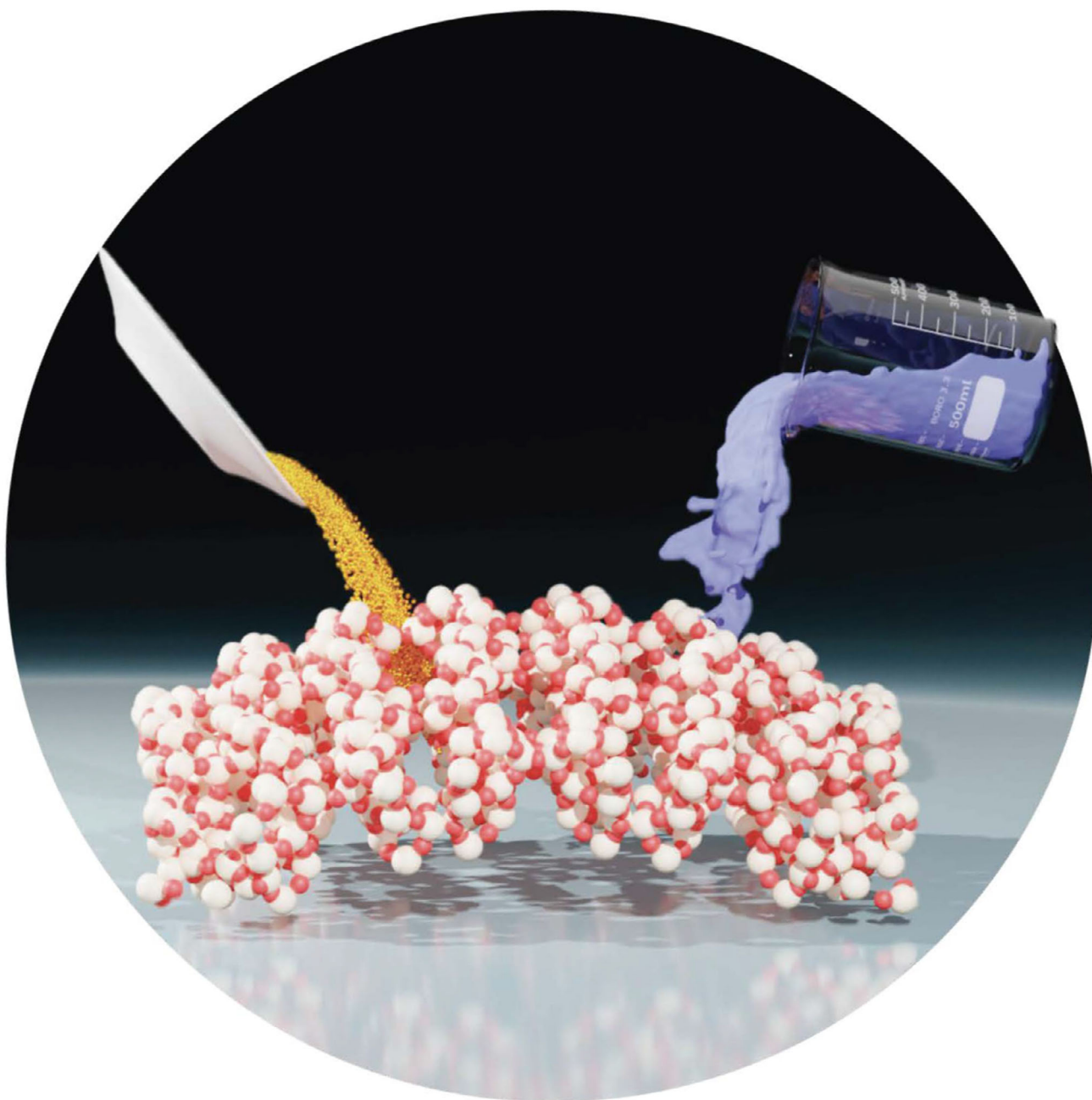


Heterogeneous Catalysis

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Isolated and Paired Metal Sites in Zeolites Using Solid-State Ion Exchange

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Abstract: Isolated and paired extraframework transition metal cations in zeolites are emerging as top candidates for numerous applications, including, but not limited to, selective methane oxidation to methanol, selective catalytic reduction of nitrogen oxides, propane dehydrogenation, propylene epoxidation, and direct air capture of carbon dioxide. Importantly, these well-defined heterogeneous catalysts offer parallels with molecular and metalloenzyme catalytic active sites. Aqueous-phase ion exchange (APIE) is the most common synthesis technique to obtain these catalysts. Solid-state ion exchange (SSIE) is an often overlooked technique that offers synthetic advantages compared to APIE. Thus, recent advances in solid-state synthesis strategies merit contemporary contextualization. In this minireview, we describe the basic principles, methods, mechanisms, challenges, and advances in solid-state ion exchange in the context of well-defined transition metal cation active sites located in extraframework positions of the zeolite.

1. Introduction

Zeolite catalysts are vital in both the petrochemical industry and the energy transition. Metal-exchanged zeolites are under development for a wealth of impactful purposes. Some recent examples include:

1. Copper cations in chabazite (CHA) for selective catalytic reduction of NO_x .^[1]
2. Iron cations in beta zeolite (BEA) for selective oxidation of methane to methanol.^[2]
3. Sodium cations in mordenite (MOR) for direct air capture of carbon dioxide.^[3]
4. Zinc cations in Mobil-5 zeolite (MFI) for propane dehydrogenation.^[4]
5. Cobalt cations in faujasite (FAU) for propylene epoxidation.^[5]

Extraframework metal sites add functionality to the zeolite in the form of Lewis acidity and catalytic redox pairs^[6] Through lines with metalloenzymes^[7–10] and molecular catalysts^[11–14] also fuel interest in these cationic active sites. Myriad applications and potential for societal impact culminates in broad interest in their preparation.^[15] Some excellent reviews cover general synthesis strategies for metal active sites in zeolites,^[6,16] where ion exchange is noted as a

powerful tool to obtain isolated, well-defined active sites on zeolites.^[6]

Ion exchange can take place between the zeolite and the metal precursor in the solid, liquid, and vapor phase. In the current minireview, our objective is to describe recent innovations in the process termed solid-state ion exchange (SSIE)—which, phenomenologically, involves solid, liquid, and vapor phase processes. SSIE represents only a small share of the relevant literature (Figure 1) but could offer predictable, reproducible, well-defined extraframework active sites with significant environmental benefits compared to the conventional approach. We aim to fill a gap in recent literature where an updated account of SSIE in zeolites has not appeared since a 2008 contribution^[17] from the late Hellmut G. Karge.^[18] The contents of the present minireview include a background on cation exchange in zeolites, a comparison with conventional exchange methods, mechanisms, challenges, advances, and a general outlook for SSIE in zeolites.

