A 314 (2006) 81.
[13] J. Diaz-Teran, D.M. Nevskaia, J.L.G. Fierro, A.J. Lopez-Peinado, A. Jerez, Micropor. Mesopor. Mater. 60 (2003) 173.
[14] J.H. Zhu, Y. Wang, Y. Chun, Z. Xing, Q.H. Xu, Mater. Lett. 35 (1998) 177.
[15] Y. Wang, W.Y. Huang, Y. Chun, J.R. Xia, J.H. Zhu, Chem. Mater. 13 (2001) 670.
[16] K. Tanabe, in: B. Imelik, C. Nacceche, G. Condurier, Y. Ben Taarti, J.C. Verdrine (Eds.), Catalysis by Acids and Bases, Elsevier, Amsterdam, 1985, p. 1.
[17] V.K. Díez, C.R. Apesteguía, J.I. Di Cosimo, J. Catal. 215 (2003) 220.
[18] F. Prinetto, G. Ghiotti, R. Durand, D. Tichit, J. Phys. Chem. B 104 (2000) 11117.
[19] P.E. Hathaway, M.E. Davis, J. Catal. 116 (1989) 263.
[20] P.E. Hathaway, M.E. Davis, J. Catal. 119 (1989) 497.
[21] N. Ballarini, F. Cavani, L. Maselli, A. Montaletti, S. Passeri, D. Scagliarini, C. Flego, C. Perego, J. Catal. 251 (2007) 423.
[22] M. Bregolato, V. Bolis, C. Buscob, P. Ugliengo, S. Bordigac, F. Cavani, N. Ballarini, L. Maselli, S. Passeri, I. Rossetti, L. Forni, J. Catal. 245 (2007) 285.
[23] Y. Wang, J.H. Zhu, J.M. Cao, Y. Chun, Q.H. Xu, Micropor. Mesopor. Mater. 26 (1998) 175.
[24] J.I. Di Cosimo, C.R. Apesteguía, J. Mol. Catal. A 130 (1998) 177.
[25] M. Vijayaraj, C.S. Gopinath, J. Catal. 243 (2006) 376.
[26] A.R. Pradhan, T.S. Lin, W.H. Chen, S.J. Jong, J.F. Wu, K.J. Chao, S.B. Liu, Appl. Catal. A: Gen. 218 (2001) 81.
[27] R. Golembiewski, J. Kornatowski, Chem. Mater. 13 (2001) 609.
[28] Z. Fan, A.P. Watkinson, Ind. Eng. Chem. Res. 45 (2006) 6428.
[29] R.C. Greenler, J. Chem. Phys. 37 (1962) 2094.
[30] R.O. Kagel, J. Phys. Chem. 71 (1967) 844.
[31] J. Shabtai, L.H. Klemm, D.R. Taylor, J. Org. Chem. 35 (1970) 1075.
[32] P. Mars, J.J. Scholten, P. Zwietering, Adv. Catal. 14 (1963) 35.
[33] U. Heiz, J. Phys. Chem. B 106 (2002) 11961.
[34] M. Ziolek, J. Kujawa, O. Saur, J.C. Lavalley, J. Phys. Chem. 97 (1992) 9761.
[35] J.S. Francisco, J. Am. Chem. Soc. 125 (2003) 10475.
[36] J. Hu, K. Zhu, L. Chen, C. Ku1bel, R. Richards, J. Phys. Chem. C 111 (2007) 12038.
[37] J. Günster, G. Liu, J. Stultz, S. Krischok, D.W. Goodman, J. Phys. Chem. 104 (2000) 5738.
[38] X.D. Peng, M.A. Barteau, Langmuir 5 (1989) 1051.
[39] N.D. Lazo, D.K. Murray, M.L. Kieke, J.H. Haw, J. Am. Chem. Soc. 114 (1992) 8552.
[40] T. Mori, S. Hoshino, A. Neramittagapong, J. Kubo, Y. Morikawa, Chem. Lett. (2002) 390.
[41] F. Cavani, L. Maselli, S. Passeri, J.A. Lercher, J. Catal. 269 (2010) 340.
[42] C.S. Huang, A.N. Ko, Catal. Lett. 19 (1993) 319.
[43] A. Borgna, J. Sepúlveda, S.I. Magni, C.R. Apesteguía, Appl. Catal. A 276 (2004) 207.
[44] A.E. Palomares, G. Eder-Mirth, M. Rep, J.A. Lercher, J. Catal. 180 (1998) 56.
[45] N. Ballarini, F. Cavani, L. Maselli, S. Passeri, S. Rovinetti, J. Catal. 256 (2008) 215.
[46] A.H. Padmasri, A. Venugopal, V. Durgakumari, K.S. Rama Rao, P. Kanta Rao, J. Mol. Catal. A 188 (2002) 255.
[47] G. Spoto, S. Bordiga, A. Zecchina, J. Mol. Catal. 49 (1988) 187.
[48] A.E. Palomares, G. Eder-Mirth, J.A. Lercher, J. Catal. 168 (1997) 442.
[49] D. Jiang, B. Zhao, Y. Xie, G. Pan, G. Ran, E. Min, Appl. Catal. A 219 (2001) 69.
[50] E.I. Becker, J. Chem. Edu. 36 (1959) 119.
[51] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New Solid Acid and Bases, Elsevier Science & Technology Publishing, Amsterdam, 1990. p. 1.
[52] A.S. Ndou, N.J. Coville, Appl. Catal. A 275 (2004) 103.
[53] Ø. Mikkelsen, S. Kolboe, Micropor. Mesopor. Mater. 29 (1999) 173.
[54] M. Bjørgen, U. Olsbye, S. Kolboe, J. Catal. 215 (2003) 30.
[55] W.C. Choi, J.S. Kim, T.H. Lee, S.I. Woo, Catal. Today 63 (2000) 229.