Synthesis of intermetallic compounds for catalytic applications

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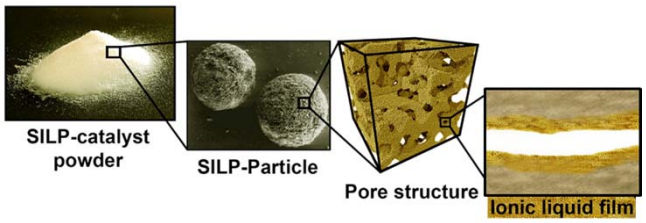
Synthesis of nano-dispersed intermetallic systems: SILP meets intermetallic

Supported ionic liquid phase (SILP) were used as precursors for the synthesis of supported intermetallic compounds (IMCs). Ionic liquids (ILs) are, by definition, salts melting below 100°C [1]. By coupling ILs with heterogeneous supports, is practically possible to merge features of homogeneous systems with those of heterogeneous ones [2]

[1] P. Wasserscheid, T. Welton (eds.) "Ionic Liquids in Synthesis", Wiley-VCH, 2nd edition, 2007
[2] S. Werner, N. Szesni, M. Kaiser, M. Haumann, P. Wasserscheid *Chemical Engineering & Technology* **35**, 1962-1967, **2012**



As IL phase, triethylammonium chlorometallate of general formula $[Et3NH]_n[MCl_m]$, so called protic ionic liquid (PILs), were chosen. They were straightforwardly synthetized according the following scheme:

$$n\,[Et_3NH]Cl + MCl_m \xrightarrow[\text{or } CH_3CN/MeOH]{CH_3CN} [Et_3N]_n[MCl_{m+n}]$$

n=m=2; **M**=Pd, Pt, Ni, Cu, Co
n=1; m=3; **M**=Au, Fe, Cr, Ir, Rh, Ru

The SILP material was then prepared allowing the PILs to adsorb on a *porous glass support*. Contacting the SILP material with an excess of a ***gallium source*** will lead to forming nano-dispersed **IMCs**, being the latter trapped in the porous network of the support.

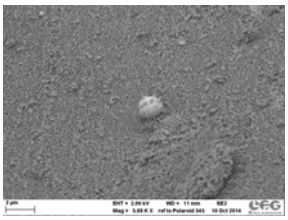
$$[Et_3NH]_n[MCl_{n+m}] + Et_3NGaH_3 \xrightarrow[Et_2O]{} M_xGa_y + n\,[Et_3NH][GaCl_4] + H_{2(g)} + Et_3N \quad (1)$$

$$[Et_3NH][GaCl_4] \xrightarrow[>300°C]{} Et_3NGaCl_{3(g)} + HCl_{(g)} \quad (2)$$

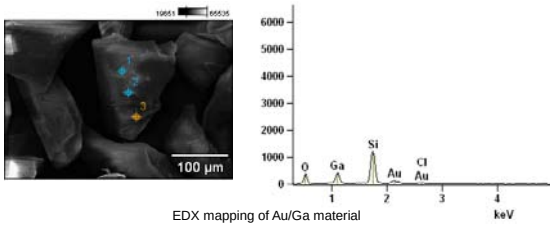
All the by-products could be easily removed by a simple thermal/vacuum treatment, leaving clean IMCs phases and eventually the excess of metallic gallium (scheme above, eq. 2)

Materials characterization

SEM and EDX: SEM showed the formation heterogeneous domains on the surface of the support (Au/Ga system in the pictures). EDX mapping showed that Ga and the active Metal are widely dispersed on the surface, i.e. also aggregate not visible with SEM

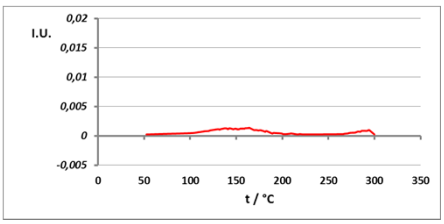


SEM imaging of Au/Ga material

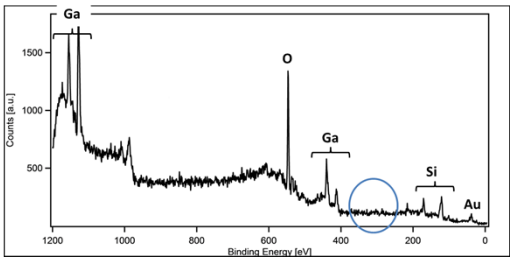


EDX mapping of Au/Ga material

TPD: the Pd/Ga containing material was investigated and CO desorption analysis indicated a modification of the adsorbing properties: substantially, **NO** CO was desorbed, indicating a strong modification of the active metal *via* IMC formation



XPS: analysis showed the synthesis produced very clean materials: traces of Cl, neither N nor C detectable (blue circle in picture below, Au/Ga sample) on the sample surface.



IMCs characterization

XRD analysis (table below) showed the presence of intermetallic phase in most of the prepared material..

Precursor	Intermetallic Phase [space group]
$[Et_3NH]_2[PdCl_4]$	PdGa [$P2_131$]
$[Et_3NH]_2[PtCl_4]$	Ga_2Pt [Fm3m]
$[Et_3NH]_2[CoCl_4]$	CoGa [Pm3m]
$[Et_3NH]_2[NiCl_4]$	Ni_2Ga [$P6_3mc$] Ni_2Ga_3 [P-3m1] Ni_3Ga_4 [a3d]
$[Et_3NH][FeCl_4]$	Fe_3Ga [Pm3m] Fe_6Ga_5 [C2/m]
$[Et_3NH][CrCl_4]$	$CrGa_4$ [Im3m]
$[Et_3NH][AuCl_4]$	Au_7Ga_4 [P-62m]*

**The attribution of this species is not yet certain*

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