

Catalysis of organic reactions by inorganic solids

Pierre Laszlo

Laboratoires de chimie fine aux interfaces, Ecole Polytechnique, 91128 Palaiseau, France; and Université de Liège, Sart-Tilman par 4000 Liège, Belgium.

ABSTRACT: Major advances have been made towards design, realization, and optimization of efficient catalytic systems based on modified aluminosilicate minerals.

INTRODUCTION

ROUGH AND READY: according to the dictionary this expression has the adjectival meaning of something "rude or unpolished in nature, method, or manner, but effective in action". This definition suits admirably aluminosilicate minerals in their function as catalysts for organic reactions. In this presentation I shall intimate at the bewildering diversity of such minerals in Nature. I shall delineate some of the principles for modifying them into potent catalysts. I shall indicate applications to the renovation of important organic reactions; such as those listed below in Fig. 1.

Fig. 1 SOME OF THE REACTIONS DRAWING BENEFIT FROM CATALYSIS BY MODIFIED CLAYS

- electrophilic aromatic substitutions:
chlorinations - nitrations - Friedel-Crafts alkylations and acylations
- Diels-Alder cycloadditions
- Michael additions
- protection - regeneration of carbonyls

One of the main goals of modern synthetic methodology is to emulate enzymatic efficiency: quantitative yields, with near 100% stereoselectivity, under very mild conditions at body temperature and at atmospheric pressure. Enzymes achieve it as micro-reactors endowed with remarkable assets. Among inorganic minerals, clays possess not-unlike favorable features as micro-reactors (Fig. 2).

Fig. 2 CLAYS ARE ALSO MICRO-REACTORS

- low-dimensional -----> fast diffusional kinetics
- pores -----> concentration of reactants
- catalytic sites -----> positioning of reactants

Clays are assemblies of tetrahedral layers of SiO_4 silicate units and of octahedral layers of AlO_6 aluminate units. The resulting sheets are planar. That adsorbates are constrained to diffuse in two-dimensional space as against a three-dimensional reaction volume makes for increased encounter frequencies between reactants, thus boosting (by up to four or five orders of magnitude) the pre-exponential term in the kinetic equations.²⁻³

The planar clay platelets stack on top of one another, not unlike a deck of playing cards. Because the platelets are offset from one another, or do not have identical horizontal dimensions, or display local orthogonal arrangements, card-house-like, their assembly has pores through which solvent and solute molecules can migrate. Compartments are also set up in this manner.⁴ Organic molecules congregate in such compartments and pores thus locally increase their activity.

The catalytic sites, besides the high Brønsted-acidic surface⁵ (a factor we shall return to), are edge sites, where the platelets break off, offering coordinatively-unsaturated aluminum (III) sites;⁶ iron (II) and iron (III) centers arising often from substitution of aluminum (III) in the octahedral layer.⁷ Furthermore, dehydrative activation of a clay, through heating in an oven at temperatures in the range of 150-300°C, results in generation of surface radical sites of the O₃SiO silyloxy type⁸. Due to the planar topology, due also to the geometrical constraint of insertion between the parallel plates of two adjacent clay layers, substrate molecules are restricted in their orientation as they chemisorb onto catalytic sites. Accordingly, stereochemical consequences of import are expected (and found).

A montmorillonite is a clay mineral in which one octahedral aluminate layer is sandwiched in-between two tetrahedral silicate layers (Fig. 3). One sees (Fig. 3) one edge aluminum (III) site with dangling bonds, as pointed out earlier. Furthermore, in the octahedral layer, if the cationic species are silicon (IV) and aluminum (III) exclusively, only two out of three octahedral sites are occupied by an aluminum cation.

But this is a highly idealized description. In reality, isomorphous substitution occurs. In the tetrahedral layer, an occasional Si(IV) is replaced by an Al(III) ion. As a consequence, the valences of the coordinated oxygens are no longer saturated. An unbalance of negative charge is set up on the oxygens. In order for electroneutrality to be maintained, cations come to the interlamellar space, in-between two adjoining platelets. These counterions are condensed next to the negatively-charged silicate sheet. Likewise, there are substitutions in the octahedral layer. In random manner, an Al(III) is replaced with a divalent ion such as Mg(II), Mn(II), or Fe(II). This sets-up an excess of negative charge localized next to the site of substitution. And again counterions in the interlamellar space compensate exactly the electrical imbalance.

