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Variations of apparent activation energy based on thermodynamics analysis of zeolitic imidazolate frameworks including pyrolysis and combustion

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ABSTRACT

Thermodynamics of zeolitic imidazolate frameworks (ZIFs) in pyrolysis and combustion processes at different heating rates were analyzed and kinetic parameters were calculated using thermogravimetric tests. Related results show that TG curves of both pyrolysis and combustion processes shift to the high-temperature zone with the increase of heating rates. Differences of DTG curves reaction intensity of the pyrolysis process are not evident with the increase of heating rates, while the reaction intensity of DTG curves of the combustion process is reduced gradually. The pyrolysis process can be divided into the dehydration (30–230 °C) and the pyrolysis reaction (430–950 °C). The combustion process can also be divided into the dehydration (30–250 °C) and the combustion reaction (331–449 °C). Three stages of the pyrolysis process are carried out by dynamical analysis due to changes of slopes, while the combustion process has only one stage. Dynamical parameters, such as the most probable mechanism, the pre-exponential factor and the apparent activation energy, are acquired by the way of comparison using two methods of Coats-Redfern (CR) model based on integral form and Achar-Brindley-Sharp-Wendworth (ABSW) model based on the differential form. Some interesting phenomena are also presented that effects of heating rates on the thermal decomposition and the kinetic analysis.

1. Introduction

Recently, the greenhouse effect has been paid more and more attention to people, which derives from the increasing concentration of carbon dioxide (CO_2), water vapor and methane in the air. Some technologies have been applied in the capture and separation of related gas emitting from fossil fuel combustion [1–3], in which the development of new function materials is the crucial step. Metal organic frameworks (MOFs) as unique porous nano-materials, constructed by the coordination between metal ions and organic linkers, have been developed rapidly in some research area such as adsorption [4–6], separation [7,8], membrane [9,10], drug delivery [11], energy application [12–14] and catalysis [15–19]. Wang et al. [20] synthesized monodispersed ZIF-8 particles for CO_2 adsorption and heterogeneous catalysis. Calero et al. [21] synthesized two-layered membranes of ZIF materials for the H_2/CO_2 separation. It is a fact that reactions are performed generally at a high-temperature condition for adsorption and separation using MOFs materials [22], which leads to that the thermal decomposition analysis of samples is necessary to the application of materials. Besides, MOFs as precursors are very promising to obtain scattered nano-scale metal oxides by combustion in the air due to the fact that metal oxides are well dispersed using long chains of organic ligands [23], in which ligands are used to be bridges and metal ions are used to be centers. MOFs can also be applied to be ideal precursors for the synthesis of metal@carbon materials by a simple one-step carbonization in inert atmosphere.

Kinetics analysis of solid-state reactions is a widespread method to study the effect of the temperature on reaction processes (pyrolysis and combustion process), which is an effective way to

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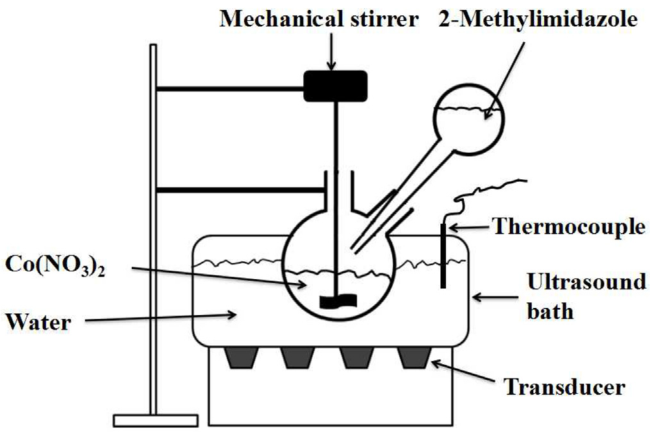

Fig. 1. The schematic diagram of synthesis apparatus of samples.

investigate thermochemical behaviors, to evaluate dynamical parameters and to design and operate the furnaces at the industrial production [24,25]. Thermogravimetric (TG) tests provide related information about the changes of samples with the temperature during reaction processes and the description of thermal characteristics of samples [26]. Related TG data is combined with various mathematical methods, such as Coats-Redfern [26], Friedman [27], starink [27], Kissinger [28], Flynn-Wall-Ozawa [29], to acquire the kinetic triplet (the most probable mechanism, the pre-exponential factor and the apparent activation energy). Though some simple thermal decomposition of MOFs have been presented in previous papers, of which the metal oxide is formed by calcining in air [30–32] and the carbon material is formed by calcining in inert atmosphere [33,34], few papers are studied in detail about thermal decomposition of MOFs materials based on dynamical analysis including pyrolysis and combustion processes at different heating rates.

