

## FTIR Study of the Methylation of Phenol with Dimethyl Carbonate over KBr/SiO<sub>2</sub>

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**Summary:** The *O*-Methylation of phenol with dimethyl carbonate (DMC) over KBr/SiO<sub>2</sub> catalyst was carried out and the reaction mechanism was investigated by in-situ FTIR. It was found that phenol was deprotonated to generate phenolate at 100 °C but DMC was found no activation even at elevated temperature except a little decompose at 200 °C. As a result anisole was formed at 150 °C. Methylation mechanism was proposed based on those, in which phenolate was generated firstly and then acted as an active phase to attack methyl carbon of DMC to yield anisole. The activation of DMC seemed to be not essential.

### Introduction

Anisole is an important industrial chemical and synthetic intermediate which is extensively used for the preparation of fragrances, pesticides, cosmetic products, dyes and antioxidants. Its traditional production involved the *O*-methylation of phenol with dimethyl sulphate (DMS), methyl halides or methanol, which either generated environmental pollutions [1] or needed severe reaction conditions [2, 3]. With the appeal of chemical technology causing minimum environmental impact, some “green” alkylating agents and heterogeneous catalysts have been developed for the alternative routes. Dimethyl carbonate (DMC) as a green reagent has recently been reported as a potential methylation and carbonylation reagent [4-6]. Amongst them, *O*-methylation of phenol and phenol derivatives with DMC has lots of advantages over the other reagents [6-9].

The synthesis of anisole by *O*-methylation of phenol with DMC had been extensively investigated using phase transfer catalysts (PTC) [10-13], organic alkali catalyst [14] or zeolites as catalysts [14-17]. Though high catalytic performance was achieved by using PTC catalysts, the reactions were generally carried out in homogeneous systems with the drawbacks of poor catalyst recovery and complicated product separation. While zeolite catalysts normally needed higher reaction temperature (250~300 °C) and often produced more side products of phenyl ring C-alkylation. Hence, there was a crucial need to exploit more highly efficient heterogeneous catalytic materials.

Recently, some eco-friendly potassium salts had attracted attention as novel and facile catalysts which require gentle reaction conditions, easy separation of products, while regeneration of catalysts is easy. K<sub>2</sub>CO<sub>3</sub> [18] was reported to give high phenol conversion and more than 96 % selectivity towards anisole. KNO<sub>3</sub> supported on alumina [19] was used as catalyst for the reaction of DMC with catechol which gave high *O*-methylation. We have found [20] that potassium bromide (KBr) is highly efficient catalyst for the *O*-methylation of phenol with DMC, too. However, the mechanism of KBr as a highly efficient catalyst for this reaction is yet to be clear. Thus, the absorption of both DMC and phenol on KBr/SiO<sub>2</sub> catalyst was carried out by using FT-IR, and then a possible reaction mechanism was proposed on the basis of IR results.

### Results and discussion

#### *Adsorption of DMC on KBr/SiO<sub>2</sub>*

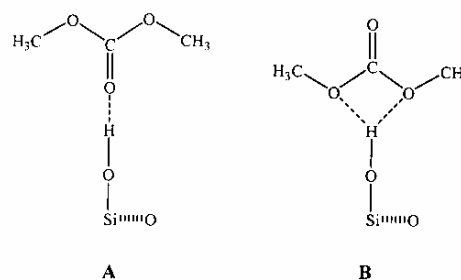
The spectra of DMC adsorption on KBr/SiO<sub>2</sub> was depicted in Fig. 1. For pure DMC, the band at 1755 and 1281 cm<sup>-1</sup> could be attributed to the C=O stretching vibration [21] and the antisymmetric stretching vibration of the O-C-O of DMC [22], respectively. The bands at 1455 cm<sup>-1</sup> and its small shoulder at 1431 cm<sup>-1</sup> were due to deformation vibrations of the DMC methyl groups. The absorbance at 2962 cm<sup>-1</sup> was assigned to C-H symmetric stretching vibrations of DMC methyl groups, and those at 3009 and 3032 cm<sup>-1</sup> were ascribed to C-H antisymmetric stretching vibrations.

