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The pore structure of chrominophosphate catalysts

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A series of chrominophosphates (CrPs) with various P/Cr ratios were prepared by the precipitation method. The pore structures of these catalysts were characterized by nitrogen adsorption and mercury-penetration porosimetry. The results indicated that the micro-pores with diameters less than 20 nm were due to the dehydration process and had a slit-shaped geometry. There were two types of large pores (meso- and macro-) with diameters greater than 20 nm. These pores had a cylindrical pore-shape. The meso-pores can be attributed to the packing of particles and the macro-pores are essentially due to the packing of the aggregates of the particles.

Keywords: Chrominophosphate; pore structure; catalyst characterization

1. Introduction

The catalytic properties of phosphates, both stoichiometric and nonstoichiometric, have excellently been reviewed by Moffat [1]. Although considerable work has been done on materials containing phosphorus, especially on alumina-aluminum phosphate [2–4], relatively few reports of studies on the cation chromium in such materials have appeared.

Chrominophosphates (CrPs) have porous surface characteristics and relatively large surface areas and pore volumes [5–12]. They have been used as solid acid catalysts in many reactions such as dehydration, dehydrogenation, hydrolysis, isomerization, alkylation, and oxidation. However, the study of the pore structure of CrPs has received little attention in the open literature. The present investigation was to study the pore size distributions and pore geometries of CrPs.

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2. Experimental

A series of chrominophosphates with various P/Cr ratios were prepared by mixing aqueous solution of $Cr(NO_3)_3.9H_2O$ (Merck) and H_3PO_4 (85 wt%, Merck) with aqueous ammonia as a neutralizing agent. Chromium nitrate and phosphoric acid were dissolved in a common solution which was added together with an aqueous ammonium hydroxide solution into a well-stirred container. The rate of addition of the two solutions was regulated to maintain a constant pH of 8.0 (± 0.1). The precipitation was carried out at 298 K. After allowing the obtained gel to settle, it was filtered, washed, ground, oven dried at 373 K, and then calcined in air at 773 K for 16 h.

The elemental analysis was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The results indicated that the P/Cr ratios of the precipitates were the same as those of the starting materials within the experimental error ($< 2\%$).

The composition of the chrominophosphate catalyst is denoted throughout this paper by use of stoichiometric shorthand $Cr_A.CrP$, where A is the molar ratio of chromia to chrominum phosphate. For example, a sample with $P/Cr = 0.2$ is chemically equivalent to a stoichiometry of $2Cr_2O_3.CrPO_4$. It will be denoted as $Cr_2.CrP$.

The surface areas (SA) of these catalysts were measured by the B.E.T. method using a Micromeritics 2600. Pore size distributions of these catalysts were determined by the mercury-penetration measurement and the nitrogen adsorption method. The pore size distribution can be divided into two parts. The first part is the small pores (micropores) having diameters less than 20 nm and it was adopted from the nitrogen adsorption measurement results. The second one is the large pores (meso- and macropores) having diameters greater than 20 nm and it was adopted from the mercury-penetration results.

3. Results and discussion

Pore size distributions

The pore size distributions of these catalysts are shown in figs. 1 and 2 in terms of dV/dD_{po} (the differential increase in pore volume with increase in pore diameter). Fig. 1 is the distribution of micro-pores of CrPs around a diameter of 4 nm for each CrP. There was a peak in the range of 7 and 15 nm. The value of the pore diameter, at which the peak is a maximum, increases as the A value increases. It is clearly shown that the pore volume of the small pore (< 20 nm) is decreased with increasing A values. The large pores of these samples as shown in fig. 2 are widely distributed around diameters of 10^2–10^3 nm (mesopores) and 10^5 nm (macropores). The pore volumes of the large pores reach a maximum at A value of 2.

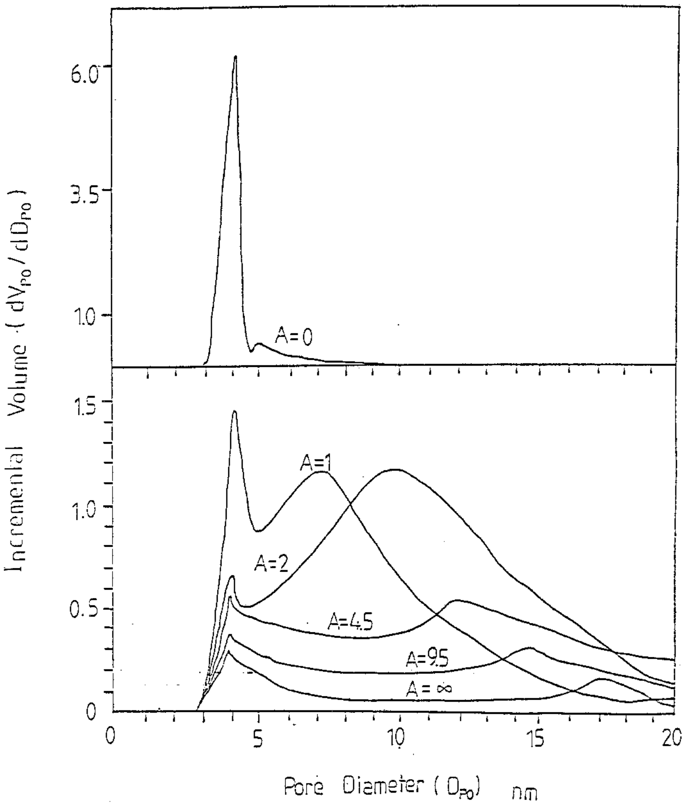

Fig. 1. Pore size distribution of small pores of chrominophosphates. (The A value is the molar ratio of Cr_2O_3 to $CrPO_4$.)