2. Background and Motivation

The corner-sharing tetrahedra that compose the zeolite framework (TO_4 where $T = \text{Al, Si}$) possess a negative charge imparted by the isomorphous substitution of Al^{3+} in place of Si^{4+} . Extraframework cations compensate the negative charge, anchoring to the channels, pores, and pockets near framework aluminum (Al_F).^[19] Counter-balancing cations typically include H^+ (Brønsted acid sites), NH_4^+ , alkali metals, alkaline earth metals, and transition metals. Under strict ion exchange conditions, divalent cations (e.g., Co^{2+}) exchange at paired Al_F sites and monovalent cations (e.g., Na^+) coordinate with all available Al_F sites (Figure 2). Here, we define paired Al_F as sites within a “visible” distance, as explained by Wichterlová and coworkers.^[20] The distribution of isolated and paired Al_F in the zeolite is controlled by the topology, hydrothermal synthesis conditions, structure directing agents, and the Si/Al ratio.^[21] Thus, control over the Al_F site distribution, in turn, enables precise cation placement in the zeolite.^[22] Controlling the distribution of Al_F in zeolites, while not the focus of the present review, is a topic with many pertinent achievements.^[20,23–26]

It is important to point out that the metal cation sites formed during ion exchange do not always match the active site involved in catalysis. For example, to obtain the active copper species required for selective catalytic reduction (SCR) of nitrogen oxides, Cu-CHA is pretreated at 500 °C in oxygen (to remove organic material and oxidize the Cu sites) and then exposed to a reaction mixture of NO , O_2 and NH_3 .^[1] Cu-SAPO-34 is pretreated at 750 °C in air prior to SCR to drive the migration of Cu into the pores.^[27] Thermal pretreatments are required prior to stepwise conversion of methane to methanol (MTM) as well: Cu-MOR is activated in O_2 at 450 °C, He at 500 °C, and O_2 again at 250 °C to enable binuclear $\text{Cu}^+/\text{Cu}^{2+}$ cycles^[28] (Figure 3a); Fe-BEA is activated in He at 900 °C, H_2 at 700 °C, and N_2O at 250 °C to enable mononuclear $\text{Fe}^{2+}/\text{Fe}^{4+}$ cycles^[29] (Figure 3b); and more recently, Fe-BEA (or Fe-FER) is activated under

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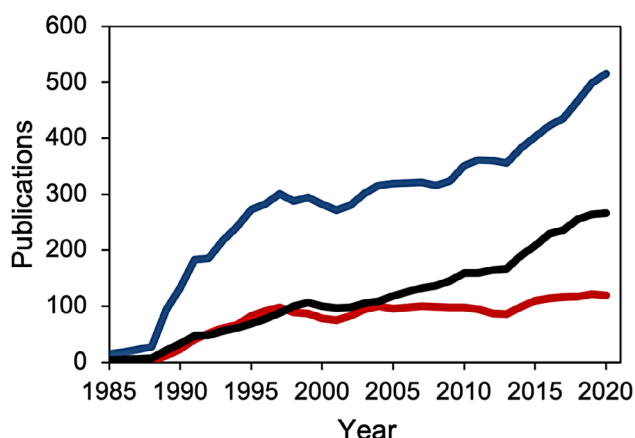


Figure 1. Comparing publishing trends in aqueous-phase and solid-state ion exchange indicates that a gap is widening between the two synthesis routes. Search details: source: Web of Science; all fields; “zeolite + exchange” (blue); “zeolite + water + exchange” (black); “zeolite + solid + exchange” (red).

vacuum (10^{-3} Pa) at 450 °C, calcined at 420 °C in O_2 and cooled to room temperature to enable binuclear Fe^{2+}/Fe^{4+} cycles^[30,31] (Figure 3c) before reacting with CH_4 . Clearly, thermal activation is important in obtaining the correct oxidation state and location of the metal cations. Thus, a synthesis technique that combines the metal addition process with the inevitable thermal post-processing could alleviate the need to expose the sample to additional treatment steps and may open opportunities to embed cations in locations prohibited by solution-based approaches. Additionally, with recent accomplishments in site-specific spectroscopy of transition metal ions in zeolites,^[32] an opportunity to directly compare the abundance of reactive species (and not ensemble averages) obtained from various synthesis techniques should be possible.

Among the synthesis techniques employed to append extraframework metal sites to zeolites, aqueous-phase ion exchange (APIE) is the most common. This is owed in part to its 1850s discovery^[33] and to the well understood thermodynamics, kinetics, and exchange mechanisms.^[34] In a typical APIE, the zeolite is combined with a dilute aqueous metal precursor and allowed to equilibrate. Although this ion exchange system appears simple, diligence is required to gen-

erate reproducible catalysts with cations in the desired position. The most important considerations are the solvent stability of the zeolite (pH dependent), surface charge of the zeolite (pH dependent), speciation of the metal cation (pH dependent), solvation shell size of the entering/exiting metal cation, incubation time required to reach equilibrium (temperature dependent), and the number of repeated treatments required to reach the desired exchange capacity. These complexities are discussed in detail by Townsend and coworkers.^[34] In addition to APIE, one-pot synthesis is a common approach to obtain transition metal zeolites where Si, Al, and Na precursors, structure directing agents, and transition metal precursors are combined in a hydrothermal treatment.^[6] Depending on the coordination of the metal heteroatom, this approach leads to either isomorphous substitution (primarily from the boron group)^[35] or cation exchange.^[36]

