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MICRO FLUIDIZED BED REACTION ANALYSIS AND ITS APPLICATIONS

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ABSTRACT

Micro Fluidized Bed Reaction Analyzer (MFBRA), which was developed by IPE, CAS, employing micro fluidized bed as reactor to strength mass and heat transfer, realized the plug flow of gas and mixing flow of solid in the reactor. Typical applications (reaction character), including combustion of carbon, capture of CO₂ with Ca(OH)₂, pyrolysis of biomass and combustion of graphite were illustrated in this study to justify the technique advancement of MFBRA.

INTRODUCTION

Gas solid reactions widely existed in the fields of chemical engineering, chemistry, environmental science, material and fuels conversion. The accurate and reliable reaction kinetics are very important to understand the chemical reactions and develop reactors. Instruments for reaction kinetics researches could separate to isothermal and non-isothermal conditions based on the heating rate of sample. Thermogravimetric analyzer (TGA) typifies the non-isothermal analysis tool and approach widely used for gas-solid reactions [1]. For establishing a kind of isothermal reaction analysis instrument and approach that can be applied to various highly exothermic quick and complex reactions, micro fluidized bed (MFB) in diameter and particle bed height of about 20 mm has been used to develop the so-called micro fluidized bed reaction analyzer (MFBRA)[2-4], as shown in the figure 1(b), in Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS), China. By enabling the on-line pulse feeding of milligrams of fine reactant and its subsequent quick mixing and heating of the reactant powder by interacting with bed material particles at a preset temperature, it has been proven that the MFBRA provides readily an isothermal, differential and diffusion-minimized reaction analysis tool. It is also highly suitable for analyzing the gas-solid reactions in special circumstances such as steam, while this analysis is difficult for TGA.

This paper is devoted to summarize the successful applications of the MFBRA to some typical gas-solid reactions including pyrolysis of coal and biomass, combustion of graphite, CO₂ capture by Ca(OH)₂, steam gasification of char, decomposition of CaCO₃, reduction of CuO and iron oxides and so on. These applications demonstrated that the MFBRA not only provides an efficient tool and approach to determine the isothermal kinetics of gas-solid reactions that is closer to the intrinsic kinetics, but also allows a deep insight of the involved reaction mechanism by online monitoring the formed gas product via a differential isothermal method.

Principle and Operation of Instrument

The MFBRA, as shown in figure 1, consisted of a solid sample jet-transfer device, a two stage micro fluidized bed reactor of 20 mm in diameter and an online MS with capillary sampling. The bed material was quartz sand of 0.2-0.25 mm size, and a software system controlled the actions of the MFBRA and monitored the formed gas composition change.

The experimental procedure was as follows. Three grams of bed material (quartz sand) were loaded into bottom gas distributor of the reactor. Under fluidization by a gas stream with a definite composition and flow rate, the quartz glass reactor was heated to form the desired bed temperatures below 1100 °C. The reaction was initiated by injecting 10-50 mg particle sample into the inside of the fluidized quartz sand particles. The reaction occurred simultaneously. Therefore, any gas-solid reactions could be tested in MFBRA under selected conditions. And the intrinsic conditions could also be easily realized for thinning gas film around solid under high gas velocity and collision of fine particles.

