The rational design of a Cr/AlPO$_4$-5 molecular sieve

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Chromium(III) and chromium(VI) species have been deposited on the external surface of an AlPO$_4$-5 molecular sieve *via* gas-phase deposition of Cr(acac)$_3$.

The neutral character of the AlPO$_4$ molecular sieve framework[1] precludes the introduction of metal ions by ion exchange, which could be of interest for catalytic applications. Therefore, the direct incorporation of metal ions in the AlPO$_4$ framework *via* substitution of aluminium or phosphorus atoms during hydrothermal synthesis[2,3] is used. A relationship between catalytic properties and localisation of metal ions in the molecular sieves of the AlPO$_4$ family can be clarified once materials of well-defined structure are compared. Therefore, an alternative approach for their synthesis has to be developed which results in metal localisation at the external surface of the molecular sieve. For this purpose a reaction of the transition metal precursor with the surface hydroxyl groups terminating the AlPO lattice[4] can be envisaged. To our knowledge, this possibility has not yet been realised since it is not clear if they are reactive enough to be used for the anchoring of transition metal precursors. In the case of AlPO$_4$-5,[5] the outer surface terminal P–OH and Al–OH groups were found to be stable up to 900 °C.

This communication describes an approach to the rational design of a Cr/AlPO$_4$-5 molecular sieve. In this way, chromium(III) and chromium(VI) species were attached to the external surface of AlPO$_4$-5 *via* interaction of its terminal hydroxyl groups with a volatile chromium precursor which is too bulky to enter the AlPO$_4$-5 pores. For this purpose Cr(acac)$_3$, whose molecular diameter of 0.90 nm[6] exceeds the free diameter of the AlPO$_4$-5 unidimensional channels close to 0.80 nm,[1] was selected.

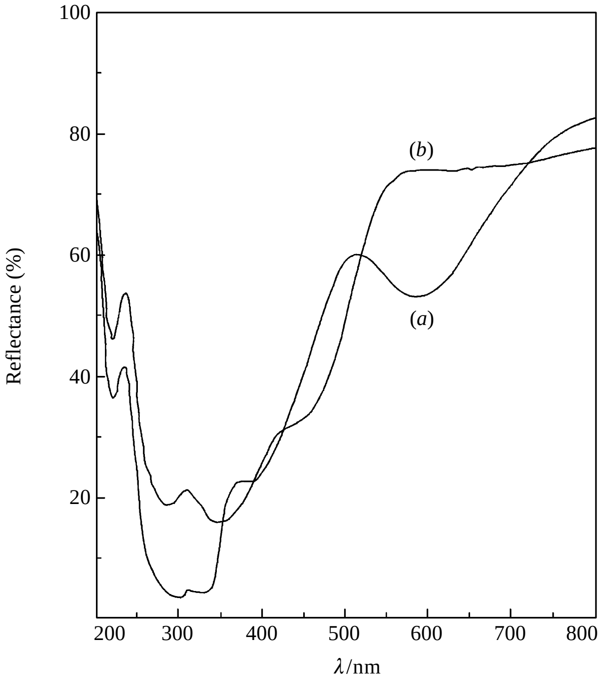

Figure 1 Diffuse reflectance UV-VIS spectra of AlPO$_4$-5 molecular sieve after deposition of Cr(acac)$_3$ at 200 °C (*a*) and consequent calcination in air at 500 °C (*b*).

