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Hole-growth phenomenon during pyrolysis of a cation-exchange resin particle

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Key words:

Non-catalytic gas-solid reaction; Cation exchange resin; Pyrolysis; Central hole expansion; Temperature difference; Transformation

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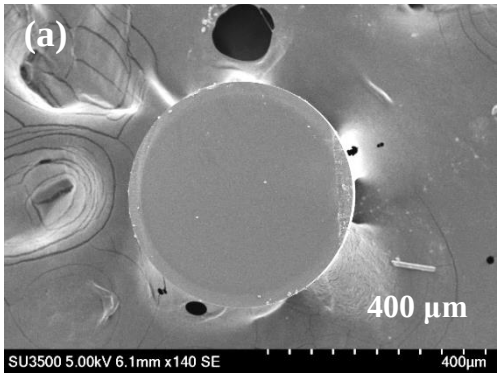
Background introduction

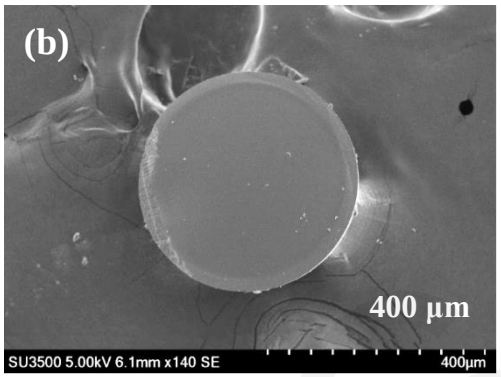
Non-catalytic gas-solid reaction models

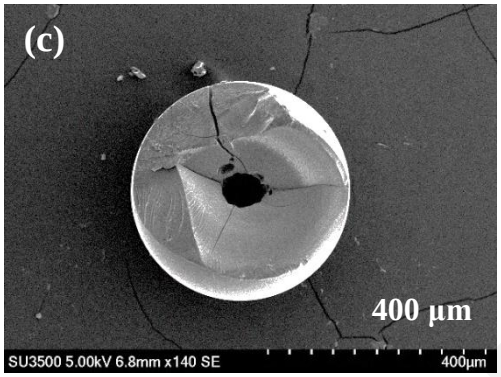
- The shrinking core model
  - The reaction proceeds from the outside to the inside of the solid reactant
- The pore model, zone reaction model…
  - The gas enters the interior of the solid reactant through pore channel and makes internal and external reactions occur simultaneously

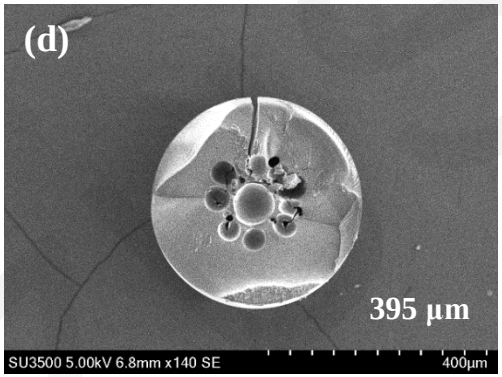
New model proposal → The central hole expansion mode

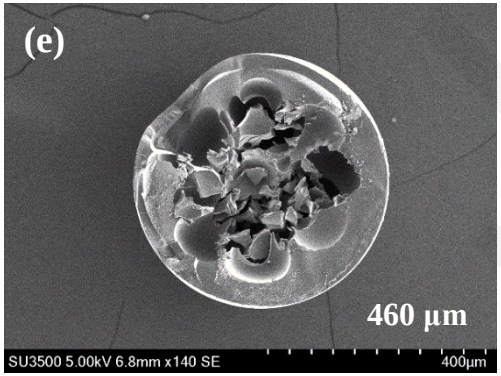
Discovery of central hole expansion mode