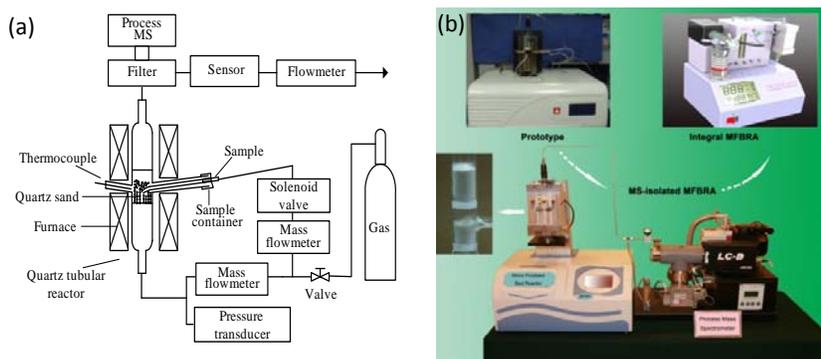


Fig.1. Schematic (a) and Photographs (b) of MFBRA

Typical Applications

Direct reaction of CO_2 and Ca(OH)_2

Reaction of CO_2 with Ca(OH)_2 provides an effective and inexpensive capture for CO_2 , which cause lot of studies on the reaction in recent years[5-7]. However, because Ca(OH)_2 is easy to decompose into CaO , it is difficult to measure the direct reaction of CO_2 with Ca(OH)_2 in the traditional reaction characterization devices, such as TG and DSC.

The resulting gas release characteristics at 610 °C are shown in Fig. 2. The initial quick decrease of CO_2 concentration represented the surface reaction of CO_2 with Ca(OH)_2 , and the successive slow rebound of the CO_2 concentration suggested that the reaction was gradually blocked by the internal gas diffusion. Thus, the chemically controlled reaction was only at the stage with low conversion. Another interesting finding was that the steam release started later than the CO_2 quick adsorption, implicating that an intermediate compound was formed in the reaction process, and the reaction of CO_2 with Ca(OH)_2 did not form CaCO_3 and H_2O directly.

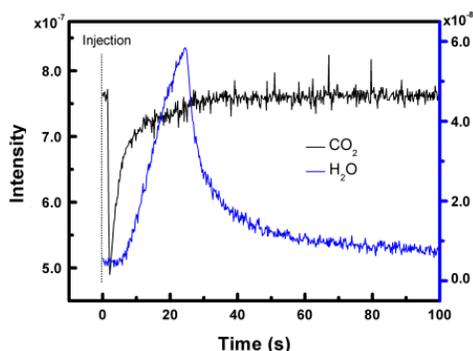


Fig.2. Release characteristics of gas components

Reaction kinetics was calculated from the variation of CO_2 concentration according to shrinking core model. Figure 3 shows that the reaction rate quickly increased at the beginning to denote the heating period for $\text{Ca}(\text{OH})_2$ particles. Then, the rate decreased with the progress of the reaction. The reaction rate and conversion both increased with elevating the temperature at the test values. The conversion x was calculated from the absorbed CO_2 according to the reaction between $\text{Ca}(\text{OH})_2$ and CO_2 . One can see that the curves had good linearity in $x=0.02$ to $x=0.1$ to the determination of the reaction rate constant $k(T)$. Further from the Arrhenius equation it resulted in the activation energy of about 40 kJ/mol for the reaction of CO_2 with $\text{Ca}(\text{OH})_2$, which is much lower than the literature-reported value for the CO_2 capture by CaO [8,9]. The new results in this experiment exhibit the micro fluidized bed reaction analysis could be applied in direct reaction test of unstable materials.

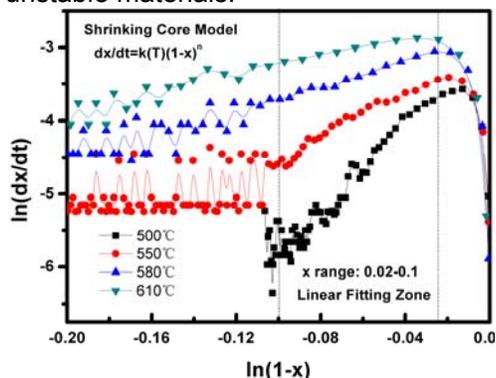


Fig. 3. Correlation of data on shrinking core model

Pyrolysis of Beer Lees

Biomass pyrolysis is essentially important to the utilization of biomass energy. By far, TG method has been generally used to characterize the biomass pyrolysis process and deduce its reaction kinetics. Nonetheless, testing biomass in TG suffers a serious drawback resulting from the instability of the fuel and seriously the interfacial gas diffusion inhibition [10].

