Promotion and inhibition of gas hydrate formation by oxide powders

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ABSTRACT

In this work we studied the activity of powders of silicon, aluminium, zinc, titanium and magnesium oxides as promoters of natural gas hydrate formation. We found that the activity of powder as a promoter of heterogeneous gas hydrate nucleation depends on the properties of powder particle surface, in particular on functional groups that are present on the surface. For example, the addition of powdered aluminium oxide into water resulted in both the maximal and close to minimal induction times of the hydrate formation depending on the surface chemical composition of powder particles. Our results show that the formation of hydrates is favored by the presence of carbon-containing groups (in particular carbonate) on the surface of the particles. Consequently, the modification of the surface of oxide particles can be used to obtain the promoters of gas hydrate formation.

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1. Introduction

Gas hydrates are inclusion compounds in which the molecules of gas or easily volatile liquid are located in the cavities of a polyhedral framework composed of water molecules. The guest–host interactions are of van-der-Waals type [1,2]. Natural gas hydrates contain huge reserves of fuel gas, which makes them prospective source of energy [3]. The methods of storage and transportation of natural gas and hydrogen involving gas hydrates are under development, as well as hydrate-based methods of gas mixture separation, in particular the mixtures of methane and carbon dioxide, or carbon dioxide and hydrogen [4–7]. Many works focus on the kinetics of hydrate formation in the systems liquid water–gas [1,8,9]. Nucleation of gas hydrates and the induction periods of hydrate formation were considered in detail [10,11]. Here and below the induction time are understood as the time since the establishment of thermobaric conditions for gas hydrate formation till the formation of detectable hydrate phase. It is assumed that the main part of this period is the time necessary for the formation of the first hydrate nucleus able to grow spontaneously. Induction times in gas hydrate crystallization with the promoter of nucleation are still poorly studied.

It follows from the nucleation theory [12,13] that the induction time (or period) is a random value, with the maximum of its distribution corresponding to the most probable time of the start of new phase formation. As was demonstrated for hydrate formation processes, the induction time and the width of distribution function decrease with increased degree of supercooling [14–17]. The formation of the nuclei of the new phase can proceed via the homogeneous or heterogeneous mechanism. Homogeneous nucleation occurs under substantial supercooling of the system; in this case the nucleus of the new phase is formed due to density fluctuation in the initial phase. The dependence of the free energy of this nucleus on its size runs through a maximum. Nucleus radius corresponding to the maximum of the free energy is called the critical radius, and the nucleus itself is called critical. The addition of new atoms or molecules to the critical nucleus decreases its free energy. This nucleus is able to grow spontaneously. A nucleus with the radius less than the critical one dissolves. So, the formation of the critical nucleus is connected with overcoming the potential energy barrier. The height of the potential barrier is proportional to the value of the free energy of the nucleus. In the case of heterogeneous nucleation, the nucleus of the new phase is formed on some extraneous surface present in the initial phase (later referred to as the surface of the inducer). This may be a particle suspended in the initial phase, vessel wall and so on. Sticking of the nucleus to the inducer surface decreases its surface free energy. In this case, nucleation can be considered as adsorption or epitaxial growth of the crystal of new phase [18,19].

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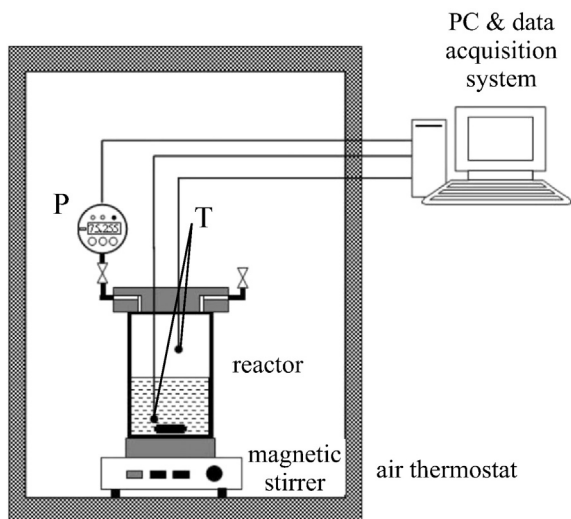**Fig. 1.** Schematic of the experimental setup.

Fig. 3. Gas consumption in a typical experimental run with pure water. The upper and lower curves correspond to gas consumption due to gas dissolution in water + hydrate formation and hydrate formation only, respectively. t_n is the onset of gas hydrate formation.

