

自由基辅助粉煤灰合成沸石分子筛的研究进展

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摘 要: 沸石分子筛(简称沸石)在吸附、分离和催化等领域具有广阔应用前景, 但沸石合成速率慢、工业化生产效率低; 同时高品质沸石主要由化学原料合成, 制备成本高, 因此, 利用自由基提高合成速率, 以粉煤灰为硅铝源降低合成成本, 对沸石的工业化生产和大宗固废的消纳具有重要的现实意义。本文对自由基促进沸石合成的作用机理进行调研, 同时探究自由基促进粉煤灰硅铝活化的可能机制, 挖掘自由基在沸石合成体系中的产生及存在, 并针对粉煤灰来源广、成分杂问题, 系统梳理了各类预处理方法, 在此基础上, 提出了利用自由基有望解决粉煤灰中硅铝活化难的问题, 这将为粉煤灰大规模、高值化利用提供可能途径。

关键词: 沸石分子筛; 自由基; 粉煤灰; 催化机理; 硅铝活化

中图分类号: TQ536.4 文献标志码: A 文章编号: 0454-5648(2024)01-0347-12

网络出版时间: 2023-12-01



沸石分子筛(简称沸石)是由硅氧、铝氧四面体(TO₄)通过共顶点连接形成的具有规则孔道结构的无机晶体材料, 具有良好的孔隙结构、高的比表面积和优异的化学稳定性, 在吸附、分离以及催化剂等领域有大量应用^[1-4]。沸石合成的方法多样, 如水热合成法、二次生长法、离子热合成法, 其本质是硅铝源先解聚再聚合形成硅铝酸盐凝胶后, 在结构导向剂的作用下通过一定时间的室温老化及高温晶化, 形成具有不同孔道结构的沸石晶体。其中, 结晶过程主要包括晶体成核和生长 2 个阶段, 但长时间的晶体成核和生长导致沸石的合成速率慢、工业化生产效率低^[5]。其次, 沸石合成的原料多种多样, 组成结构性质迥异的硅铝源不仅影响着沸石前驱体的形成, 还会影响沸石的表面形貌、孔道结构和化学性质等^[6]。目前, 高品质沸石主要利用化学原料合成, 制备成本较高。因此, 提高沸石的合成效率, 寻找价格低廉的硅铝源极具现实意义。

随着沸石合成方法的不断发展, 除微波法外^[7], 在合成过程中引入自由基可以大幅提高沸石的合成速率^[8]。与此同时, 粉煤灰^[9]、气化渣、煤矸石^[10-13]、尾矿^[14-15]中均含有丰富的硅铝元素, 以其为原料不仅能够降低沸石的制备成本, 还能为此类煤基固废

的高值化利用提供可行途径^[16]。由于这些与煤相关的固废成因、结构和性能方面相差较大, 考虑到粉煤灰产量大且硅铝含量高, 适合用于沸石合成^[17], 因此, 本文以其为例进行详细探讨, 这也为后续其他类似固废的资源化利用提供借鉴。

研究发现, 粉煤灰经历了高温燃烧, 硅铝等元素存在于莫来石、石英等惰性物质中, 导致其活性差、直接利用难^[11]。自由基能否对这些活性差的硅铝源起作用及如何作用需要深入探究。同时, 沸石合成常在高温高压及强碱性条件下进行, 采用紫外、 γ 射线、超声等物理辐射法, 或添加引发剂如芬顿试剂、过硫酸根等化学方法, 虽然可以向沸石合成体系中引入自由基, 但是物理法受限于沸石合成需要耐温耐压设备; 常用的引发剂受 pH 值影响大, 在碱性环境中易失效。此外, 粉煤灰中不可避免的存在一些金属氧化物和未燃尽的碳等, 这些均影响着合成沸石的纯度和结晶度。

针对上述问题, 本文系统梳理了自由基提高沸石合成速率、促进硅铝源发生反应的作用机理, 详细探究了自由基促进粉煤灰硅铝活化的可能, 深入挖掘了在沸石合成条件下产生自由基的有效手段, 并针对粉煤灰来源广、成分杂的问题, 评价了对其

收稿日期: 2023-05-05。 修订日期: 2023-08-14。

基金项目: 国家自然科学基金(22008255); 国家重点研发项目(2022YFC3701901, 2022YFD2200904); 中央高校基本科研业务费(2022XJHH06)。

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Received date: 2023-05-05. Revised date: 2023-08-14.

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开展的预处理方法,在此基础上,发现并构建了适合粉煤灰这类低品位硅铝源制备沸石的可行路径。

1 自由基辅助合成沸石分子筛机理及其对结构性能影响

2016 年,于吉红院士课题组^[18]首先在沸石合成体系发现了自由基,并将羟基自由基($\bullet\text{OH}$)引入沸石合成,提高了沸石的合成速率,创建出除微波法外另一种实现沸石高效合成的方法^[19–20]。此后,围绕自由基加速沸石合成开展了大量研究。Feng 等^[18]将 NaA 沸石的合成时间从 55 h 降低到 40 h,形成的沸石晶体具有高结晶度。Cheng 等^[21]将 Silicalite-1 的合成时间从 24 h 缩短到 16 h。Guo 等^[22]在不同温度下合成 Y 型沸石,将诱导期缩短了 1~8 h 不等。Tiffany 等^[23]将 RHO 沸石的合成时间从常规水热需要的 8 d 缩短至 2 d。这些研究证实,通过 $\bullet\text{OH}$ 作用,大大加快了 NaA、NaY、Silicalite-1 和 ZSM-5 等沸石的结晶过程,尤其加速了晶体的成核阶段^[24]。

鉴于 $\bullet\text{OH}$ 高效合成沸石已被证实, $\bullet\text{OH}$ 加速沸石合成速率的作用机理同样被深入研究。研究表明,相较于 OH^- ,对于成核阶段 Si—O—Si 键、 Si—O—Al 键的解聚和聚合,尤其在解聚方面 $\bullet\text{OH}$ 表现