SSIE is an alternative cation templating technique that was first reported in 1973.^[37] In its simplest form, a zeolite with a volatile counter-balancing cation (H^+ or NH_4^+) is intimately mixed with a metal precursor and heated in an inert atmosphere or under vacuum. Ion exchange using solid-state precursors avoids considerable quantities of heavy metal waste typically produced during conventional APIE. SSIE is also useful in synthetic situations where APIE is inadequate. For example, to prevent Fe^{3+} from precipitating, the exchange solution must be below pH 2.2.^[8] These conditions are too acidic for many important zeolites and dealumination would be unavoidable.^[38] Another notable challenge with APIE is the diameter of the incoming metal aquo complexes (e.g., $[M(H_2O)_6]^{2+}$) (Figure 4), which vary significantly in size depending on the cation, are generally unable to pass through 6 MRs or smaller,^[8] and struggle to migrate into hydrophilic micropores.^[27] Another experimental complexity of APIE is the remaining need to thermally activate the catalyst after exchange (see above). For these reasons (and others),^[16] we see a notable opportunity to investigate SSIE as an alternative metal cation–zeolite synthesis method for broad, present-day applications in catalysis and adsorption.

3. Basic Principles of SSIE

For successful exchange of the zeolite and metal cation using SSIE, specific criteria must be met. Chiefly, the parent zeolite



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James Crawford obtained his BS in chemical engineering at Montana State University in 2016. He completed his PhD in chemical engineering at the Colorado School of Mines under the advisory of Professor Moises A. Carreon and completed his postdoc with Dr. Matthew M. Yung at the National Renewable Energy Laboratory. He joined the faculty of Montana State University as an assistant professor in 2023, where he studies porous catalysts applied to environmentally important chemical reactions.

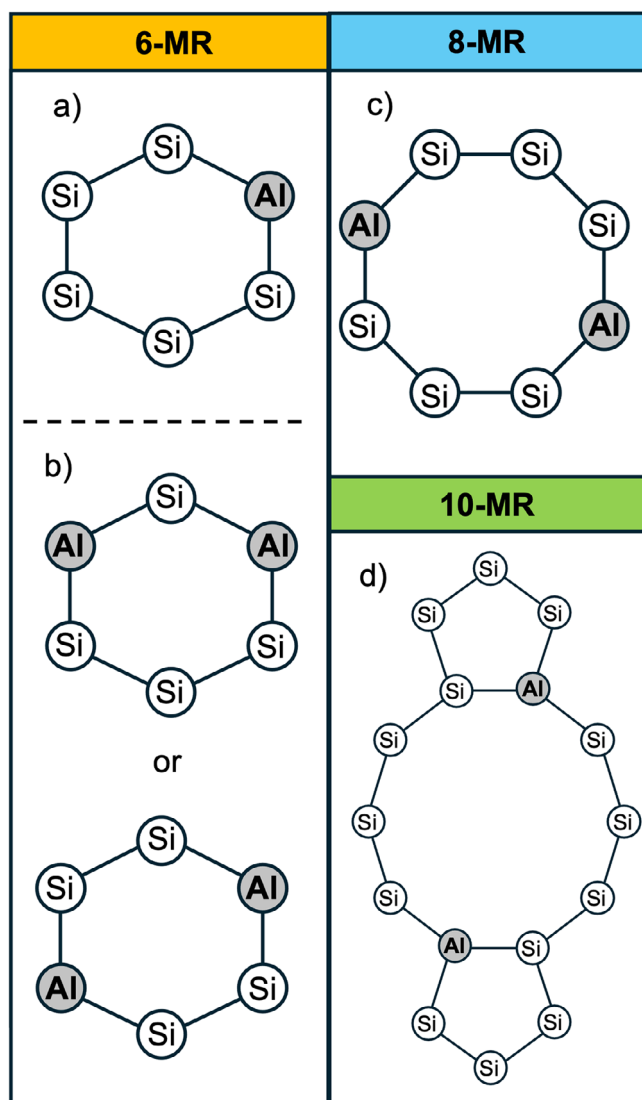
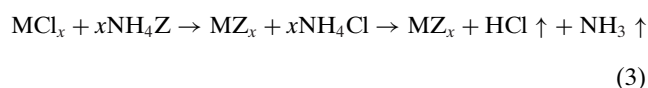
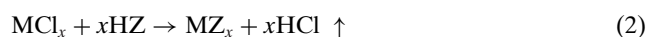


Figure 2. Zeolite Al_F influence the cation exchange properties. Common forms of Al_F include a) isolated 6 MR and b) paired 6 MR observed in chabazite (CHA), c) paired 8 MR observed in mordenite (MOR), and d) visible distance 10 MR observed in Mobil five (MFI) zeolites.

must be in the H or NH_4 form. This is owed to the importance of the SSIE reaction product, best illustrated in a comparison of a Na-, H-, and NH_4 -zeolite in a stoichiometric reaction between monovalent zeolitic exchange sites (Z) and x -valent metal chloride (MCl_x).^[34]



When the Na-zeolite is exchanged, NaCl is the product (Equation 1). Even at high temperatures (typical range for SSIE is between 200–800 °C), NaCl has a relatively low volatility and is slow to leave the system. NaCl can be removed by washing, but more convenient is the use of H- or NH_4 -zeolite. As shown in Equations 2 and 3, volatile HCl or NH_4Cl (which decomposes to HCl and NH_3 under SSIE reaction conditions^[39]) leave the system and permit rapid forward progress of the reaction. This is a key difference between APIE and SSIE, where the former is equilibrium limited, and the latter could reach complete conversion of the metal chloride. For this reason, SSIE generally achieves higher degrees of exchange than APIE.^[4,17,40]

