Substitution of Divalent Cobalt into Aluminophosphate Molecular Sieves

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Substitution of divalent cobalt into the crystal framework of the microporous aluminophosphates '$AlPO_4$-5' and '$AlPO_4$-11' has led to the formation of new acidic catalysts.

Synthetic molecular sieves made up of alternating AlO_2^- and PO_2^+ units and forming structures similar to zeolites represent a new class of microporous inorganic solids, the $AlPO_4$'s.[1] Incorporation of silicon into the aluminophosphate framework with subsequent production of acid sites indicates predominant substitution for phosphorus, although some 'paired substitution' may also occur.[2] We now report the synthesis of aluminophosphates in which substitution of divalent ions (in particular, cobalt) into the tetrahedral sites has occurred. The presence of acid sites has been confirmed, showing that Co^{2+} must predominantly substitute for Al^{3+}.

The substituting cobalt ion is added to an aluminophosphate gel and is incorporated into the framework during subsequent hydrothermal crystallisation of the gel. The gel is prepared by mixing phosphoric acid and a reactive aluminium hydroxide. A cobalt salt is added, followed by the appropriate templating agent necessary to form the desired structure. Our work has concentrated on two of the crystal forms of the $AlPO_4$-*n* series;[1] namely $AlPO_4$-5 and $AlPO_4$-11, for which there are a number of possible templating agents. We have found that triethylamine is the most suitable for the production of substituted $AlPO_4$-5 and di-isopropylamine for the production of substituted $AlPO_4$-11. The reaction mixture is stirred thoroughly until homogeneous, sealed in a stainless steel bomb and heated at 200 °C until crystallisation occurs, after approximately 24 hours. The resulting crystalline product, the precursor, must be calcined in air to obtain a usable, substituted $AlPO_4$.

When Co^{II} is added as a substituting ion the product is an intense blue-coloured powder, indicating that cobalt is in a tetrahedral environment.[3] This would be expected for Co substitution into the $AlPO_4$ framework. There are no major differences in the *X*-ray powder diffraction patterns of the substituted and unsubstituted $AlPO_4$'s, and no other crystalline phases which might contain cobalt were observed. Analysis with scanning electron microscopy/energy dispersive *X*-ray analysis showed crystal sizes *ca.* 10 μm and indicated no sign of any Co-rich phases.

Thermogravimetry/mass spectrometry studies of the precursors show that the templating agent is either evolved intact at slightly above room temperature, or decomposes at a high temperature (350—500 °C) forming the corresponding alkene and ammonia. This mode of decomposition has been observed[4] in zeolites and has been attributed to a Hofmann type degradation of the protonated amine. This type of decomposition indicates the presence of acid sites, and is also observed in the silicon substituted aluminophosphates (SAPO's), prepared according to reference 2, but does not occur in the unsubstituted $AlPO_4$'s.

The thermal desorption of ammonia from calcined samples, which have been exchanged with aqueous NH_4NO_3 and dried over silica gel, can be monitored by thermogravimetry/mass spectrometry in argon carrier gas. An initial water loss is always observed and this is consistent with the known hydrophilicity of the $AlPO_4$'s.[1] Figures 1a and 2a show the temperature programmed desorption (tpd) of ammonia from the cobalt substituted $AlPO_4$-5 and the cobalt substituted $AlPO_4$-11, hereafter named Co-$AlPO_4$-5 and Co-$AlPO_4$-11 respectively. Included for comparison are the NH_3 tpd curves from SAPO-5 and SAPO-11,[2] and also the appropriate unsubstituted $AlPO_4$'s.[1] Clearly, cobalt substitution results in the production of acid sites within the crystal framework.

The ammonia desorption curve can be resolved into two peaks by assuming a symmetrical high temperature peak, with the second peak deduced by subtraction. This suggests sites of different acid strengths. Pore size analysis[1] of these materials shows that NH_3 (kinetic diameter = 2.6 Å) is unlikely to undergo any diffusional steric hindrance, so comparison of the temperatures at which the peak maxima occur suggests that of the two structures, the stronger acid sites exist in the Co-$AlPO_4$-11 (Figures 1a and 2a).

