

FT-IR and catalytic characterization of the acidity of imogolite-based systems

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Introduction

Proper imogolite (from the Japanese “Imogo”, clay soil) is a material of volcanic origin [1], with chemical composition $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$ and a fascinating nanotubes structure [2]. Its formation can be described considering a single $\text{Al}(\text{OH})_3$ gibbsite sheet and substituting, on one side only, three OH groups with an orthosilicate unit O_3SiOH . Being Si-O bonds shorter than Al-O bonds, the gibbsite-like sheet curls up, eventually forming nanotubes. When the process is not successful, an amorphous phase forms, proto-imogolite. Imogolite may also be obtained via sol-gel synthesis [3,4]. Electron diffraction measurements [2] and computer models [5] showed that the most likely structures for natural and synthetic imogolite are nanotubes with 10 and 12 gibbsite units in the cross-section, respectively. Dehydroxylation at 500°C is accompanied by breakdown of the tubes [6] and formation of a lamellar aluminosilicate (L-IM), with new surface functionalities. NMR studies shown that in imogolite nanotubes only tetrahedral Si atoms and octahedral Al atoms are present, whereas after structural dehydroxylation new environments create for both Si and Al, the latter being present also as tetrahedral and five-coordinated aluminium.

Materials and Methods

Imogolite (IM) was synthesised according ref. 3; reaction conditions are rather strict, and unsuccessful syntheses lead to amorphous proto-imogolite (PR-IM). Samples will be hereafter identified by the acronym of the solid followed by the temperature (in Celsius) of the pre-treatment, *e.g.* IM-150 stands for imogolite heated at 150°C. Note that IM-500 coincides with L-IM (L = lamellar). Materials were characterized by means of XRD; N_2 isotherms at 77 K; FESEM microscopy and FT-IR spectroscopy of absorbed probes: CO (at nominal 77 K); NH_3 , methanol and phenol were dosed on samples outgassed at temperatures in the 150 – 500°C range to study the acidity and accessibility of surface species. The catalytic behaviour in the gas phase methylation of phenol with methanol was tested and compared to that of a commercial silica (Grace Silica Catalyst Support) and of a $\gamma\text{-Al}_2\text{O}_3$ used as reference materials.

Results and Discussion

As a hydrated aluminosilicate, the behaviour of imogolite is very sensitive to thermal pre-treatments: molecular water is only removed at 300°C, so rendering inner silanols accessible to probes like CO, ammonia, methanol and, partially, to phenol. CO adsorption at nominal 77 K on IM-300 showed that silanols are as acidic as those of amorphous silica, but

their abundance enhances the interaction with adsorbed molecules: on the one hand, ammonia is observed to form ammonium species, on the other hand, diffusion is difficult. At temperatures around 500°C, the nanotubes structure is lost, with formation of a lamellar phase, with new stronger acidic properties, resembling those of amorphous aluminosilicates with high Al content, as shown by FT-IR spectroscopy of adsorbed CO and ammonia on L-IM material. Catalytic tests of gas-phase phenol reaction with methanol showed that the aromatic compound has a limited access to inner silanols of IM at high temperature, whereas methanol interacts with both inner silanols and outer $\text{Al}(\text{OH})\text{Al}$ groups. PR-IM shows a remarkable acid-type behaviour in phenol methylation, which, however, rapidly declines because of deactivation phenomena. A peculiar reactivity is shown by L-IM, presenting medium-strength acidic and basic surface features, which result into an “amphoteric” catalytic behaviour: FT-IR spectroscopy showed, on the one hand, the presence of acidic Brønsted –like sites, similar to hydroxyls in high Al-content alumina-silicates and mildly acidic zeolites: on the other hand, the presence of basic sites is shown by the formation of phenolate species upon phenol adsorption. Basic properties, indeed, lead to phenol de-protonation and to the preferred formation of o-cresol, with negligible formation of p-cresol, as usually observed with basic-type solids.

Table 1. Relevant textural properties of materials, as derived from XRD and N_2 isotherms at 77 K

Catalyst	BET SSA ($\text{m}^2 \text{g}^{-1}$)	Total Pore Vol. ($\text{cm}^3 \text{g}^{-1}$)	Micropores Vol. ($\text{cm}^3 \text{g}^{-1}$)	Inner diameter (nm)	Outer diameter (nm)
IM-150	213	0.20	0.01	-	-
IM-300	362	0.26	0.04	0.98	2.44
IM-500	197	0.16	0.02	-	-
PR-IM	178	0.09	0.03	-	-

Significance

From a catalytic point of view, most interesting features are: i) the nanoporous structure; ii) the outer surface covered by $\text{Al}(\text{OH})\text{Al}$ groups; iii) the inner surface lined by $\equiv\text{SiOH}$ groups. Though less famous than its organic counterpart, *ie.* Carbon NanoTubes, imogolite presents as well an intriguing nanotubes structure and a remarkably high silanols density at the inner surface (9.1 OH nm^{-2} , *ca.* twice as much as the average silanols density at the surface of hydrated amorphous silicas (*ca.* 5 OH nm^{-2}), and could be exploited in selective adsorption and/or gas storage applications.

References

1. Yoshinaga, N., Aomine, A. *Soil Sci. Pl. Nutr.* 8, 22 (1962).
2. Cradwick, P.D.G. et al. *Nature Phys. Sci.* 240, 187 (1972).
3. Farmer, V.C. et al. *Clay Miner.* 18, 459 (1983).
4. Wada, S.I. et al. Proceedings of the International Clay Conference (M.M.Mortland and V.C. Farmer Ed.) Elsevier, Amsterdam (1978) 348.
5. Pohl, P.I. et al. *Langmuir* 12, 4463 (1996).
6. MacKenzie, K.J. et al. *Clays and Clay Miner.* 37, 317 (1989).