Boron doped g-C_3N_4 as an effective metal-free solid base catalyst in Knoevenagel condensation

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Abstract: We first report here boron-doping is an effective strategy to enhance the basicity of g-C_3N_4 in Knoevenagel condensation as metal-free solid base catalyst.

Keywords: g-C_3N_4, boron-doping, Knoevenagel condensation

1. Introduction

Base-catalyzed Knoevenagel condensation between an aldehyde and an active methylene-containing reagent is one of the most primary processes to synthesize unsaturated carbonyl compounds[1]. Considering the issues of separation and recycling, heterogenous solid base catalysts, i.e. hydrotalcite, metal phosphates, are preferred over homogeneous bases. However, the use of such metal-containing solid base materials leads to inevitable metal contamination of the products[2]. Therefore, alternative metal-free heterogenous base catalysts for Knoevenagel condensation are highly desirable. Carbon materials, due to its various structure and facile modification, have been intensively investigated as potential metal-free base catalysts. And nitrogen-doping is normally regarded as an effective way to enhance the basicity of carbon materials[3]. Recently, a nitrogen-rich graphitic carbon nitride has attracted much attention. In fact, allotropes of graphitic carbon nitride may be constituted of two types of tectonic units. They are s-triazine and tri-s-triazine to construct g-CN and g-C_3N_4, respectively[4]. Although some publications indicated that g-CN materials have exhibited basicity due to the free amine groups in Knoevenagel condensation. However, the low nitrogen content and stability of g-CN limit its practical application. Therefore, it is more meaningful to enhance the basicity of g-C_3N_4 which possesses intrinsically high nitrogen content and stability. Owing to the weak electron delocalization in the tri-s-triazine ring, g-C_3N_4 shows only weak basicity. Therefore, it is highly desired to develop a facile and effective strategy to modulate the electron delocalization in the tri-s-triazine ring to enhance the basicity of g-C_3N_4. In the present work, we investigated the effect of boron, phosphor, sulfur doping on the basicity of g-C_3N_4 in Knoevenagel condensation. Correlating their catalytic performance and characterizations, it is concluded that boron-doping is an effective strategy to enhance the basicity of g-C_3N_4 as metal-free solid base catalysts.

2. Experimental (or Theoretical)

The g-C_3N_4 sample was synthesized by dicyandiamide or urea precursor condensation at 550℃ for 4h at a heating rate of 2.3℃ min^{-1}. The g-C_3N_4 doped by heteroatoms including boron, phosphor and sulfur were prepared with the similar method in reference. The obtained samples were denoted as CNMF-*x*, where M represented the type of doped atom (B, P, S). *x* represented the mass ratio of ionic liquid to dicyandiamide (*x*=0.1,0.3,0.5,0.7).

3. Results and discussion

FT-IR spectra, XRD, XPS, and HRTEM images indicate the successful doping of boron into g-C_3N_4 matrix. B 1s spectrum of CNBF-0.3 in Fig.1(a) displays one peak at 192.0 eV attributed to the boron substitution of the carbon atoms in the g-C_3N_4 framework. Correspondingly, N-B=N bonds are formed between the doped boron atoms and surrounding N atoms. The ^{11}B solid-state MAS NMR result in Fig.1(b) suggests two peaks in 4.56 ppm and 15.14 ppm, corresponding to the boron substitution of bayer carbon site and the corner carbon site, respectively. The basicity of materials in Fig.1(c,d) indicate that g-C_3N_4 has the weak basicity with the basic site concentration of 18.81 μmol/g. When phosphor is doped into g-C_3N_4, the basicity disappears completely probably due to the neutralization of acidity and basicity in CNPF. On the contrary, the basic site concentration increases when sulfur or boron is doped into g-C_3N_4. Especially, for boron doped g-C_3N_4, except for basic site concentration, the base strength is enhanced reflected by the shift of the peak position from 120.3℃ to 130.0℃.