出更高的催化活性^[18]。通过采用电子顺磁共振(EPR)技术对 $\bullet\text{OH}$ 进行捕捉,并利用密度泛函理论(DFT)进行理论计算, $\bullet\text{OH}$ 催化沸石合成的机理被挖掘^[25]。研究者构建了不同模型体系,如 $\text{Si}(\text{OH})_3\text{ONa}$ 和 $\text{Al}(\text{OH})_4\text{Na}$ 单体^[26]或 $[\text{SiO}_2(\text{OH})\text{—O—SiO}_3]\text{Na}_5$ 计算模型^[18],来模拟引入 $\bullet\text{OH}$ 后体系中 SiO_4 单元与 SiO_4 或 AlO_4 单元分别缩合成 Si—O—Si 、 Si—O—Al 的机理。这里以 $\text{Si}(\text{OH})_3\text{ONa}$ 或 $\text{Al}(\text{OH})_4\text{Na}$ 单体与 $\text{Si}(\text{OH})_3\text{O}\bullet$ 和 $\text{Si}(\text{OH})_2\text{ONaO}\bullet$ 自由基之间的缩合反应为例进行分析,如图 1 所示。对比这些过程所需的吉布斯自由能, $\text{Si}(\text{OH})_3\text{O}\bullet$ 和 $\text{Si}(\text{OH})_2\text{ONaO}\bullet$ 自由基的存在均加速了 Si—O—Si 键和 Si—O—Al 键的形成,其中 $\text{Si}(\text{OH})_2\text{ONaO}\bullet$ 自由基与 $\text{Si}(\text{OH})_3\text{ONa}$ 和 $\text{Al}(\text{OH})_4\text{Na}$ 的缩合需要更高的活化能,且 Si—O—Al 键的形成比 Si—O—Si 键的吸热性高 15.4 kcal/mol,说明 $\bullet\text{OH}$ 优先加速 Si—O—Si 键的形成。除硅铝沸石外,研究发现,在 $\bullet\text{OH}$ 存在下 SAPO-34 沸石的结晶机制可能不同,而这正是由于 $\bullet\text{OH}$ 可以加速硅氧键的解聚和新硅氧键的形成,有利于硅(0Al)岛的形成,从而改变了晶化过程中硅原子的化学环境^[27],同样证实了 $\bullet\text{OH}$ 在沸石合成过程中对硅铝溶解和聚合的作用。

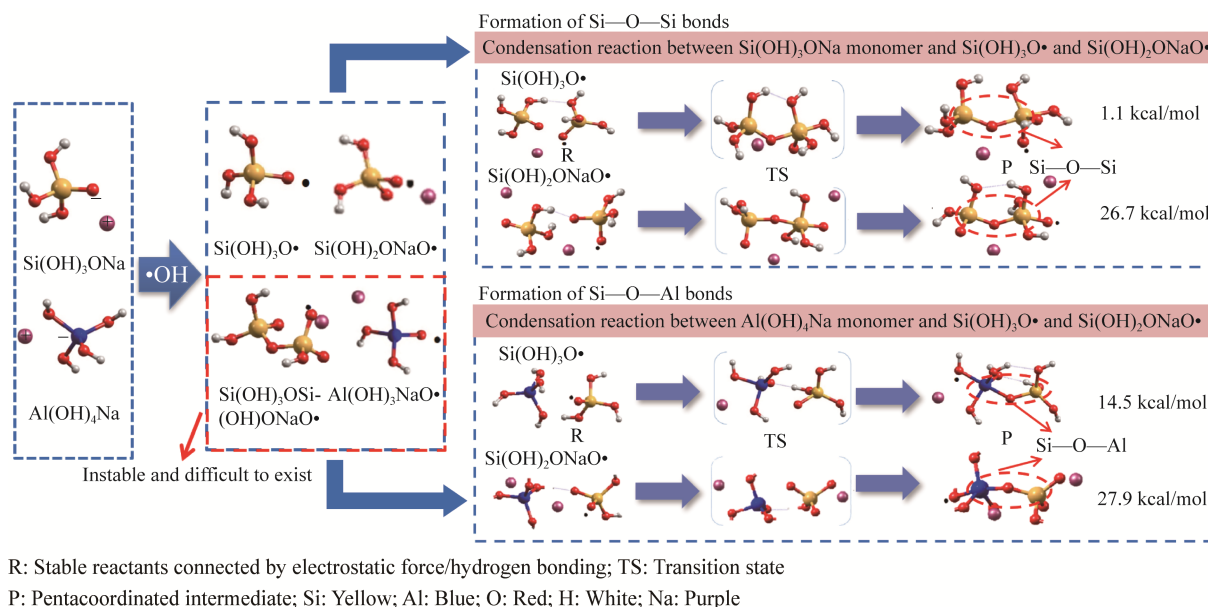


图 1 $\text{Si}(\text{OH})_3\text{ONa}$ 和 $\text{Al}(\text{OH})_4\text{Na}$ 单体模拟
Fig. 1 $\text{Si}(\text{OH})_3\text{ONa}$ and $\text{Al}(\text{OH})_4\text{Na}$ monomer simulation

根据自由基加速沸石合成机理,自由基促进 Si—O—Si 、 Si—O—Al 键的解离和聚合,尤其是优先加速 Si—O—Si 键的断裂和形成,这导致合成过程中硅铝比增加的可能性,促进了高硅沸石的形成。

除此之外,于吉红院士课题组在研究 Silicalite-1、SBA-15 及 NaA 沸石的合成中分别表明, $\bullet\text{OH}$ 的引入可以有效减少合成体系中模板剂或酸碱用量^[21, 24],符合绿色合成。并且由于自由基的存在沸石性能得

到显著提高,所制备的 NaA 沸石具有更大的孔体积和更高的比表面积,对纯 CO_2 的吸附能力增加了 6 倍(质量分数从 1.98% 提高到 12.83%)^[28]; ZSM-5 获得了更多的 B 酸中心,显著增强了甲醇制汽油反应(MTG)的传质和催化性能^[29]。

随着研究不断深入,除 $\bullet\text{OH}$ 外,其他氧化活性物质,如活性氧(ROS),超氧自由基($\bullet\text{O}_2^-$)、和硫酸根自由基($\text{SO}_4^{\bullet-}$)、单线态氧($^1\text{O}_2$),在沸石合成领域也被应用。有研究者在利用超声辐射引入自由基时发现,超声波形成的气泡崩塌为结晶提供了巨大的

