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INVESTIGATION OF SURFACE PHENOMENA ON SOLID CATALYSTS BY THERMOGRAVIMETRY

2. COMPARISON OF ADSORPTION MEASUREMENTS BY DYNAMIC THERMOGRAVIMETRY ON AN OPEN SYSTEM WITH RESULTS OBTAINED ON A STATIC SYSTEM

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NH_3 and CO_2 adsorptions were measured for seven silica–alumina catalysts, containing various concentrations of sodium ion. The measurements were carried out in two different ways: with the classical volumetric method, and a dynamic one, taking DTA, TG and DTG curves simultaneously. Great similarities are observed between the results obtained with these methods. Adsorption measurement by thermal analysis may be useful for semiquantitative studies.

In the course of our studies on industrially applied catalytic processes we attempted to investigate the surface phenomena on solid catalysts. This was done by means of a relatively easy and straightforward technique: dynamic adsorption measurements with a Paulik–Paulik–Erdey Derivatograph (MOM, Budapest). This method [1, 2] records the mass changes (TG and DTG) jointly with thermal effects (DTA). The latter occur on increase of temperature in the system solid catalyst–gaseous reactant.

The data obtained are reproducible, but of low accuracy. In order to evaluate this, NH_3 and CO_2 adsorption was measured by two independent methods: thermal analysis, and the classical volumetric method.

Experimental

Apparatus

Adsorption by the dynamic method was measured with a Derivatograph (MOM, Budapest, Hungary), and adsorption by the static method with a conventional volumetric apparatus with gas pressure in the range 0–800 mm Hg.

Materials

Seven silica–alumina catalysts were prepared with constant silica/alumina ratios but different sodium ion concentrations. Amorphous Ketjen 25 silica-alumina was used as a basic catalyst. The other six adsorbents were prepared by impregnation of this with aqueous sodium hydroxide solutions of various concentrations. Detailed data are given in Table 1.

Table 1

Catalyst no.	Sodium content		Specific surface area* m^2/g
	mole Na/g	μmole Na/m^2	
1	0.00	0	665
2	0.14	0.23	615
3	0.25	0.52	583
4	0.36	0.66	555
5	0.55	1.05	525
6	0.81	1.64	495
7	1.00	2.13	445

* Specific surface area was calculated from point *B* of the isotherm of N_2 adsorption at – 196°.

Gases of technical grade were used. Ammonia was dried over sodium, and carbon dioxide with phosphorus pentoxide. The gases were finally passed through a dry-ice freezer.

Measurements

Measurements by the dynamic method were carried out for 100 min. in an open system at atmospheric pressure and at temperatures varying from room temperature up to 600°. Before the experiment was started, the samples were subjected to the same heat treatment as was applied subsequently, in order to clean the surface. The samples were heated and then cooled to room temperature under dry argon. At the moment of injection of NH_3 or CO_2, the flow of argon was stopped. The content of air in the system during the cooling and heating of the sample was negligible. The results of measurements with a constant gas flow and rate of heating are given in the TG, DTG and DTA diagrams.

In the static system adsorption was measured by the volumetric method at constant temperature by means of a vacuum apparatus. Before the experiments, catalyst samples were degassed under reduced pressure (ca. 10^{-5} torr at 400°). After lowering of the temperature to that selected for the experiment, a definite portion of gas was introduced portionwise to the apparatus. When equilibrium was reached the quantity of gas adsorbed was calculated from the difference in the pressures before and after adsorption. The quantities of gas adsorbed at 30, 100, 200 and 300° and a pressure of 755 mm Hg were taken for comparison.

Results and discussion

The quantities of NH_3 and CO_2 adsorbed are shown in Figs 1–4 as a function of the sodium concentration of the catalyst. The method of evaluating the results was published previously [3].