Important aspects regarding the zeolite, metal precursor, exchange temperature, and gas atmosphere (vacuum, inert, oxidizing, reducing) have been discussed previously in great detail.^[17,41] Here, we emphasize three of these important considerations: 1) the metal precursor must have a non-zero vapor pressure at the selected exchange temperature to volatilize and adsorb on the zeolite surface,^[40,42] 2) the metal precursor must not undergo oligomerization prior to exchange as polymeric species are often unable to penetrate zeolitic micropores,^[43–45] and 3) the ligands of the metal precursor must form a volatile reaction product with the zeolitic exchange site while maintaining a sufficiently small kinetic diameter to exit the micropore.^[39,46] These three considerations largely prohibit SSIE of complex organometallic precursors or low volatility metal oxides.^[39,42] Importantly, SSIE has enabled the addition of cations that typically show low equilibrium exchange concentrations in APIE. Some examples of SSIE advantaged systems are Cs^+ ,^[47] Ni^{2+} ,^[48] La^{3+} ,^[49] Ce^{3+} ,^[40] Ga^{3+} ,^[50] and noble metal cations.^[51]

4. Methods of Exchange

Under the umbrella of SSIE, there are two predominant processes that are a direct result of mixing and heating the zeolite and metal precursor: contact-induced (CIE) and vapor-phase exchange (VPE), as depicted in Figure 5. CIE was first observed when mixing two separate phases of Li- and Na-LTA zeolites. After only a brief mixing period at room temperature, the two phases formed a uniform LiNa-LTA phase.^[52] However, it was later demonstrated that under the exclusion of water, CIE did not occur.^[41,53,54] Thus, it is generally agreed that CIE proceeds through equilibrium-controlled dissolution/diffusion of the metal precursor in pore-bound water.^[52,55] In many ways, CIE follows the same mechanism as APIE, but with a limited quantity of water.

For VPE, a metal precursor passes through the vapor phase to react with the zeolite. This process is similar to chemical vapor deposition, but with the key difference being selective titration of Brønsted acid sites. Examples of VPE include $FeCl_3$ on H-MFI,^[56,57] $CuCl$ on H-MFI,^[58–60] $GaCl_3$ on H-MFI,^[50,57] $ZnCl_2$ on H-MFI,^[4,57] Zn^0 on H-FAU,^[61] and Cd^0 on H-FAU.^[62] This list of examples helps to point out that metal precursors with low vapor pressures are still able to volatilize and titrate the zeolite. Applying medium/high

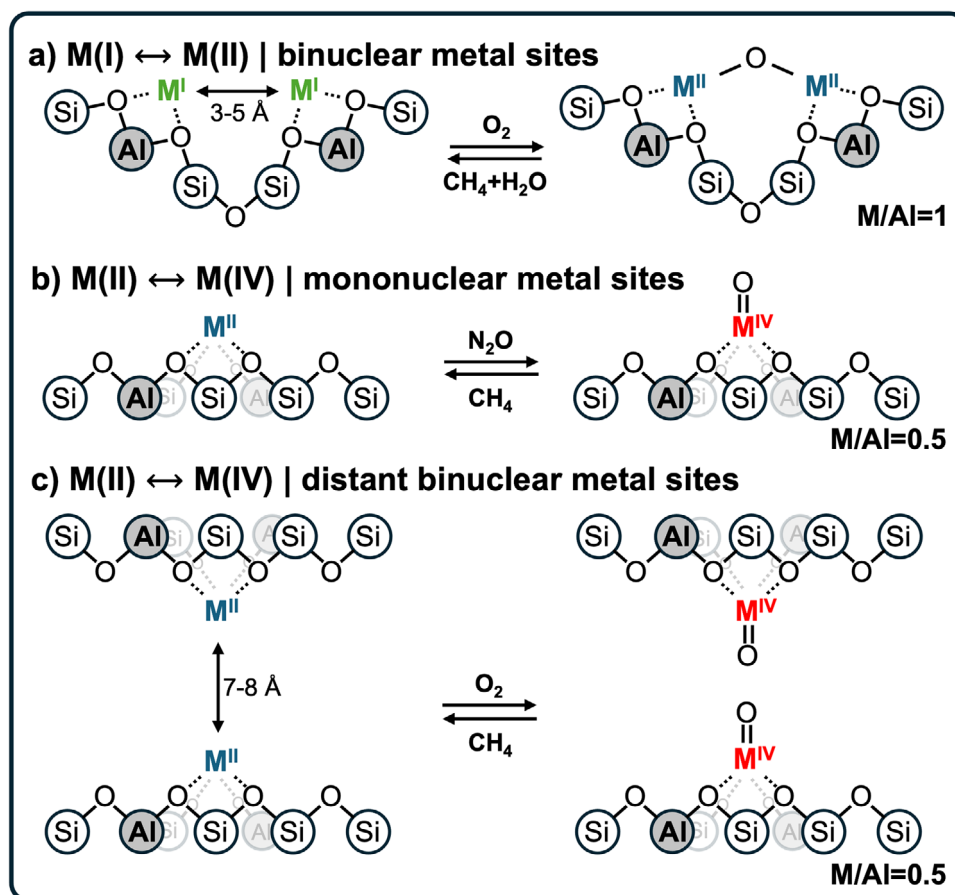


Figure 3. Selected mononuclear and binuclear cationic metal sites involved in the stoichiometric conversion methane to methanol. Redox pairs include a) binuclear $M(I) \leftrightarrow M(II)$, b) mononuclear $M(II) \leftrightarrow M(IV)$, and c) binuclear $M(II) \leftrightarrow M(IV)$. The nuclearity and oxidation state impacts the reactivity with gas-phase oxidants and reductants.