能量密度^[30],可以同时激发和解离水分子和氧分子产生氢原子、 $\bullet\text{OH}$ 和 $\bullet\text{O}_2^-$ 这类反应性物种。利用这些强氧化剂和还原剂,可以在反应介质中完成 $\text{Si}-\text{O}-\text{Si}$ 和 $\text{Si}-\text{O}-\text{Al}$ 键的形成(图 2)^[31-32]。其他研究者也相继发现如 ROS ^[33]、 $^1\text{O}_2$ ^[34] 和 $\bullet\text{O}_2^-$ ^[35] 可以通过催化 $\text{Si}-\text{O}(\text{Al}-\text{O})$ 键的断裂和重整来促进沸石的晶化,且研究表明它们的协同作用比单独的 $\bullet\text{OH}$ 具有更高的催化活性。这种自由基反应机理为促进沸石结晶开辟了新的途径,并暗示着通过在合成系统中提供氧化活性物质来生产沸石的巨大潜力^[36]。

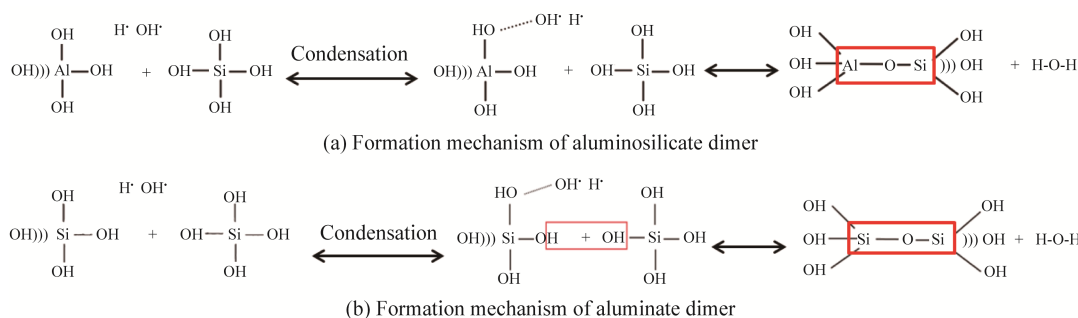


图 2 铝硅酸盐二聚体(a)和铝酸盐二聚体(b)的形成机理

Fig. 2 The proposed mechanism for the formation of aluminosilicate dimer (a) and aluminate dimer (b)

综上所述,自由基在高效合成沸石中的作用已经被发现,同时自由基的潜力被不断发掘,针对目前高品质沸石制备成本较高的问题,自由基方法的引入,可能为一些活性较低的廉价硅铝源实现高品质沸石的合成开辟一种新途径。

2 自由基辅助粉煤灰合成沸石分子筛机制、结构和性能

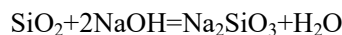
粉煤灰作为一种典型煤基固废,产出量巨大,且集中在西部地区,建材需求量小,大量研究着眼于利用粉煤灰制备沸石,但大多局限于实验室规模,因此,该技术的高效高值规模化利用亟待实现^[37]。表 1 分别总结了我国粉煤灰的化学成分及矿物组成^[38],可以看出与普通硅铝源不同^[39-40],粉煤灰成分复杂、硅铝存在状态多样,主要以晶质矿物石英、莫来石和非晶矿物玻璃体形式存在,结构稳定,需活化处理,并且粉煤灰表面的致密的玻璃质外壳,阻碍了 Si、Al 元素的溶出^[41],其组成和结构如图 3 所示。因此,粉煤灰合成沸石的关键问题是如何使硅和铝被充分活化,并得到有效利用。

研究指出,晶相结构的不同决定了粉煤灰活化步骤的复杂程度,利用机械研磨法,可以使其内部

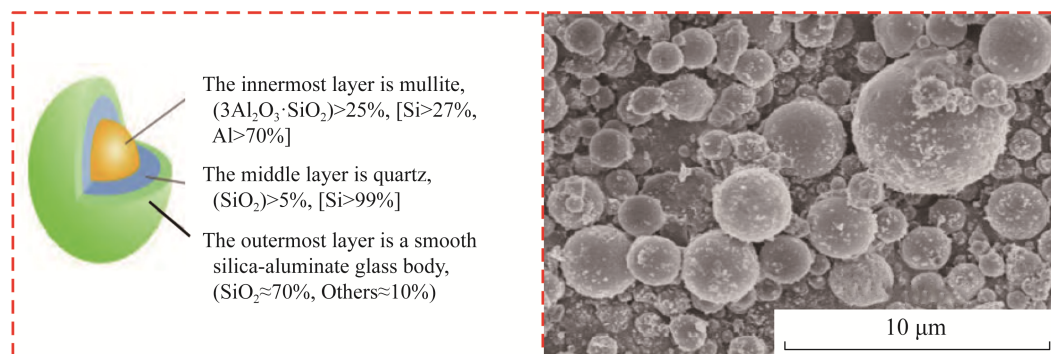
表 1 我国粉煤灰化学成分和主要矿物组成及范围
Table 1 Chemical composition, mineralogical composition and range of Fly Ash in China

Coal-based solid wastes	Chemical components	Mineralogical composition
Fly Ash	24.0%–65.0% SiO_2	11%–35% Mullite
	16.0%–50.0% Al_2O_3	1%–16% Quartz
	1.5%–16.2% Fe_2O_3	42%–70% Amorphous phase
	0.4%–16.8% CaO	
	0.2%–3.7% MgO	
	5.0%–20.0% C	

的 SiO_2 和 Al_2O_3 外露,增加硅铝的溶解率^[16]。并且研磨作用通过产生缺陷位点和促进粉煤灰的溶解,提高粉煤灰的化学反应性。但研磨不能破坏粉煤灰中如莫来石的一级结构,活化效果较差,通常需要与其他活化方法结合使用。水热合成法、碱融-水热合成法是粉煤灰合成沸石的常用方法。水热合成法是将粉煤灰与碱液混合,达到硅铝活化的作用,并经过晶化形成沸石。碱液活化反应式如下:



研究表明,碱度是决定粉煤灰合成沸石总反应速率的主要因素,较高的碱度可以促进硅铝相的溶

图3 粉煤灰组成和结构示意图及形貌(SEM)照片^[41]Fig. 3 Schematic composition and structure of pulverized coal furnace fly ash and morphology (SEM) diagram^[41]

解^[42]。但由于石英、莫来石等都是惰性物质,难以参与水热反应,导致硅铝的溶出率低,沸石产率偏低。为改善水热法不能充分活化的问题,将粉煤灰与碱或碱与盐的混合物混合均匀后在高温下进行焙烧活化,即碱熔融活化法,可以将粉煤灰中含硅铝的矿物组分活化,再经水热合成结晶形成沸石,提高原料利用率,进而提高沸石产率和纯度。Chang^[43-44]、Gollakota^[45]、Verrechia^[46]、He^[47]等以粉煤灰为原料,采用碱融-水热法分别合成了X型、ZSM-22、X型、A型沸石。证明碱作为助溶剂与粉煤灰中的莫来石和石英反应,破坏了石英和莫来石的晶体结构,生成可溶性硅酸盐和铝酸盐。并且,在随后的水热反应中与硅和铝反应,促进沸石的结晶。碱融-水热法是传统方法中较为成熟的方法,但该方法的耗碱量很大,并且需要很高的煅烧温度,增大了粉煤灰制备沸石的成本。随着技术的发展,超临界水合成法、转晶法、微波和超声辅助等方法被应用于粉煤灰沸石化上,其中,微波和超声的引入,可以加速Si和Al的溶解,缩短活化和结晶时间^[9, 48-52]。但仅用微波活化法或超声活化法从粉煤灰中提取Si和Al的效率仍然不够高,Chen等发现微波和超声协同法(MUCA)具有明显优越性,具有更高效的溶解粉煤灰中硅铝物种的能力,合成了高度结晶的K-MER分子筛^[53]和LTA分子筛^[54]。但微波和超声辅助法所需较严格的试验条件及特殊装置设备,目前仅在实验室进行,很难进行工业化生产。由此可见,现有活化方法仍面临众多问题,利用自由基对粉煤灰中硅铝物质的活化过程进行强化,或可解决上述难题。

为明晰自由基能否对惰性硅铝物质的活化起到积极的促进作用,学者们开展了大量研究。Kubicki等^[55]用量子力学方法研究了水分子与石英断裂表

面团簇模型的相互作用。根据计算, $\bullet\text{OH}$ 参与到 $\text{Si}-\text{O}-\text{Si}$ 键的断开,得到的产物硅氧自由基($\text{Si}-\text{O}\bullet$)比 OH^- 催化 $\text{Si}-\text{O}-\text{Si}$ 键断开生成的硅氧负离子($\text{Si}-\text{O}^-$)反应活性更高,其中 $\text{Si}-\text{O}\bullet$ 自由基与水反应需要跨越的能垒是27.6 kJ/mol,而 $\text{Si}-\text{O}^-$ 负离子为61.2 kJ/mol。Yuichi等^[56]计算了石英和无定形硅粉等硅物种在碱性条件下的解聚能垒为18.30~20.95 kcal/mol。随后,Konecny等^[57]模拟真实石英表面 $\text{Si}-\text{O}$ 亚表面键合的 $\text{Si}-\text{OSiH}_3$ 键的解离,表明 $\bullet\text{OH}$ 活化石英表面层的可能性。如图4, $\bullet\text{OH}$ 活化过程的计算能垒(4 kcal/mol)显著低于 OH^- 催化石英表面溶解速率控制步骤的预测能垒(19 kcal/mol)。并且 $\text{Si}-\text{O}-\text{Si}$ 键断裂后在表面形成 $\text{Si}-\text{O}\bullet$ 自由基为化学惰性、硅醇封端的老化石英表面的再活化提供了一种可能的机理。除此之外,也有研究者发现自由基在其他废弃物合成沸石中的应用,以工业废硅(LSF)为原料,采用钠盐辅助碱脱硅和真空紫外(VUV)引发ROS的方法在4 h内制备了结晶良好的介孔方钠石(SOD)^[58],对Cu(II)有较好的吸附和选择性。由此,证实了自由基在以固体废弃物为原料制备沸石的研究具有重要的科学价值。

综上所述,现有活化方法,如机械法、水热法、碱熔融、微波和超声等辅助水热合成沸石,粉煤灰中的硅铝被一定程度的活化,但这些方法仍面临如活化不充分,用碱量大、能耗高、实验装置及实验条件要求苛刻等问题。而自由基在粉煤灰中促进惰性物种硅铝活化的作用已通过模拟计算被证明,推测自由基可以为粉煤灰合成沸石中硅铝活化及重排起到一定作用,改善以粉煤灰为代表的煤基固废合成沸石面临的问题。但相关实验性研究缺乏,需进一步验证,特别是寻找适合粉煤灰合成沸石体系的自由基引入方法。