Application of the MFBR to biomass pyrolysis demonstrated that the reactor led the pyrolysis to have higher gas yield and less remaining carbon than the test

in TG, and at 1173 K the reaction finished in 10 seconds. The time span to release an individual gas component appeared longest for H₂, shortest for CO₂ and equivalent for CH₄ and CO in between (Fig. 4). These results indicate that the reaction temperature significantly affected the formation of pyrolysis gaseous products, especially for hydrogen, because of the severe tar secondary thermal cracking reaction at high temperature.

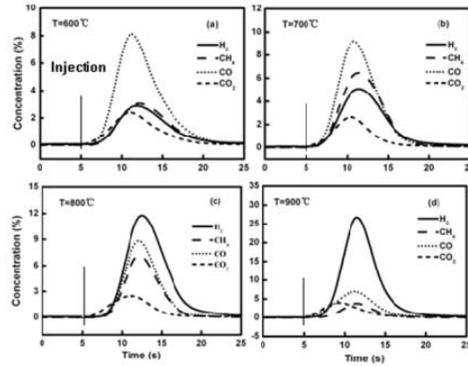


Fig. 4. Pyrolysis gas releasing characteristics in MFBRA

Reaction kinetics was investigated with respect to the formation of individual gas component and pyrolysis gas mixture. All the correlation curves in Fig. 5 have good linearity above 0.97, and the resulting apparent activation energy E fell into a range of 10-30 kJ/mol. The activation energy represents the difficulty for forming the gas component. For H₂ it has the largest activation energy and this justifies that it was more difficult to generate H₂ in pyrolysis. In comparison, the formation of CO₂ is obviously easier for it has the lowest activation energy.

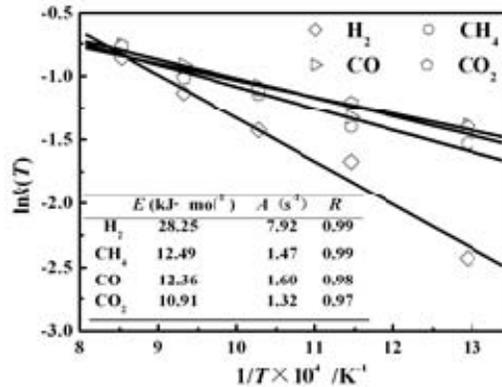


Fig. 5. Linear fitting of $\ln(k(T))$ and $1/T$ and corresponding E

Combustion of Graphite

The measured conversions versus time in MFBRA at different preset temperatures are illustrated in Fig. 6. The reaction finishing time decreased from 500 s to about 20 seconds responding to the elevation of temperature from 700 to 850 °C. When the temperature was over 950 °C the reaction ended in 6 seconds, which represents the fast reaction of graphite combustion.

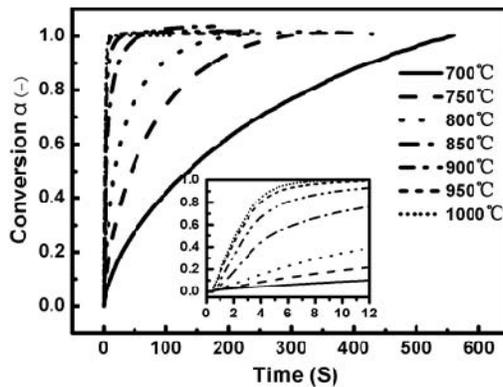


Fig. 6. Conversion α versus time t at different temperatures

Figure 7 shows that the correlation of $\ln(da/dt)$ versus $1/T$ according to iso-conversional method under isothermal conditions, where the conversion α was taken as a parameter. This enabled the determination of the activation energy for each of the plotted conversion from the slope of the linear correlation curve. The resulting data were tabulated in Fig. 8 via digital values. Obviously, the activation energy was lower when the conversion was below 0.2, but in $\alpha=0.2-0.9$ the acquired activation energies are almost the same. The former reveals again that during the first period of reaction in MFBRA the reaction was subject to reactant heating so that the data in this period cannot be used for kinetic analysis. Averaging the activation energies for $\alpha=0.2-0.9$, which varied in 154-179 kJ/mol, led to an average of 165.3 kJ/mol that represents essentially the activation energy of the tested graphite combustion.