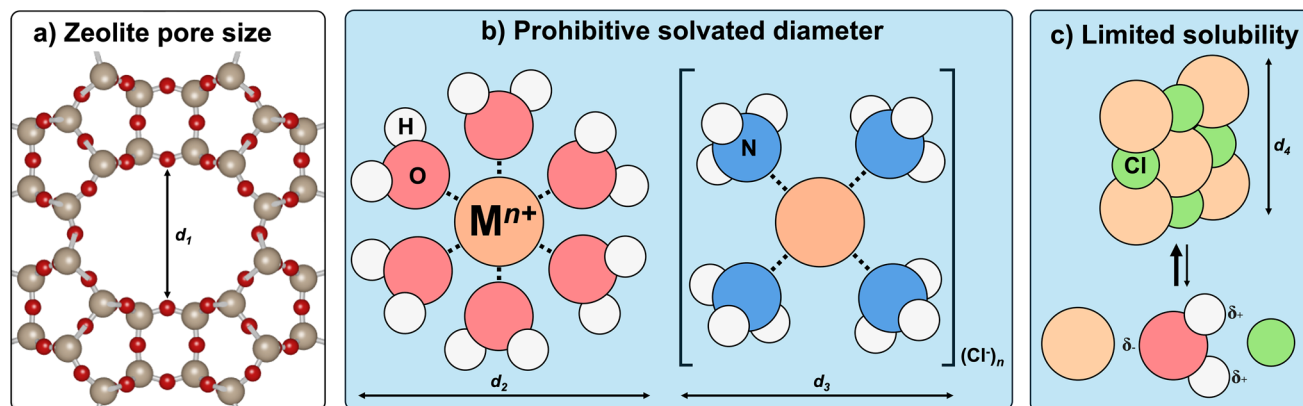


Figure 4. Challenges experienced in aqueous-phase ion exchange where cations are excluded from a) the zeolite micropore with limiting dimension, d_1 , owed to b) prohibitively large solvation shells, d_2 , or bulky ligands, d_3 , or c) sparing solubility in water, where crystallites remain intact, d_4 .

vacuum to low volatility metal precursors aids in the VPE process. It is important to note that VPE does not rely on the presence of pore-bound water. Under strict exclusion of water, VPE is the primary driver of exchange. However, when heating to elevated temperatures, zeolite dehydroxylation

cannot be disregarded and may contribute small quantities of water that are involved in the SSIE chemistry.^[63] Most existing SSIE zeolite catalysts syntheses involve both CIE and VPE, as strict exclusion of water from zeolitic micropores requires complicated handling.

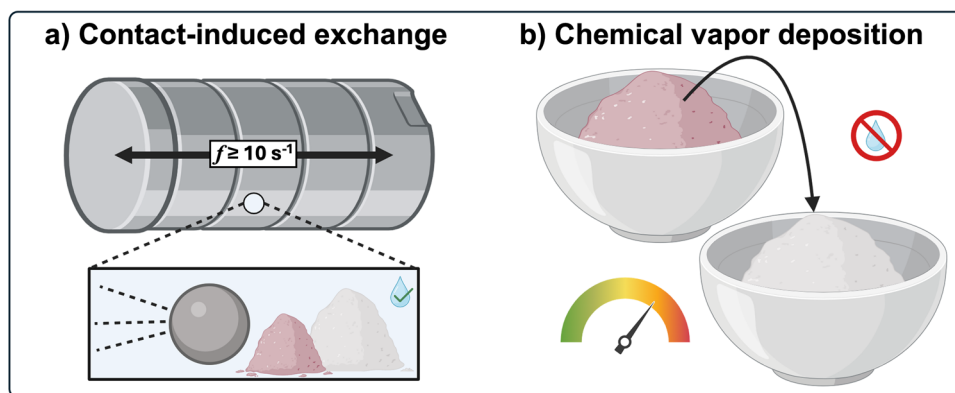


Figure 5. Methods of SSIE on zeolites include a) contact-induced ion exchange where a high frequency ball mill is employed to obtain an intimate mixture and b) vapor-phase exchange where the metal precursor is volatilized and reacts with the H-sites in the zeolite. Combining these techniques often leads to shorter reaction times.

Table 1: Recent studies in solid-state ion exchange.

Metal precursor	Zeolite	References
CuCl	H-USY, H-Y, H-MOR, H-BEA, H-MFI, H-CHA,	[44, 71–77]
CuCl ₂	Na-USY, NH ₄ -USY, H-SAPO-34	[44, 78]
CuCH ₃ CO ₂	Na-USY, NH ₄ -USY	[44]
Cu(CH ₃ CO ₂) ₂	H-CHA	[79]
Cu(acac) ₂	H-SAPO-37, NH ₄ -CHA	[80, 81]
Cu(NO ₃) ₂	Na-USY, NH ₄ -USY, NH ₄ -CHA, NH ₄ -SAPO-18, NH ₄ -SAPO-34	[44, 81, 82]
Cu ₂ O	NH ₄ -BEA, Na-BEA, H-CHA, Na-USY, NH ₄ -USY	[44, 83, 84]
CuO	NH ₄ -BEA, H-SAPO-34	[78, 83, 85, 86]
TiCl ₂ Cp ₂	H-BEA	[87]
Ce(NO ₃) ₃	NH ₄ -Y	[88, 89]
NiCl ₂	NH ₄ -MFI, NH ₄ -BEA	[90]
Ni(NO ₃) ₂	H-BEA, NH ₄ -Y, H-MFI, H-Y	[69, 88, 91, 92]
FeCl ₃	NH ₄ -BEA, NH ₄ -MOR, NH ₄ -FER, H-MFI	[56, 93, 94]
Fe(NO ₃) ₃	H-BEA, H-MCM-22	[45, 95]
AgNO ₃	H-Y, H-BEA	[75, 77, 96]
Sn(CH ₃ CO ₂) ₂	H-BEA	[97, 98]
Pd	H-SAPO-34	[99]
PdO	H-SAPO-34	[99]
ZnCl ₂	H-MFI	[4]
SrCl ₂	Na-SAPO-34, NH ₄ -SAPO-34	[46]
In ⁰	H-MOR	[63]
In ₂ O ₃	H-CHA, H-MFI, H-MOR, H-BEA, NH ₄ -BEA	[63, 96, 100–103]
In(NO ₃) ₃	NH ₄ -CHA, NH ₄ -MOR	[104, 105]
ZrOCl ₂	H-BEA	[106]
Ga(NO ₃) ₃	H-MOR, H-CHA	[107]

To follow Karge, 2008.^[17]

