Catalysis Science & Technology

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

View Article Online
View Journal | View Issue

Cite this: *Catal. Sci. Technol.*, 2024, **14**, 4740

Influence of binders and matrices on zeolite-containing catalysts

Ke Zhang, *[a] Xiao Jiang,[a] Michael J. Forte,[a] Miao Sun,[b] Mohammad AlAbdullah,[b] Mohammed AlAmer,[b] Mohammad Aljishi, [c] Essam AlSayed,[d] Wajdi AlSadat,[a] Bruce C. Gates [e] and Alexander Katz [f]

Received 12th June 2024,
Accepted 27th July 2024

DOI: 10.1039/d4cy00737a

rsc.li/catalysis

Industrial solid catalysts are rarely pure materials consisting solely of catalytically active species; many are complex multiphase composites. This complexity is exemplified by zeolite catalysts, which are widely applied in industry. Given the proprietary nature of industrial catalysis, the fundamental chemistry and materials science of binder-catalyst combinations have been largely neglected. Although binders might be considered to be inert components, they often significantly influence catalyst behavior. Over the preceding decade, academic awareness has increased significantly, bridging the knowledge gap between fundamental zeolite research and the practical use of zeolite catalysts. Building on these advances, we aim to summarize the state of this field, focusing on understanding of the role of binders in zeolite catalysts, both with and without metals, and presenting insights into how binders affect acid density, porosity, and the control of the proximity between metal and acid sites within shaped zeolite catalysts. We anticipate that binders will continue to play crucial roles in zeolite catalysis and offer a perspective on emerging topics and recommendations for future work on the subject.

Introduction

Industrial solid catalysts are rarely pure materials. Rather, they are complex composites, incorporating components that provide desirable properties in addition to the intrinsic activity and selectivity of the catalytically active species—such as texture and porosity, robustness, and physical strength to withstand high temperatures and abrasion. The components of catalyst particles often include the following:

1. The catalytically active species, such as proton-donor sites or metal-containing nanoclusters or crystallites. These are usually only a small fraction of the catalyst—with a metal typically constituting less than 1 wt% of a catalyst.[1,2]

2. Supports (carriers), platforms on which the catalytically active species are dispersed; supports usually have high surface areas and are robust, inexpensive, and available with tailored physical properties such as surface area and pore size distribution. Supports may be essentially inert, but often they present surface groups that interact with catalytically active species such as metals, participating in the catalytic cycles. Supports are typically the major components in catalysts.[3,4]

3. Promoters, components that improve the activity or selectivity of a catalyst without themselves being catalytically active. Most promoters (chemical promoters) are dispersed on catalyst surfaces at only low loadings (much less than 1 weight percent), but some (textural promoters) are present at much higher loadings and help to stabilize the catalysts and their textural properties.[5]

4. Binders, which are components that stabilize the catalysts and provide improved physical properties such as crush strength and resistance to abrasion. There is much less literature of catalyst binders than of the other catalyst components. Often binders serve as glues that hold together catalyst components such as metal oxide and zeolite crystallites, stabilizing the porous catalyst particles (with a general compositional range of 10–50 wt%).[6–10] Commonly used binders (and binder precursors) are clays, which, upon heating in the presence of the other catalyst components, may spread and form bonds with the other catalyst components to stabilize them. Clays may undergo a range of chemical changes during catalyst preparation, such as vitrification (whereby they take on a glass-like state) and

---

[a] *Aramco Americas: Aramco Research Center—Boston, 400 Technology Square, Cambridge, MA 02139, USA. E-mail: ke.zhang@aramcoamericas.com*
[b] *Saudi Aramco, Fuels & Chemicals Division, Research and Development Center, Dhahran 34464, Saudi Arabia*
[c] *Saudi Aramco, Catalyst Center of Excellence Division, Research & Development Center, Dhahran 34464, Saudi Arabia*
[d] *Saudi Aramco, Oil & Gas Treatment R&D Division, Research & Development Center, Dhahran 34464, Saudi Arabia*
[e] *Department of Chemical Engineering, University of California, Davis, California 95616, USA*
[f] *Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, USA*

transformation into other components.[11] Transition aluminas and silicas are themselves used as catalysts and catalyst supports, and they can be used without additional binders, because the functional groups (*e.g.*, hydroxyl groups) on alumina and silica surfaces readily bond with such groups on neighboring particles—thereby taking on the function of the binder by themselves.[12] The fine particles create interparticle void spaces through which reactants and products are transported. In contrast to transition aluminas, α-Al_2O_3, which typically has a low surface area and is used as a support for silver particles in ethylene epoxidation catalysts,[13] lacks a high density of surface functional groups and benefits from binders that glue the support particles together and provide integrity and strength to the catalyst bodies. Zeolites are another important class of catalysts and catalyst supports that benefit from binders, and they are used on an enormous scale. This essay focuses on zeolite-containing catalysts that incorporate binders.