The negatively-charged sheets, with the electronic density delocalized on a large number of equivalent oxygen atoms through fast migration of protons (from water molecules for instance) on the surface, are reminiscent of the conjugate bases of strong inorganic oxyacids such as nitric or perchloric acids. This is a major reason for the high surface acidity of many clays. A natural montmorillonite has a surface acidity measuring (using the Hammett H₀ acidity function⁹) between 1.5 and -3. Simple washing with mineral acid such as 0.1M HCl brings H₀ down to between -6 and -8, i.e. to values intermediate of concentrated nitric acid and of oleums of sulfuric acid!

Fig. 3 MONTMORILLONITE (2:1)

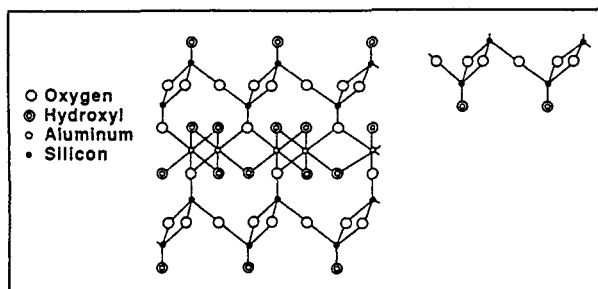
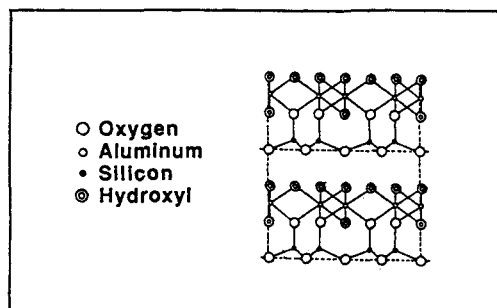


Fig. 4 KAOLINITE (1:1)



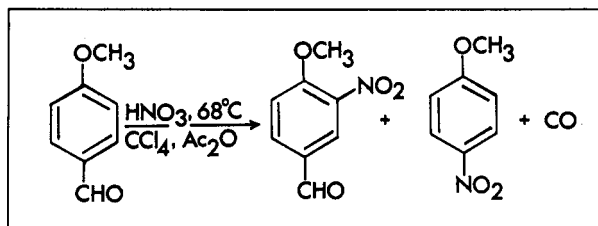
PUTTING THE HIGH SURFACE ACIDITY TO ADVANTAGE

With such high surface acidities, that are evocative of superacidic media, Brønsted acid catalysis of some reactions can be spectacular. An example is the cyclohexadienone-phenol rearrangement. Crawford and Curtin had determined its kinetics in hydrocarbon solution with sulfuric acid as the homogeneous catalyst: the half-life was five hours at 80°C.¹⁰ When we replaced the homogeneous catalyst with the K10 montmorillonite - an industrial catalyst (Süd-Chemie, Munich) with well-defined and highly reproducible characteristics -, the half-life remained the same, but at room temperature. Upon drying carefully this clay catalyst in an oven prior to use, in order to benefit from maximum Brønsted acidity, the half-life decreased to five minutes, still at room temperature. If the Brønsted acidity is yet heightened by exchanging Fe(III) into the clay (coordination of the Lewis acidic cations by the interstitial water molecules renders them better proton donors), and this is combined with clay drying, the half-life is again decreased, to five seconds, still at room temperature¹¹.

We shall detail now the reasoning behind the choice of one such inorganic mineral as a catalyst, so that it be apparent that rational design is not only feasible but also brings with it success. Kaolinities i.e. clays from which china ware is made are (Fig. 4) 1:1 clays associating one tetrahedral and one octahedral layer.

Successive platelets stack due to hydrogen-bonding between the surface alanol groups as donors and the silicate oxygens as acceptors. Due to this network of very strong hydrogen-bonds, kaolinities intercalate highly polar molecules, such as water, formamide, N-methylformamide, dimethyl-sulfoxide and -selenoxide¹². It is thus a tempting extrapolation that kaolinite clays might be capable of stabilizing highly-polar transition states, as well. In order to test this working hypothesis, we elected to examine the nitration of p-anisaldehyde I (Fig. 5).

Fig. 5 CATALYSIS OF A NITRATION



Nitration occurs either *ortho* or *para* to the methoxy group. In the former case, it suffices for the Wheland intermediate to lose a proton and it goes to product. In the latter case, when the nitro substituent is introduced *ipso* to the aldehyde function, the Wheland intermediate has to expulse a positively-charged formyl group before it can be converted into product. Accordingly, under homogeneous conditions *ortho* nitration prevails and **2** is the vastly predominant product. The electric dipole moments of the two transition states for *ortho* and *para* nitration were calculated (Fig. 6).