The work was focused on discussing differences in thermochemical behaviors of MOFs in pyrolysis and combustion processes at different heating rates. ZIFs materials as prepared samples were chose from typical representatives of MOFs. Thermogravimetric tests were carried out to obtain TG curves and DTG curves. Two methods of the Coats-Redfern and the Achar-Brindley-Sharp-Wendworth were employed to calculate kinetic parameters, which is supposed to accelerate researches of pyrolysis and combustion processes of ZIFs materials.

2. Materials and methods

2.1. Materials

Samples were synthesized using a complexation reaction between rigid organic molecules and metal ions with ultrasonic treatment derived from our previous studies [35]. A certain amount of 2-methylimidazole and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in a mixture solution of methanol and ethanol, respectively. Then, two solutions were mixed under ultrasonic radiation. Mixed solution was aged at ambient conditions for 24 h. Precipitates were aggregated, washed and centrifuged using ethanol with several times. Precipitates were dried at 65 °C overnight to obtain samples. A schematic diagram of samples synthesis was exhibited in Fig. 1 [36].

2.2. Thermogravimetric tests

Thermogravimetric (TG) tests were carried out using a Netzsch thermobalance (STA 449F3). Baseline was calibrated by comparing with pre-determined baselines obtained in absence of samples. A certain number of samples were distributed into an alumina

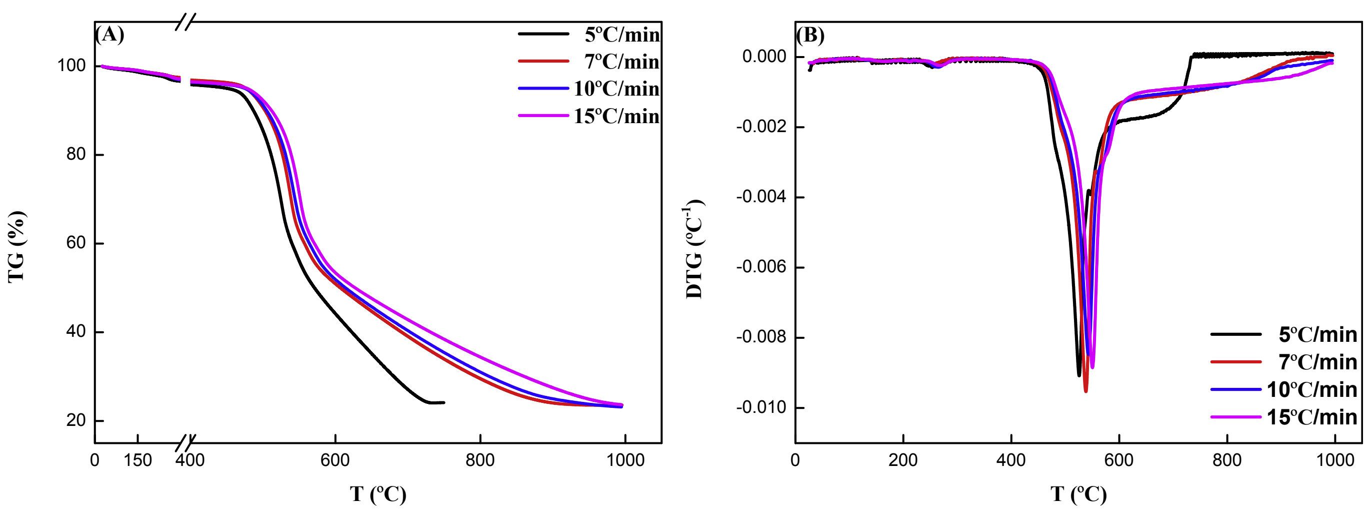

Fig. 2. Curves of ZIFs pyrolysis process at different heating rates: (A) TG, (B) DTG.

Table 1
Weightlessness rates and temperature regions of different stages of ZIFs pyrolysis process at different heating rates.

Weight loss (%)	T (°C)	5 (°C/min)	T (°C)	7 (°C/min)	T (°C)	10 (°C/min)	T (°C)	15 (°C/min)	Mean (%)
First	30–220	1.96	30–210	1.48	30–230	1.75	30–231	1.76	1.74
Second	431–528	28.49	451–540	27.48	440–544	26.26	460–554	28.06	27.57
Third	528–565	15.49	540–588	16.16	544–600	18.48	554–616	16.42	16.64
Fourth	565–730	27.35	588–880	28.02	600–860	23.59	616–950	26.37	26.33
Total	–	73.30	–	73.13	–	70.09	–	72.60	72.28