The substituted aluminophosphates convert methanol into

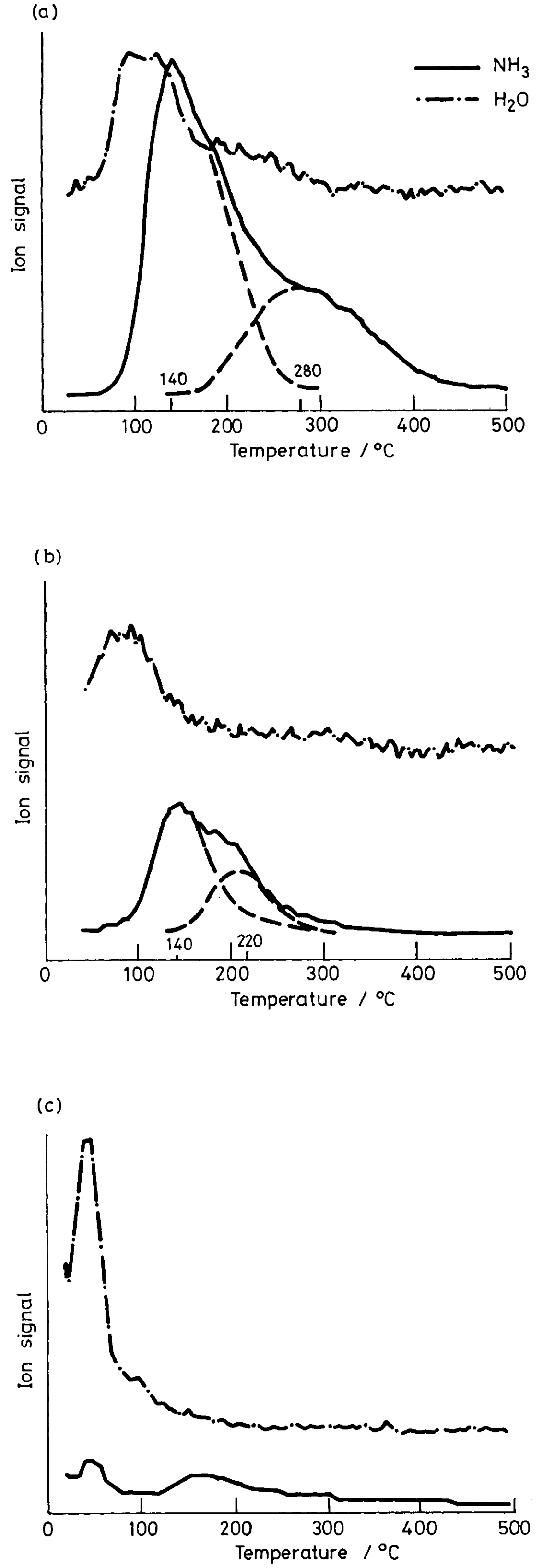

Figure 1. Temperature programmed desorption of ammonia (——) and water (–·–) from NH_4NO_3(aq) exchanged samples (a) Co-$AlPO_4$-5, (b) SAPO-5, (c) $AlPO_4$-5. The dotted line shows the curves resolved into two peaks, and temperatures of peak maxima are shown. The ion signals are directly comparable.

