A review on the solid sorption mechanism and kinetic models of metal halide-ammonia working pairs

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ABSTRACT

Solid sorption and kinetic models are important for both experimental and theoretical analysis of chemisorption refrigeration and energy storage. This review attempts to present clear overview of the reaction kinetics of chemisorption working pairs (mainly the metal halide-ammonia working pairs). The typical equilibrium principles and phenomena in metal halide-ammonia working pairs are introduced. The advantages and shortcomings of several classical non-equilibrium models have been analyzed comprehensively and new chemisorption phenomena of metal halide-ammonia working pairs that have been recently discovered are discussed. Finally, new directions for the development of kinetic models for metal halide-ammonia working pairs are proposed.

1. Introduction

Solid sorption refrigeration systems, which can be powered by solar energy [1–4] or low-grade waste heat [5–8] and utilize working pairs with zero Ozone Depletion Potential (ODP) and Global Warming Potential (GWP), have received increasing attention since the 1990s. Solid sorption phenomena can be divided into physical adsorption [9–11] and solid chemisorption [12–14]. Physical adsorption is a consequence of van der Waals forces [15] while solid chemisorption is a complexation reaction between sorbates and the surface molecules of sorbents [16]. Compared to physical adsorption, solid chemisorption has a larger sorption capacity, which is beneficial for increasing the specific cooling power per kilogram sorbent (SCP) and decreasing the volume of the reaction bed.

Solid chemisorption working pairs consist of metal halide-ammonia, hydride-hydrogen, and oxide-oxygen. Hydride-hydrogen is mainly used for the storage of hydrogen, oxide-oxygen working pairs are optimal for high-temperature heat storage, and metal halide-ammonia working pairs are extensively used for refrigeration, heat pumping and energy storage [17]. In pursuit of improving the heat and mass transfer performance of chemical sorbents, composite sorbent matrices have been widely studied [18,19] for the past three decades, with a special focus on expanded natural graphite (ENG) and expanded natural graphite treated with sulfuric acid (ENG-TSA) [20–22]. Other composite sorbents such as 'CaCl$_2$ confined to silica gel', have been used to improve the SCP or coefficient of performance (COP) [23,24].

The classic solid sorption theories include the Langmuir adsorption theory [25], the Gibbs approach [26], the Polanyi potential theory [27–29], and the Brunauer-Emmett-Teller (BET) equation [30]. Of these, the BET method is widely used to study the surface area of porous materials such as silica gels [31], whereas the Dubinin-Radushkevich (D-R) equation [32,33], established according to the Polanyi potential theory, is extensively applied in physical adsorption. For materials with novel structures, a physical model called the 'multilayer model with saturation' has been successfully used to interpret the adsorption equilibrium of ethanol on metal organic frameworks [34]. In the case of composite solid sorbents, it was recently proposed that kinetics similar to physical adsorption can account for the existence of multiple pores in the matrix [35,36], the D-R (Dubinin-Astakhov (D-A)) equation was also used for the establishment of kinetic models [37].

Since the 1990s, several types of kinetic models have been proposed to explain the chemisorption working pair mechanisms. Stitou and Crozat divided solid chemisorption kinetic models into three groups, viz. local models, global models, and analytical models [38]. Local models [39–41] are based on the local heat and mass transfer laws and consider uniform variables in small volumes; the problems in space and time need to be discretized and numerically solved because they can generate a set of partial derivatives. Global models [42–46] consider uniform values on the same scale with the reactor. Since global transformations like permeability, heat conductivity and thermal capacity are averaged in reference to the volume of the reactor, these models lead to a set of differential equations, which only need discretization in the time scale of the problem. Analytical models [38,47] consider the variables to be averaged during the entire reaction time, which means that the characteristic variables are only relevant to the space variables in the resolution of a set of differential equations. In some cases, by

Nomenclature

A	surface of heat exchange, m^2
Ar	Arrhenius term
C_p	specific heat at constant pressure, $J\,kg^{-1}\,K^{-1}$
E	pseudo-energies of activation, J
K	kinetic parameter
K_s	gas permeability
M	kinetic parameter
m	mass of salt, kg
m_2	pseudo-orders of reaction II
N	number of moles of gas adsorbed per mole of salt
N_g	molar adsorption capacity, $mol\,mol^{-1}$
n	mole
n_1	pseudo-orders of reaction I
n_2	pseudo-orders of reaction II
p	pressure, Pa
R	universal gas constant, $J\,mol^{-1}\,K^{-1}$
r	radius, m
S	exchange surface, m^2
s	Arrhenius constant
T	temperature, K
t	time, s
V_m	molar volume, $m^3\,mol^{-1}$
$X(x)$	conversion degree of reaction I
$Y(y)$	conversion degree of reaction II
U	global heat exchange coefficient, $W\,m^{-2}\,K^{-1}$