The geometry of the pores

The characteristics length is defined as the pore width for a slit-shaped pore and pore diameter for a cylindrical one. The characteristic length L of a slit with width X, length Y and depth Z is:

$$L = 2XYZ/2YZ = 2V/SA \tag{1}$$

where V is pore volume and SA is surface area. The characteristic length of a cylindrical pore can also be calculated from its pore volume and its surface area as:

$$L = 4V/SA. \tag{2}$$

Thus one can distinguish pore shapes by these two equations. We can conclude that the voids of particles and aggregates are cylindrical-shaped pores because of the corresponding results from nitrogen adsorption and mercury-penetration measurements. This cylindrical idealization is widely used in many materials of large pores forming by the packing of particles [14].

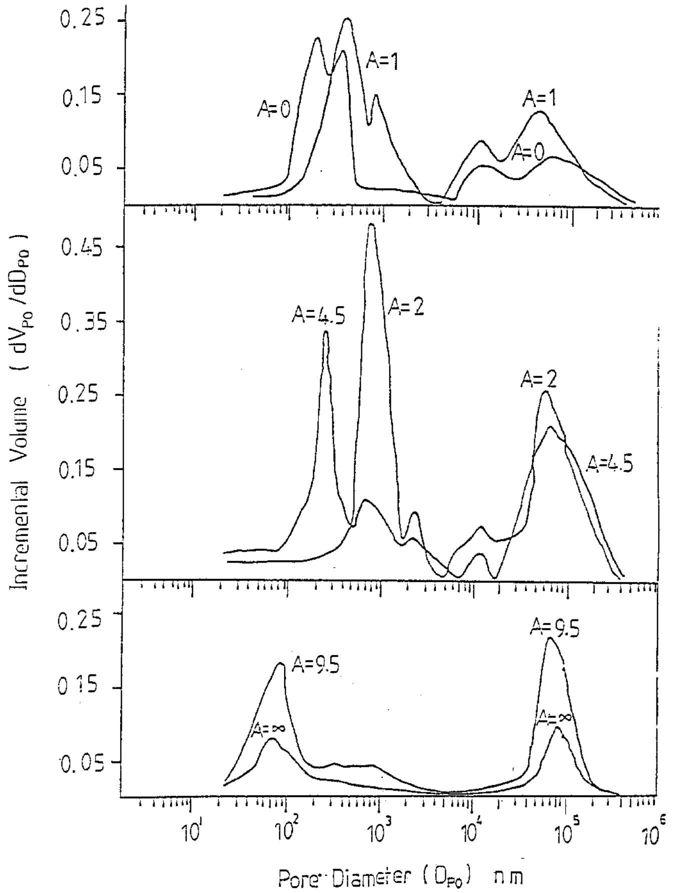

Fig. 2. Pore size distribution of large pores of chrominophosphates. (The A value is the molar ratio of Cr_2O_3 to $CrPO_4$.)

In order to calculate the characteristic length of the small pores and verify their geometry, we need to find the correlation between pore volume, surface area and characteristic length.

The experimental pore size of small pores from nitrogen adsorption were listed in table 1. Calculation of the surface area of small pores is more complicated and the procedure of the calculation is as follows. From the pore volume data of mercury penetration, we could calculate the surface area for each pore diameter ($4V/D_{\mathrm{po}} = SA$) because mercury penetration measurement is based on the assumption of a cylindrical pore model. In this way, we can obtain the surface area of large pores by summation of surface area at large pore diameter ($\Sigma SA_{\text{large pores}}$). Substracting the surface are calculated above from the total surface area data of BET ($SA_{\mathrm{BET}} - \Sigma_{\text{large pores}}$), one can obtain the surface area of the small pores. It should be noted that the BET surface area measurement is only based on the assumption of multilayer adsorption, never

Table 1
Comparison of measured and calculated average pore diameters of micropores

P/Cr ratio	A value [a]	surface area (m^2/g)	pore size (nm) [b]	L (nm) [c]	error (%)
1	0	34.8	4.7	5.0	6.4
0.33	1	39.7	7.2	6.8	5.6
0.20	2	36.2	10.3	9.6	6.8
0.10	4.5	25.3	11.0	10.8	1.8
0.05	9.5	14.2	11.2	10.8	3.6
0	∞	10.1	12.1	12.7	5.0

[a] A value is the molar ratio of Cr_2O_3 to $CrPO_4$.
[b] Experimental pore size from nitrogen adsorption measurement.
[c] Characteristic length of the slit calculated from $2V/SA$.

deals with any assumption of pore geometry. These calculated surface areas for small pores are listed in the third column of table 1. From these data, the geometry of the small pore can be determined from the above criteria (eqs. (1) and (2)]. The results showed that the small pores are slit-shape and have a characteristic length of $2V/SA$ within 7% error.

It has been reported that the small pores of alumina-aluminum phosphates and alumina are slit-shaped from the dehydration of water in the layer structures of hydrates [15–17]. The free moisture contained in the doughs of the precipitates was dehydrated and the slit pore was formed.

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