

Characterization of some catalysts using vacuum balances

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Abstract

A vacuum quartz-spring balance was used to determine the nitrogen adsorption isotherms at -196°C of silica–titania, silica–alumina, silica–magnesia and chromia–alumina catalysts. The surface acidities of these acid catalysts were determined by following the desorption of pyridine using an electronic vacuum balance.

Good agreement was found between the nitrogen adsorption isotherms determined by the vacuum quartz-spring balance and those followed by conventional volumetric methods.

The adsorption of pyridine at 35°C was found to be of the physical type where the sorbed pyridine was completely expelled by prolonged out-gassing at the adsorption temperature. The adsorption of pyridine at 150°C on the catalysts investigated is mainly chemical and the amount of pyridine chemisorbed determines the number of acid sites per unit weight of the catalyst or per unit surface area. The thermal desorption of pyridine was found to be related to the strength of the surface acid sites.

A fairly good relationship was found between the surface acid density (number of acid sites per cm^2) and the catalytic activity towards isopropanol dehydration.

INTRODUCTION

Solid acid catalysts are the backbone of major refining and petrochemical processes, including cracking, hydrocracking, reforming, isomerization, and disproportionation of aromatics. In the near future, these catalysts should also play a significant role in the synthesis of functional compounds. Natural acid solids (in particular, clays) are also known to participate in many catalytic processes [1].

There are a large variety of solid acids [2]: natural clay minerals, mounted acids (H_3PO_4 mounted on diatomaceous earth), cation exchange resins, oxides, mixed oxides, salts and zeolites. The acidic properties (acid amount and acid strength) of these solids can be completely different.

The performance of acid catalysts depend on their textural properties (surface area and pore volume distribution) [3]. However, the activity, selectivity and stability of acid solids are obviously determined to a large

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extent by their surface acidity, i.e. the number, nature, strength and density of their acid sites [4, 5].

The textural properties are determined from the adsorption of nitrogen, which seldom enters into specific interaction with the surface, at -196°C . The adsorption isotherm allows the determination of the surface area by applying the conventional Brunauer–Emmett–Teller (BET) equation [6]. The pore volume distribution can be obtained by application of one of the methods developed for this.

Several methods (chemical titration, spectroscopic and thermal methods) are used to evaluate the acidity number and strength of sites. The first has received the greatest attention. It involves titration with a base in the presence of coloured indicators [7]. However, chemical titration cannot determine the type of acidity, which is one of the drawbacks of the method. Catalytic reactions on solid catalysts take place at temperatures higher than ambient and, therefore, measurements of acidity are preferred at, or at least close to, reaction temperatures. The high-temperature adsorption of an organic base followed by thermally programmed desorption (TPD) of this base at high temperatures, is mainly chemical, thus determining the acid sites on the catalyst surface. On desorption, one may assume that weak acid sites desorb the base at relatively lower temperatures.

Of the organic bases, pyridine has proved to be the most appropriate for probing acid sites on the surface of solid catalysts [8].

In the present investigation, various mixed oxides were characterized in terms of their surface area and pore structure as well as in terms of their acidic character. The mixed oxides investigated were silica–titania (ST), silica–alumina (SA), silica–magnesia (SM) and alumina–chromia (AC). The gravimetric technique was used to determine the chemisorption of pyridine and the adsorption of nitrogen. Adsorption of the latter was also followed using the conventional volumetric method, in order to investigate the validity of the gravimetric method in which vacuum balances are used for adsorption measurements. An attempt was made to relate the catalytic dehydration activity of the investigated catalysts towards isopropanol.

EXPERIMENTAL

Materials

The mixed gels were prepared by mechanically mixing precipitated, unwashed gels in different mole ratios for each mixed gel, as shown in Table 1. The required volumes of the two slurries were thoroughly mixed by mechanical stirring for 5 h, filtered, washed, dried at 110°C , and then calcined at 550°C .

Silica hydrogel was prepared from 1 M sodium silicate and sufficient 5% sulphuric acid solution to attain pH 5. Alumina, magnesia and chromia

TABLE 1

The chemical composition and the designations of the samples investigated

Sample	Chemical composition/mol%	Sample	Chemical composition/mol%
ST1	SiO ₂ , 70; TiO ₂ , 30	SM1	SiO ₂ , 70; MgO, 30
ST2	SiO ₂ , 50; TiO ₂ , 50	SM2	SiO ₂ , 50; MgO, 50
SA1	SiO ₂ , 70; Al ₂ O ₃ , 30	AC1	Al ₂ O ₃ , 70; Cr ₂ O ₃ , 30
SA2	SiO ₂ , 50; Al ₂ O ₃ , 50	AC2	Al ₂ O ₃ , 50; Cr ₂ O ₃ , 50

hydrogels were precipitated from the corresponding nitrate solution using 0.2 M NH₄OH. Titania gel was prepared by hydrolysis of TiCl₄ (Carlo Erba R.P. reagent).

