SUPPLEMENTARY DATA   JA002921F

1. *Further evidence that the nickel and zinc metals are the active sites for polymerisation in porous materials.*

In addition to the facts that no polymerisation was observed when the mesopores or zeolites did not contain the active metals, the activity in both microporous and mesoporous materials correlates with the amount of Ni or Zn incorporated.   Thus at low metal exchange the activity is lower, and less polymer is produced per unit time, and a lower total yield is obtained, e.g., in zeolite samples, where more extensive data are available:

Ion	Ion incorporation*	Carbon content	Temp/°C	Alkyne
Ni	64%	5.31	20	propyne
Ni	95%	7.81	20	propyne
Ni	64%	5.85	130	propyne
Ni	95%	13.64	130	propyne
Zn	64%	4.96	20	propyne
Zn	95%	12.09	20	propyne
Zn	64%	5.99	130	propyne
Zn	95%	15.59	130	propyne

*Percentage of exchangeable sodium replaced by nickel or zinc.

Other metal ions can be incorporated into porous materials, and though none are as active as nickel or zinc some show lower activity for the polymerisation of acetylene.   This activity does not correlate directly with the Lewis acidity of the metal ion, [in agreement with our mechanistic proposals] but again correlates with the amount of metal ion incorporated.
Nonporous aluminosilicates even when doped with nickel or zinc show no activity, so the confinement of the metals in the pores is also a requirement, as suggested by the reported data on changes of cation acidity in porous media. Baldovi, M.V.; Corma, A.; Fornés, V.; Garcia, H.; Martinez, A; Primo, J. *J. Chem. Soc., Chem. Commun.*, **1992**, 949-951.
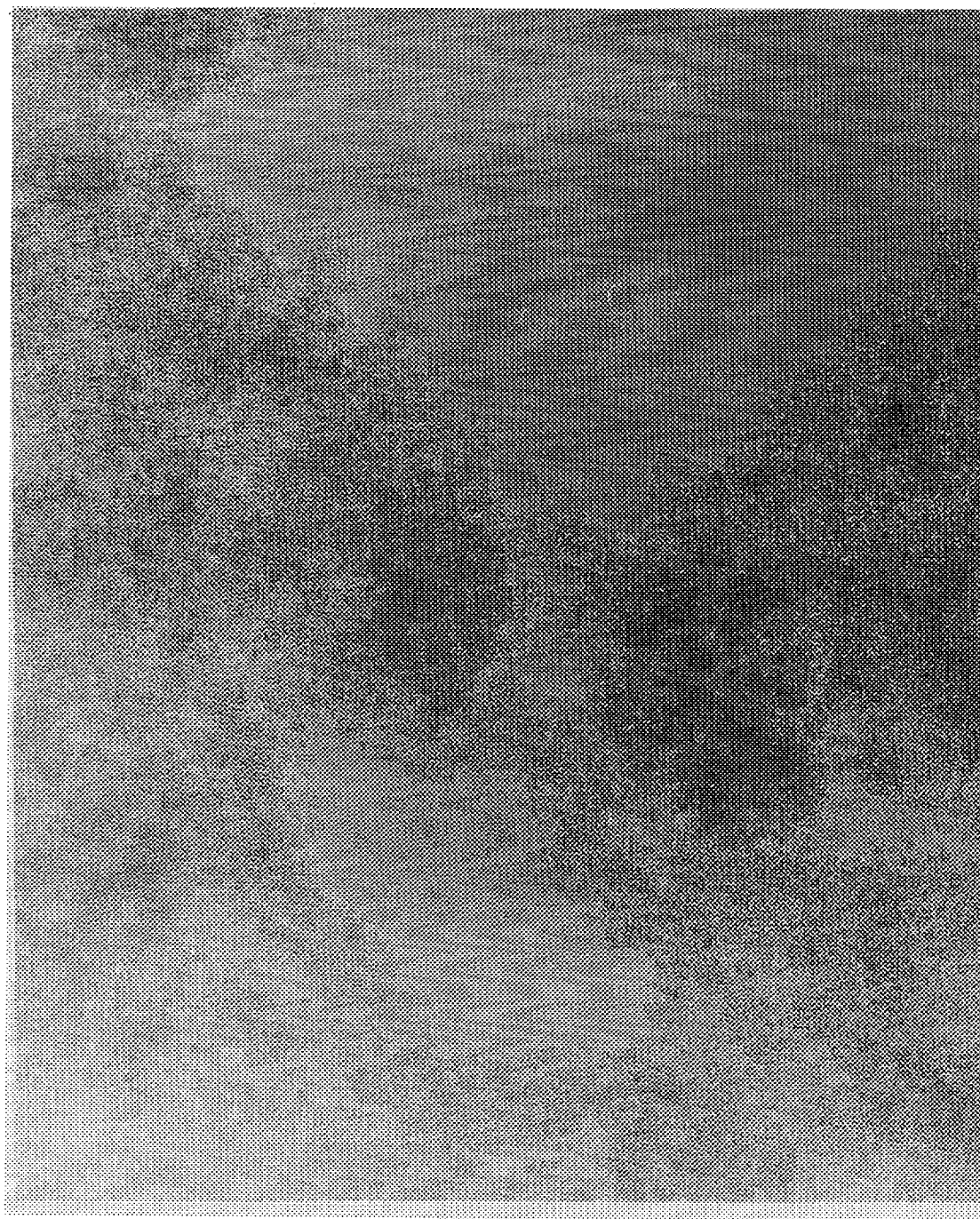
2. *Incorporation of metal ions into the mesopores.*

The metal ions were incorporated into the mesopores using aqueous solutions of the ions. Mesopores undergo structural degradation on exposure to aqueous solutions, and this was found to be minimised when the metals were exchanged from strong solutions.   Saturated solutions of nickel or zinc chloride were employed, and TEM studies showed that for strong solutions with short exposure times the mesopores retained approximately 85% of the initial structure.   Dilute solutions or long exposure times should be avoided as substantial breakdown of the pore structure can occur.