Greek symbols

θ	local dimensionless temperature
ΔH	change in enthalpy, $J\,mol^{-1}$
ΔS	change in entropy, $J\,mol^{-1}\,K^{-1}$
ν	stoichiometric coefficient of the chemical reaction

Subscripts

1	reaction I
2	reaction II
a	adsorption process
c	constraint value
cal	calculated value
d	desorption process
eq	chemical equilibrium value
exp	experimental value
i	locally finished state
sw	salt/wall

Superscripts

0	standard state
*	corrected value

considering that mass transfer in the reaction medium does not impose any limitations, only the heat transfer equation (the kinetic equation for the reaction process will not be considered because no time variables are included in this model) needs to be solved and an analytical resolution can be obtained.

On the other hand, according to Lebrun and Spinner's analysis [48], the kinetic model should be either phenomenological or analogical. The phenomenological models link with the physico-chemical properties and precision phenomena, and hence they are counted as knowledge models. On the other hand, since the properties and structure of the reaction medium need to be understood in detail, it makes the model too complex and difficult to manipulate. The analogical approach, which does not involve detailed reaction mechanisms, is only used to reproduce the overall performance and effect of solid sorbents. Since the reaction medium is considered a uniform entity, the kinetic models are no longer based on the properties and structure of the medium, but on simple physico-chemical processes and homogeneous reactions, which consist of a number of parameters. As the parameters do not evolve from the properties of the medium, they are experienced parameters and must be identified according to the experimental values. Therefore, these models are not knowledge models. Under this criterion, phenomenological models [41,49] are much lesser in number than the analogical models.

In the last 20 years, a number of reviews on sorption refrigeration have been published. Wongsuwan et al. [50] reviewed the current technologies and their applications and prospects in chemical heat pumps (CHPs). Yong and Wang [51] reviewed over a hundred patents on technologies to enhance the performance of solid sorption systems. Wang et al. [52] summarized the available physical and chemical working pairs with their basic equilibrium models. Furthermore, a review on adsorption refrigeration technology and deterioration in physical adsorption processes was presented by Wang et al. [53], in which they focused on the methods to enhance heat and mass transfer. Cabeza et al. [54] reviewed the operation principles of the technologies and materials in both absorption/adsorption heat pumps and sorption for thermal energy storage. Aristov [55] presented an overview of the available literature on several classes of working pairs. Later, Younes

et al. [56] reviewed physical adsorbent-adsorbate pairs for adsorption cooling applications and the isotherm models used to estimate the adsorption equilibrium uptake of the studied pairs. Most of the reviews published in recent years concentrate on solar sorption refrigeration [57–61], especially on the principles and physical adsorption equilibrium models used in solar sorption refrigeration systems [62].

Several kinetic models used for various chemisorption working pairs have been applied in recent years. Jiang and Guo [63] used the recently proposed Sudden Vector Projection (SVP) model to predict mode specificity, bond selectivity, normal scaling behavior, and surface lattice effects in the case of water dissociative chemisorption on Ni(111), Cu (111), Pt(111), and Pt(110)-(1 × 2) using direct plane-wave density functional theory calculations. Later, they investigated site-specific reaction probabilities on a nine-dimensional global potential energy surface (PES) (for water interacting with a rigid Ni(111) surface) using a quasi-seven-dimensional quantum dynamic model [64]. It was shown that the site-specific reactivity was largely controlled by the topography of the PES instead of the barrier height, underscoring the importance of multidimensional dynamics. Similarly, Jackson et al. [65] worked on the dissociative chemisorption of methane on metal surfaces and Liu et al. [66] studied H_2 adsorption on a Cu(111) surface; in both cases, the quantum model was used.

Even though halide-ammonia pairs, typically used for chemisorption, are widely applied in refrigeration, heat pumping and energy storage, there have been very few reviews analyzing the solid chemisorption kinetic models of halide-ammonia working pairs in detail. However, such studies are essential for designing the reactors and for theoretical and experimental analyses. In order to help other researchers achieve a clear and precise understanding of the mechanism and modeling of halide-ammonia working pairs, in this review article, we initially introduce the typical equilibrium principles and phenomena in metal halide-ammonia working pairs. In the subsequent sections, the advantages and shortcomings of several classical non-equilibrium models are analyzed. Later, several recently discovered sorption phenomena are discussed and finally, we propose several new directions for the development of kinetic models for metal halide-ammonia working pairs.