5. Experimental Considerations

5.1. Metal Precursor Selection

Metal precursors used for SSIE can have a large influence on the resultant catalyst quality. Recent studies (after 2008) have been tabulated and organized by metal precursor (Table 1). Metal chlorides are the most studied precursors

for zeolite SSIE. The relatively small size and moderate volatility of metal chlorides allow effective penetration into the zeolite pore. Additionally, the reaction product when a metal chloride exchanges with a Brønsted acid site is HCl (see Equation 2), which is sufficiently volatile to leave the zeolite pore. Several seminal studies have demonstrated that formed HCl does not damage the zeolite framework using X-ray diffraction,^[64] but further evaluations using ²⁹Si and/or ²⁷Al magic angle spinning nuclear magnetic resonance spectroscopy would aid in confirming these results. Even under excessive initial metal chloride loading, over-exchange ($M/Al > 1$) does not readily occur.^[44] Multivalent metal chlorides have been shown to exchange as subchlorides and may require additional treatments to obtain bare cationic sites.^[4,50,54] Metal oxides typically require much higher temperatures to initiate exchange compared to chlorides. This is owed to the lower volatility of metal oxides compared to metal chlorides. Thus, metal oxides are faced with significantly higher kinetic limitations for SSIE compared to chlorides. Additionally, metal oxides are prone to forming polymeric fragments with unfavorable exchange properties.^[41] For example, CuO forms oligomeric clusters under high-temperature conditions and does not readily exchange with the zeolite until heated past 800 °C.^[65] A similar result was also reported for Mn₃O₄,^[66] NiO,^[67] and MoO₃,^[43] which displayed lower exchange affinity than their respective chlorides. Generally, metal nitrates, acetates, and acetylacetonates decompose and involve complicated side reactions that result in the formation of oxidized or reduced metal nanoparticles when the zeolite and precursor are heated under inert gas flow.^[39,44,68] In a recent study, Ni(NO₃)₃ was successfully combined with dealuminated H-BEA and heated in flowing air. The resulting catalyst was highly dispersed Ni on zeolitic silanol defects obtained through dealumination.^[69] Although the obtained Ni-silanol sites were significantly different than the isolated or paired extraframework sites targeted here, this was a successful alternative approach using SSIE of a metal nitrate precursor to obtain high quality catalytic materials. Reduced metals are an attractive precursor for SSIE as the theoretical exchange product would be H₂ (Equation 4, assumes that the exchanged metal takes

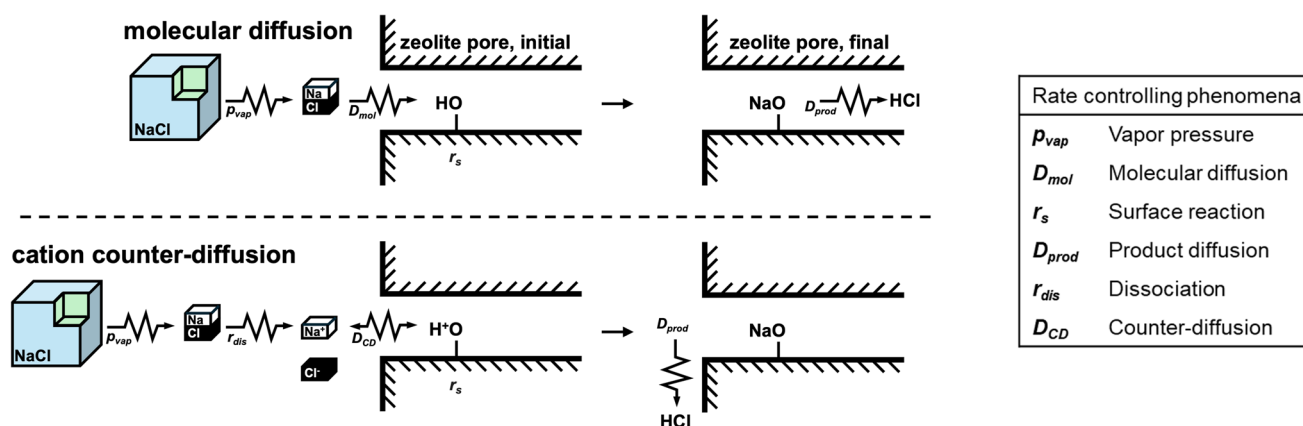


Figure 6. Proposed mechanisms of exchange include molecular diffusion and cation counter-diffusion with resistances from potentially rate controlling phenomena.

on a 1+ charge upon exchange) and the ingoing neutral metal atom would be minimal in size. From the limited studies available (Zn, Cd, In), the volatility of the metal was shown to influence the ease of exchange.^[61–63,70] The exchange mechanism of zero-valent metal species entering the protonic zeolite pore is a subject of ongoing discussion.



5.2. Zeolite Selection

Typically, H- and NH_4 -zeolites are preferred for SSIE (see section Basic Principles of SSIE). The crystallite size and topology of the zeolite also impact the ease of exchange. This was demonstrated with $MoCl_3$ exchanged H-MFI zeolites where the smaller crystallite MFI exchanged at a lower temperature than the larger crystallite MFI. Comparing the exchange of 1D zeolite H-LTL with the intersecting pores in H-MFI, higher-dimensional systems were found to exchange more rapidly.^[41]