For decades, zeolite catalysts have found applications in petroleum refining and petrochemical conversion, facilitating the large-scale worldwide production of a diverse range of products.[14–16] The industrial importance of zeolites reflects their distinctive properties, including high surface areas, ion-exchange capabilities, acidity, and thermal stability. Further, the regular molecular-scale channels in these crystalline materials facilitate shape-selective reactions and precise discrimination of reactants, products, and transition states.[17–20] Confinement within zeolite micropores is thought to endow the Brønsted-acid sites in them with catalytic properties that rival those of materials with much stronger acid sites, such as polyoxometalates and mineral acids.[21–24]

Zeolites are unusual among industrial catalysts in being crystalline (and having pore structures that are determined by the crystal structures). The relative structural simplicity of crystalline powder zeolites has made them widely appealing to researchers, and consequently much of the zeolite catalysis literature—both experimental and theoretical—is based on the investigations of zeolites in this form. Industrial applications of zeolite catalysts, in contrast, rely on formed (shaped) catalysts (bodies) that contain components other than the zeolites themselves, prominently including binders (Fig. 1). Binders are commonly used in the scale-up and manufacture of zeolite catalysts, to shape the crystalline zeolite powders into bodies that have the necessary mechanical strength and attrition resistance. The binding of discrete particles into products suitable for industrial use is pivotal in numerous engineering materials, not just catalysts. The strength and attrition resistance of the formed catalytic materials are especially important when they are used in fluidized-bed reactors—as in fluid catalytic cracking (FCC), a process that is practiced on an enormous scale and requires catalysts worth billions of dollars annually.[25]

In catalyst manufacture, binders are predominantly applied as colloidal solutions; these incorporate finely dispersed particles to ensure a nearly uniform distribution in the catalyst during the application. In zeolite catalyst formulation, a binder serves as the soluble component responsible for binding zeolite crystallites during the shaping process. The typical production of a zeolite catalyst begins with the creation of a shaped preform and culminates in high-temperature treatments, such as drying and calcination, which transform the initial preformed particles into technologically useful bodies having the necessary mechanical properties. During the drying/calcination, volatile components are removed, and the transformations may include phase changes of the inorganic binders. The changes may result in dense or porous solid matrices having various structures, which can be either amorphous or crystalline.

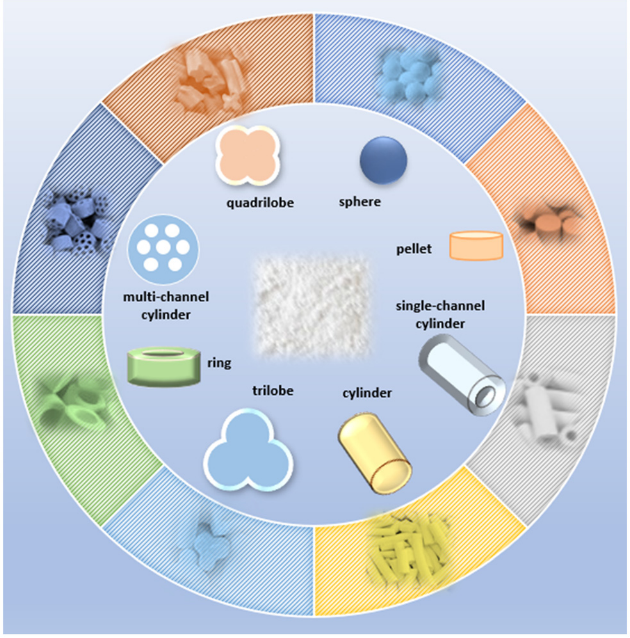

Fig. 1 Schematic illustration of variously shaped commercial catalysts and supports.

The terms "binder" and "matrix" are sometimes used interchangeably, especially when the matrix is derived from the binder. For example, binders derived from silica or alumina lead to the formation of porous particulate matrices in which particles are held together by oxygen bridges, with the pore-size distribution of the matrix determined by the size distribution of the particles that form it. Clay minerals are widely used as binders, and, provided that they exhibit sufficient wettability and hydrophilicity, they can be used alone to shape zeolite catalysts. Then, the distinction between a soluble binder and a solid additive becomes blurred. Furthermore, a clay can also function as a component of the matrix, contributing to the formation of a multi-component matrix—with the clay then sometimes being referred to as a filler or a matrix, because of its role in modifying the porosity and density of the resultant catalysts.[25]

Although binders may be essentially inert components within composite catalytic materials, they instead often significantly influence catalyst behavior. Binders may either enhance or detract from catalyst performance, and commonly the behavior of a zeolite-binder composite is not determined by a simple weighted sum of the properties of the individual phases. Because of this complexity, the scale-up and production of zeolite catalysts are typically complex. And, given the proprietary nature of industrial catalysis, the fundamental chemistry and materials science of binder-catalyst combinations have been largely neglected—although academic awareness of the issues has grown in the preceding decade, as is evident in a series of articles that have substantially bridged the knowledge gap between fundamental zeolite research and the practical use of zeolite catalysts.[6–10] Building on these advances, we aim in this essay to summarize the understanding of the incorporation of binders in zeolite catalysts and to provide insights into the influence of binders on acid density, porosity, and control of the proximity of metal and acid sites within shaped zeolite catalysts. We also offer a perspective on emerging topics and recommendations for future work.