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The band at  $2855\text{ cm}^{-1}$  was accounted for the combination band of two C-H deformation vibrations [17]. Compared with pure DMC, the bands of DMC adsorbed on  $\text{KBr/SiO}_2$  at  $25^\circ\text{C}$  showed a series of blue or red shifted. For instance, the band of O-C-O anti-symmetry stretching vibration of DMC had a blue shift to  $1307\text{ cm}^{-1}$ . The C=O stretching vibration was split into two peaks, one showed a red shift to  $1749$  and the other was blue shifted to  $1778\text{ cm}^{-1}$ , which revealed different adsorption states of DMC appeared on  $\text{KBr/SiO}_2$ . Moreover, a small shoulder at  $1725\text{ cm}^{-1}$  was observed, due to C=O stretching vibration of crystal DMC [23]. This suggested that some of DMC molecules disposed directionally or had some character of crystal after the adsorption on  $\text{KBr/SiO}_2$ .

Obviously, such a change of DMC was due to its interaction with  $\text{SiO}_2$  rather than  $\text{KBr}$  because the spectrum of DMC on  $\text{KBr/SiO}_2$  was almost the same as that on  $\text{SiO}_2$  (not shown here). This was in accordance with the point that DMC could be easily activated by acidic sites [17, 24] rather than by basic sites [25]. It was most likely that the DMC had an interaction with  $\text{SiO}_2$  via its oxygen atoms interacting with the hydroxyl group on the silica surface. The possible adsorption states of DMC on  $\text{SiO}_2$  could be described in Scheme 1. The band of C=O stretching



Scheme 1: Phenol states transformation on  $\text{KBr}$ .

vibration at  $1749\text{ cm}^{-1}$  corresponded to state **A**, in which carbonyl oxygen atom of DMC was bonded with a hydrogen atom of silica hydroxyl. This would weaken the C=O band and strengthen O-C-O band; and the band at  $1778\text{ cm}^{-1}$  was responsible for state **B**, in which one or two ester oxygens of DMC were bonded with silica hydroxyls [17]. This could strengthen O-C-O band but weaken C-O band. State **A** was dominant on the adsorption of DMC on  $\text{SiO}_2$  because the band at  $1749\text{ cm}^{-1}$  was much stronger than that at  $1778\text{ cm}^{-1}$ .

All the bands of DMC on  $\text{KBr/SiO}_2$  gradually diminished with heat treatment in vacuum (see Fig. 1). Heating up to  $150^\circ\text{C}$ , the band at  $1778$