Techniques

The adsorption of nitrogen was carried out using both the conventional volumetric apparatus and the vacuum quartz-spring balance. Quartz springs are inert with respect to all the adsorbates and their extension is a function of the weight of the adsorbed material. Calibration is made for each spring prior to any adsorption measurements.

The adsorption of pyridine and its temperature-programmed desorption were followed by means of an S.I. Electronic vacuum balance (Mark 2B). The dehydration of isopropanol was followed using the pulse microcatalytic technique. The decomposition of this alcohol was carried out at 260°C, with a flow rate of the nitrogen carrier gas of 37.5 ml min⁻¹. Under such conditions, only three peaks were detected by a chromatograph (model 5600A Hewlett-Packard assembly): isopropanol, acetone and propene.

RESULTS AND DISCUSSION

Textural properties

The adsorption of nitrogen at -196°C on the samples investigated proved to be rapid; equilibrium was attained in 20 min. However, intervals of 30 min were left between successive measurements to ensure equilibrium conditions.

The isotherms are of type IV, which is characterized by a capillary condensation at high relative pressure [9], and obey the conventional BET equation in the relative pressure range of 0.05–0.35. The isotherms show closed hysteresis and a well developed knee at a low relative pressure. Representative isotherms are shown in Fig. 1. For the sample SA2, data obtained from volumetric and gravimetric methods are presented and they show complete agreement.

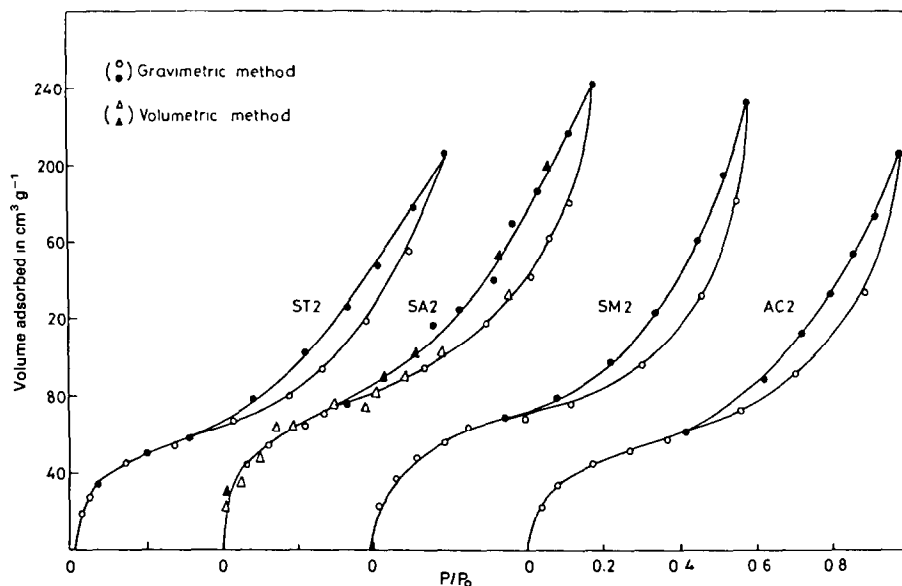


Fig. 1. Representative adsorption-desorption isotherms of nitrogen at 77 K.

The textural parameters of the investigated catalysts are listed in Table 2. Column 2 of this table summarizes the BET surface areas (S_{BET} in $\text{m}^2 \text{g}^{-1}$). The S_{BET} surface areas are $\pm 2\%$ of those calculated from the knee points on the isotherms. The total pore volume V_{T} (the volume of liquid nitrogen taken by one gram of catalyst in ml g^{-1}) was calculated using the equation

$$V_{\text{T}} = V_{\text{st}} \times 15.47 \times 10^{-4}$$

where V_{st} is the volume of nitrogen gas adsorbed at or very close to the saturation vapour pressure in $\text{cm}^3 \text{g}^{-1}$. The calculated V_{T} values are listed in