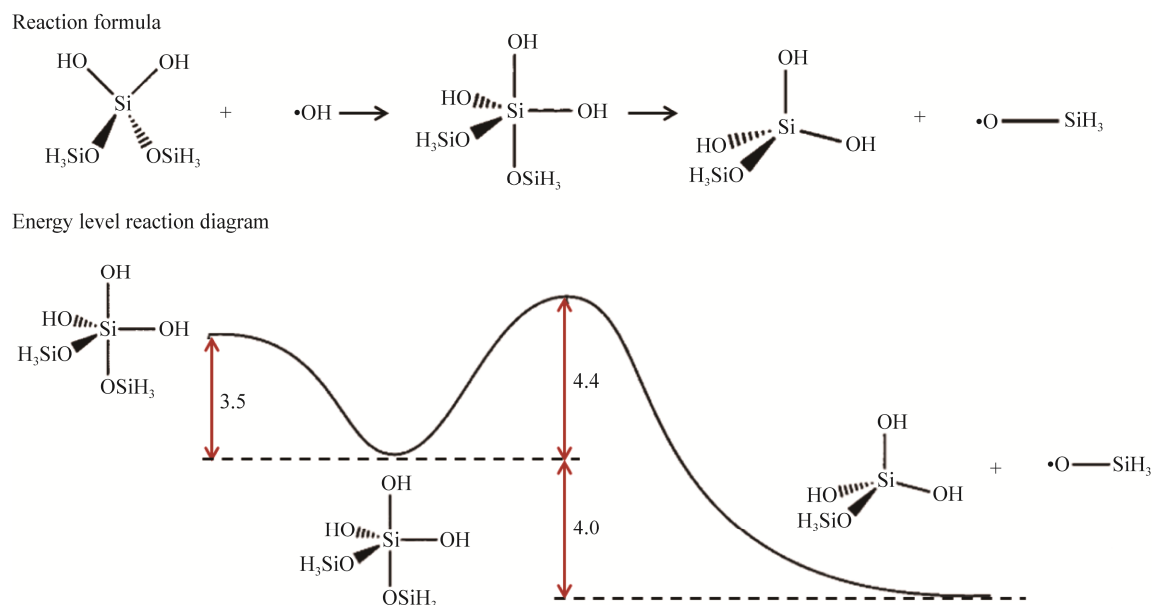


图 4 Si—O—Si 键与 $\cdot\text{OH}$ 自由基反应方程式及能级图(B3LYP/6-31G**方法计算)

Fig. 4 Equation and energy level diagram for the reaction of Si—O—Si bond with $\cdot\text{OH}$ radical (calculated by B3LYP/6-31G** method)

3 粉煤灰合成沸石分子筛用自由基的发生机制、种类和性质

$\cdot\text{OH}$ 是目前在沸石合成中应用最广泛的自由基。引入 $\cdot\text{OH}$ 的方法多样, 包括物理法和化学法。常用的物理方法, 如紫外辐射^[59-60]、 γ 射线辐射^[28, 61] 及超声处理^[23, 62-64] 等, 是通过对合成前驱体溶液或对放有合成液的反应釜等进行物理辐射, 从而在合成体系产生 $\cdot\text{OH}$ 的过程。但物理法要配备额外的辐射设备持续辐照合成液^[18], 而沸石合成的反应器需要耐温、耐压、耐腐蚀, 金属外壳导致这些反应器很难被辐射穿透, 因此使用物理法需要对反应器进行重新设计, 实现起来难度大、成本高。

相较于物理法而言, 化学法对于反应器要求较低, 不需要使用其他额外设备, 仅是通过在合成液中加入 $\cdot\text{OH}$ 引发剂来产生 $\cdot\text{OH}$ 。如芬顿(Fenton)试剂, 利用芬顿反应产生 $\cdot\text{OH}$, 即在酸性介质($\text{pH}=3.0\sim 3.5$) 中利用二价铁离子和三价铁离子作为催化剂分解过氧化氢从而产生 $\cdot\text{OH}$, 并引发更多其他活性氧^[65]。且 H_2O_2 在不高于 $80\text{ }^\circ\text{C}$ 的温度下会发生自分解产生 $\cdot\text{OH}$, 所以芬顿试剂在较低温度下的促进作用比在较高温度下的促进作用强的多^[66]。虽然芬顿反应条件温和、操作方便, 但由于在中性和碱性的环境中 Fe^{2+} 会产生氧化铁沉淀而失去催化能力, 不能催化氧化 H_2O_2 产生 $\cdot\text{OH}$, pH 值适用范围窄的问题限制

了芬顿试剂在沸石合成强碱环境中的应用^[67], 针对这一问题, 可以借鉴在污水处理, 染料降解等领域中的研究, 利用类芬顿高级氧化技术尝试解决^[68]。大量研究证实, 有机螯合剂与铁离子形成的铁螯合物可以拓宽芬顿体系的 pH 值范围。这些有机螯合剂的结构通常含有氧和/或氮原子, 如草酸盐(O_x)、草酸(OA)、酒石酸(TA)、乙二胺四乙酸(EDTA)和乙二胺-N, N'-二琥珀酸(EDDS)等, 作为铁螯合剂, 是用于在中性条件下应用光芬顿工艺的策略之一^[69-71]。例如, 一些研究报告称, EDTA 可用作防止 Fe 沉淀和调节 Fe 浓度的配体, 通过螯合作用控制了体系中游离 Fe^{2+} 的浓度, 减少了 Fe^{2+} 对自由基的消耗, 拓宽了 pH 值范围, 避免了 Fe^{2+} 的大量浪费^[72]。因此, 利用螯合物螯合 Fe^{2+} 可能是利用芬顿反应催化沸石碱性条件下合成的可能方法。

此外, 有研究指出 $\text{S}_2\text{O}_8^{2-}$ 容易生成 pH 值范围广泛的自由基($\text{SO}_4\cdot^-$), 产生的 $\text{SO}_4\cdot^-$ 自由基可以进一步生成 $\cdot\text{OH}$ 加速沸石的合成^[21, 73]。溶液中的 $\text{SO}_4\cdot^-$ 自由基会发生一系列自由基链式反应, 最终达到与 $\cdot\text{OH}$ 共存的状态, 而两者的相对含量由溶液 pH 值决定。在酸性及中性溶液中($\text{pH}\leq 7$), 以 $\text{SO}_4\cdot^-$ 自由基为主, 在弱碱溶液中($\text{pH}=8\sim 9$), 二者共存, 而在强碱溶液中($\text{pH}>10$), $\cdot\text{OH}$ 则开始成为主导^[74]。因此用过硫酸根作为 $\cdot\text{OH}$ 引发剂能够较好的适应沸石合成的碱性环境。图 5 即为自由基引入的不同方法及特点。

