A Concise Review on Hypercrosslinked Polymers with Catalytic Applications

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ABSTRACT

In this review article, the main methods of synthesizing and applications of hypercrosslinked materials are studied. Porous structure, high specific surface area, and pore volume make these materials an excellent choice for different applications including gas storage, carbon capture, and molecular separation, removal of pollutants, catalysis, and drug delivery and sensing. In this review article, catalytic applications are particularly considered.

INTRODUCTION

Porous organic polymers have drawn considerable attention. They are alternatives for the conventional porous materials and providing a new opportunity for synthesizing porous materials with particular specifications. Different synthetic methods are proposed for synthesizing porous organic polymer networks with different structures including covalent organic frameworks (COFs) [1,2], Hypercrosslinked Polymers (HCPs) [3], Conjugated Microporous Polymers (CMPs) [4,5], polymers of Intrinsic Microporosity (PIM) [6,7], Covalent Triazine Frameworks (CTFs) [8-10], and (PAFs) [11,12].

Historically, the porous structures begin from inorganic frameworks and then developed to organic materials. The inorganic porous frameworks began with zeolites, a group of crystalline aluminosilicates with channels and pores. In zeolite structures, aluminate and silicate tetrahedrons are connected by bridging oxygen atoms in a corner-sharing arrangement. The linkage of these tetrahedrons results in rings, cavities, and eventually open frameworks extending three dimensionally. They have attracted much attention over the past few decades, with applications in adsorbent ion and catalysis [13-15]. Although the synthesis of covalent organic frameworks (COFs) in 2005 is considered to be the starting point of porous framework construction from entirely organic units [16] but hyper-cross-linked polymers (HCPs) were first synthesized by Davankov, et al. at early 70s via Friedel–Crafts alkylation [17,18]. The bridges between the phenyl rings (for example styrene) can be made by a halogen containing compounds as crosslinker. For CMP synthesis, monomer

molecules with three or more cross-coupling sites are needed. The monomers are connected by rigid strut molecules such as 1,4-substituted benzene nodes via a Sonogashira–Hagihara cross-coupling reaction. In contrast to the porous polymers with their ineffectively packed polymeric chains, the porosity of CMPs originates from the voids among the rigid monomer molecules that extend two- or three-dimensionally (2D or 3D). In 2009, a material with a record-high BET surface area for porous aromatic frameworks (PAFs), of 5600 m^2 g^{-1}, was synthesized. The term "aromatic" originates from the abundant benzene rings. It was synthesized by the Yamamoto type Ullmann coupling reaction of tetrakis (4-bromophenyl) methane [19].

Although hypercrosslinked polymers (HCPs) are not much novel porous polymers, however, they are still in development and have research interest. The synthesis of HCPs is mainly based on Friedel–Crafts reaction. They are a highly crosslinked network, a fast kinetics resulting with high porosity and up to 2000m^2/g BET surface area [17].

Hypercrosslinked polymers are different from traditional macroporous styrene-divinylbenzene and the essence of porosity is different. Macroporous samples are a result of micro phase separation in the course of free radical copolymerization of the comonomers, in the presence of an inert diluent. The catalytic applications of styrene-divinylbenzene resins back to these macroporous resins as selective catalysts compared to the homogeneous analogue [20]. Hyper crosslinking reaction is done at the swollen state of the polymer. The bridges of crosslinker between the phenyl rings of precursor polymer (or monomer) make the porosity. In comparison to Macroporous resins, hypercrosslinked version shows much higher surface area with much lower pore size [17].

The hypercrosslinked polymers were first developed by Tsyurupa and Davankov in the early 1970s in which polystyrene-based precursors such as linear solvated polystyrene or gel-type swollen polystyrene-co-divinylbenzene (polyst–DVB) were post-crosslinked by external crosslinking agents (external electrophiles) in the presence of a Lewis acid catalyst and an appropriate solvent through a Friedel-Craft reaction [18]. Post-crosslinking of polystyrene or polystyrene-divinylbenzene (low DVB content) with rigid connections through a Friedel-Craft reaction makes the hypercrosslinked network. A nearly uniform porosity is distributed throughout the entire volume of the polymer. In the course of reaction the crosslinker connects phenyl rings of neighboring styrene units.

In this review article, the synthesis methods of HCPs and catalytic applications are presented. Although there is some other porous materials with same or better properties, like those mentioned at the beginning of introduction, however, HCPs can be simply synthesized based on polystyrene precursor as well as other precursors. There are two main strategies for synthesizing Hypercrosslinked polymers and other methods are sub-divisions of these two main methods. (1) post-crosslinking polymer precursors, (2) direct condensation reaction of functional monomers (direct polycondensation). (Another method is also developed known as knitting strategy).