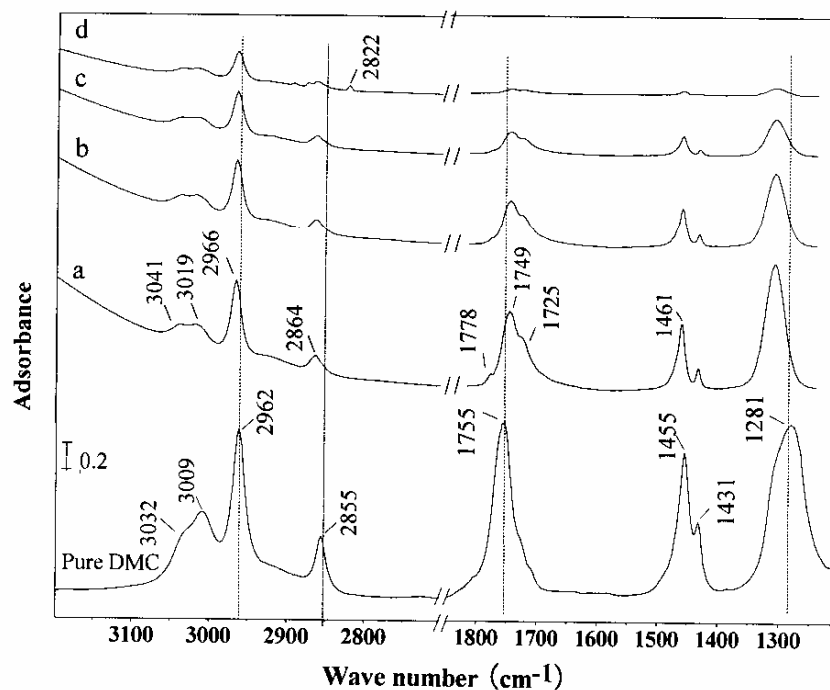


Fig. 1: FTIR spectra after adsorption of DMC on  $\text{KBr/SiO}_2$  at (a)  $25^\circ\text{C}$ , (b)  $100^\circ\text{C}$ , (c)  $150^\circ\text{C}$  and (d)  $200^\circ\text{C}$ .

$\text{cm}^{-1}$  disappeared, and at  $200^\circ\text{C}$ , only a small amount of DMC was kept on  $\text{KBr/SiO}_2$ , indicating a weak interaction between DMC and  $\text{KBr/SiO}_2$ . Besides, a new small band at  $2822\text{ cm}^{-1}$  appeared at  $200^\circ\text{C}$ , which could be ascribed to C-H vibration of the intermediate of DMC decomposition [17].

#### Adsorption of Phenol on $\text{KBr/SiO}_2$

Fig. 2 showed the FTIR spectra of phenol adsorbed on  $\text{KBr/SiO}_2$  at  $25^\circ\text{C}$ , and strong absorption was observed at  $1473$ ,  $1500$  and  $1597\text{ cm}^{-1}$  in the region of aromatic ring vibration. The bands at  $1473$  and  $1500\text{ cm}^{-1}$  could be contributed to normal modes 19a and 19b vibration of aromatic ring of phenol. The absorbance at  $1597\text{ cm}^{-1}$  and its shoulder at  $1605\text{ cm}^{-1}$  were ascribed to the 8a and 8b deformation vibrations of the ring [26-27]. Three broad bands at  $1365\text{ cm}^{-1}$ ,  $1358$  and  $1345\text{ cm}^{-1}$  were also detected and were due to the in-plane C-O-H bending vibration of phenol. The bands at  $3052$  and  $3025\text{ cm}^{-1}$  in the C-H stretching region were assigned to the C-H stretching vibrations of the phenyl ring. It was noticeable that all the above bands of phenol adsorbed on  $\text{KBr/SiO}_2$  were the same as that in  $\text{CCl}_4$  solution [27], suggesting that phenol was mainly bonded by its H atom to  $\text{KBr/SiO}_2$  at  $25^\circ\text{C}$ .

Heating the sample stepwise from  $50$  to  $200^\circ\text{C}$ , all bands obviously decreased because of desorption (see Fig. 2). As the temperature increased to  $100^\circ\text{C}$ , the band of C-O-H deformation vibration at  $1366$ ,  $1358$ , and  $1345\text{ cm}^{-1}$  diminished more quickly than that of aromatic ring vibration at  $1597\text{ cm}^{-1}$ . The exceptional diminishment of C-O-H deformation vibration suggested that the O-H bond of phenol was weakened on  $\text{KBr/SiO}_2$ . Besides, a new absorbance at  $1494\text{ cm}^{-1}$  appeared at  $100^\circ\text{C}$  accompanied by the decreasing of the bands at  $1500$  and  $1473\text{ cm}^{-1}$ , suggesting the formation of phenolate [17]. Thus, phenol could be deprotonated on  $\text{KBr/SiO}_2$  at  $100^\circ\text{C}$ . Meanwhile, the C-H stretching vibrations of phenyl ring showed a red shifted from  $3052$  and  $3025\text{ cm}^{-1}$  to  $3045$  and  $3011\text{ cm}^{-1}$ , respectively. Since the deprotonation of phenol to phenolate would increase the negative charge on the oxygen atom and weaken the C-H bond of phenyl ring by conjugative effect, the red shift of C-H bands could further confirm the deprotonation of phenol. At  $200^\circ\text{C}$ , the three broad bands of phenol C-O-H in plane deformation vibration disappeared, and the band of  $1494\text{ cm}^{-1}$  responsible for phenolate became stronger while bands at  $1500$  and  $1473\text{ cm}^{-1}$  were almost invisible. These indicated that the adsorbed phenol had been completely deprotonated and transformed to phenolate on  $\text{KBr/SiO}_2$  at  $200^\circ\text{C}$ .