There are great similarities between corresponding curves taken by static adsorption and thermogravimetry. Extrema are observed on both curves at the same sodium concentration on the catalyst. However, there are quantitative differences (more clear at lower temperatures) in the intensities of the peaks which characterize the minima and maxima of adsorption. Above 100°, curves obtained with the dynamic and static methods approach each other and coincide. In conclusion, one can say that the results of adsorption measured with the thermobalance are

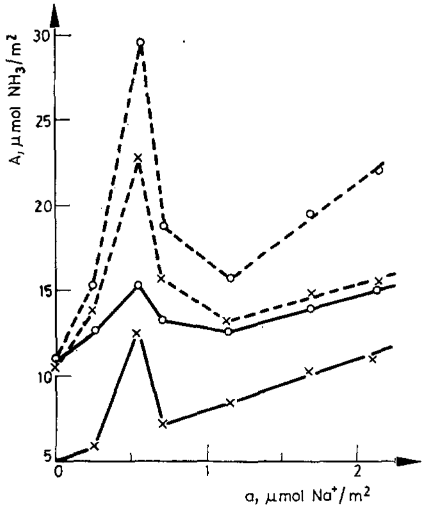

Fig. 1. Relation between the quantity of NH_3 adsorbed at 30° and 100° and the amount of sodium added to the catalyst; ———— volumetric method; - - - - thermogravimetry; ○: 30°, ×: 100°

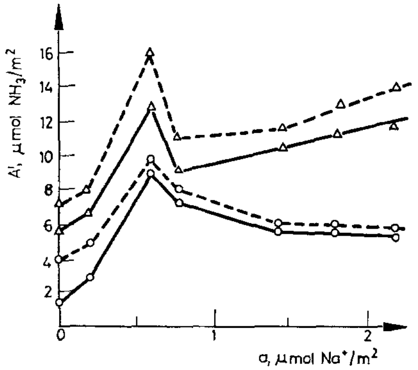

Fig. 2. Relation between the quantity of NH_3 adsorbed at 200°, and 300° and the amount of sodium added to the catalyst; ———— volumetric method; - - - - thermogravimetry; △: 200°, ○: 300°

higher than those obtained with the static method. Considering that the system does not reach equilibrium in the dynamic method, we had rather expected the opposite situation.

It seems that the increased values of adsorption of NH_3 and CO_2 as measured with the dynamic method result from the presence of moisture on the surface of

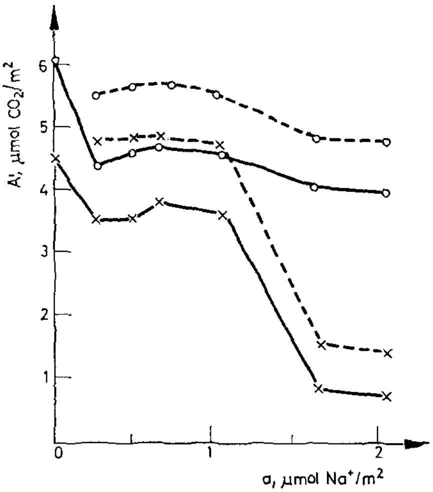

Fig. 3. Relation between the quantity of CO_2 adsorbed at 30° and 100°, and the amount of sodium added to the catalyst; ——— volumetric method; - - - - thermogravimetry; × : 100°, ○: 30°

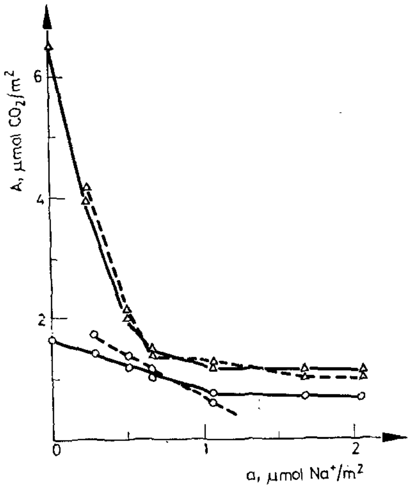

Fig. 4. Relation between the quantity of CO_2 adsorbed at 200° and 300° and the amount of sodium added to the catalyst; ——— volumetric method; - - - - thermogravimetry; △: 200°, ○: 300°