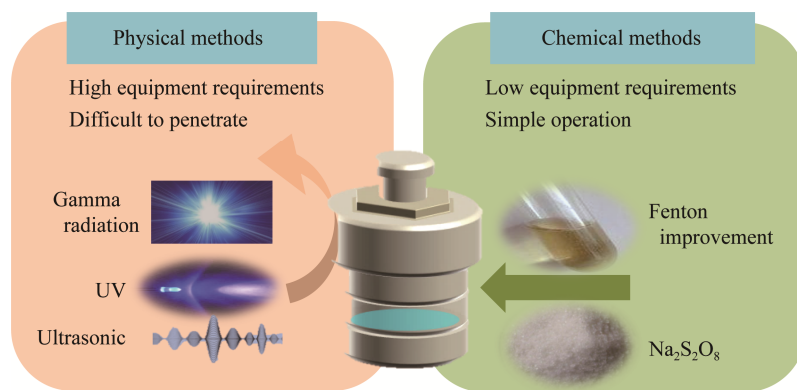


图5 自由基引入方法及特点

Fig. 5 Methods and characteristics of introducing free radicals

如前所述,除了 $\bullet\text{OH}$ 在沸石合成中的引入,其他氧化活性物质,如 $\bullet\text{O}_2^-$ 、 $^1\text{O}_2$ 在沸石合成中的引入方法被调研。Chen 等^[33]将氧化石墨烯(GO)引入合成体系通过紫外辐射产生 $\bullet\text{OH}$ 、 $\bullet\text{O}_2^-$,直接从硅灰锂(LSF)废料中快速合成了介孔方钠石(SOD)沸石和杂化 SOD 沸石。Lu 等^[34]表明可以用特定引发剂 $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$,同时向体系中引入 $\bullet\text{OH}$ 和 $^1\text{O}_2$,促进一锅法合成高度有序的介孔结构。利用紫外辐射

氧化石墨烯的方法能够在碱性条件下产生自由基,但面临着上述提到的设备要求高等问题;特定引发剂 $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ 也并不能很好的适用于大多沸石合成的碱性环境。而 Liu 等^[35]通过将石墨氮化碳($\text{g-C}_3\text{N}_4$)作为可见光催化剂,对 ROS 的产生表现出高活性,尤其是在碱性溶液中,能够较好适用于大多数沸石的合成。表 2 对不同自由基在合成沸石时的引入方法及作用进行了总结。

表 2 不同自由基在合成沸石时的引入方法及作用

Table 2 Introduction methods and effects of different free radicals in zeolite synthesis

Free radical types	Introduction method	Free radical generation	Free radical generating environment	Synthetic zeolites	Free radical action
$\bullet\text{OH}$	UV radiation	$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$ $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2(\text{hot})$ $\text{H}_2\text{O}_2(\text{hot}) \rightarrow 2\bullet\text{OH}$ $\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O}$	Alkalinity	ZSM-5, Silicalite-1, NaA, SAPO-34, Beta, MCM-14, SBA-13	$\bullet\text{OH}$ radical has higher activity than OH^- ion. Theoretical calculations show that $\bullet\text{OH}$ is more favorable to the breaking and formation of Si—O—Al and Si—O—Si bonds in the system; Especially the formation of Si—O—Si bonds. It can improve the zeolite Si—Al ratio and reduce the amount of template agent and alkali.
	Ultrasonic radiation	$\text{H}_2\text{O} \xrightarrow{\text{Ultrasonic wave}} \text{H}\bullet + \bullet\text{OH}$ $\text{O}_2 \xrightarrow{\text{Ultrasonic wave}} 2\text{O}\bullet$ $\text{O}\bullet + \text{H}_2\text{O} \rightarrow 2\bullet\text{OH}$ $\text{H}\bullet + \text{O}_2 \rightarrow \text{HO}_2\bullet$	Alkalinity	4A, RHO, DDR	
	Gamma radiation	$\text{H}_2\text{O} \xrightarrow{\gamma\text{-ray}} \bullet\text{OH}$	Alkalinity	NaA, NaY, Silicalite-1 and ZSM-5	
	Fenton	$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}\bullet + \text{OH}^-$ $\text{H}_2\text{O}_2 + \text{HO}\bullet \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$	Acidity	Y, ZSM-5	
	Sodium persulfate	$\text{S}_2\text{O}_8^{2-} + \text{Heat/UV} \rightarrow 2\text{SO}_4^{\bullet -}$ All pH: $\text{SO}_4^{\bullet -} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \bullet\text{OH} + \text{H}^+$ Alkaline pH: $\text{SO}_4^{\bullet -} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \bullet\text{OH}$	Acidity, Alkalinity	NaA, silicalite-1, ZSM-5, ZSM-48	
$^1\text{O}_2$	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Reduction of Ce^{4+} to Ce^{3+} by water on the active surface of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ crystals induces the formation of $^1\text{O}_2$ and $\bullet\text{OH}$ molecular species of reactive oxygen species	Acidity	SBA-15	Synergistic interaction of singlet oxygen with $\bullet\text{OH}$ radical has higher catalytic activity for ethyl orthosilicate hydrolysis than that of $\bullet\text{OH}$ radical alone.
$\bullet\text{O}_2^-$ and $\bullet\text{OH}$	Vacuum UV radiation +GO	$\text{OH}^- + \text{O}_2 \rightleftharpoons \bullet\text{O}_2^- + \bullet\text{OH}$ $\text{O}_2 + \text{eaq} \rightleftharpoons \bullet\text{O}_2^-$ $(\text{r})\text{GO} \rightarrow (\text{r})\text{GO}^*$ $(\text{r})\text{GO}^* + \text{O}_2 \xrightarrow{\text{Energy transfer}} (\text{r})\text{GO} + ^1\text{O}_2$ $(\text{r})\text{GO} + \text{eaq} \rightarrow (\text{r})\text{GO}^{\bullet}$ $(\text{r})\text{GO}^{\bullet} + \text{O}_2 \rightarrow (\text{r})\text{GO} + \bullet\text{O}_2^-$	Alkalinity	SOD	Promote zeolite crystallization by catalyzing the cleavage and recombination of Si—O (Al—O) bonds.
	$\text{g-C}_3\text{N}_4$ photocatalysis	$\text{C}_3\text{N}_4 + h\nu \rightarrow \text{e}^- + \text{h}^+$ $\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+$ $\text{h}^+ + \text{OH}^- \rightarrow \text{OH}$ $\text{e}^- + \text{O}_2 \rightarrow \bullet\text{O}_2^-$	Alkalinity	Na-A and NaZ-21	