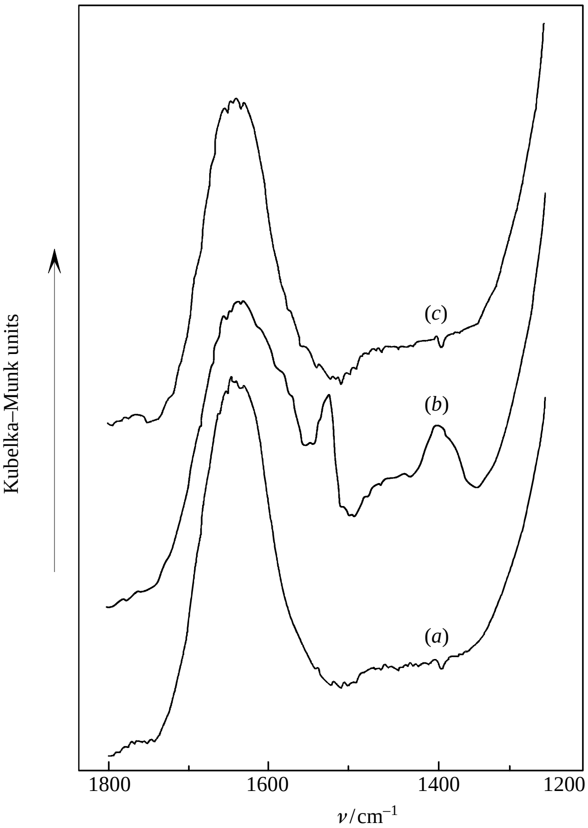

Figure 2 Diffuse reflectance FTIR spectra of the initial AlPO$_4$-5 molecular sieve (*a*), after deposition of Cr(acac)$_3$ at 200 °C (*b*) and consequent calcination in air at 500 °C (*c*).

AlPO$_4$-5 was prepared from a gel of composition 1.5Pr$_3$N : 1.0Al$_2$O$_3$: 1.05P$_2$O$_5$: 50H$_2$O. Pseudoboehmite (Pural SB, Condea Chemie, 75.0% Al$_2$O$_3$) was used as an aluminium source. Crystallisation was carried out at 150 °C for 4 h in a Teflon-lined autoclave placed into a preheated oven.[7] The template was removed by calcination of the as-synthesized material in air at 500 °C for 20 h which resulted in the formation of a highly pure and crystalline AlPO$_4$-5 molecular sieve.

X-ray powder diffractograms were measured on a Philips PW 1840 diffractometer using CuKα radiation. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried out with a STA-1500 H thermobalance (PL Thermal Sciences). Diffuse reflectance UV-VIS and FTIR spectra were measured with a Cary 3 UV-VIS and a Magna FTIR spectrophotometer, respectively.

The deposition procedure included preliminary dehydration of the AlPO$_4$-5 sample (4.0 g) in a Pyrex tube reactor under a flow of dry nitrogen at 500 °C for 2 h. Subsequently, 0.1 g of Cr(acac)$_3$ was introduced into the cooled reactor where the modifier and the AlPO$_4$-5 sample were separated by a porous plate. During deposition of Cr(acac)$_3$ on AlPO$_4$-5 surface the

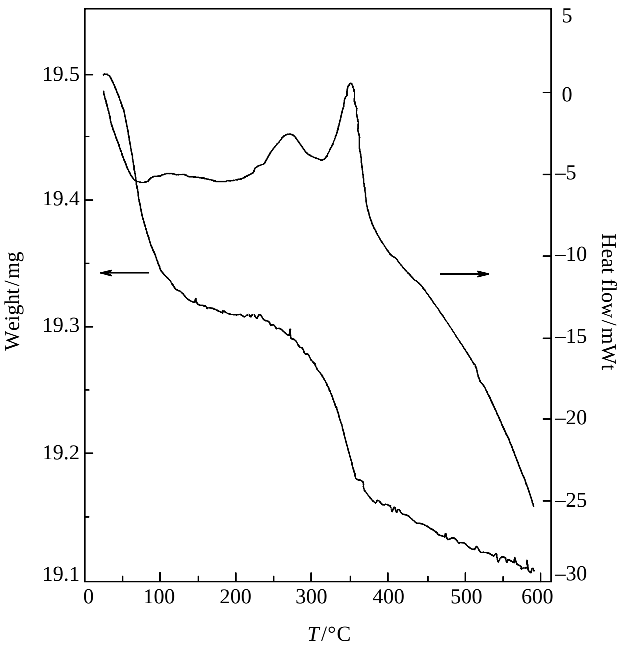

Figure 3 TG/DSC profiles of $AlPO_4$-5 molecular sieve with the deposited $Cr(acac)_3$.

temperature was kept at 200 °C for 3 h to ensure complete sublimation of $Cr(acac)_3$ and its passage through the $AlPO_4$-5 sample. Condensation of the modifier near the outlet of the reactor indicated that a sufficient excess of the modifier was used and when deposition was complete. The sample was subsequently subjected to a flow of dry nitrogen at the same temperature for 3 h in order to remove all unbound modifier from $AlPO_4$-5 sample and the reactor was cooled to room temperature.