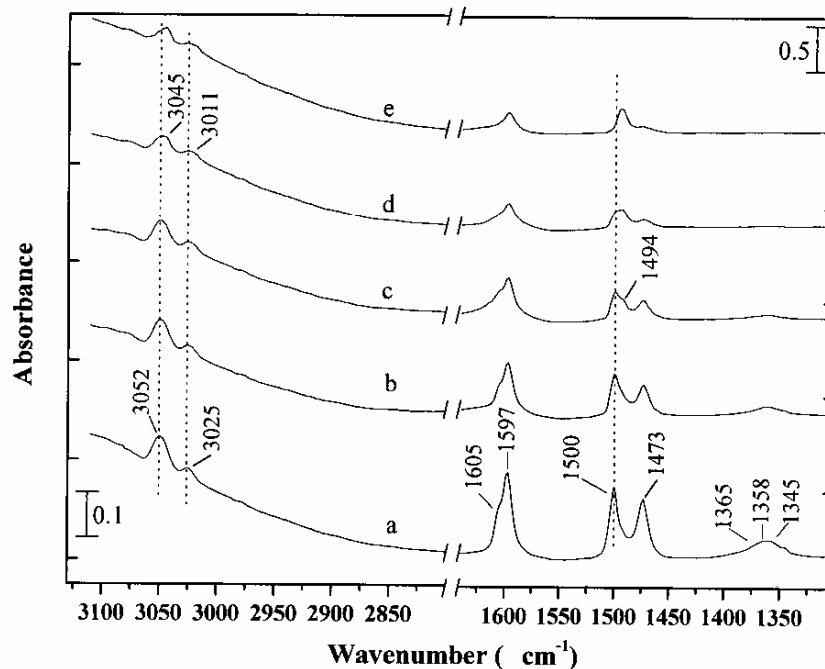
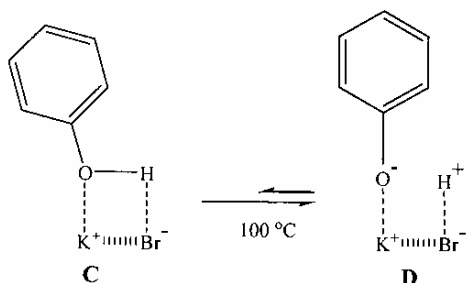


Fig. 2: FTIR spectra after adsorption of phenol on  $\text{KBr/SiO}_2$  at (a)  $25^\circ\text{C}$ , (b)  $50^\circ\text{C}$ , (c)  $100^\circ\text{C}$ , (d)  $150^\circ\text{C}$  and (e)  $200^\circ\text{C}$ .

It should be pointed out that the deprotonation of phenol was not found over pure  $\text{SiO}_2$  (not shown here). Thus, it was KBr which caused deprotonation of phenol. KBr has a strong Bronsted basic site,  $\text{Br}^-$ , and a strong Lewis acid site,  $\text{K}^+$ , which are prone to interact with the hydrogen atom and oxygen atom of phenol hydroxyl, respectively. The interaction of KBr with phenol could be speculated as scheme 2. At  $25^\circ\text{C}$ , phenol was adsorbed on KBr mainly by its hydroxyl hydrogen bonded on  $\text{Br}^-$  and oxygen atom bonded with  $\text{K}^+$  (state C, Scheme 2). When the temperature increased up to  $100^\circ\text{C}$ , the hydroxyl bond of phenol was weakened or totally broken to form phenolate as shown by state D.