Influence of binder/matrix on acidity

Acidic sites within the microporous frameworks of zeolites play pivotal roles in many catalytic reactions, and so it is important to understand how shaping and the incorporation of binders influence zeolite acidity. The effects of binders are significant; to explain them, we focus on three major classes of binders: clays, silica, and alumina. We summarize results of experiments characterizing acidities of the resultant catalysts and contrast these results with estimates based on the simple assumption that the number of acid sites in the catalyst is just the sum of the numbers of such sites in the components (Fig. 2). When we use the term "acidity" here we refer to the number (and not the strength) of the proton–donor sites, unless otherwise specified.

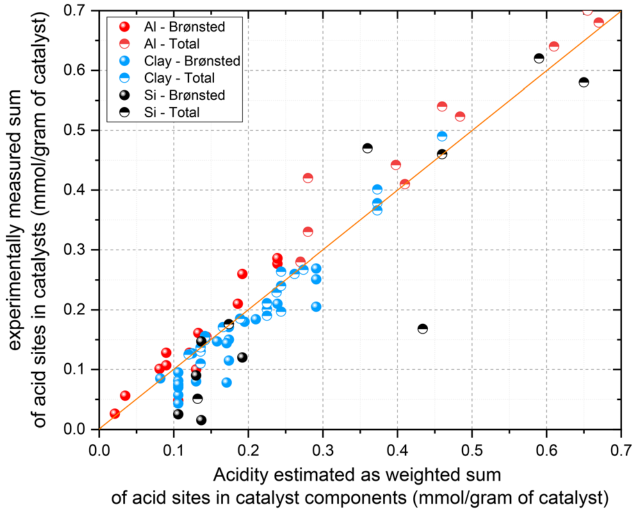

Fig. 2 Data showing that experimentally measured numbers of acid sites do not generally match these estimated as the weighted sums of acid sites in the zeolite and binder components. The original data are collected from ref. 26–45.

The literature[26–45] shows that the influence of binders on catalyst acidity is determined predominantly by the type of binder. Notably, alumina is distinct from silica and clays. In the following, we emphasize clays as binders, reflecting their importance in practice and the relative lack of reports characterizing them. We draw contrasts among three types of clays that are commonly used as binders for shaping zeolite catalysts and offer insights and suggestions for best practices in their application.

Alumina

The results summarized in Fig. 2 show that the measured acidities of zeolite catalysts with alumina binders often exceed those estimated as the weighted sums of the acidities of the alumina and the zeolite. When alumina is used as the matrix—and severe zeolite dealumination does not occur—the increase in acidity is attributed to the formation of new Brønsted acid sites resulting from the migration of aluminum from the binder into the zeolite framework during heating.[46–49] Pioneering research on aluminum migration from external aluminum sources into zeolites involved experiments characterizing the reaction of anhydrous high-silica ZSM-5 with aluminum halide vapors or aluminate solutions.[50] Subsequent investigations showed that alumination occurs primarily through the interaction of aluminum ions with zeolite defect sites such as silanol nests, external silanol groups, and defective (*i.e.*, non-intact) Si–O–Si bonds—and not by replacement of framework silicon ions with aluminum ions.[51] Alumina binder-induced alumination typically results in an increase in catalytic activity for Brønsted acid-catalyzed reactions.[46–49]

The newly created Brønsted acid sites have been found at the interface between the zeolite and the matrix or, alternatively, within the zeolite framework. The surface Brønsted acid sites have characteristics akin to those of such sites on amorphous silica-alumina, and they result from the dehydroxylation reaction involving silanol groups and aluminum species, which form new Si–O–Al sites.[52] On the other hand, the presence of structural defects is essential for aluminum insertion into the Brønsted acid sites within the zeolite framework. These defects can arise from imperfect crystallization or various post-synthetic treatments, as well as from calcination-induced structural defects, which act as sites for alumination. A recent investigation of FCC catalysts shed light on the source of calcination-induced defects, demonstrating that new Brønsted acid sites are created at the expense of strong Lewis acid sites originating from distorted tetrahedral aluminum sites near the external zeolite surfaces.[26] In other words, not all tetrahedral aluminum sites function as Brønsted acid sites in zeolites. Some can act as Lewis acid sites, provided that they can accept electron density and expand their coordination spheres. These tetrahedral aluminum sites with strong Lewis acidity are located near hydroxyl groups at the outer layers of zeolite crystals and can be highly reactive. They can be removed by heating and replaced with aluminum from the binders, resulting in the formation of new Brønsted acid sites.[26]