Post Crosslinking or Davankov Method

This method is based on hyper crosslinking of polymer precursor. Macroporous poly (styrene-co-divinylbenzene - PS-DVB) is prepared by suspension polymerisation, together with an appropriate amount of a suitable solvent (porogen). Nodehi, et al. [21] showed that by increasing DVB to 40% and a combination toluene and n-heptane a specific surface area (SSA) of 350 m^2/g can be achieved. However, when very high levels of crosslinker are used then a significant number of vinyl groups remain unreacted. Steric congestion and phase separations are an inhibition to their complete consumption in the course of crosslinking reaction. The products of polymerisation have lower levels of crosslinking than one would anticipate based on the monomer feed. Davankov [22] introduced a distinctly new method for the production of porous polystyrenes, a method which comprised the extensive post-crosslinking of linear PS chains by means of a Friedel-Crafts reaction. This process installed numerous structural bridges between neighbouring aromatic rings whilst the PS dissolved (or PS-DVB is in swollen state), and yields resins with hypercrosslinked (HCL) structure, high micropore content and high SSA (up to ~ 2,000 m^2 /g) [23]. The first polymer precursor used was linear PS [24]. To produce spherical particles the PS precursor can be a lightly crosslinked with DVB (0.3-2%) as crosslinker.

In a different approach, PS-DVB macroporous polymers (containing up to 30 % of DVB) were also hypercrosslinked. Poly(vinylbenzyl chloride-co-DVB) (VBC-DVB) has been shown to be another excellent precursor polymer for the synthesis of HCL materials. The chloromethyl (–CH$_2$Cl) substituent is the source of the internal electrophile used for bridging adjacent aromatic rings [25].

Precursor Polymers

The post crosslinking can be done on the gel type polystyrene-divinylbenzene copolymer or on macroporous sample. Both are synthesized by conventional suspension polymerization. Some works applied just DVB as precursor. By using macroporous sample it is stated that the double bonds in the microgels are crosslinked and makes more surface area [26]. But using macroporous precursor results in bimodal pore size distribution [23]. Except for these polystyrene-based resins, some other heterochain polymers were also hypercrosslinked to form highly porous networks such as polysulfone[27], polyarylates [27], polyaniline[28], and polypyrrole [29]

Catalyst

Usual catalysts that are widely used are $FeCl_3$, aluminium chloride ($AlCl_3$), tin chloride ($SnCl_4$), zinc chloride ($ZnCl_2$). Nevertheless, $FeCl_3$ is still one of the most widely used catalysts. Based on the surface area results, $FeCl_3$ exhibits the best catalytic efficiency compared with $AlCl_3$ and $SnCl_4$ in dichloroethane (DCE), which can be ascribed to a better compromise between solubility and the molecular size [30]. The highest surface area of up to 2090 m^2/g using a gel-type precursor with only 2% DVB was achieved. precursor resins with a higher DVB content (20%) may present an inherent limitation for the solvent and catalyst accessibility, resulting in a significantly lower surface area even when matching the functional degree of chloromethyl groups with gel-type precursors (1055 m^2 g^1 vs. 1706 m^2/g). A hypercrosslinked network from the gel-type 2% DVB precursor with a 3:1 monomer ratio (St: VBC) resulted in extremely low surface area polymers of only 2 m^2/g. Interestingly, a much higher surface area (474 m^2 g^1) was obtained using the 20% DVB precursor with the same monomer ratio. These results imply that precrosslinked DVB plays an important role and can influence the porous structure and surface area, however, more meticulous experiments are required to validate these conclusions [30].

Crosslinkers

There is a wide range of external crosslinkers. Changing the external crosslinker can modify the resulting HCP both structurally (variations in the bridge length and rigidity impact on the porous morphology) and chemically (installation of a moiety from the external crosslinker) [30]. commonly used crosslinkers were halogen containing compounds such as bifunctional monochlorodimethyl ether

(MCDE), tetrachloromethane (CCl4), dichloroxylene (DCX), bis(chloromethyl)biphenyl (BCMBP), p,p0-bischloromethyl-l,4-diphenylbutane (DPB), trifunctional tris-(chloromethyl)-mesitylene (TCMM) can perform better. For instance, compared with bifunctional crosslinkers, TCMM can join three polymer chains simultaneously thus creating enhanced rigidity in the final network and a much higher apparent surface area at a relatively low crosslinking degree [30].