They were found to differ enough to encourage us to attempt differential "solvation" of these two competing transition states. Indeed the minor pathway is enhanced by one order of magnitude with the introduction (Fig. 7) of the K10 montmorillonite and by more than a factor 20 with that of a kaolinite. (Fig. 8) The catalytic turnover, from the Brunauer-Emmet-Teller BET specific surface of $8.8 \text{ m}^2 \cdot \text{g}^{-1}$ and from a Langmuir isotherm, plotting the % yield of **3** as a function of the ratio of catalyst to substrate **1**, is at least a factor 300^{13} .

Fig. 6 DIPOLE MOMENTS, D^a

ortho	4.49
para	5.57
a MINDO-3	

Fig. 7 ROLE OF THE BRONSTED SURFACE ACIDITY

	% p-nitroanisole
HOMOGENEOUS	1.1
HETEROGENEOUS	
K10	9.6
K10-Cu(II)	13
K10-Al(III)	15
K10-Ti(IV)	16
K10-Zr(IV)	21

Fig. 8 SUPERIORITY OF A KAOLINITE CATALYST

	-Ho	% p-nitroanisole
HOMOGENEOUS	-	1.1
HETEROGENEOUS		
K10 montmorillonite	6 - 8	9.6
kaolinite	3 - 6	27

Other rewards of rational design based upon careful consideration of the relevant physico-chemical factors have been catalysis by zeolites of the chlorination of aromatic hydrocarbons by sulfuryl chloride: because of its high Brønsted acidity (Si/Al ratio) ZF520 is the choice catalyst for nuclear chlorination, in 86% yield and with 300:1 selectivity; with its low Si:Al ratio, conducive to the presence of silyloxy chain carriers, the NaX (13X) zeolite gives rise conversely to almost exclusive side-chain radical chlorination (80% yield and 400:1 selectivity) (the values stated are with toluene as the substrate)¹⁴.

MAKING USE OF THE LEWIS ACIDITY

A major reaction both in the laboratory and in industry is the Friedel-Crafts. We teach students, over-enthusiastically, that it is *catalyzed* by Lewis acids such as aluminum chloride. In fact, secondary products (e.g. chloride ions from alkyl or acid chlorides) poison the catalyst by coordination to the π orbital. As a consequence *stoichiometric* rather than catalytic amounts are required. Recourse to Lewis acidic sites in clays, either exchanged or impregnated with Lewis acidic cations, provides extremely efficient catalysis of Friedel-Crafts alkylations¹⁵⁻¹⁶ and acylations¹⁷ (Fig. 9), with the environmental asset of vastly reduced (by factors up to a thousand) amounts of catalyst as compared to the standard procedures using aluminum chloride, at least one industrial plant takes advantage of this breakthrough.

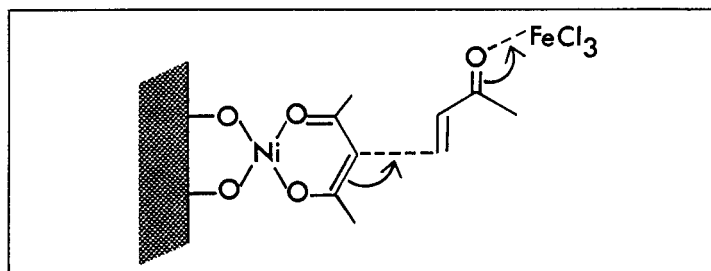
Lewis acid catalysis is a mainstay for Diels-Alder cycloadditions. With normal electron demand Diels-Alder's the Lewis acid lowers the LUMO for the dienophile thus narrowing the HOMO-LUMO gap, hence the catalysis. This key reaction of organic synthesis has also been catalyzed successfully using doped clays¹⁸⁻²⁰; for instance, with furans as dienes, reactions can be run at *ambient temperature and pressure*²¹, instead of requiring 15kbars of applied pressure to give significant yields of reaction products.