Scheme 2: DMC adsorption states on  $\text{SiO}_2$ .

#### *Coadsorption and Reactivity of DMC and Phenol on $\text{KBr}/\text{SiO}_2$*

The spectra of phenol adsorption on  $\text{KBr}/\text{SiO}_2$  preadsorbed with DMC were shown in Fig. 3, and the same spectra (not shown here) were observed when the adsorption order was changed. Except that the band at  $1778\text{ cm}^{-1}$  of DMC wasn't present, the spectrum of coadsorption at  $25^\circ\text{C}$  did not show any difference comparing with that of DMC (see Fig. 1) or phenol (see Fig. 2) adsorbed on  $\text{KBr}/\text{SiO}_2$ . The absence of band of  $1778\text{ cm}^{-1}$  indicated that state B was not formed when phenol coexisted, which was in accordance with the results of Beutel on NaX [17] that the formation of chelating DMC complex with catalyst was sterically hindered with the existence of phenol. Obviously, a shoulder at  $1456\text{ cm}^{-1}$  appeared at  $150^\circ\text{C}$  and replaced the band at  $1461\text{ cm}^{-1}$  completely at  $200^\circ\text{C}$ . Simultaneously a new band at  $3077\text{ cm}^{-1}$  appeared at  $150^\circ\text{C}$ . Both bands at  $1456$  and  $3077\text{ cm}^{-1}$  were absorption bands of anisole, which was checked by comparison with absorption of anisole on  $\text{KBr}/\text{SiO}_2$ . Their appearance revealed the formation of anisole at  $150\text{--}200^\circ\text{C}$ . The aromatic ring vibration of anisole at  $1494\text{ cm}^{-1}$ , the same as that of phenolate, became exceptionally stronger accompanied by the disappearance of bands

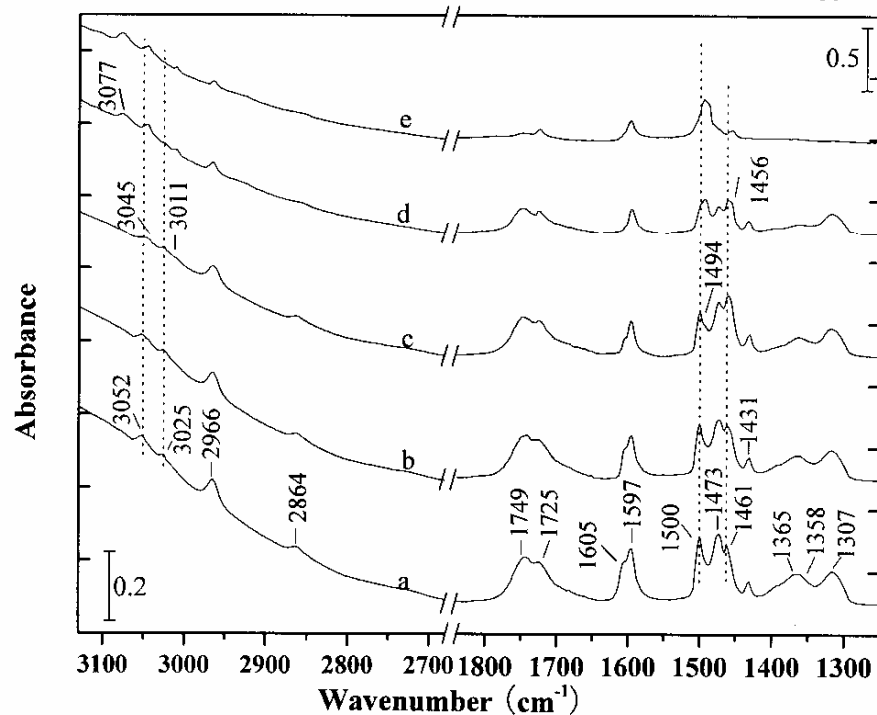


Fig. 3: FTIR spectra after coadsorption of DMC and phenol on  $\text{KBr}/\text{SiO}_2$  at (a)  $25^\circ\text{C}$ , (b)  $50^\circ\text{C}$ , (c)  $100^\circ\text{C}$ , (d)  $150^\circ\text{C}$  and (e)  $200^\circ\text{C}$ .

at 1500 and 1473  $\text{cm}^{-1}$  at 200 °C. This further confirmed the formation of anisole.