Based on davankov method it is reported that using PS or PS-DVB materials can gain up to 1000 m^2/g SSA using DCX [31], CME [32], BCMBP [33] and up to 700 by using ccl_4 [34]. Using macroporous PS-DVB sample as precursor provide higher surface area. Azanove and Hradil reached a surface area of more than 900m²/g by hypercrosslinking of macroporous sample of about 600 m^2/g SA and CCl_4 as crosslinker [35]. The crosslinker plays an important role in the crosslinking reaction. For instance, CCl_4 reacts more slowly and gives a lower overall conversion than CME [23],

Intramolecular crosslinkers

Ahn, et al. [36] showed that by using VBC-DVB as precursor, the crosslinking process is intramolecular which leads to extremely efficient reactions as reported. They found that a gel-type, VBC-DVB resin prepared by suspension polymerisation could be almost fully hypercrosslinked within 15 minutes only. From gel-type polyVBC precursors crosslinked with 2% DVB under suspension polymerization conditions a SSA of up to 2090 m^2/g were reported [36].

Sherrington and co-workers have prepared a series of vinylbenzyl chloride–divinylbenzene copolymers (polyVBC–DVB) with well-defined functional compositions (with 2% and 20% DVB content respectively) [23]. Using VBC-DVB precursor can provide much more SSA up to 2000 m^2/g as the data shows [36,37].

Tan and co-workers [38] by varying the DVB content from 0 to 10% demonstrated a particular control over the pore structure from macroporosity to microporosity in the resulting hypercrosslinked divinylbenzene–vinylbenzyl chloride polymers (HCP-DVB–VBC). By increasing the DVB content, initially the surface area of HCP-DVB–VBC is increased and then it is decreased by further increasing the DVB content. The highest surface area of 2060 m^2/g was obtained with a 2% DVB content. By using this precursor there is no need to use macroporous precursor to achieve high SSA and a uniform micropores can be obtained.

Instead of using VBC-DVB as precursor, it is possible to use chloromethylated PS–DVB. Veverka [25] used commercial chloromethylated PS–DVB resins and then crosslinking is performed via the internal condensation of chloromethyl groups [25,39]. Bussing and Peppas [40] used cationic polymerization of styrene using dichloroethane and SnCl4 at 25°C (low molecular weight polystyrene) and then postcrosslinking at 50°C through Friedel-Craft reaction.

Direct polycondensation

The hypercrosslinking of polymer precursor not only includes an extra step of polymerization prior to hypercrosslinking but also limited functional monomers can be selected to satisfy the combined conditions from reactions of radical polymerization and Friedel–Crafts alkylation. The self-condensation method was not much explored until further investigation was made by Cooper and co-workers [41]. In this strategy the hypercrosslinked polymer is synthesized directly by polymerization of appropriate monomers and crosslinkers.

Except for the self-condensation reaction, bis(chloromethyl) aromatic monomers can also act as external crosslinkers to link other substances (like DCX). Condensation of crosslinker (DCX) with a monomer like fluorene results in hypercrosslinked polymer. Microporous polytriphenylamine networks were prepared from triphenylamine (TPA) and DCX crosslinkers using a $FeCl_3$ promoted oxidative polymerization and Friedel–Crafts alkylation process. The resulting polymer has amine functionality and SSA can be controlled from 318 to 1530 m^2/g with the pore width maximized around 0.55 to 1.8 nm [42].

Hypercrosslinked hybrid materials can be achieved by selfcondensation of benzyl chloride containing building blocks. Excluding the chloromethyl groups, hydroxymethyl can also act as functional moieties to form networks via self-condensation. For example Luo, et al. [43] chose two kinds of aromatic hydroxymethyl monomers i.e. 1,4-benzenedimethanol (BDM) and benzyl alcohol (BA) as the starting building blocks. A high surface area of up to 847 m^2 g^{-1} was obtained using the bifunctional monomer BDM with a predominant microporous architecture.

Tan and co-workers [44] proposed an approach for the synthesis of microporous polymers from a wide range of low functional aromatic building blocks. This approach directly links adjacent phenyl rings by eliminating two aryl-bound hydrogen atoms and forming a new aryl–aryl bond in the presence of an anhydrous $AlCl_3$ catalyst (sometimes Brønsted acid such as hydrogen chloride is also needed). The method is based on the Scholl coupling reaction. Msayib, et al. used DCE as a solvent that also plays the role of crosslinker in providing methylene bridges. Greatly enhanced microporosity was obtained in the resulting amorphous porous polymers with highest surface area of 2435 m^2/g [45]. This work can be seen as a new approach in synthesizing microporous network polymers with high surface areas even more than commercially activated carbons.

