

《解説》

MOLECULARLY ENGINEERED LAYERED STRUCTURES: AN EMERGING TECHNOLOGY

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I. Introduction

Layered structures have long been recognized as compounds with significant commercial potential. Clays, such as montmorillonite and bentonite, have numerous applications as sorbents, thickening agents, ion exchangers, and catalysts. Graphite and molybdenum disulfide have widespread use as lubricants. While such materials are attractive due to their low cost relative to performance, the range of structural, chemical and surface properties is rather limited. Clays can be modified by ion exchange with organo-ammonium cations to increase dispersibility in solvents, or surface-treated with silanes or titanates to improve compatibility with organic media such as polymers. However, these treatments are somewhat limited in scope and the materials often suffer from poor hydrolytic stability of the introduced organo-function. True organic/inorganic compounds in which the two functions are connected covalently throughout the solid are relatively rare; even more so in the case of layered compounds.

Catalytica is developing a novel class of materials which are called Molecularly Engineered Layered Structures (MELS)[®]. These compounds are lamellar structures comprising metal phosphonates or metal organophosphates. The original invention of the materials was carried out at Occidental Research; Catalytica contributed to their development as consultants and subsequently obtained exclusive worldwide rights to the compounds when they were made available by Occidental. MELS are covered

broadly by a substantial patent estate; sixteen U.S. patents describe several hundred compositions of matter and several processes of preparation. Because of their tremendous physical and chemical flexibility, MELS have the potential for a broad range of applications including catalysis, sorption, adhesion and coatings.

II. Structure and Synthesis

The structure of MELS is that of a metal phosphate core layer with pendant organic groups attached to this core and extending perpendicular to the plane of the layer (Fig. 1). The combination of the two functions results in a unique material which combines the properties of both the organic and inorganic components: the particulate and morphological properties of the solid device substantially from the inorganic core; the surface properties are dictated mainly by the organic component. MELS are solid materials typically synthesized under aqueous conditions by the reaction of a

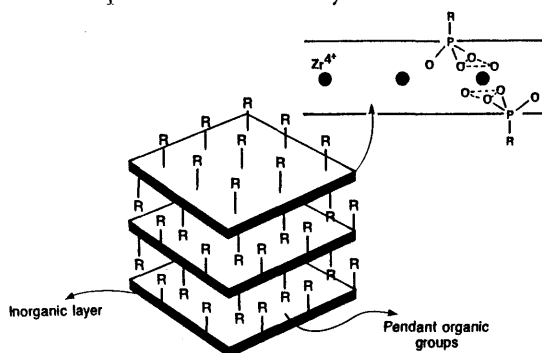
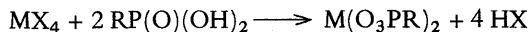


Figure 1. Simplified structure of a typical MELS.

soluble salt of a tetravalent metal and a phosphonic acid or an organophosphoric acid:



where R generically represents an organic group. Unless the organic function is substantially hydrophilic, MELS precipitates readily from solution and can be filtered or centrifuged. Phosphonates are generally preferred as they provide exceptional hydrothermal stability and acid resistance. The metals most commonly employed in synthesizing MELS are titanium and zirconium, but any tetravalent metal which favors octahedral coordination can be used. The organic moiety is chosen to tailor the surface and chemical properties of the material to match the performance required for a particular application.

Typical examples of organic groups and metals that have been incorporated in these compounds are shown in Figure 2. The limitations which can arise in the scope of the materials are based mainly on the ability to obtain or synthesize the desired phosphonic

Representative Pendant Groups	M (IV) Ions
- H	Zr
- CH ₂ Cl	Ti
- C ₆ H ₅	Pb
- O(CH ₂) ₂ CN	U
- (CH ₂) ₂ COOH	Ce
- C ₆ H ₅ SO ₃ H	Th
- (CH ₂) ₂ NH ₂ -C ₆ H ₄ N	Sn
- (CH ₂) _n SH	
- C ₆ H ₄ -C ₆ H ₄ -	



Figure 2. Representative examples showing the scope of MELS compounds.