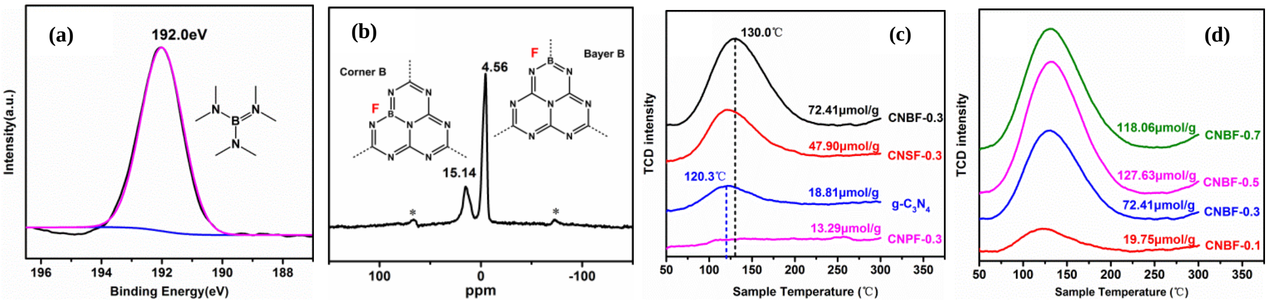

Fig.1 XPS B 1s spectrum (a) and ^{11}B solid-state MAS NMR spectra (b) of CNBF-0.3, CO_2-TPD profiles of g-C_3N_4, CNSF, CNPF and CNBF-*x*(c,d).

The comparison of the catalytic performances of Knoevenagel condensation over various catalysts is summarized in Table 1. The blank reaction between benzaldehyde and malononitrile gives almost no product (entry 1). Using g-C_3N_4 as catalyst, the conversion increases to 5.57 % together with a selectivity of 98.81% (entry 2). If we exclude the effect of S_{BET} and adopt the turn number of benzaldehyde per surface area of catalyst per hour (TON, with the unit of $mmol_{bezaldehyde}/m^2_{catalyst}.h$) to evaluate the intrinsic activity of catalyst, it is indicative that all the TON values of g-C_3N_4 is fairly low. Compared with g-C_3N_4, the boron-doped samples with various boron contents (entries 3-6) present the significantly increased conversion. Especially, the sample CNBF-0.5 delivers a highest conversion of 78.55 %, featured with almost both the highest boron content and S_{BET} among all the boron-doped samples. Excluding the effect of S_{BET}, the TON values of boron-doped samples follow the order CNBF-0.1< CNBF-0.3< CNBF-0.5< CNBF-0.7, which is the same as that of boron content and basic site concentration shown in Table 1. As contrast, when sulfur or phosphor is doped into g-C_3N_4, the conversion is quite low (entries 7-8).

Table 1 Comparison of the catalytic performances of knoevenagel condensation over pure and doped g-C_3N_4 materials

Entry	Catalyst	Conversion, %	Selectivity ,%	S_{BET} of catalyst,m^2/g	TON
1	--	0.17	--	--	--
2	g-C_3N_4	5.57	98.81	8.57	27.07
3	CNBF-0.1	19.67	99.14	13.26	61.67
4	CNBF-0.3	38.02	99.27	21.27	74.47
5	CNBF-0.5	78.55	99.78	42.87	76.33
6	CNBF-0.7	63.61	99.81	25.27	104.87
7	CNSF-0.3	16.57	98.35	21.52	32.07
8	CNPF-0.3	1.41	99.27	9.45	6.21

4. Conclusions

In summary, heteroatoms including boron, sulfur and phosphor doped g-C_3N_4 materials were prepared by thermal copolymerization of dicyandiamide and imidazole ionic liquids. Among them, boron-doped g-C_3N_4 materials exhibit significantly enhanced activity in base-catalyzed Knoevenagel condensation. The characterizations showed that boron was doped in tri-s-triazine rings of g-C_3N_4 by substituting carbon atoms. In addition, the basic site concentration of boron-doped g-C_3N_4 is proportional to the doped boron content. Correlating the catalytic performance and characterizations, it is concluded that boron-doping is an effective strategy to enhance the basicity of g-C_3N_4. We envision that the study will constitute an insight for further application of boron-doped or boron-dominant two dimensional materials towards metal-free base catalysis.

References

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