6. Mechanisms of Exchange

The mechanisms governing SSIE are largely unknown.^[108] Infrared spectroscopy shows that heating metal precursors under anaerobic/dry conditions titrates the Brønsted acid sites in the zeolite while gaseous reaction products effervesce (e.g., HCl when metal chlorides are exchanged with H-zeolite), confirming that metal cations are transported and anchored to acid sites. This result does not clarify how the precursors move through the pore. Two possible mechanisms (Figure 6) have been proposed: 1) vapor-phase transport of intact metal salt molecules and/or 2) surface counter-diffusion of metal cations and pore-bound cations (also referred to as T-jump, where the cations hop from T-site to T-site). In both cases, intercrystallite diffusion rates would be anticipated.^[17,109] Bell and coworkers thoroughly characterized the exchange of zinc and gallium chlorides on H-MFI zeolite under anaerobic/dry conditions and observed the formation of substoichiometric

chlorides at cation exchange sites (e.g., $ZnCl_2$ converted to $[ZnCl]^+$ in Reference [4] and $GaCl_3$ converted to $[GaCl_2]^+$ in Reference [50]). This result points to mechanism (1), where intact molecules diffuse to Brønsted acid sites and react. However, this result does not rule out the possibility that the MCl_x dissociates to Cl^- and $[MCl_{x-1}]^+$ that counter-diffuses against H^+ . In a study from Sulikowski and coworkers, $LaCl_3$ was thermally exchanged (anaerobic/dry) with H-MOR, H-FAU, and H-FER.^[110] La- was successfully exchanged in MOR and FAU but was not exchanged in FER. The bare La^{3+} cation, if dissociated from its parent chloride, would have a diameter of ~ 0.23 nm,^[111] which would be small enough to enter the 0.54×0.42 nm FER pore (International Zeolite Association, Database of Zeolite Structures). The absence of La- in FER indicated that $LaCl_3$ did not dissociate; the intact salt was too large to enter the H-FER pore. This study provides strong evidence for mechanism (1). We have found more experimental evidence supporting intact molecular diffusion (mechanism (1)), but cannot rigorously exclude the possibility that T-jump cation counter-diffusion occurs (mechanism (2)). Additionally, the mechanism of exchange is likely to vary with the precursor, gas-phase environment, and zeolite cation. A meaningful computational study would aid in evaluating diffusion mechanisms for metal precursors under configurational confinement in a zeolite.

7. Current Challenges

One obvious challenge with SSIE is the use of metal chlorides as the catalyst precursor. It is generally agreed that Cl^- is a difficult contaminant to manage in heterogeneous catalysts.^[112–114] Below, we discuss recent advances in SSIE that facilitate either the removal of chlorine from the catalyst or the use of alternative metal precursors. Another challenge during SSIE is the need for zeolite thermal stability coincident with metal precursor volatility. In some cases, high temperatures are required to drive the exchange. Under these conditions, dealumination of the zeolite may occur. Although dealumination is important for many catalytic applications, in the pursuit of model catalysts, it creates

additional heterogeneities that complicate structure–function relationships. Some exciting examples of low-temperature SSIE could provide a practical solution to this problem, also discussed in the recent advances section. Critically, pretreatments used to obtain NH_4 - or H-zeolites can also cause severe dealumination. Rigorous dealumination studies are available for many industrially relevant zeolites,^[115–118] which provide guidance for appropriate pretreatments.

Complications in controlling the metal speciation during SSIE are reported when water and oxygen are present in the reaction mixture.^[39] This is especially important when mixing the zeolite and metal precursor, where water-free, anaerobic environments are difficult to obtain. These situations have been addressed with Schlenk line and glovebox handling.^[4,50,54] However, from an industrial perspective, the presence of water and air are likely unavoidable in large scale syntheses. Thus, additional efforts focused on comparing the quality of catalysts obtained under ambient versus anaerobic/dry conditions are required. This brings us to a closing challenge, which is not reserved to SSIE: site-specific characterization of the metal-zeolite active site. Great improvements have been made in this area,^[8,32] but expanding this spectroscopic skillset to the greater catalysis community remains a bottleneck. Applying advanced spectroscopies to both the obtained materials after SSIE and in situ will certainly aid in understanding the molecular process.

8. Recent Advances

8.1. Removal of Excess Chlorine

Thermal treatments for SSIE zeolites vary widely and rationale for the selected synthesis conditions are often omitted.^[72,119,120] Unverified thermal treatments lead to unknown catalyst speciation, residual chlorine, and unreproducible catalytic activity. Early efforts from Karge and coworkers focused on the gas-phase products during SSIE (referred to as temperature programmed evolution, TPE).^[121] TPE studies are valuable in understanding the ideal SSIE synthesis conditions. As shown by Bell and coworkers, CuCl exchanges with H-MFI first between 300 and 400 °C and again between 400 and 800 °C (Figure 7). By halting the exchange at different synthesis temperatures and evaluating the catalyst composition, they demonstrated that the CuCl/Al ratio decreased, and the zeolite bound Cu/Al ratio increased as the treatment temperature increased.^[54] Studies that thoroughly investigate the composition of the catalyst at varied SSIE synthesis temperatures are generally unavailable. These systems are especially well suited for modern in situ techniques including X-ray and optical spectroscopies.

Aside from heating the catalyst under inert conditions, reductive gas treatments also aid in the removal of chlorine. Bell and coworkers demonstrated that after mixing ZnCl_2 and H-MFI, heating to 500 °C positioned subchlorides of zinc at the acid sites. After exposing the catalyst to an additional treatment in 2.5% H_2 at 500 °C, chlorine was largely removed from Zn sites.^[4] Care must be taken in selecting the reduction conditions as M^0 agglomerates can

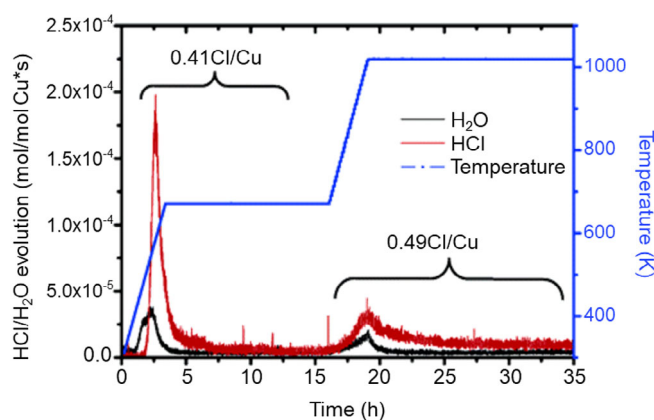


Figure 7. Evolution of HCl and H_2O during temperature programmed heating of a mixture of CuCl and H-MFI. Adapted with permission from Ref. [54] Copyright 2006 American Chemical Society.