Compound	Interlayer Spacing, Å
Zr(O ₃ P-H) ₂	5.61
Th(O ₃ P-CH ₃) ₂	8.9
Zr(O ₃ P-CH ₂ Cl) ₂	10.0
Zr(O ₃ P-CH ₂ CH ₂ COOH) ₂	12.8
Zr(O ₃ P-CH ₂ CH ₂ SH) ₂	15.5
Zr(O ₃ P-CH ₂ -O-C ₆ H ₅) ₂	19.0
U(O ₃ P-CH ₂ CH ₂ CH ₂ SO ₃ H) ₂	29.4
Th(O ₃ P(CH ₂) ₁₇ CH ₃) ₂	42.0

Figure 3. Correlation of lattice spacing of MELS with chemical composition.

acid; however, we have not seen this to be a significant limitation. The x-ray data in Figure 3 confirm the expected correlation of interlayer spacing with the size of the pendant organic group.

Solid products consisting of layered sheets with ordered arrays of the pendant organic groups on both sides of the layer are obtained with most phosphonic acids. The generic structures of these materials fall into three classes, as depicted in Figure 4. In addition to single component MELS (i.e., using a single phosphonic acid), structures with multiple functionality can be prepared by incorporating more than one phosphonic acid during the synthesis step. This is useful for example in catalysis, where one phosphonic acid can supply the catalytic activity while a second function can alter the surface properties such as surface hydrophilicity. Pillared MELS are made using diphosphonic acids, usually in combination with a second smaller phosphonic acid, thereby creating an open microporous structure. This ensures access to each layer in the structure and can in principle provide a two dimensional analog to zeolites.

In addition to chemical variations, Figure 5 shows that the physical properties of MELS can also be altered. By careful control of the synthesis conditions, solids ranging from x-ray amorphous to highly crystalline can be produced. Crystal sizes range from submicron to tens of microns. In addition to solids,

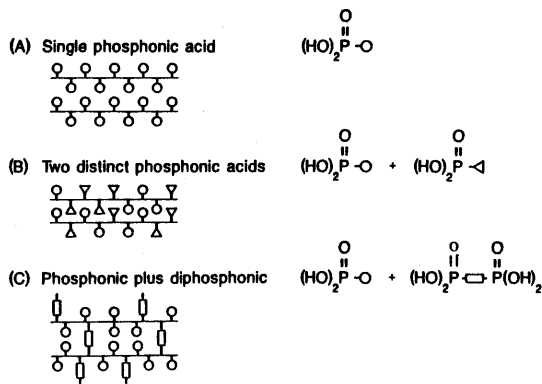


Figure 4. Generic structures of MELS: single component; two component; pillared.

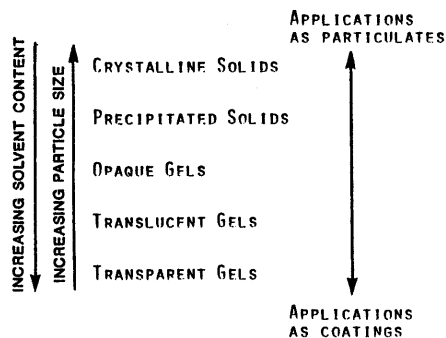


Figure 5. Potential variations in morphology and particle size of MELS.

gelatinous MELS can be formed in aqueous or organic media.

III. Application as Acid Catalysts

Figure 6 depicts a schematic of a MELS acid catalyst. In this case, the MELS has an aryl sulfonic acid functionality, somewhat analogous to the acid site of conventional strong acid ion exchange resin catalysts. The MELS, however, have several potential advantages over the resins.