Table-1 demonstrated the catalytic performance of  $\text{KBr}/(\text{SiO}_2)$  catalyst for the synthesis of anisole from the reaction of phenol with DMC. The reaction of DMC and phenol over  $\text{KBr}/(\text{SiO}_2)$  catalyst was highly selective towards anisole, even if a small amount of methoxycarbonylation product (MPC) was detected. It was found that  $\text{SiO}_2$  had no activity towards the reaction, but  $\text{KBr}$  gave 94.76 % of phenol conversion and about 99.97 % anisole selectivity. This indicated that  $\text{KBr}$  was efficient catalyst towards this reaction.  $\text{KBr}$  supported on  $\text{SiO}_2$  hardly improved the phenol conversion as shown Table-1.

Table-1: Reactivity of phenol and DMC on  $\text{KBr}$ ,  $\text{KBr}/\text{SiO}_2$  and  $\text{SiO}_2$  catalyst.

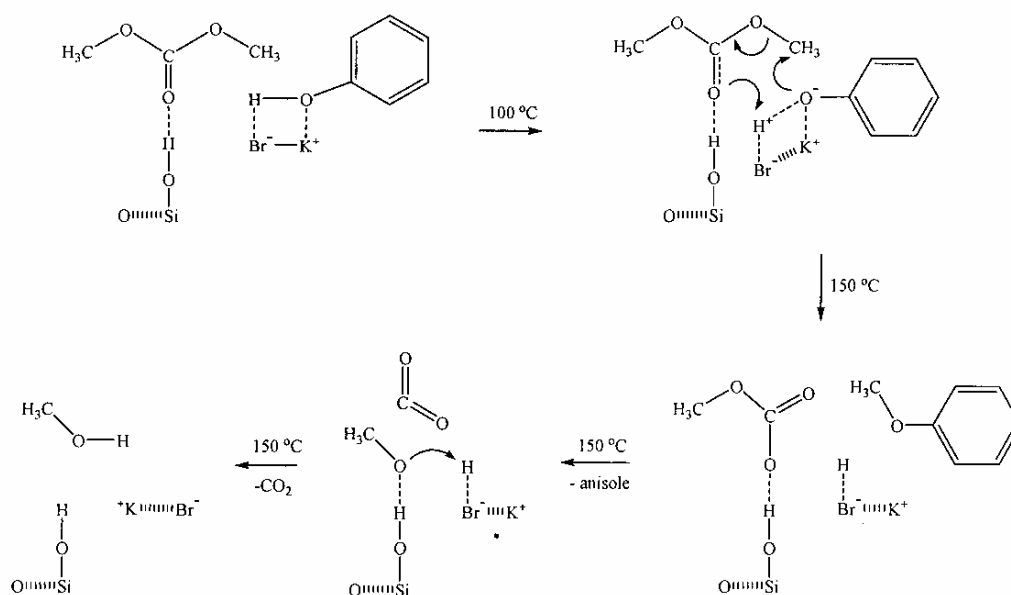
Catalyst	Temperature (°C)	Phenol conversion (%)	Anisole yield (%)	MPC yield (%)
$\text{KBr}^a$	130	0	-	-
	150	3.65	1.23	2.42
	180	65.9	64.16	1.74
	200	94.76	94.73	0.03
$\text{KBr}/\text{SiO}_2^b$	130	0	-	-
	150	3.37	1.09	2.28
	200	94.68	94.60	0.08
$\text{SiO}_2^c$	200	0	-	-

(DMC 0.2 mol, phenol 0.1 mol. a,  $\text{KBr}$  1wt %; b, 10wt% $\text{KBr}/\text{SiO}_2$  10wt %; c,  $\text{SiO}_2$ , 1wt %, 8h).