Fig. 9 BENZOYLATION OF AROMATIC SUBSTRATES BY BENZOYL CHLORIDE (K10-Fe(III) CATALYSTS)

	TIME	TEMP. °C	YIELD.%
anisole	5mn	160	100
mesitylene	15mn	160	98
p-xylene	3 h	140	100

The Michael reaction, with conjugate bases of β -diketones as donors and with α,β -unsaturated ketones as acceptors, is efficiently catalyzed by a combination of clay supported nickel bromide (heterogeneous) and ferric chloride (homogeneous) (Fig. 10)²²

Fig. 10 PLAUSIBLE PICTURE FOR CATALYTIC SYSTEM



During the course of this work, we became aware of a blatant lack: there is neither a good measure of the acidity of a Lewis acid, nor a good correlation with its catalytic power. We have provided theoretical justification²³ for the nmr method based on the chemical shift (H_3) of crotonaldehyde complexed by a Lewis acid.²⁴

CONCLUDING REMARKS

The achievements of clay micro-reactors are already notable. Quantitative yields and high selectivities are accomplished under mild conditions. Work-up is no sweat: filter off the supported reagents and/or catalysts, evaporate the solvent, and pure product will show up. Through rational design, catalysts can be tailored to the particular reaction they are meant to rouse. And these are, literally, dirt-cheap. Of negatives, there are few. The complexity of the catalytic surfaces precludes full understanding of the whole sequence of catalytic events. Humidity is a rather omnipresent threat to catalytic activity. The aluminosilicate micro-reactors are sometimes destroyed¹⁴, they are always affected by the reactions to which they offer seats.

Thus, to resume with our opening metaphor of the rough and ready, clay-supported reagents and catalysts may give a rough ride but they will get you there in a jiffy.

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REFERENCES

- 1 *The Merriam-Webster Pocket Dictionary*, Collector's Ed., Pocket Books, Inc., New York, 1947, p. 297.
- 2 G. Adam and M. Delbrück, in *Structural Chemistry and Molecular Biology*, A. Rich and N. Davidson, eds., W.H. Freeman, San Francisco, 1968, p. 198.
- 3 S. L. Hardt, *Biophys. Chem.*, 1979, 10, 239-243.
- 4 J. Fripiat, J. Cases, M. François, and M. Letellier, *J. Coll. Interface Sci.*, 1982, 89, 378-400.
- 5 H.A. Benesi, *J. Am. Chem. Soc.*, 1956, 78, 5490-5494.
- 6 G.A. Somorjai, *Pure Appl. Chem.*, 1988, 60, 1499-1516; and references herein cited.
- 7 P. do Souza Santos, *Ciencia e Tecnologia de argilas*, 2.^a ed., Edgard Blücher Ltda., Sao Paulo, Brazil 1989.
- 8 F. Freund and F. Battlo, in *Structure and Active Sites of Minerals*, ACS Symposium Series 145, Washington DC, 1989, 310-329.
- 9 L.P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1970, 267-273.
- 10 D.Y. Curtin and R.J. Crawford, *J. Am. Chem. Soc.*, 1957, 79, 3156-3159.
- 11 S. Chalais, P. Laszlo, and A. Mathy, *Tetrahedron Lett.*, 1986, 27, 2627-2630.
- 12 for instance, P. M. Costanzo and R. F. Giese, Jr., *Clay & Clay Min.*, 1990, 38, 160-170.
- 13 C. Collet, A. Delville, and P. Laszlo, *Angew. Chem. Int. Ed. Engl.*, 1990, 29, 535-536.
- 14 L. Delaude and P. Laszlo, *J. Org. Chem.*, in press.
- 15 P. Laszlo and A. Mathy, *Helv. Chim. Acta*, 1987, 70, 577-586.
- 16 J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow, and P. Landon, *J. Chem. Soc. Chem. Comm.*, 1989, 1353-1354.
- 17 A. Cornélis, A. Gerstmans, P. Laszlo, A. Mathy, and I. Zieba, *Catal. Lett.*, in press.
- 18 P. Laszlo and J. Lucchetti, *Tetrahedron Lett.*, 1984, 25, 1567-1570.
- 19 P. Laszlo and J. Lucchetti, *Tetrahedron Lett.*, 1984, 25, 2147-2150.
- 20 P. Laszlo and H. Moison, *Chem. Lett.*, 1989, 1031-1034.
- 21 P. Laszlo and J. Lucchetti, *Tetrahedron Lett.*, 1984, 25, 4387-4388.
- 22 P. Laszlo, M.T. Montaufer, and S.L. Randriamahefa, *Tetrahedron Lett.* in press.
- 23 P. Laszlo, and M. Teston, *J. Am. Chem. Soc.*, submitted for publication.
- 24 R.F. Childs, D.L. Mulholland, and A. Nixon, *Can. J. Chem.*, 1982, 60, 801-808.