

## **MICROCALORIMETRIC INVESTIGATION OF ZEOLITES FOR APPLICATIONS IN HETEROGENEOUS CATALYSIS, ADSORPTION OF POLLUTANTS AND AS THERMAL ENERGY STORAGE MATERIALS**

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The unique surface properties of zeolites have led to their many applications in catalysis and other areas of chemistry. These properties are governing the energetics of the adsorption, reaction and desorption steps, which represent the core of a catalytic process. A fundamental understanding of the great diversity of chemistry occurring at the surface requires familiarity with molecule-surface interaction. The energetics of chemical events occurring on the surface play an important role in determining the catalytic properties of the surface, since different surfaces will cause a substance to react in different ways. Study of adsorption of probe and reactive gas molecules onto surface of zeolites leads to the better understanding of the nature of gas-solid interactions and gives valuable information about the properties of the adsorbent surface and thus is of primary importance in catalytic reactions, adsorption of pollutants and development of thermal energy storage materials.

Adsorption is an exothermic process and when a reactive molecule interacts with the surface of the solid heat is evolved. This heat is related to the energy of the bonds formed between the adsorbed species and the adsorbent and hence to the nature of the bonds and to the chemical reactivity of the surface. From a number of techniques used to study this interaction only a few provide information about the strength of adsorption itself. The determination of the differential heats evolved, by means of a microcalorimeter linked to a volumetric line or another analytical technique such as GC, TG, MS, when known amounts of gas probe molecules (ammonia, pyridine, etc.) are adsorbed on catalytic surface is the most suitable and accurate method which allows the determination of the number, strength and energy distribution of the adsorption sites [1, 2]. The effective use of this technique in heterogeneous catalysis depends on the choice of the probe molecule, since the nature of the probe determines which surface property is going to be investigated.

Catalytic processes in which zeolites are used are mostly reactions catalysed by acid sites [3]. In other words, acidity with a controlled distribution of acid sites strengths is probably the most important property observed in the zeolite catalyst. Therefore, the estimation of features related to acidity is evidently crucial for understanding the reactivity of zeolites. The understanding of zeolites' acidity comprised knowledge of related concepts: a) nature of the acid sites, b) number of the acid sites, c) acid strength of the sites, and d) distribution of the acid strength of the sites [3]. Adsorption microcalorimetry allows an accurate determination of amount, strength and the strength distribution of surface sites, based on the heats of adsorption of appropriate probe molecules and differential heats as a function of surface coverage [3]. The number of cases where adsorption microcalorimetry has been successfully applied to this end has increased in recent years, especially in the field of determination of the acidic function of molecular sieves. Besides basic zeolites have their importance too in catalysis. More recently the acid-base properties of zeolites have been also determined in liquid phase such as n-decane or water using n-butylamine or phenylethylamine as probe molecules.

Adsorption of various pollutants from aqueous phase on zeolites materials have also been studied by calorimetry and associated UV-vis spectrometry. This technique is a promising

method to study adsorption phenomena on the surface of a solid in contact with a liquid phase for two main reasons: (i) the expected physical quantities are directly measured, and (ii) the experiments provide both thermodynamic (the heat evolved) and quantitative (the amount of adsorbed substance) data [4, 5]. Therefore, the adsorption capabilities of various synthetic and natural zeolites were investigated for the removal of phenol, nicotine and different pharmaceutically active compounds from water solutions by calorimetry technique [6].

One of the recent applications of zeolites is as materials for thermal energy storage. The energy storage is one of the critical problems of present solar energy application research. Due to their structure, zeolites are able to store solar energy and to be showed off due to their propriety of adsorbing/desorbing water without damaging the structure. The great advantage of thermal energy storage methods based on adsorption/desorption processes consists in the possibility of storing thermal energy, even for long time. Zeolites answer to requirements of large availability and most stringent environmental regulations. However, Alefeld *et al.* [7] and Kato *et al.* [8] ruled out the use of zeolites alone in seasonal storage for economical reasons. On the other hand, salt hydrates such as magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) have shown great potential as thermochemical heat storage materials. Endothermic dehydration of the salt hydrate occurs *via* heat obtained from a solar collector, before rehydrating the material using humid air, which releases the stored heat *via* an exothermic reaction. However, a significant obstacle when using  $\text{MgSO}_4$  is that upon hydration, a crust of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  forms over the surface of the bulk material, limiting further sorption of water. Therefore, a composite material was developed using a microporous zeolitic matrix to offer a high specific surface for reaction and a high magnesium sulphate impregnation. In this way optimization of the heat stored/released by the composite material can be achieved [9].

## References

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