Adducts of Heteropoly Acids (HPA) with Neutral Al(III) Complexes
Potential Use as Strong Solid Acid in Catalysis

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Introduction – Concept - Strategy

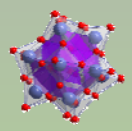
Sugar fatty acid esters are high value compounds for personal care products, emulsifiers in food manufacturing and lubricants. In the ester, as for the product of the exemplified target reaction of D-sorbitol with oleic acid, a high OH-level is favorable; therefore the mono-ester is the most desired product. The target reaction is performed on a commercial scale applying homogeneous catalysts as mineral acids. The aim of the present contribution is the implementation of heterogeneous catalysts to replace the mineral acids for environmental and processing benefit.

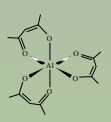
HPA are solid acids with the strength of mineral acids and thus suitable systems. However, the free acids (fa) are soluble in organic solvents used for the target reaction and generally have low surface areas in the range of 1 [m^2g^{-1}]. Bulky cations (Cs^+ or alkyl-ammonium ions) form stable and insoluble salts with HPA, the so called type-B-salts. The surface area of these salts typically ranges up to more than 100 [m^2g^{-1}]. The (partial) replacement of the acid protons of the HPA on the other hand, reduces the number of acidic (Brønstedt) centers required for catalysis. As a consequence, the best HPA solid catalyst is a compromise, where about half of the protons is substituted.

The intension of our work was the implementation of Lewis-acidic cations (Al^{+3}) to create additional acidic centers in the solid catalyst. Aluminum salts of HPA are not accessible as precipitates from aqueous solution: The radius of Al^{3+} (57 pm) is to small in relation to the KEGGIN type HPA anion (more than 550 pm). To overcome this difficulty, we tended to wrap the Al^{3+} in a bulky complex. The convenient acetyl-acetonate [$Al(aca)_3$] is a neutral complex, insoluble in water but soluble in organic solvents. As the free acids of KEGGIN-type HPA are readily dissolved in some organic solvents, there is a way to combine the both parts.

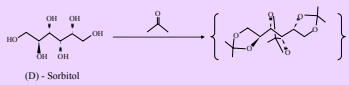
The unified solution containing HPA and $Al(aca)_3$ – in the ratio 1:1 – leave behind a kind of xero-gel after complete drying. Thermal treatment (calc), at temperatures above the decomposition of the Al-complex, generated insoluble dark materials, which have been tested for the target reaction. As HPA compound, the KEGGIN-type tungsto systems [GeW], [SiW] and [PW] are used. For comparison, in addition to the described Al-based concept, the generation of an analogous Ag-system was tempted, using the corresponding Ag(aca) complex.

apr. size ratio:

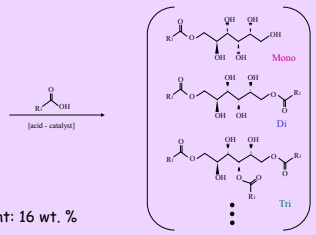




Target Reaction: Esterification of D – Sorbitol with Oleic Acid



(D) - Sorbitol



T: 408 K

Catalyst amount: 16 wt. %

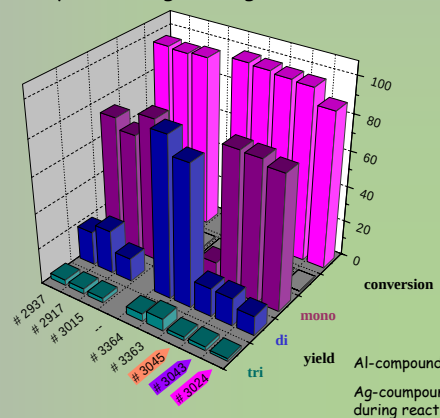
Ratio oleic acid / ketal sorbitol: 1/1

Time: 24 h

Sample Designation

# 2937	$[N(eth)_4]$ (2) [GeW]	
# 2917	$[N(prp)_4]$ (2) [SiW]	
# 3015	$[N(prp)_4]$ (2) [PW]	
# 3364	Ag(aca) ~ [GeW] (calc)	
# 3363	Ag(aca) ~ [GeW] (calc)	
# 3024	$Al(aca)_3$ ~ [GeW] (calc)	(iii)
# 3043	$Al(aca)_3$ ~ [SiW] (calc)	(iii)
# 3045	$Al(aca)_3$ ~ [PW] (calc)	(iii)
# 3017	$Al(aca)_3$ ~ [GeW]	(ii)
# 3038	$Al(aca)_3$ ~ [SiW]	(ii)
# 3039	$Al(aca)_3$ ~ [PW]	(i)
# 2667	[GeW] (fa)	(i)
# 2665	[SiW] (fa)	(i)
# 2805	[PW] (fa)	(i)
# 2985	$Al(aca)_3$	(i)

Catalyst Testing in Target Reaction



Al-compounds act as type-B-salts;

Ag-coumpounds are partly dissolved during reaction: Inverted selectivity;

Conclusion

Intimate interaction of Al-complex with HPA in solution;

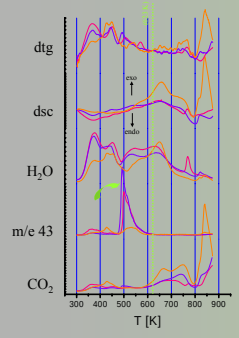
Thermal decomposition generates non-soluble Al-HPA compounds of medium surface area;

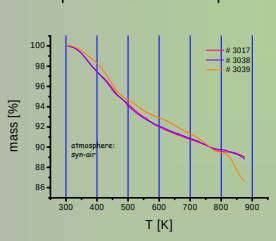
These compounds behave as other solid (acid) catalysts and give access to the preferred product in high yield;

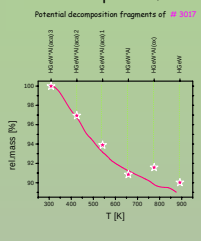
Thermal treatment: TG/MS samples level (ii)

Decomposition of Al-complex, indicated by m/e 43, starts below calcination temperature and is lower than for the pure complex (ca. 588 K);

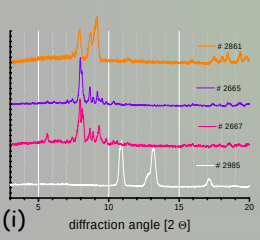
Decomposition of adducts depends on KEGGIN composition;

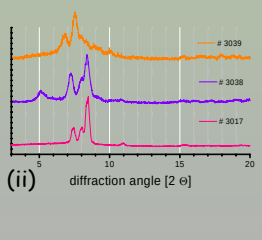


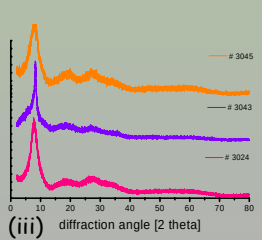




(i) HPA (fa) + $[Al(aca)_3]$ (combined solution (EtOH / benzene 1:1)) → evaporation of solvent → (ii) xero gel (yellow to orange) → Calc. (air) 623 K → (iii) insoluble black solid (target catalyst)





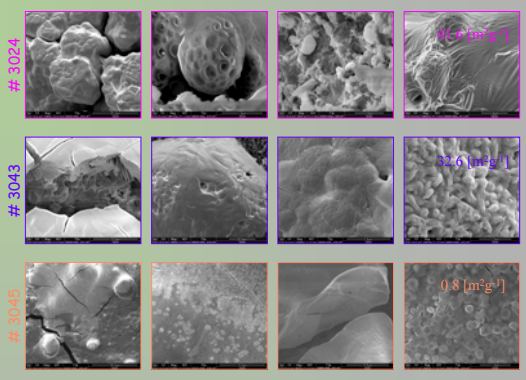


Bulk structure: XRD

Xero-gel (ii) shows features of parent HPA (i) with additional large distances;

Pattern of parent Al-complex (i) disappeared upon interaction with HPA (ii);

Calcination destroys almost long-range order in the material (iii);



Morphology: SEM

In accordance to XRD the material shows no crystalline arrangement;

Morphology is mostly characterized by the coexistence of smooth planes with domaines of highly unordered small particles and especially the absence of larger Al-agglomerations;

EDX revealed the presence of carbon and uniform distribution of elements;