As an example of different external crosslinker, Li, et al [46] proposed a new strategy which consists of the "knitting" of rigid building blocks of an aromatic monomer (including benzene, phenol or chlorobenzene), the crosslinker (FDA) and the catalyst ($FeCl_3$) were dissolved in DCE, with an external crosslinker. Formaldehyde dimethyl acetal (FDA) yields methanol as a byproduct of the reaction rather than the typical chloromethyl functionalities which release HCl. SSA of 1400 m^2/g is reported. Similar approaches using FDA as crosslinker is also applied by other groups [23,42,47]. Schwab et al [48] used Fluorene as precursor, BCMBP as precursor, DCE solvent and $FeCl_4$ as catalyst a surface area of 1800 m^2/g is reported.

Other strategies

Tan and co-workers proposed a method known as the knitting strategy. In this method active formaldehyde dimethyl acetal (FDA) was used as an external crosslinker to combine simple aromatic compounds like benzene or biphenyl with rigid methylene bridges via the anhydrous $FeCl_3$ catalyzed Friedel–Crafts reaction [46]. The benzene knitting networks displayed the highest apparent surface area of up to 1391 m^2/g.

Applications

HCP materials are promising candidates for potential applications in gas storage, carbon capture, molecular separation, removal of pollutants, catalysis, drug delivery and sensing. Perhaps one of the most interesting application is CO_2 capture. HCP with 437 m^2/gr and 11.9% (2.7 mmol/g) CO_2 adsorption [49] to 4334 m^2/g (under carbonization of hypercrosslinked polymer) and 15.4 % (3.5 mmol/g) [50] is observed. As can be seen no considerable change in adsorption capacity in spite of more than nine fold increase in the surface area (273k and 1 bar) is achieved. This can be attributed to its narrower pore size compared to other polymer networks which is helpful for the adsorption of small molecules. However, at a high pressure of 15 bar, surface area plays a more important role [51]. At a high pressure of more

than 1 bar, the adsorption capacity of CO_2 is very dependent on the surface area [30].

Catalytic applications of HCP

HCPs with a high surface area and a large pore volume have already been regarded as superior supports for heterogeneous catalysis. A number of applications are presented mainly based on the knitting method proposed by Tan and coworkers [46]. The enthusiasm of researchers to use HCPs in catalysis may be triggered by immobilization of a homogeneous metal complex catalyst with this easily accessible and designable material. In 2012, Li and Tan, et al. [52] fabricated on the basis of the first knitting model, a rigid HCP with a fragment of PPh3 (triphenylphosphine) by knitting this ligand with benzene in the presence of FDA in one step. With the obtained HCP material, a stable, highly active, and recoverable palladium–phosphine heterogeneous catalyst, HCP–PPh$_3$–Pd, was prepared. SSA was high up to 1025 m^2 g^{-1} with 0.7 wt% loading of Pd.

An HCP–PPh$_3$–Ru developed by Jia et al can be used in the construction of many heterocyclic compounds [53]. The metal loading of the HCP–PPh$_3$–Ru is 0.15 mmol g^{-1}. The HCP–PPh$_3$–Ru catalyst exhibited outstanding catalytic performance, even than that of the homogeneous counterpart, PPh$_3$/RuCl$_3$.

To demonstrate the great ability of this one-step knitting strategy for catalysis uses, various arene-based ligands were then tested. A great success was achieved with commonly used N-heterocyclic carbenes (NHCs). Through incorporation of different NHC units into the HCPs backbone by the first knitting model followed by a post-modification to induce Pd^{2+}, Tan and Li, et al. fabricated an HCP–NHCs–Pd catalyst with high S$_{BET}$ up to 569 m^2 g^{-1} [54].

Wang et al. [55] tried to use the second knitting model to incorporate metal complex onto HCP skeleton, and the proof-of-concept was verified by knitting Pd(PPh$_3$)$_4$ and benzene with FDA to prepare an HCP. The resulting material has nearly single-atom dispersed Pd species in its 3D network.

Hypercrosslinked Polymers for Acid/Base Catalyst

Traditionally, ion exchange materials based on PS-DVB resins is used for water treatment [20]. Gel type resins with no porosity is used for water treatment but for catalytic applications macroporous precursors is used [56]. Sulfonic acid functional PS-DVB resins, so called "strong-acid cation-exchange resins" have also found extensive use as solid acid catalysts in many

chemical processes, such as dehydration of alcohols to olefins or ethers [57], alkylation of phenols [58.], addition of alcohols to olefins [59], manufacturing of bisphenol-A from phenol and acetone [60] and so on.

