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Adsorption models and heat of adsorption of adsorbed ortho di-methyl benzene and 1-propanol species in competitive adsorption on silica by using temperature programmed adsorption equilibrium methods

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ABSTRACT

Single and binary adsorptions of ortho di-methyl benzene and 1-propanol on silica at 300 K and at various adsorption pressures were studied using temperature programmed adsorption equilibrium (TPAE) procedure. The evolutions of the surface coverage with the adsorption temperature ($\theta_e = f(T_a)$) were compared to the Temkin and Langmuir models in order to determine the heats of adsorption and to reveal the presence of mutual interactions between adspecies. It has been shown that in single adsorption equilibrium of 1-propanol on silica, the heats of adsorption were found to be dependent to the surface coverage. In contrast, of single adsorption equilibrium of ortho di-methyl benzene on silica, the heat of adsorption was found independent to the surface coverage. However, in the competitive adsorption, the heats of adsorption of the adsorbates were found varied with the surface coverage. The variation of heats in single and in binary adsorption characterizes the mutual interactions between the adspecies.

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Introduction

It is well known that volatile organic compounds (VOCs) are involved in the degradation of the air quality and their effects on human health are diverse (toxic, carcinogenic, mutagens, etc.) [1]. Actually, several processes are used to prevent their emission in the atmosphere. The adsorption-desorption-condensation or destruction (reaction) constitutes the most processes studied and currently used in VOCs removal from the exhaust gas [2–7]. Because of its harmfulness to the environment and human health, removal of VOCs from a bulk gas stream by an adsorption process is a common engineering practice that has been receiving increasing attention during the past few years [2–7]. Numerous adsorbents are currently used into these processes, which include zeolite, activated carbon and metallic oxides [8,9]. The most widely utilized adsorbent for the exhaust gas cleaning is the high surface area activated carbon and zeolite. However, those materials present some drawbacks, such as difficulties in the regeneration in air, selectivity in the case of multicomponent in a stream and adsorbed molecules could be destroyed due to the chemisorptions at high temperatures [3,5,10–12]. Activated carbon and zeolite

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have high capacity to remove large amount of VOCs due to various surface properties (porosity, potential barrier, etc.) that lead to strong interactions implying surface function groups and condensation into pores at high partial pressures. Flat surface of nonporous materials permits to study the interactions between adsorbate and adsorbent without taking into account the effects of diffusion and condensation into pores. For this reason, the present work will focus on measuring the interactions between VOCs and non-porous silica gel surface that has polar surface and may adsorbs molecules from the gas phase and keeps them on the surface via interactions with silanol groups and acidic sites which act as adsorption sites [11,13,14]. In addition, silica gel often serves as a catalyst support and its silanol groups are analogous to those that exist in reinforcing siliceous glass fibers [15]. Moreover, due to the industrial use of chemicals, various compounds are often present in the exhaust emissions. Among them, ortho di-methyl benzene (denoted OX) and 1-propanol (denoted PrOH) are selected for this investigation. The choice of these VOCs is based on the fact that these compounds are main components in the exhaust emissions of painting automobiles industry and are involved in different industrial catalytic processes such as isomerization and oxidation [2,15–19]. Furthermore, the OX and PrOH molecules are characterized by different dipole moment 0.64 D and 1.68 D, respectively [20-22]. This characteristic may lead to different affinity with the silica surface sites and subsequently promotes their adsorption [23,24]. In fact, the adsorption of PrOH and OX on silica could occur via silanol groups on the silica surface involving

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hydrogen bonding [16,25–28] and benzene ring π -orbitals [29– 31]. Therefore, it is of great scientific and practical interest to study the adsorption properties of non-porous silica with respect to different adsorbates (polar and/or non-polar). Such investigations could provide evidence for the importance of some adsorbent parameters including the surface heterogeneity and polarity of adsorbate. This basic knowledge is important for the development of improved models for the prediction of the equilibrium in case of multi-component adsorption [27].