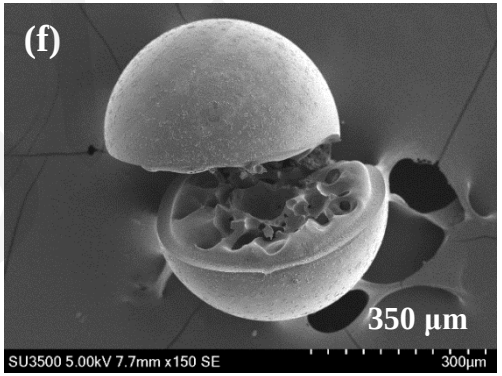








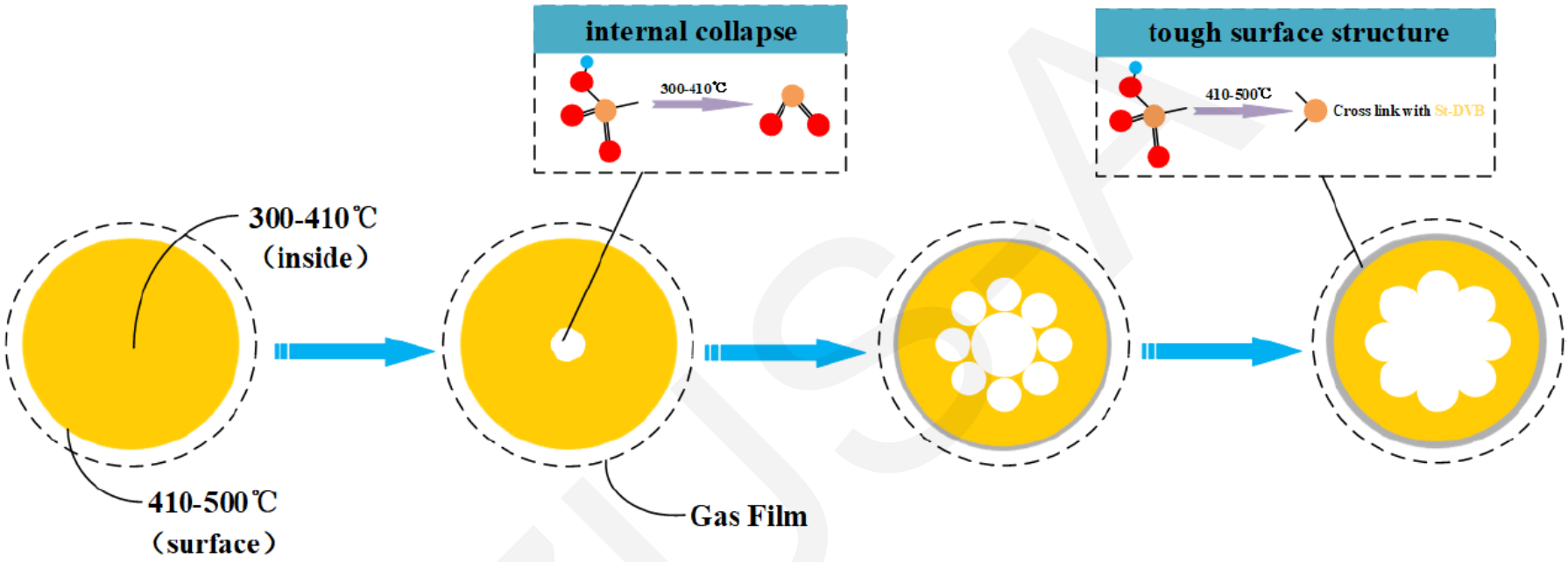




(a) IRN-97H cation exchange resins and products pyrolyzed at 450℃ in 3%O_2 for (b) 5 min, (c) 10 min, (d) 20 min, and (e, f) 30 min.

In this study, the reaction always starts from the exact center of the spherical particles and then spreads uniformly around.

The schematic diagram of the central hole expansion mode



The gas coats the solid surface to form a gas film and enters the interior of the solid during the reaction.

The reaction starts from the center, and a hole is formed there at first.

The volume of hole increases, and the surrounding sites continue to form a distributed hole group.

The hollow particle with many holes inside is formed but the surface remains intact.

Formation mechanism of the central hole expansion mode

$$(\text{St-DVB-SO}_3\text{H})_n \rightarrow (\text{St-DVB-SO}_2\text{-})_n + (\text{St-DVB-S-})_n + (\text{St-DVB})_n + \text{SO}_2$$

$$(\text{St-DVB-SO}_2\text{-})_n + (\text{St-DVB-S-})_n + (\text{St-DVB})_n \rightarrow \text{C}_x\text{H}_y + \text{SO}_2 + \text{H}_2\text{O} + \text{Residue}$$

The first stage is the decomposition and transformation of the sulfonic acid groups, which are bonded to the copolymer matrix polystyrene-divinylbenzene (St-DVB), and releases part of SO_2, as shown in the following formula (up).

The second stage is the pyrolysis of the organic skeleton to form hydrocarbons and residue, which is shown in formula (down).

Conclusion

The cation exchange resins always follow the same pyrolysis law (the central hole expansion mode) at 400-500℃ under different oxygen content atmospheres, different crosslinking degrees and particle sizes, different doped metal ions, different surface roughness and pore structure, which has certain universality.

The central hole expansion mode proposed in this study may provide guidance for the verification and development of non-catalytic gas-solid reaction models due to its regular reaction process and predictable reaction sites.