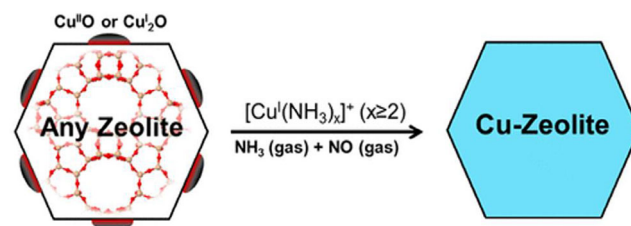


Figure 8. Gas-phase chemical reactions ($\text{NH}_3 + \text{NO}$ or NH_3 only) with the metal oxide precursor (CuO or Cu_2O) enable low-temperature SSIE of copper over various zeolites. Adapted with permission from Ref. [123] Copyright 2015 American Chemical Society.

form under harsh reduction conditions, and in some cases, irreversibly form metal nanoparticles.^[41] Similar reductive treatments have been applied to Cu-MFI^[122] and Ga-MFI^[50] to obtain high quality SSIE catalysts with exceptional catalytic activity.

8.2. Avoiding Chlorides Through Ammonia-Facilitated Exchange

Although chlorides exhibit optimal volatility for SSIE, they present challenges in mitigating unwanted residual Cl^- that is known to poison redox active sites.^[112,113] Alternative precursors, discussed above, open opportunities to avoid Cl^- . Metal oxides would be an ideal exchange candidate for SSIE, but are often limited by low volatility. Interestingly, SCR reaction conditions were observed to redistribute Cu species into CHA.^[79] In response to this observation, Vennestrom and coworkers studied the influence of gas-phase reactants on SSIE of copper oxides.^[123] Specifically, CuO and Cu_2O were exchanged with BEA, CHA, and MFI zeolites while varying the gas composition of NO , NH_3 , H_2O , and O_2 . Under ~500 ppm NH_3 /500 ppm NO /balance N_2 , CuO and Cu_2O were both able to exchange with the zeolite at 250 °C (Figure 8).

An in-depth analysis revealed that only NH_3 was required to facilitate Cu_2O exchange, whereas NO and NH_3 were required to facilitate CuO exchange. They explained this

fundamental difference with the hypothesis that NO aided in reducing CuO to Cu₂O that ultimately formed mobile [Cu^I(NH₃)_x]⁺ ($x \geq 2$) complexes that enter the zeolite pore.^[83] The same authors later confirmed that the formation of linear, high mobility [Cu^I(NH₃)₂]⁺ was essential for the exchange process in the range of 150–300 °C. Above 350 °C, [Cu^I(NH₃)₂]⁺ decomposed and limited Cu exchange.^[84] Later, NH₃-assisted low-temperature exchange of Cu(NO₃)₂ and Cu-acetate was also demonstrated.^[81] The opportunity to form mobile, exchangeable species through gas-phase reactions is an exciting new area that has not yet been generalized to other metal oxide precursors or been thoroughly studied to obtain isolated/paired transition metal active sites.

8.3. Modified Vapor Phase During Exchange

The vapor phase above the solid-state mixture has a significant influence on the mobility of transition metals in zeolites. Vacuum atmospheres drive the sublimation of metal precursors while positive pressure atmospheres can drive restructuring events. Restructuring is well documented for thermochemical SCR,^[27] MTM,^[124] and CO₂ reduction^[103] reactions using transition metal zeolite catalysts. In many ways, modifying the vapor phase during SSIE is analogous to adsorbate-induced restructuring.^[125] We have already discussed the influence of NO and NH₃ for exchange of copper oxides above. Oxidative and reductive treatments have been thoroughly discussed previously.^[17] Additional examples of modified gas atmospheres that can lead to cation exchange in zeolites (depending on the choice of zeolite, precursor, and exchange conditions) include H₂O, Cl₂, CO, CCl₄, and volatile hydrocarbons.^[41] As an example, MoO₃ is a particularly challenging precursor for SSIE as it forms polymeric fragments in the vapor phase when heated. However, under partial pressures of CCl₄, MoO₃ was successfully exchanged via SSIE in several protonic zeolites at moderate temperatures ($T < 300$ °C).^[126] The authors attributed this result to the formation of high mobility cationic oxychloride fragments that successfully penetrated the zeolite pore. Metal carbonyls are another high mobility transition metal complex that can undergo ion exchange. An example in the context of SSIE is the exchange of RhCl₃ on a protonic zeolite. Under CO partial pressure, the extent of exchange was much higher under partial pressures of CO.^[127] The authors attributed the enhancement to the formation of high mobility carbonyls. This process would likely be amenable to other metal precursors with a propensity to form carbonyls.

9. Summary and Outlook

Upon reviewing the past and present zeolite SSIE literature, we have identified several important themes. We imagine that additional research in SSIE will result in more precise synthesis strategies for isolated and paired extraframework metal sites in zeolites, which continue to find new and

impactful applications. Additional computational studies targeting the influence of the metal precursor, zeolite topology, zeolite cation, and the gas atmosphere (reactive, inert, or vacuum) will aid in understanding the underlying mechanisms of exchange and enable new experimental paths forward. Among the experimental research themes, the formation of mobile metal species through gas-phase chemical reactions (such as SCR reaction conditions) is an exciting development. This result has only been demonstrated for copper zeolites, but could be extended to other transition metals known to form ammine complexes. Additionally, the opportunity to template metal precursors completely through vapor-phase exchange (under vacuum) has not been broadly explored but may result in high-quality catalysts. Regarding the characterization of the obtained metal–zeolite catalysts, new opportunities are emerging that allow the researcher to understand the functionality of the active site involved in the chemical reaction via site-specific spectroscopy. By avoiding ensemble averaging and probing the species involved in the reaction, one can identify the desired active site and optimize the synthesis strategy used to obtain these sites. Thus, we see SSIE playing a key role in the preparation of next-generation isolated/paired transition metal cation zeolite catalysts.

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The authors have nothing to report. [Correction added on May 3, 2025, after first online publication: Figure 3 was updated.]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Active site • Catalyst synthesis • Solid-state ion exchange (SSIE) • Transition metal ion • Zeolite

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