Cyanometallates: an Underestimated Class of Molecular Sieves

Gosse Boxhoorn, Jan Moolhuysen, Joop G. F. Coolegem, and Rutger A. van Santen

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research B.V.), Badhuisweg 3, Amsterdam, The Netherlands

Cyanometallates display molecular sieving properties, which can be predicted on the basis of their specific structure; very effective separations of C_6 isomers and of CO_2–CH_4 mixtures are reported.

Adsorption properties of cyanides with the general formula $M^1_x[M^2(CN)_6]_y$ (x and y depend on the valency of M^1 and M^2) have been reported.[1—4] As far back as 1912, the uptake of moisture from air and ammonia by ferrocyanides was measured.[1] The adsorption of gases can be explained by assuming the cyanides to have an open-channel structure.[2c] So far no data have been published on the use of cyanometallates in actual physical separations, although the data in the literature suggest the existence of attractive molecular sieves based on these complexes.

Here we report some initial results on the molecular sieving properties of the cyanometallates. We restrict ourselves to two

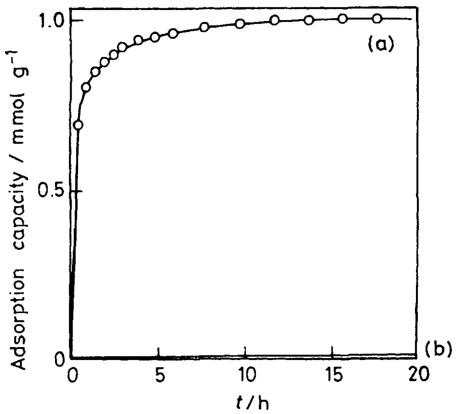

Figure 1. Gravimetric analysis of the adsorption of (a) 3-MP (2.2 kPa) and (b) 2,2-DMB (40 kPa) at 50 °C in $Zn_3[Co(CN)_6]_2$ after dehydration at 310 °C for 1 h.

separation problems: (i) the separation of C_6 isomers: n-hexane (n-C_6), 3-methylpentane (3-MP), and 2,2-dimethylbutane (2,2-DMB); (ii) the separation of CO_2 and CH_4.

The complexes referred to in this study were prepared by ion exchange in water solutions using standard procedures;[1—4] some are commercially available. Two methods were used to obtain information on adsorption capacities and diffusion rates: gravimetric analysis† and mass spectrometry.‡ The former measures only the total uptake of the adsorbates, whereas the latter provides information on the actual separation process. Prior to the adsorption measurement, all the complexes were dehydrated completely and their crystallinity was verified by *X*-ray diffraction. Sorption equilibria and diffusion rates were determined under various conditions of pressure and temperature. Diffusion rates and diffusion coefficients were calculated using the equations of ref. 5.

(i) Figure 1 gives an example of adsorption studies of 3-MP and 2,2-DMB on $Zn_3[Co(CN)_6]_2$ at 50 °C (gravimetric analysis), and shows that $Zn_3[Co(CN)_6]_2$ does not adsorb 2,2-DMB, whereas for 3-MP an adsorption capacity of 1 mmol/g was measured, with a diffusion rate of $0.3 \times 10^{-4}\ s^{-1}$. (For n-$C_6$ a similar adsorption capacity was measured with a diffusion rate of $21.0 \times 10^{-4}\ s^{-1}$ under the same conditions of pressure and temperature.) The adsorption characteristics of $Zn_3[Co(CN)_6]_2$ can be explained by its cubic structure[6] (Figure 2). As can be deduced from the structure and its stoicheiometry, vacancies are created by the omission of 33% of the $[Co(CN)_6]^{3-}$ ions (0.88 nm) in a NaCl-type lattice, charge neutrality being maintained. This structure is preserved after dehydration. Channels can be formed by connecting these vacancies, with pore openings of *ca.* 0.56 × 0.86 nm. These openings are large enough for adsorption of both n-C_6 and 3-MP (with kinetic diameters of 0.43 and 0.55 nm, respectively), but too small for adsorption of 2,2-DMB (0.62 nm). This and the fact that the diffusion coefficients are independent of the grain sizes of the crystallites indicate that $Zn_3[Co(CN)_6]_2$ is a true molecular sieve.

(ii) When the cyanide complex possesses no vacancies, *e.g.* in $Zn[Fe(CN)_5NO]$, small openings in the cubic structure are still present, which might enable mixtures of small molecules such as CO_2 and CH_4 to be separated. Results for mass spectrometric measurements of the adsorption of a CO_2–CH_4 gas mixture (1 : 1 v/v) at 20 °C and 1.2 bar are shown in Figure 3, and show that with a $Zn[Fe(CN)_5NO]$ type cyanide complex, having no vacancies, it is possible to separate small molecules *via* the openings in its cubic structure. A CO_2 adsorption capacity of 1.3 mmol/g with a diffusion rate of $1.3 \times 10^{-4}\ s^{-1}$ was measured (1.2 bar; 22 °C). For other cyanometallates under the same conditions of temperature and pressure, CO_2 adsorption capacities of up to 3.6 mmol/g with virtually no CH_4 adsorption were measured; these will be reported elsewhere.[7]