3. *Structural integrity of the composites.*

Following cation exchange [see above] some structure of the mesopore is lost.   The residual structure is largely retained during polymerisations carried out under controlled temperature conditions.
Even at the highest temperature for which graphite is not formed, viz. 300 °C, much of the mesopore structure is retained.   The transmission electron micrograph shown below is for a sample of MCM-41, nickel exchanged, in which acetylene was polymerised at 300 °C.

4. *Aluminium content of the mesopore following cation exchange.*
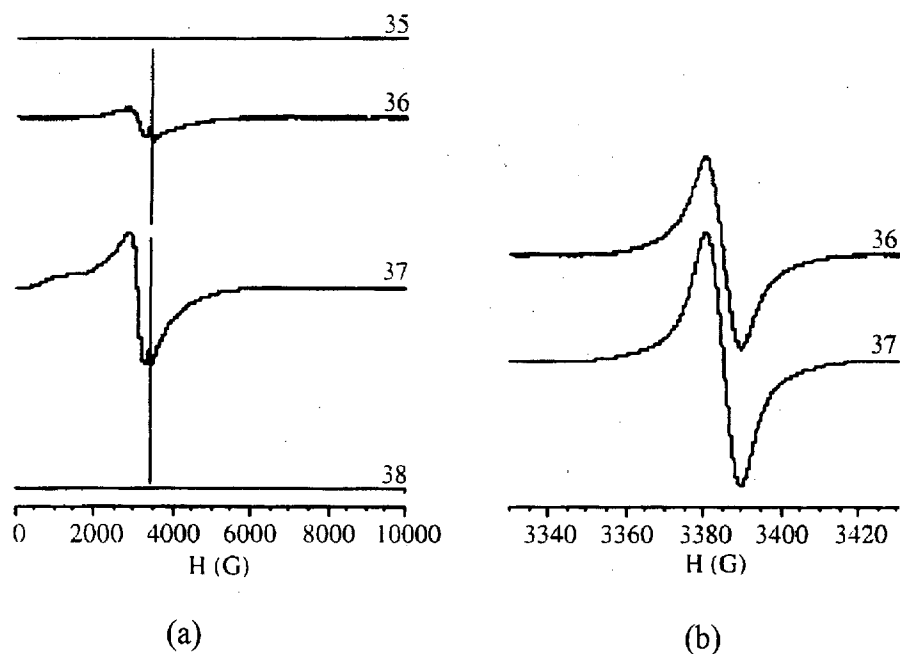
Exchange of nickel or zinc ions for sodium in the mesopore does not affect the aluminium content of the host. However, we can not be certain that the aluminium ions retain the same positions in the mesopore after exchange as they occupied before. For example, it could be that aluminium ions migrate from sites in the cavities to the surface. A referee has suggested that possibly the aluminium is behaving like the original Shirakawa catalyst. The fact that no analytical change is observed, however, does at least suggest that the aluminium is not directly involved, and the gross chemical difference between the Shirakawa materials and aluminium in an aluminosilicate do not suggest any parallels here.

5.Catalyst Activity

The mesopore containing the zinc or nickel salts are highly reactive unless controlled thermally. Uncontrolled reactions are highly exothermic and lead to graphite formation on the outside of the particles. It is estimated that 80-90% of the polymerisation takes place in the first two minutes during the initial exotherm of even controlled reactions. For example a loading of 10% Zn(II) and a polymer loading of 39% [no graphite formation] corresponds to an activity of 0.39g polymer/ 100mg catalyst/120 sec. Uncontrolled reactions are substantially faster, but do not give pure encapsulated polymer. Nickel systems give a higher reaction rate, and are more exothermic, but produce graphite more easily. The zinc systems are easier to control, but are still capable of yielding filled mesopores. It should be noted that this catalysis is different from a conventional polymerisation in that the product once formed is bound at the site of production, and not released into solution or precipitated, so activities must be substantially lower than in these cases.

6 ESR Spectra

Below are shown the ESR spectra of mesopore samples containing polyethyne. Spectrum (a) shows a wide range scan with the broad metal [Ni] signal and the sharp organic polymer signal superimposed upon it. Spectrum (b) shows an expanded view of the central polymer signal. Full details of the ESR spectra will be published separately.

(a)

(b)

7. Filling of the pores in mesoporous and microporous media.

The pore filling has been calculated based on the carbon analysis of the composite, which gives the total polymer present. Hydrogen analyses were not included for the reasons given above associated with adventitious water. The carbon content in a mesopore can be compared with the carbon content of the material immediately prior to calcination of the template. This clearly represents the maximum occupancy of the pore, since it is formed around the template. In this sense, estimates based on the template will be pessimistic as to channel filling. The question then arises as to whether the template and polymer have comparable densities: if they have the analysis is sound. Our mesopores have been prepared using

cetyltrimethlammonium chloride, and available data indicate that the template fills the channels like a long hydrocarbon chain. For details see Elworthy, P.H.; Florence, A.T.; McFarlane, C.B. *Solubilisation by surface acive agents and the applications in chemistry and the biological sciences*, Chapman and Hall, London, 1968 pp 37-46.

Because of the uncertainty in the density of polyethyne [literature values range from 0.45 to nearly 1.0], it is not possible to obtain an accurate occupancy based on this.

It is noteworthy though, that the BET measurements support the complete or near-complete filling of the channels.