Because of the inorganic core in MELS, the materials do not melt or deform at the temperatures where this is encountered with polymeric resins. By virtue of the oxidative stability of the metal-oxygen-phosphorus backbone and direct bonding of phosphorus to the aromatic ring, MELS have higher thermal resistance to desulfonation and oxidation compared to analogous ion exchange resins, as well as greater hydrothermal stability. Whereas sulfonated styrenedivinylbenzene resins will desulfonate at 140°C. and decompose at 300°C., arylsulfonic acid MELS desulfonate at 330°C., as measured by thermogravimetric experiments. Figure 7 compares the resistance

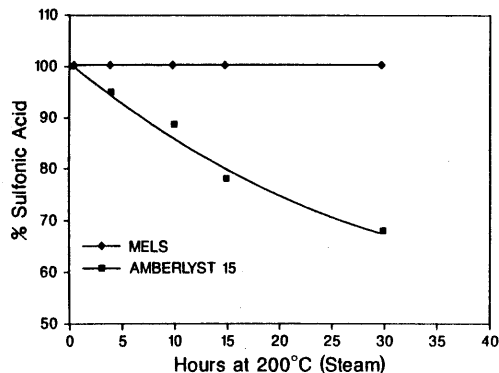


Figure 7. Comparative steam stabilities (relative to desulfonation) of MELS arylsulfonic acid catalyst and strong acid ion exchange resin (Amberlyst 15).

of Amberlyst 15 and an arylsulfonic acid MELS to desulfonation in steam at 200°C. After 30 hours, Amberlyst lost 30% of its sulfonic acid sites whereas the MELS showed no measurable desulfonation.

The ability to control both structure and composition allows MELS to be tailored for optimum performance in a given chemical reaction. Not only can the acid strength be varied by choice of the functional group (e.g., carboxylic acids and sulfonic acids), but also secondary moieties can be added to alter the environment around the catalytic site. Figure 8 shows the performance of arylsulfonic acid MELS catalysts compared with Amberlyst 15 for the synthesis of MTBE. When a hydrophobic secondary group is incorporated into the MELS structure, the MELS catalyst has an 80% higher rate per SO_3H group than Amberlyst 15; if the secondary group is hydrophilic, the rate of the MELS catalyst is 130% higher. This ability to tailor the catalytic site to enhance reactivity or other properties repre-

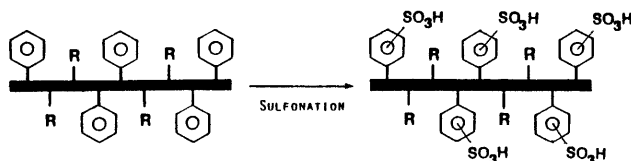


Figure 6. Simplified schematic of MELS arylsulfonic acid catalyst and its synthesis.

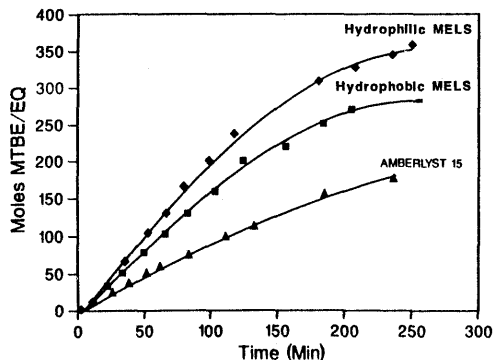


Figure 8. Relative performance of MELS and Amberlyst 15 for the synthesis of MTBE.

sents an exciting form of molecular engineering.

MELS with acidic functional groups such as the arylsulfonic acid described above can be applied to a variety of catalytic applications in both polar and non-polar media. Other

catalytic reactions which have been demonstrated in the laboratory include esterifications, aromatic alkylations, isomerizations and condensations.

IV. Summary

MELS represent an exciting new class of materials with a broad range of applicability in several fields of technology. They are unique organic-inorganic composites in which these distinct functions are bonded at the molecular level. The ability to control particle size, surface area and porosity, and surface chemistry in unique ways, as well as the scope and range of possible distinct compositions, make these materials especially attractive. The commercial possibilities of these materials are just beginning to be appreciated and exploited.