The present work focuses on the characterization of the competitive adsorption of selected VOCs on non-porous silica under quasi-equilibrium using the temperature programmed adsorption equilibrium (TPAE) method [32,33] and modeling of the surface coverage variation with the temperature of adsorption by theoretical models such as Langmuir [34] and Temkin [35] models. The development of the microkinetic approach of heterogeneous catalytic processes goes through the validation by experimental procedures of mathematical expressions for the kinetic parameters of the different surface elementary steps. The present study contributes to this development by showing that the adsorption coefficient K and the $\theta_e = f(T_a, P_a)$ curves linked to localized adsorbed species constitute a robust support to characterize the adsorption equilibrium of the adsorbate that can be either a strongly adsorbed diatomic molecules [32] or a more complex weakly adsorbed species [33]. In addition, discussions about competitive adsorption of alcohol and benzenederived compounds on silica are limited in the open literature.

Experimental

Materials

Silica solid: SiO₂ Aerosil 200 from Degussa (BET = $220 \text{ m}^2/\text{g}$) has been selected for two main interests: (a) it is a non-porous solid preventing the contribution of condensation in the pores to the experimental data and (b) at low temperatures, it has non-reactivity with OX or PrOH excepted the adsorption. Same sample of material was used for several experiments and it was pretreated before each adsorption in order to regenerate the silica surface and to remove eventual trace of adsorbates, as follows: He, 300 K \rightarrow He, 723 K (2 h) \rightarrow O₂, and 723 K (1 h) \rightarrow He, 723 K (10 min) \rightarrow He, 300 K. For the adsorption experiments, ortho di-methyl benzene (Alfa Aesar, 99%) and 1-propanol (VWR BDH Prolabo, 99%) were used as adsorbates. Dry helium was used as carrier gas with purity greater than 99.999%.

Analytical procedures

The temperature programmed adsorption equilibrium (TPAE) [32,33] was used in the present work in order to evaluate silica gel efficiency of removing multi component gas from bulk stream, and to determine the heats of adsorption for each component. The TPAE experiments carried out in a dynamic adsorption/ desorption process using a purpose-built device consisting of a gas chromatography (GC) and flame ionization detector (FID) as detector for transient experiments. The assembly (Fig. 1) permits (i) to prepare gas mixture in the inlet reactor and to control feeding flow rate, (ii) to perform in situ pre-treatment, adsorption and desorption steps in quartz micro reactor (1 cm³) and (iii) to monitor OX and PrOH concentrations in the outlet reactor by the mean of GC-FID.

In order to avoid condensation into tubing after condenser/ saturator system, the pathways to the GC system were heated to 373 K and the partial pressure of each adsorbate was predetermined to less than 2.9% and 0.96%, respectively, for PrOH and OX.

In the case of single adsorbate, a flow of 100 cm³/min of He controlled by mass flow controller (MFC) (way1) was passed through saturator/condenser system at desired temperature of Dewars under atmospheric pressure to fix the partial pressure of the adsorbate. The saturated flow was directed either to GC-FID for concentration determination or to the silica bed in the reactor then to the GC-FID. While way-2 may was served either to perform dilution of way-1 or to prepare mixture of adsorbates. Several valves permitting to select the gases mixture and to permute between two ways used to feed the sample. The gas mixture was passed through the fixed bed material (0.31 g of silica) supported by quartz wool in a quartz microreactor. A furnace and its controller system permitted to perform a linear increase in the temperature of adsorption at a constant heating rate. The temperature inside the reactor was measured with a type K thermocouple (0.25 mm). The online analysis system (GC-FID) was equipped with an injection loop $(1 \mu l)$ and with a capillary column



Fig. 1. Scheme of experimental device equipped with GC allowing single and binary adsorption of 1-propanol and ortho di-methyl benzene on silica.

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