### Reaction Mechanism

A possible mechanism of *O*-methylation of phenol with DMC on  $\text{KBr}/(\text{SiO}_2)$  was thus proposed as shown in Scheme 3. Phenol adsorbed on  $\text{KBr}$  to generate phenolate by hydroxyl H atom bonded with  $\text{Br}^-$  and O atom bonded with  $\text{K}^+$ . Phenolate thus formed, as a strong nucleophile reagent ( $\text{PhO}^-$ ), attacked methyl carbon of DMC, then a six-member ring was formed, readily followed by electron rearrangement and led to the formation of anisole and methyl hydrogen carbonate at higher than 150 °C, the latter may further decompose to  $\text{CO}_2$  and methanol.

The activation of phenol to phenolate was ever reported by Ouk *et al.* [10] on tetrabutylammonium (TBTA) catalyst. Phenolate was formed by phenol hydroxyl-H atom bonded with  $\text{Br}^-$  atom and O atom bonded with  $\text{N}^+$  of TBTA, a mechanism in which this phenolate attacked methyl carbon of DMC to give yield of anisole was speculated. Beutel [17] also found deprotonation of phenol on  $\text{NaX}$  zeolites catalyst. Phenol interacted with  $\text{NaX}$  by H bonding to zeolites hydroxyl group and O bonding to  $\text{Na}^+$  ions. The mechanism was also speculated as phenolate attacked methyl carbon of DMC to generate anisole. While there was a little difference of the mechanism on  $\text{NaX}$  with that on



Scheme 3: Possible reaction mechanism of *o*-methylation of phenol with DMC on  $\text{KBr}/(\text{SiO}_2)$ .

KBr/(SiO<sub>2</sub>) catalyst of this paper and TBTA catalyst was that DMC was also activated by NaX catalyst.

### Experimental

#### Catalyst preparation

KBr/SiO<sub>2</sub> catalyst with 10 % of KBr was prepared by impregnation method. Typically, SiO<sub>2</sub> was calcined at 400 °C for 4 h before use. So-pretreated silica (529m<sup>2</sup>/g) was dipped in a KBr solution with a suitable concentration and kept for 24 h, and then the sample was dried at 80 °C and calcined at 300 °C for 4 h in N<sub>2</sub>. So-prepared 10 % KBr/SiO<sub>2</sub> catalyst and KBr catalyst were calcined at 200 °C before reactions.

#### In-situ FTIR

FTIR spectra were recorded on a Nicolet Magna 550II Fourier-transform infrared spectrometer in the region of 4000-400cm<sup>-1</sup>. 128 scans with a resolution of 4 cm<sup>-1</sup> were collected. The sample was pressed at 7×10<sup>8</sup> N·m<sup>-2</sup> with 15-20 mg into a self-supporting wafer of Φ13mm and mounted in an in-situ cell equipped with CaF<sub>2</sub> windows. The reactants, DMC and phenol, were adsorbed on catalyst at 25 °C and then heated stepwise in vacuum to observe their interactions.

#### Reactivity test

The reactions of phenol with DMC were carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. After reactants and catalyst were introduced in, the autoclave was sealed and heated to preset temperature, and then it was kept at this temperature for a certain time under autogenous pressure for reaction. After the reaction, the reactor was cooled down to room temperature and the liquid products were filtered from the catalyst and were analyzed by a chromatograph (GC-920, Shanghai Haixin Chromatograph Instrument Co. Ltd.) with a flame ionization detector and a HP-5 column. The product yield was defined as  $m_i/m_{\text{phenol}} \times 100$ , where  $m_i$  was the weight of product of  $i$ , and  $m_{\text{phenol}}$  was the total weight of phenol added into the reactor.

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