TABLE 2

Textural and acidic properties of the investigated catalysts

Sample	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{T}}/\text{ml g}^{-1}$	$r/\text{\AA}$	Pyridine adsorbed/ mg g^{-1}	Total acidity/ mmol g^{-1}	Surface acid density/ $\text{N acid per cm}^2 \times 10^{13}$
ST1	260	0.364	28	34.0	0.430	9.96
ST2	180	0.324	36	20.0	0.252	8.43
SA1	340	0.408	24	78.0	0.986	17.46
SA2	278	0.375	27	55.0	0.695	15.05
SM1	320	0.384	24	24.0	0.303	5.70
SM2	240	0.360	30	14.0	0.177	4.44
AC1	218	0.360	33	20.0	0.159	4.39
AC2	170	0.323	38	8.0	0.101	3.58

column 3 of Table 2. This table also gives the mean pore radii calculated from the equation

$$r(\text{\AA}) = 2 \times V_T \times 10^4 / S_{\text{BET}}$$

The mean pore radii are given in column 4 of Table 2. Inspection of this table reveals that for the mixed oxides in which silica is one of the components, the surface area and the total pore volume decrease, and the mean pore radius increases, with a decrease in silica content from 70 mol% to 50 mol%. Also, for alumina–chromia samples the same trend was reported with a decrease in alumina from 70 mol% to 50 mol%. Therefore, in mixed oxides, silica and alumina contribute mainly to the surface area and total porosity. This is not surprising because these oxides are frequently used as carriers for many catalytic systems. They are also characterized by their resistance to heat treatment and exposure to different atmospheres.

Application of the gravimetric technique (vacuum quartz-spring balance) for nitrogen adsorption measurements has the following advantages.

(i) The amount of mercury used for the measurements is small, being limited to the manometer reservoirs, and equals approximately one third of the quantity of mercury used in the volumetric apparatus. In the latter, mercury is contained in the burettes used for volumetric determinations. Mercury is becoming expensive and may not be available in large quantities in some laboratories.

(ii) With the increase in the amount of mercury used in an adsorption apparatus, the possibilities of strains on the different components of the apparatus increase, causing either leaks or damage.

(iii) The use of only small amounts of mercury in gravimetric apparatus minimizes the health hazard due to exposure of the investigators to mercury vapours when breaks or damages occur.

(iv) The gravimetric technique provides a visual display of the adsorption and desorption changes, either using the naked eye at high relative pressures or using a cathetometer at low pressures.

Acidic properties

The adsorption of pyridine was measured at 150°C, assuming that the adsorption of this organic base at lower temperatures is mainly physical [10]. Using a vacuum balance and by a gradual, continuous rise in desorption temperature, the thermally programmed desorption of the base could be followed. TPD curves are shown in Fig. 2 (upper curves). It was also possible to construct representative acid strength distribution curves from the assumption that the greater the strength of the acid site, the higher the temperature at which it desorbs pyridine or any other adsorbed base. Differentiation of the TPD curves in Fig. 2 (upper curves) gives the acid strength distribution curves. Representative acid distribution curves are

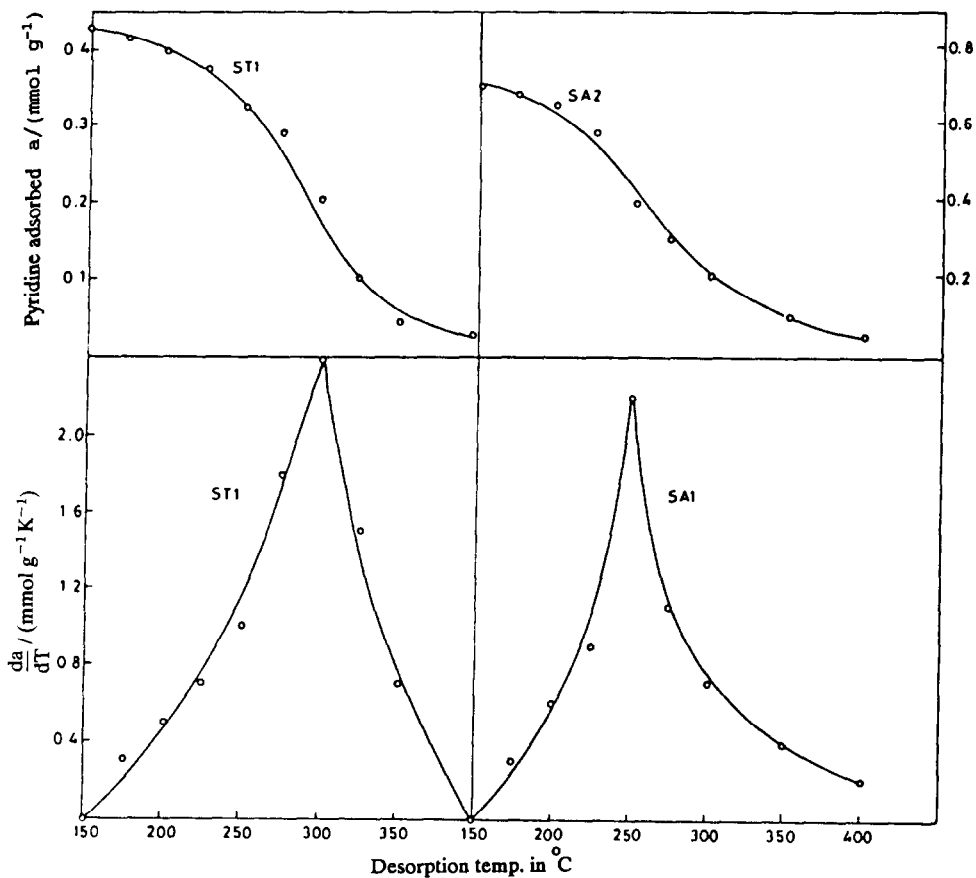


Fig. 2. Representative thermal desorption curves (upper curves) and acid distribution strength curves (lower curves).