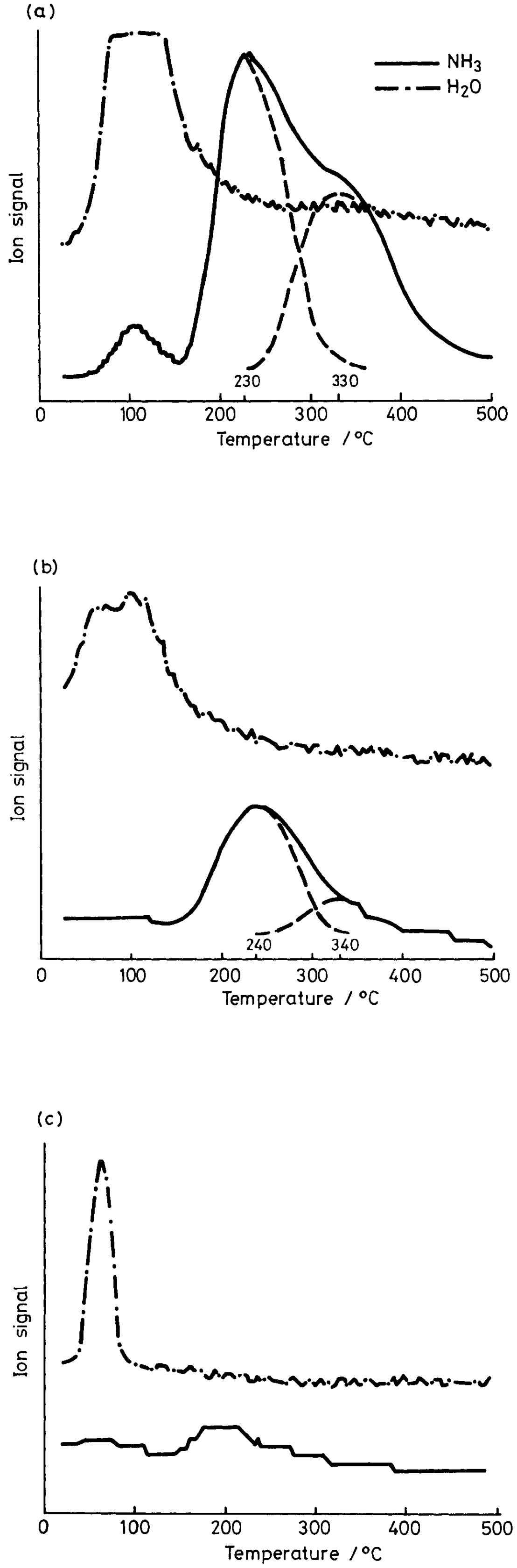

Figure 2. Temperature programmed desorption of ammonia (——) and water (–·–) from NH_4NO_3 (aq.) exchanged samples (a) Co-$AlPO_4$-11, (b) SAPO-11, (c) $AlPO_4$-11. The ion signals are directly comparable.

hydrocarbons under our conditions [pressure = 1 atm, temperature = 360 °C, liquid hourly space velocity = 2]. Co-$AlPO_4$-5 and SAPO-5 yield similar products, having the following typical hydrocarbon distribution (wt%): light olefins 45, higher aliphatics 15, aromatics 40, $CH_4 < 1$. The aromatic composition is largely penta- and hexa-methylbenzene. Formation of coke causes these catalysts to deactivate. SAPO-5 remains active for approx. 300 g methanol/g catalyst while Co-$AlPO_4$-5 deactivates more rapidly, having a lifetime of approx. 30 g/g. The product yield from the methanol reaction with Co-$AlPO_4$-11 and SAPO-11 is similar to that from H-ZSM-5.[5] Thus, the acid sites produced promote typical hydrocarbon conversion reactions such as alkylation, aromatisation, and isomerisation. The production of penta- and hexa-methylbenzene from Co-$AlPO_4$-5 and SAPO-5 is consistent with the conversion occurring within the pores of the catalyst. The parent $AlPO_4$-5 has been shown to have a structure containing 12-membered rings with a pore diameter of 8 Å.[1]

The hydrocarbon products from Co-$AlPO_4$-11 and SAPO-11 contain essentially none of these higher alkylated aromatics. The pore size of the parent $AlPO_4$-11 has been estimated to be only 6.1 Å and we consider that this smaller pore size restricts the production of species such as hexamethylbenzene which has a kinetic diameter of 7.7 Å.

In contrast to these results the unsubstituted aluminophosphates $AlPO_4$-5 and $AlPO_4$-11 convert methanol, under the same conditions, into dimethyl ether and water only. No detectable hydrocarbons are formed.

The presence of acid sites in these substituted aluminophosphates indicates that cobalt(II) substitutes for aluminium in the crystal framework. Our initial studies have indicated that a number of other divalent ions able to be accommodated in a tetrahedral environment, such as Zn^{II}, Mn^{II}, and Mg^{II} also substitute in the $AlPO_4$ framework. These results will be published elsewhere.

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