Effect of surfactant on morphology, chemical properties and catalyst activity of hydroxyapatite

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Abstract

Hydroxyapatite (HAp) with chemical formula $Ca_5(PO_4)_3(OH)$ is a naturally occurring mineral form of calcium and phosphate with interesting properties. It can be used in many catalytic reactions both, as a support or active catalyst. In this research we investigate the effect of using surfactants as template to optimise or tailor the chemical properties of this material to be suitable for specific reaction. We found a correlation between type of surfactant, chemical properties of HAp and thus activity of this material as catalyst for CO oxidation.

Keywords: Hydroxyapatite, surfactant, CO oxidation

1. Introduction

Hydroxyapatite (HAp), with chemical formula $Ca_5(PO_4)_3(OH)$, has interesting properties such as flexible structure, and superior ion-exchange capacity and acid-base properties. Recently, it has been used as a biomaterial (1) , adsorbent (2) and catalyst (3). HAp has been used in many catalytic reactions both as a support or active catalyst. When used as a support for precious metals, the resulting heterogeneous catalyst is found to be active in a number of reactions. HAp can be synthesised by different methods such as hydrothermal, precipitation, sol-gel or microemulsion; however synthesis of nano-particles with high surface area always has been a challenging process. The main problem with HAp synthesis is the agglomeration of particles, which leads to HAp having irregular shapes and specific surface areas typically less than 100 $m^2 g^{-1}$. It has been shown that optimising the wet process parameters can improve the particles size to synthesise HAp with surface area up to 150 $m^2 g^{-1}$ (4). Alternatively, it is possible to increase the surface area of HAp by using either a single surfactant or a mixture of surfactants(5). However, the effect of surfactant on chemical properties of HAp has not been studied. Here, we investigate the effect of surfactant type on both morphology and chemical properties of synthesised HAp. The activity of HAp samples are tested and compared in CO oxidation.

2. Experimental method

HAp (with no template) was synthesised by a conventional precipitation method through reaction between its precursors, $Ca(NO_3)_2.4H_2O$ and $(NH_4)_2.HPO_4$ in an aqueous solution. The Ca/P molar ratio was kept at 1.67 in all samples, which corresponds to the stoichiometry of HAp. Under stirring condition, $Ca(NO_3)_2.4H_2O$ was added dropwise to t $(NH_4)_2.HPO_4$ solution, while the pH was monitored and maintained at 10 by adding NH_4OH (30 wt.%). A white precipitate was formed, which was then stirred for 24h at room temperature. Subsequently, the solution was filtered, washed and dried at room temperature for 24h, followed by calcination at 550 ºC for 4 h at 5 ºC/min ramping rate. Table 1 lists the template reagents that used for HAp synthesis.

Table 1. Templates used for HAp synthesis

Sample #	Template	Chemical name	Type
1	no template	---	---
2	PEG	Polyethylene glycol	Non-ionic
3	P123	Poly(ethyleneglycol)-poly(propyleneglycol)-poly(ethylene glycol)	Non-ionic
4	PVA	Polyvinyl alcohol	Non-ionic
5	TWEEN 80	Polyoxyethylene Sorbitan Monolaurate	Non-ionic
6	CTAB	Hexadecyl-trimethyl-ammonium bromide	Cationic
7	HDA	hexadecylamine	Cationic
8	PAM	polyacrylamide	Cationic

To synthesis HAp using templates, a 2 wt.% solution of template was prepared by dissolving the appropriate amount of template reagent in water. Once a clear and uniform template solution was obtained, $(NH_4)_2.HPO_4$ was added dropwise to the template solution under stirring. Subsequently, under stirring, $Ca(NO_3)_2.4H_2O$ was added dropwise while pH was maintained around 10. The remainder of the synthesis method was conducted in an identical manner to that used for HAp synthesis with no template. Samples were characterised by XRD, SEM, EDX, nitrogen adsorption/desorption at 77K, FTIR and NH_3-TPD.

3. Results and discussion

The activity of the HAp catalysts were evaluated in the oxidation of CO (Figure 1). Results shows that the template has a significant influence on the catalyst activity of Hap, which have been synthesised with same material but different templates. For instance, the catalyst activity was higher in the case of PVA, TWEEN and PEG as surfactant than that for HAp with no template (as reference). Other templates had a negative effect on catalyst performance. For instance, P123 and CTAB reduced the catalyst activity to less than half of that recorded for the reference. It is well understood that surfactants are the best shape directing agents in the synthesis of crystallite materials, which is mainly related to the adsorption of surface active molecules on different crystal planes of nucleating centres, thus controlling their overall shape and morphology (6). Therefore, it can be assumed that such differences in activity of HAp for CO oxidation is due to the differences in morphology and/or surface area of the HAp sample. However, our results suggest that the difference in catalyst activity is due to change in acid site strength and distribution of HAp rather than change in morphology. Figure 2 shows NH_3-TPD profiles of different HAp samples. It is clear that the template alters the acid sites by either increasing the total acid sites (e.g. CTAB or HDA) or differing the acid sites distribution (e.g. TWEEN).