The height of the potential barrier for the formation of the critical nucleus of the new phase becomes less than that in the case of homogeneous nucleation. Accordingly, the induction period of the new phase formation decreases, as well as supercooling which is necessary for nucleation. In practice, researchers more frequently deal with heterogeneous nucleation. Because of the impossibility to control the presence and types of inducers in the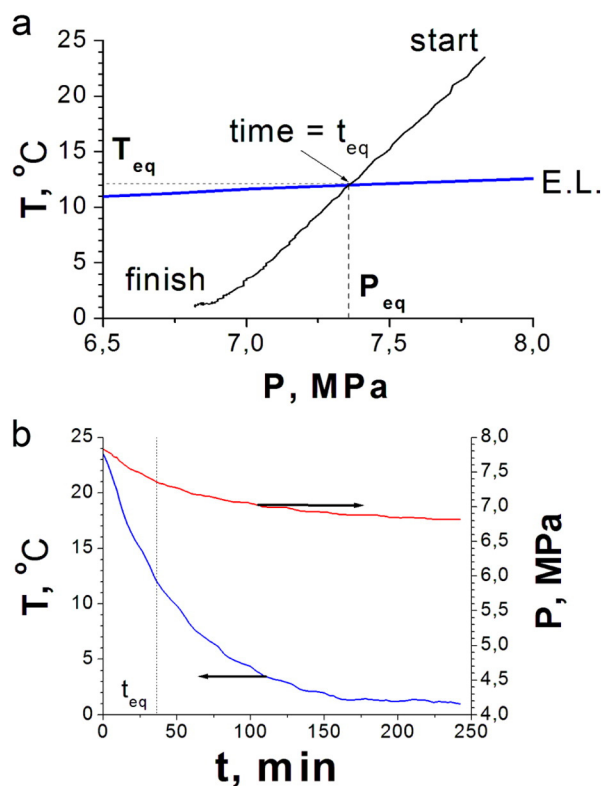 system, induction times of gas hydrate formation measured under different conditions and in different experimental facilities are poorly reproducible.

At present, the possibilities to control crystallization by introducing the centers of heterogeneous nucleation (nucleation promoter or inducer) are under investigation [20–27]. It is known that the activity of a promoter can depend on its crystal structure, particle size, topological and chemical inhomogeneity, and the nature of surface functional groups [28–30]. For instance, great curvature of inducer surface (small particle radius) prevents the growth of the new phase on it, while the pores on the surface, quite contrary, favor this process [28]. The possibility to use the powders of different substances as the promoters of gas hydrate formation was considered in Refs. [31–36]. Experimental studies of gas hydrate formation showed that the induction time decreases in the presence of the powders of SiO_2, hematite and graphite and a mixture of hematite and graphite [31–33]. Additionally it was found that the induction time of hydrate formation in porous media depends on the composition of the medium [34]. Calculations showed that the surface of hydroxylated silica does not favor the growth of gas hydrates [35]. The synergic effect of silver nanoparticles and sodium dodecyl sulfate on the gas hydrate formation rate and storage capacity was revealed in Ref. [36].

In the present work we studied the dependence of induction time of the gas hydrate formation on the nature and characteristics of the surface of oxide particles suspended in water.

Fig. 2. (a) Typical P–T experimental trajectory in isochoric cooling process. E.L. — equilibrium line of the gas hydrate [1]. START, FINISH — P,T conditions at the start and finish of the experiment, respectively; t_{eq} is the time when the equilibrium pressure (P_{eq}) and temperature (T_{eq}) of hydrate formation are reached in the reactor. (b) Changes of temperature (blue line) and pressure (red line) with time in the same experiment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
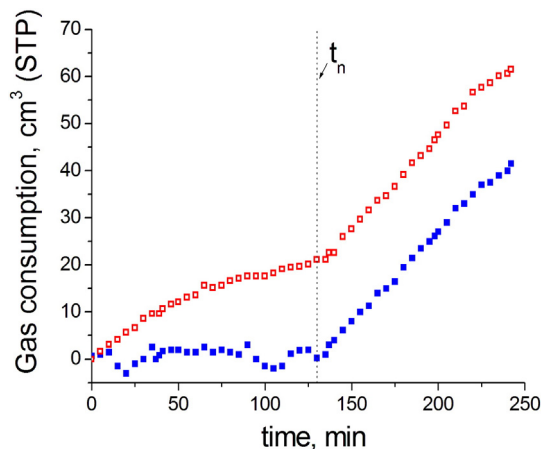
2. Materials and methods

Seven randomly chosen powdered samples were taken for experiments: silicon oxide (2 samples), aluminium oxide (2 samples), zinc oxide, titanium oxide and magnesium oxide. The SiO_2-2 and Al_2O_3-1 powders were manufactured by «Degussa» company; the samples of other powders were taken from laboratory experimental batches. Distilled water was used in experiments on hydrate formation. To avoid changes of the background concentration of hydrate formation centers, water for experiments was taken from the same vessel filled at the beginning of the series of experiments. Natural gas from the Urengoy gas field (vol.%: C_1—98.06, C_2—0.46, C_3—0.24, i-C_4—0.02, n-C_4—0.04, $C_{5+\ more}$—0.02, CO_2—0.15, N_2—1.01) was used to obtain gas hydrates.

The induction times of hydrate formation were determined in the series of experiments on the formation and dissociation of hydrates without recharging the reactor. To obtain hydrates, we used a home-made stainless steel cylindrical reactor with the inner volume of 50 cm³ which was designed for a pressure up to 15 MPa. The reactor was mounted at a magnetic stirrer. In a typical experiment, 20 g of