综上所述, 自由基的引入方法在不断涌现, 其中利用化学法在沸石合成中加入引发剂产生自由基是较为可行的方法, 但同样也仍面临着部分引发剂不能较好适应沸石合成的碱性环境等问题。因此, 适用于沸石合成环境的自由基产生方法亟待探究, 这将为构建适合低品位硅铝源制备沸石可行方法, 降低合成成本, 实现绿色发展提供可能。

4 存在问题

迄今, 有关粉煤灰合成沸石已经开展了大量研究^[75-77], 除了上述硅铝活化难的问题有待解决外, 来源广、成分杂是其资源化利用要解决的另一难题。由于原煤种类、燃烧工况等生产条件的不同, 影响着粉煤灰的理化性质, 造成其化学组成复杂, 如循环流化床锅炉燃煤因采用炉内脱硫方式, 在燃烧过程中添加生石灰等脱硫剂, 其燃烧后所形成的粉煤灰中氧化钙含量更高, 呈暗黄色或黄褐色; 而粉煤灰炉粉煤灰则呈灰白色或灰黑色^[78-80]。由表 1 可知, 粉煤灰中不可避免含有不同含量的有机质及各种无机组分, 如未燃尽的碳、金属氧化物等成为合成沸石的杂质, 危害结晶过程, 影响产物纯度和结晶度^[81-83]。因此, 在粉煤灰合成沸石时首先要解决的就是除杂问题。表 3 对不同国家及不同杂质含量的粉煤灰合

成沸石情况进行了总结。粉煤灰中的杂质可以利用高温煅烧、酸洗等过程被去除。通过高温煅烧去除了粉煤灰中的有机质, 而酸洗则去除了金属氧化物。除此之外, 经高温煅烧和酸洗除杂后, 硅铝含量被提高, 矿物中的晶相结构也可能被改变, 使其中的硅铝化合物等有价元素易于溶出, 有利于沸石的合成^[84]。陈彦广等^[85]通过煅烧、活化、酸洗等分级处理从粉煤灰中提取铝元素, 得到高纯度的氢氧化铝, 其中铝元素提取率为 80.89%。并以此为原料, 在动态水热晶化下合成了 ZSM-5 沸石。利用煅烧、酸洗等方法虽提高了其硅铝含量, 但受限于粉煤灰原料所含硅铝元素的比值, 所得沸石种类较少、硅铝比范围较窄, 且多为 P 型沸石或低硅铝比的 A 型沸石, 因此, 添加额外硅铝源、利用转晶法或寻找其他手段拓宽粉煤灰合成沸石种类及产物硅铝比范围是未来研究粉煤灰沸石化的另一方向。

综上所述, 在利用高温煅烧、酸洗等方法去除粉煤灰中的杂质后, 利用络合物改进芬顿或过硫酸根在水热合成过程引入自由基, 可以改善并强化粉煤灰中硅铝物质的活化过程, 弥补相关实验性研究的匮乏, 以此实现自由基辅助下粉煤灰制备沸石的高效、低成本合成, 并为其他类似固废提供借鉴, 如图 6 所示。

表 3 粉煤灰合成沸石分子筛
Table 3 Synthesis of zeolite from Fly Ashs

Sources of Fly Ash	Impurities	Removal methods	Silicon to aluminum ratio	Activation methods	Zeolite types	References
China, Morocco	C	High temperature calcination	Si/Al=0.71~2.64	Lye activation	FAU	[42, 86–87]
India	2.54%–12.82% Fe ₂ O ₃	Magnetic separation, acid washing		Alkali melting activation	ZSM-22, FAU	[45–46]
Japan, China	1.60%–11.00% CaO			Hydrothermal-microwave activation	P, LTA	[50, 54]
China	0.06%–2.90% MgO	Acid washing		Supercritical water activation	ZSM-5	[88]
Poland, China	1.860%–4.419% TiO ₂			Ultrasonic activation	P, SOD	[89–91]

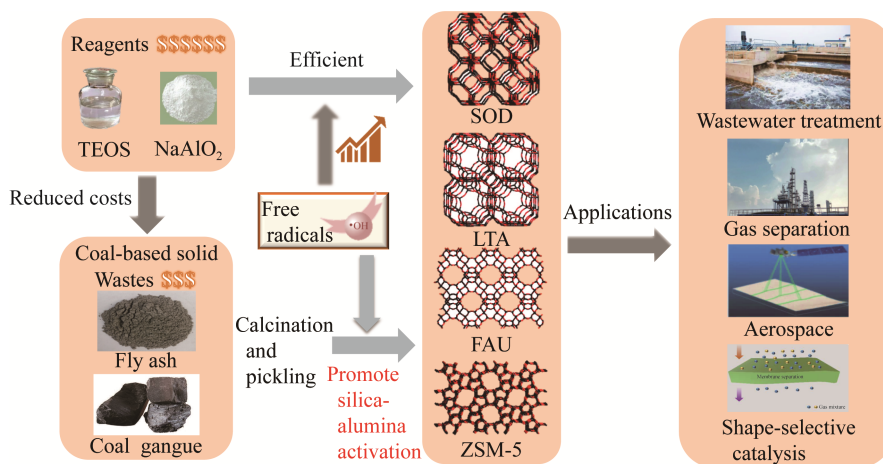


图 6 自由基在实现沸石高效合成及降低沸石合成成本中的作用

Fig. 6 Role of free radicals in achieving efficient zeolite synthesis and reducing the cost of zeolite synthesis

5 结论与展望

沸石分子筛在吸附、分离等领域具有广泛应用前景, 针对其合成速率慢、合成成本高的问题, 论文调研了自由基在实现沸石分子筛高效合成中的作用, 评估了自由基在粉煤灰合成沸石中应用的可能, 挖掘了自由基在粉煤灰合成沸石中的产生及存在, 综述了粉煤灰沸石化过程中面临的问题, 在此基础上构建自由基辅助粉煤灰合成沸石的可行方法, 得到以下主要结论, 并对未来的研究方向提出展望。