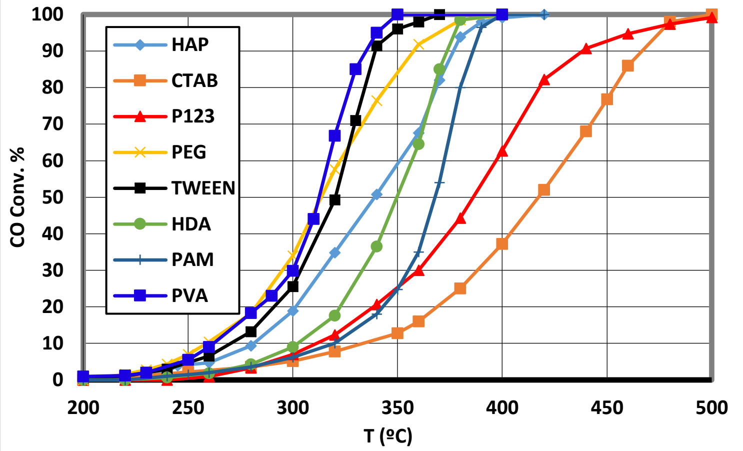

Figure 1. CO oxidation of HAp samples

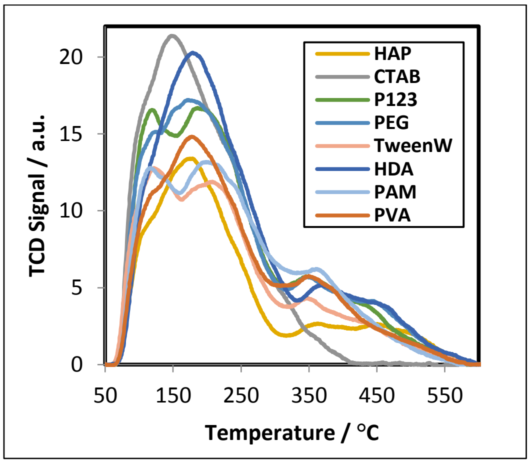

Figure 2. NH_3-TPD of different HAp samples

4. Conclusion

Hydroxyapatite (HAp) was synthesised with various surfactants as template. Results confirmed that the surfactant not only changes the morphology of crystalline material and surface area, but also it can significantly influence the chemical properties of material in terms of acid sites strength and distribution. These findings are relevant to the application of HAp as a heterogeneous catalyst.

References

1. Zhou H, Lee J. Nanoscale hydroxyapatite particles for bone tissue engineering. Acta Biomaterialia. 2011;7(7):2769-81. doi: 10.1016/j.actbio.2011.03.019. PubMed PMID: WOS:000292226000001.
2. Lin KL, Pan JY, Chen YW, Cheng RM, Xu XC. Study the adsorption of phenol from aqueous solution on hydroxyapatite nanopowders. Journal of Hazardous Materials. 2009;161(1):231-40. doi: 10.1016/j.jhazmat.2008.03.076. PubMed PMID: WOS:000262328000031.
3. Dinglin Z, Huawen Z, Xianying Z, Yimin L, Hua C, Xianjun L. Application of hydroxyapatite as catalyst and catalyst carrier. Prog Chem. 2011;23:687-94.
4. Verwilghen C, Rio S, Nzihou A, Gauthier D, Flamant G, Sharrock PJ. Preparation of high specific surface area hydroxyapatite for environmental applications. Journal of Materials Science. 2007;42(15):6062-6. doi: 10.1007/s10853-006-1160-y.
5. Uota M, Arakawa H, Kitamura N, Yoshimura T, Tanaka J, Kijima T. HIGH SURFACE AREA HYDROXYAPATITE NANOPARTICLES SYNTHESIZED VIA CALCIUM STEARATE ENCAPSULATION BY MIXED SURFACTANT-MEDIATED APPROACH. Phosphorus Research Bulletin. 2005;19:288-93. doi: 10.3363/prb1992.19.0_288.
6. Bakshi MS. How Surfactants Control Crystal Growth of Nanomaterials. Crystal Growth & Design. 2016;16(2):1104-33. doi: 10.1021/acs.cgd.5b01465.