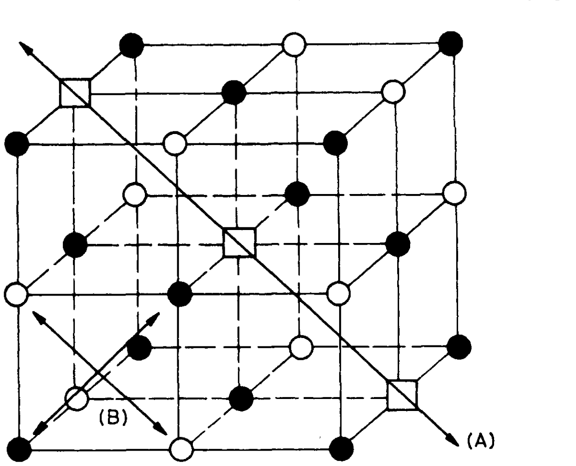

Figure 2. Lattice structure of $M_3[Co(CN)_6]_2$: ●, M^{2+} ions; ○, $Co(CN)_6{}^{3-}$ ions with the ligands bonded as Co^{3+}–CN–M^{2+}; □, vacancies. (A), channel direction; (B), small openings, which make separation of small molecules *via* $M^1[M^2(CN)_5(NO)]$ type complexes possible. In principle, a more random distribution of vacancies over the lattice can exist in such a way that 4/3 of the 4 $Co(CN)_6{}^{3-}$ positions in the lattice are unoccupied.

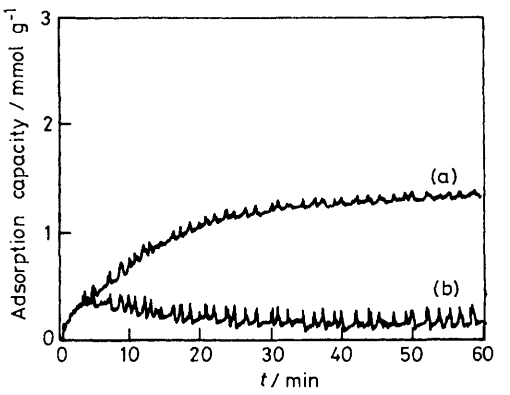

Figure 3. Mass spectrometric measurements on the separation (1.2 bar; 20 °C) of (a) CO_2 and (b) CH_4 on $Zn[Fe(CN)_5(NO)]$ after dehydration at 120 °C for 1 h.

Thus, the cyanometallates $M^1{}_x[M^2(CN)_6]_y$ form an attractive family of complexes, exhibiting zeolite-like properties. As compared to classical silica–alumina molecular sieves, they have the advantage of allowing a more flexible change of both geometry and dimensions of their pore system, since not only the metal ions, but also the number of vacancies and even the

---

† Sartorius microbalance, type 4410; reading accuracy 1 μg; typical sample weights 0.5—1 g.

‡ During the adsorption of the gases the composition of the gas mixture was measured every 10 s with a Balzer quadrupole mass spectrometer. From the change in relative concentrations, the adsorption capacities of the adsorbates can be calculated.

ligand can be varied (*e.g.* NO or OH for CN). It is of interest that the building unit is the octahedron, instead of the tetrahedron as is the case for zeolites having similar properties. Finally, most cyanometallates undergo a colour change when they are completely dehydrated, which provides an important visual check on their activity.

We conclude that cyanometallates might be attractive in a wide range of molecular sieve applications, for the separation not only of small molecules (N_2–O_2; CO_2–CH_4) but also of larger ones (*o*-, *m*-, and *p*-xylene).

We thank Ir. A. G. T. G. Kortbeek, Dr. J. Kuyper, and Dr. R. P. van der Werf for helpful discussions.

Received, 21st June 1985; Com. 875

References

1 H. E. Williams, *Chem. World,* 1912, **1**, 43; W. Peters, *Z. Anorg. Chem.*, 1912, **77**, 137.
2 G. B. Seifer, *Russ. J. Inorg. Chem.*, (a) 1959, **4**, 841; (b) 1962, **7**, 899; (c) 1962, **7**, 621.
3 P. Cartraud, A. Cointot, and A. Renaud, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1561.
4 W. P. Cummings and C. W. Chi, 'Natural Gas Purification with Molecular Sieves,' presented at 27th Canadian Chemical Engineering Conference, Calgary, Alberta, 1978.
5 R. M. Barrer, *Adv. Chem.*, 1970, **102**, 1.
6 D. F. Mullica, W. O. Milligan, G. W. Beall, and W. L. Reeves, *Acta Crystallogr., Sect. B*, 1978, **34**, 3558.
7 B. Pat. Appl. 84/00796 (Shell Int. Research Mij., 1984); J. Kuyper and G. Boxhoorn to be published.