the cooled samples. It was found that the amount of this moisture could reach 2 wt.% of the catalyst used. The measurements of NH_3 or CO_2 adsorption on a hydrated surface lead to reaction between the gaseous phase and loosely-bound water molecules; in order to confirm this, two additional experiments were carried out. First we determined the molar heat of ammonia adsorption from the DTA curve. This was checked against the isosteric heat of adsorption calculated according to the Clausius–Clapeyron equation from data given by the static method. Figure 5 shows the heats of adsorption for NH_3 and CO_2 as functions of the sodium concentration.

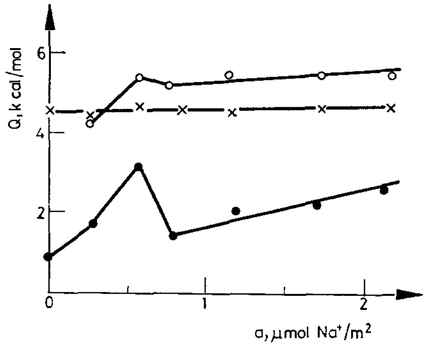

Fig. 5. Molar heats of adsorption of NH_3 and CO_2 as functions of the amount of sodium added to the catalyst. + CO_2, volumetric method; ● NH_3, volumetric method; ○ NH_3, thermogravimetry

The molar heat of NH_3 adsorption as determined from the DTA curve includes the heat of the reaction between gaseous ammonia and water. It is twice as big as the isosteric heat of adsorption calculated on the basis of data obtained for the static system. For the latter the heat values approach the thermal effects of a Lewis-type acid–base neutralisation reaction.

This calculation could not be performed for CO_2 adsorption because of significant experimental errors. To support our hypothesis, measurements of NH_3 and CO_2 adsorption on dry and moist catalyst surfaces were carried out in a closed system by the static method. At atmospheric pressure NH_3 and CO_2 adsorption on a moist surface considerably exceeds that on a dry one.

The results described above confirm the importance of surface-bound water in the adsorption process.

If one takes the results of adsorption measurements obtained by the generally accepted static method as a reference, it can be concluded that measurements with a thermobalance may be useful for semiquantitative comparative studies, in particular at temperatures above 100°, when water loosely bound by physical adsorption does not influence the studied process significantly.

References

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Résumé — On a mesuré l'adsorption de NH_3 et de CO_2 sur sept catalyseurs à base de silice et d'oxyde d'aluminium avec différentes teneurs en ions sodium. Les mesures ont été effectuées suivant deux procédés: par la méthode volumétrique classique et par ATD, TG et TGD simultanées. On peut observer une grande analogie entre les résultats obtenus par les deux méthodes. Les mesures d'adsorption par analyse thermique peuvent être utiles dans le cas d'études semiquantitatives.

Zusammenfassung — Die Adsorption von NH_3 und CO_2 wurde an sieben Silica-Aluminiumoxid-Katalysatoren gemessen, welche verschiedene Konzentrationen von Na-Ionen enthielten. Die Messungen wurden nach der klassischen volumetrischen Methode und mit der dynamischen Methode, bei welcher die DTA, TG und DTG-Kurven simultan aufgenommen wurden, durchgeführt. Eine große Ähnlichkeit der mit den zwei Methoden erhaltenen Resultate kann beobachtet werden. Die Adsorptionsmessung mit der Thermoanalyse kann für semiquantitative Untersuchungen von Nutzen sein.

Резюме — Была измерена адсорбция NH_3 и CO_2 для семи кремний-алюминиевых катализаторов, содержащих в разной концентрации ионы натрия. Измерения были выполнены двумя различными способами: классическим объемным методом и динамическим, привлекая одновременно кривые ДТА, ТГ и ДТГ. Наблюдается большое сходство между результатами, полученными этими двумя методами. Адсорбционные измерения, проведенные с помощью термического анализа, могут быть использованы для полуколичественных исследований.