Because of the unique microporous structure, HCPs obtained with direct knitting method are good supporting materials for heterogenizing acid or base catalysts. By using dichloromethylbenzenes as starting materials and anhydrous FeCl$_3$ as catalyst, Wang, et al. [61] synthesized some porous HCPs which underwent a sulfonation with chlorosulfonic acid to give some heterogeneous solid acid catalysts. Phenol and bisphenol have also been used as precursors to make SO$_3$H funtionalized HCPs in conjunction with employing FDA as cross-linking reagent and chlorosulfonic acid as sulfonation reagent [62].

CO_2 Conversion

CO_2 adsorption and conversion technique has attracted a lot of attention and it is the most catalytic application of HCPs. Zhang and co-workers [63] designed two kinds of hypercrosslinked porous polymers incorporated by phosphonium salt and imidazolium salt within the polymer networks which showed a high surface area of 1168 and 926 m^2/g respectively. With incorporated salts as catalytic sites, these polymers revealed high catalytic activity even after several cycle reactions for the conversion of CO_2 by converting propylene oxide into propylene carbonate.

A series of bifunctional ionic hyper-cross-linked polymers were synthesized by the Friedel-Crafts reaction and ionic post-functionalization. The as-prepared polymers had high Brunauer-Emmett-Teller surface areas (S$_{BET}$, 623–1345 m^2/g), considerable bifunctional ionic groups, namely bromide anions, and carboxyl groups. The polymer namely DHI-CSU-3-Br had a good CO_2 capture capacity (134 mg/g, 273 Ҟ and 1.0 bar), moderate isotopic adsorption heat (28–38 kJ/mol), and excellent CO_2 cycloaddition ability. The catalytic experiments showed that 99% of propylene oxide was successfully converted to cyclic carbonate (70 °C, 0.1 MPa CO_2, and 4 h) [64].

Wang, et al. [65] reported a well-defined porous hypercrosslinked polymer-TiO$_2$-graphene composite structure with relatively high surface area i.e., 988 m^2/g and CO_2 uptake capacity i.e., 12.87 wt%. This composite shows high photocatalytic performance especially for CH$_4$ production, i.e., 27.62 μmol /g. h, under mild reaction conditions without the

use of sacrificial reagents or precious metal co-catalysts.

Hydrazine (HZ) was successfully introduced into metalloporphyrin-based hypercrosslinked polymers (HCPs) by post-modification to create abundant CO_2 chemisorption sites in structures for efficient adsorption (Qst value up to 34.7 kJ/mol) and chemical conversion of CO_2 under ambient conditions. The HZ-modified material (HCP-TPP-Co-HZ) exhibits high catalytic performance for different molecular sizes of epoxide substrates with excellent yields (reaching 98 % of propylene oxide), much superior than that of HCP-TPP-Co-SO_3H (64 %), which can be ascribed to the abundant chemisorption sites for CO_2 reactants [66]

A kind of pyridine-based ionic hyper-cross-linked polymers (Py-HCP-X, X = Cl, Br) with high surface area, plentiful hierarchical pores and abundant catalytic active units were prepared via a one-pot method. Adsorption measurements showed that the as-prepared Py-HCP-X exhibited high CO_2 capture capacity (up to 1.72 mmol g^{-1}, 273 K and 1 bar). Importantly, Py-HCP-Br displayed excellent catalytic activity for the cycloaddition of CO_2 to epoxides under metal/cocatalyst/solvent-free conditions [67]

A series of hyper-crosslinked polymers with the high specific surface area and tunable ion-pair active sites are fabricated by using a one-pot method with simultaneous quaternization and Friedel-Crafts reactions. These IHCPs can also be used as recyclable catalysts for cycloaddition of CO_2 and epoxides under metal- and cocatalyst-free conditions, affording corresponding cyclic carbonates in excellent yields [68].

CONCLUSION

Since the first attempts by davankov at 1970s considerable improvements have been experienced in this field particularly by works of Sherrington and his team and the direct polycondensation method which gives much wider selection of materials to have hypercrosslinked polymers.

Different application has been proposed for these materials. Incorporating functional groups can enhance hydrophilicity and adsorption of polar compounds. It seems that more applications and synthesis methods can be expected in future. For example implementation of HCP materials as electrode materials in sensing devices is expected having huge potential. Because of the designability and a great structural diversity of HCPs, there still is a big room for developing new HCP based catalysts with emphasis of different functions and task-specific uses.

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