shown in Fig. 2 (lower curves). One can determine the acidity of the catalyst after prolonged outgassing at a certain temperature. This represents the acidity of the catalyst at this particular temperature; moreover, this gives at least a qualitative indication of the strength of the existing acid sites. The total acidity could perhaps be measured by the amount of pyridine adsorbed at 150°C, expressed either in milligrams of pyridine taken by one gram of catalyst (mg g^{-1}) or in the number of millimoles of pyridine per unit weight of the catalyst (mmol g^{-1}). These values are calculated for the samples investigated and are given in columns 5 and 6 of Table 2, respectively. It was also possible to calculate the surface acid densities of the investigated catalysts, i.e. the number of acid sites located on a unit area of the surface (N acid per cm^2). This is based on the assumption that every acid site will chemically hold one pyridine molecule. The surface acid densities are listed in column 7 of Table 2.

It is evident from Table 2 that for the catalyst containing silica, the amount and strength of the acidity decrease with a decrease in silica

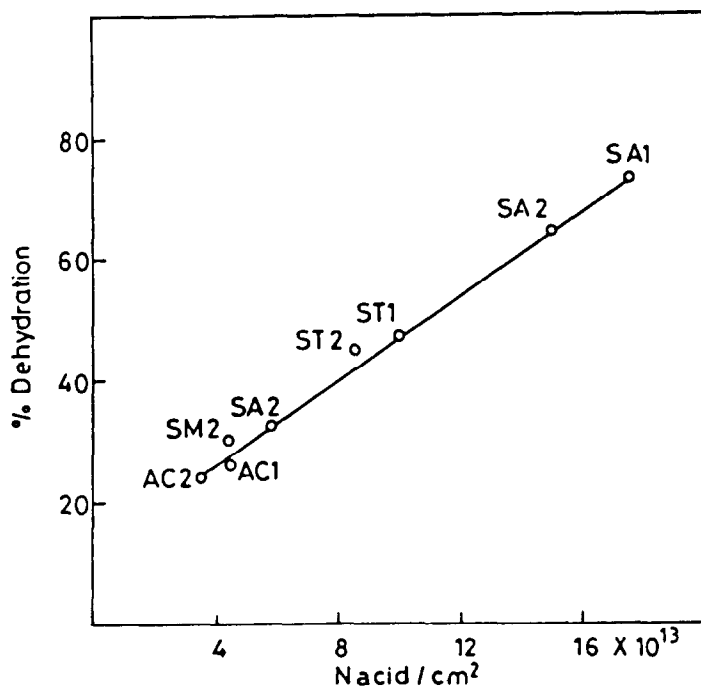


Fig. 3. Dehydration versus acid density.

content. For alumina–chromia catalysts, the acid amount and strength increase with an increase in alumina.

From the previous discussion on the acidic properties determined by pyridine adsorption using vacuum balances, it can be concluded that valuable information can be obtained, including the amount of acid at any given heat treatment temperature, the total surface acidity, the surface acid density and, moreover, the construction of acid strength distribution curves.

Catalytic properties

The catalytic properties are not one of the main concerns of this investigation. However, preliminary studies have been made to relate the textural and acidic properties of the investigated catalysts to their activity in alcohol conversion.

The data obtained from the catalytic conversion of isopropanol were not sufficient to lead to a concrete conclusion. However, the authors were able to trace a good relationship between the catalytic dehydration activity towards isopropanol and the surface acid density. A straight line was obtained and is shown in Fig. 3. Because the surface acid density does not involve the function of the surface area of the catalyst, one can suggest, therefore, that the dehydration of isopropanol, and possibly of other alcohols, is a struc-

turally insensitive catalytic reaction that depends on the number of acid sites per surface area and not on the extent of the surface area.

CONCLUSIONS

It can be concluded that vacuum balances are efficient in determining the textural properties of the catalysts via low-temperature adsorption of nitrogen and provide a more or less complete, clear pattern of the surface acidity of solid catalysts.

The catalytic dehydration of isopropanol is related to the surface acid density and is a structurally insensitive catalytic reaction. Silica–titania, silica–alumina, silica–magnesia and chromia–alumina are good catalysts for the dehydration of isopropanol and possibly of other alcohols. Their surface acidity is an important parameter in determining their activity towards dehydration.

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