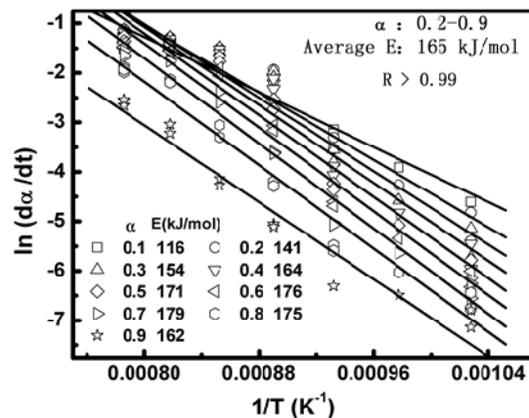


Fig. 7. Correlation of $\ln(da/dt)$ and $1/T$ and corresponding E

Reduction of CuO with CO

Reaction of CuO in CO was tested with TG and the MFBRA to compare their realized reaction rates at a given reaction temperature. The MFBRA measured the formed CO_2 in its effluent gas, while TG monitored the sample weight change. Figure 8 shows the realized conversion as a function of reaction time. The TG tests were carried out for different sample amounts (5 to 40 mg), demonstrating that increasing the sample mass decreased the reaction rate (see the slope of each curve, or the rate data of 0.04 to 0.005 1/s). This reveals that the

reaction with TG suffered greatly from the diffusion of CO into the CuO sample held in the TG cell. The test in the MFBRA used 40 mg of sample, the largest mass amount used in the TG tests, but the realized reaction rate (0.044 1/s) was even higher than that from testing 5 mg sample in TG (i.e., curve e against curve a). This suggests that the influence of external diffusion was much smaller in the MFBRA than in TG, as a result of using a fluidized bed reactor in the MFBRA. This corroborates the advantage of the MFBRA in suppressing the external diffusion, a significant limitation for TG.

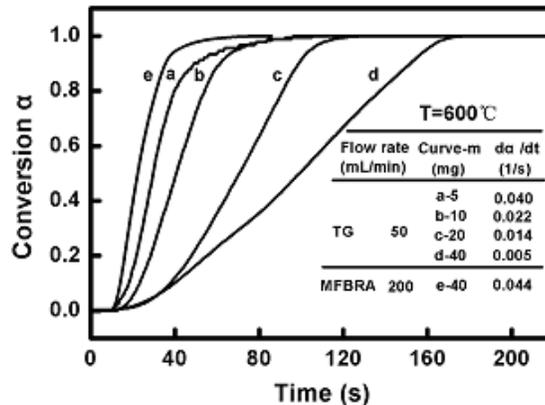


Fig. 8 Reduction rate and conversion of CuO in CO measured in both TG and MFBRA.

Conclusions

Using MFBRA provided an effective approach to measure gas-solid reactions and determine their reaction kinetics. Some interesting conclusion could be obtained as follows.

Direct reaction of Ca(OH)_2 with CO_2 in MFBRA justify that the MFBRA possess in-situ reaction characteristics. It could also be suitable for the similar reactions, such as the reaction of CaCO_3 and SO_2 .

It was shown that the pyrolysis of beer lees in the MFBRA finished in about 10 seconds at 800 °C with activation energy of 11-28 kJ/mol, which is much less than that in fixed or fluidized bed reactor. These demonstrate that the MFBRA enabled the fast reactions like pyrolysis for investigating the reaction characteristics and estimating the kinetics.

Under minimized diffusion inhibition, the kinetics graphite combustion in the MFBRA is almost same as literature report value of 165.0 kJ/mol. The accurate activation energy clarified in fact that the MFBRA possess isothermal differential reaction characteristics and is effectively applicable to fast (catalytic) combustion reaction.

Comparison test of CuO reduction in CO using TGA and MFBRA, the difference of reaction rate shows the lower gas diffusional inhibition of reaction in MFBRA than that in TG.

Above mentioned characteristics possessed in MFBRA were mainly resulted in minimizes the gas diffusion inhibition, realizing quick heating and strengthening mass and heat transfer performance by using micro fluidized bed reactor.

Acknowledgements

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