The as-synthesized $Cr/AlPO_4$-5 material had a greyish green colour which changed to yellow after calcination in air at 500 °C. Chromium loading determined by chemical analysis was found to be 0.20 wt.%.

The initial $AlPO_4$-5 support retains its crystallinity during $Cr(acac)_3$ deposition and subsequent calcination. The X-ray diffraction patterns for all samples examined correspond to those reported for the AFI-type structure.[1]

The presence of surface Cr^{III} species in the as-synthesized and Cr^{VI} oxo-species in the calcined samples was established by chemical analysis as well as diffuse reflectance UV-VIS spectroscopy (Figure 1). Strong Cr^{III} d-d bands are observed at 390 and 580 nm in the as-synthesized sample that by analogy with $Cr(acac)_3$ can be attributed to ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transitions,[8] respectively, in the octahedrally coordinated chromium(III) ions. Calcination of the as-synthesized sample results in the complete disappearance of these d-d bands owing to Cr^{III} oxidation to Cr^{VI} ions which are characterised by a low intensity oxygen to Cr^{VI} charge transfer band at 450 nm ($1t_1 \rightarrow 2e$) which is symmetry forbidden and two symmetry allowed high intensity bands at 350 nm ($1t_1 \rightarrow 2e$) and 280 nm ($6t_2 \rightarrow 2e$).[9]

IR studies confirm the presence of acac ligands coordinated to Cr^{III} ions in the surface species. The diffuse reflectance FTIR spectrum of the as-synthesized sample (KBr) contains distinct bands at 1380 and 1528 cm^{-1} (Figure 2) which correspond to $C\overset{\cdots}{-}O_{as}$ (1383 cm^{-1}) and $C\overset{\cdots}{-}C\overset{\cdots}{-}C_{as}$ (1522 cm^{-1}) vibrations[10] of the acetylacetonate ligands in $Cr(acac)_3$. Their complete disappearance is observed upon sample calcination at 500 °C in air. This means that removal of the acac ligands from the chromium(III) acac surface species occurs under these conditions.

Displacement of the acetylacetonate ligands from chromium(III) surface species starts at 220 °C and is complete at 380 °C. This is clearly seen from the TG curve of the modified sample recorded in air (Figure 3). Disappearance of the acetylacetonate ligands is accompanied by their oxidative destruction which is reflected by two exothermic peaks in the DSC curve.

The chromium loading in the as-synthesized sample and the observed weight loss associated with the removal of the acac ligands allow calculation of the acac/Cr ratio in the chromium surface species. The ratio was close to **3** which means that $Cr(acac)_3$ upon deposition on the $AlPO_4$-5 surface retains all its acac ligands. The most obvious explanation of the nature of $Cr(acac)_3$ affinity to $AlPO_4$-5 surface is the existence of hydrogen bonds between $AlPO_4$-5 terminal hydroxyl groups[5] and two acac ligands of $Cr(acac)_3$[11] that seems to be sterically favourable. Consequently, the acac ligands in the attached $Cr(acac)_3$ molecule appear to be non-equivalent. Thus, under thermal treatment in air, the acac ligands undergo removal, accompanied by oxidative destruction, at different temperatures that is clearly indicated by two distinct peaks in the DSC curve (Figure 3).

In summary, $Cr(acac)_3$ can be deposited from the gas phase on the external surface of $AlPO_4$-5 molecular sieve, presumably *via* the formation of hydrogen bonds between acac ligands and hydroxyl groups which terminate the $AlPO_4$-5 lattice. It has been determined that the $Cr(acac)_3$ deposited retains all three acac ligands which are removed under thermal treatment in air. This is accompanied by oxidation of Cr^{III} ions to the surface Cr^{VI} oxo-species. The proposed approach, which was illustrated by the attachment of $Cr(acac)_3$ onto the external surface of $AlPO_4$-5 with a neutral framework, may be extended to other classes of molecular sieves possessing terminal hydroxyl groups.

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