1) 自由基相比于 OH 对 Si—O—Al、Si—O—Si 键的断裂和形成具有更低的能量, 能够以较低能垒打破并形成 Si—O—Al、Si—O—Si 键, 实现了沸石分子筛的高效合成。以量大富含硅铝的粉煤灰为原料合成沸石, 能够有效降低沸石合成成本, 但硅铝难活化是其合成沸石关键难题。自由基能够促进惰性硅物种 Si—O—Si 键的断裂和形成, 为自由基在粉煤灰沸石化中的作用提供了依据, 从而为改善传统活化方法面临如活化不充分, 用碱量大、能耗高等问题提供可能。

2) 通过挖掘自由基在粉煤灰合成沸石中的引入方法, 可弥补自由基辅助粉煤灰合成沸石的实验性研究匮乏的问题。其中, 物理法受限于沸石合成需要耐温耐压设备, 难以大规模使用。化学法是引入自由基较为可行的方法, 利用螯合物螯合 Fe^{2+} 可拓宽芬顿试剂应用的 pH 值范围, 或采用过硫酸根离子, 这些均能够较好的适应沸石合成液的碱性环境。此外, 粉煤灰成分复杂, 利用煅烧酸洗等方法能够去除粉煤灰中的杂质, 提高沸石产品品质。

3) 除了本文提到的除杂以及硅铝活化问题, 通过添加额外硅铝源、利用转晶法或其他手段拓宽粉煤灰的硅铝比扩大合成沸石范围也是未来粉煤灰沸石化急需解决的问题。同时, 本文自由基辅助粉煤灰合成沸石路线的研究也将为其他类似煤固废资源化利用提供借鉴作用。

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Research Progress on Free Radical Assisted Synthesis of Zeolite from Fly Ash

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Extended Abstract

Zeolites have broad application prospects in adsorption, separation, catalysis, etc.. Improving their synthesis efficiency and reducing their production cost become a challenge. The synthesis rate of zeolite is low and the production period is long due to the prolonged nucleation and growth of crystals during the crystallization process. Furthermore, commercial high-quality zeolites are mainly synthesized with chemicals as raw materials, resulting in high costs. Therefore, it is significant to develop efficient and low-cost zeolite synthesis technologies. Some previous studies indicate that the use of free radicals could achieve a rapid synthesis of zeolites. Fly ash contains a large amount of silicon and aluminum elements. As a result, the synthesis of zeolite from fly ash reduces costs, and provides a feasible way for its high-value utilization. However, there is little work on the synthesis of zeolite from fly ash assisted by free radicals. It is thus necessary to explore the mechanism of free radical assisted synthesis of zeolite from fly ash, as well as the generation, types and properties of free radicals. Meanwhile, it is revealed that free radicals solve the problem of difficult activation of inert silicon and aluminum in fly ash. The theoretical basis is provided for the development of efficient and low-cost synthesis technology for the preparation of zeolite from fly ash assisted by free radicals, and a reference is provided for other coal based solid waste.

The existence of $\bullet\text{OH}$ in zeolite synthesis systems was firstly discovered in 2016. $\bullet\text{OH}$ was introduced into the synthesis system of NaA, Y, and ZSM-5 zeolites, thus greatly accelerating their crystallization process. This is a high-efficient method for zeolite synthesis besides a microwave method. Meanwhile, electron paramagnetic resonance (EPR) was used to determine hydroxyl radicals, and density functional theory (DFT) was used for the theoretical calculations to investigate the mechanism of hydroxyl radicals accelerating the synthesis rate of zeolite. The catalytic activity by $\bullet\text{OH}$ is greater than that by OH^- for the depolymerization and polymerization of $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$ bonds during the nucleation stage, especially in terms of depolymerization. With the continuous deepening of research, the promoting effects of other oxidizing active substances (*i.e.*, reactive oxygen species, superoxide radicals, singlet oxygen, *etc.*) in zeolite synthesis were also discovered. Moreover, the introduction of free radical methods also opened up a new path for the synthesis of high-quality zeolites from some low-cost silicon aluminum sources with a lower activity. The problem of difficult activation of silicon and aluminum during the synthesis of zeolites from fly ash was discovered, and the positive effect of free radicals on the activation of inert silicon species was demonstrated through the simulation calculations. It is thus speculated that free radicals can improve the problems faced by coal-based solid waste synthesis of zeolite, represented by fly ash. However, little work on the relevant experimental research are made yet, and the further verification is needed. Therefore, free radical introduction methods suitable for fly ash synthesis of zeolite system were discovered, *i.e.*, physical and chemical methods. Among

them, adding initiators to produce free radicals in zeolite synthesis using chemical methods is a more feasible method. However, there exist still problems, *i.e.*, some initiators unavailable for the alkaline environment of zeolite synthesis. The research on free radical generation methods suitable for zeolite synthesis environment will provide possibilities for constructing feasible methods for preparing zeolite from low-grade silicon aluminum sources, reducing the synthesis costs, and achieving the green development. Furthermore, some impurities existing in zeolization of fly ash are effectively removed by calcination and acid washing, thereby increasing its silicon and aluminum content, which is conducive to the synthesis of zeolites.

Summary and prospects Compared to OH^- , the breaking and formation of Si—O—Al and Si—O—Si bonds were achieved with lower energy barriers in the presence of free radicals, thus achieving the efficient synthesis of zeolites. Fly ash as a raw material could effectively reduce the cost of synthesizing zeolite. However, activating these inert silicon and aluminum was a challenge for synthesizing zeolite from fly ash. Free radicals played a catalytic role in the cleavage and formation of Si—O—Si bonds in inert silicon species. It could be inferred that free radicals could play a similar catalytic role in the synthesis of zeolite from fly ash. The excavation of free radical introduction methods (*i.e.*, using chelates to chelate Fe^{2+} to broaden the pH range of the Fenton reagent applications or using persulfate ions) could make up for the lack of experimental research on free radical assisted fly ash synthesis of zeolite. Besides, for fly ash with wide source and complex composition, using calcination and acid washing could effectively remove some impurities in the fly ash to improve the product quality.

A reference for the resource utilization of other similar coal based solid waste could be provided *via* studying the free radical assisted synthesis route of zeolite from fly ash. In addition, widening the silicon aluminum ratio of fly ash and expanding the range of synthetic zeolite are also a challenge in the future.

Keywords zeolite; free radical; fly ash; catalytic mechanism; silica-alumina activation