A related emerging approach to understanding these phenomena involves incorporating aluminum into mesoporous Y zeolites through the condensation of an aluminum alkoxide precursor with silanols generated in the zeolite. When aluminum incorporation is conducted in the presence of water, without rigorous drying of the zeolite, a phase-separated alumina phase is synthesized. When, instead, this incorporation is conducted under rigorously dry conditions, the alumina forms a uniform nanoscale (10 nm-thick) layer along the interior of the mesoporous Y zeolite. Data summarizing these points are presented in Fig. 3.[53] When the reactants are rigorously dry, the zeta potential (approximated as the surface charge) of the resulting surface-modified mesoporous Y zeolite can be controlled by the aluminosilicate composition of the layer. This surface charge can be exploited for controlling the colloidal adhesion of the zeolite particle to the binder, as it changes to more negative zeta potentials as the Si : Al ratio of the layer increases.[53] Those binders that impart greater colloidal dispersion of the zeolite catalyst and greater accessibility of acid sites on the zeolite external surface in the shaped catalyst are those that can be preferred, particularly for acid catalyzed reactions involving large reactant molecules. Through related strong electrostatic adsorption approaches, this surface charge can be used to control the deposition of molecular catalyst precursors.[54]

Various strategies have been explored to either facilitate or impede the migration of aluminum species, including the following:

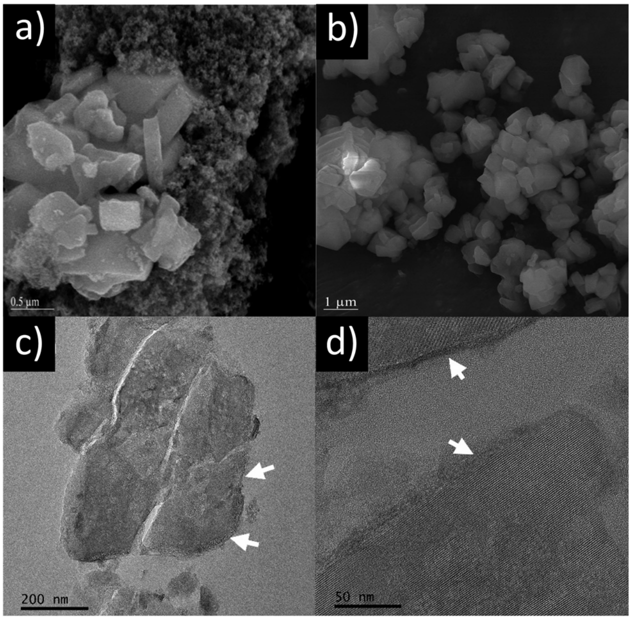

Fig. 3 Mesoporous materials incorporating zeolite Y with 4.6 wt% alumina coatings: a), synthesized under wet conditions and imaged by scanning electron microscopy (SEM), showing a distinct alumina phase separated from the zeolite; b), synthesized under rigorously dry conditions and imaged by SEM, showing a lack of phase separation; c) and d), high-resolution transmission electron microscopy images of nanoscale alumina coating of material shown in b). Adapted from ref. 53 with permission. Copyright 2023 American Chemical Society.

(1) Leveraging a wet-binding microenvironment: practically, aluminum insertion is more effective when carried out in the presence of water, involving a transfer of soluble aluminum species rather than a solid–solid reaction. The mere physical mixing of alumina and zeolite did not yield substantial alterations in total acidity, with only a minimal increase in external acidity observed at the interface where close interactions occur.[55]

(2) Regulating alumina particle size: the size of the alumina particles plays a role in aluminum migration. Experimental results suggest that both the total acidity and the acid site strength increase as the alumina particle size decreases. This result is attributed to the greater contact area between zeolites and smaller rather than larger alumina particles, enhancing the likelihood of migration of aluminum species to zeolites and generation of new acidic sites.[52]

(3) Introducing silica into alumina binder: incorporating silica into the alumina binder provides another avenue to promote aluminum migration into the zeolite. Aluminum migration occurs during calcination and takes place at temperatures below 450 °C before the transformation of the boehmite phase. The doping of silica into the alumina binder raises the boehmite phase transformation temperature, facilitating the release of aluminum species from the phase and their subsequent migration to zeolites during calcination. In this approach, the mass of silica added should be carefully optimized, as excessive silica dilutes the alumina binder and reduces the number of overall transferable aluminum species.[56]

(4) Using a plasticizer with specific functional groups: the presence of a polyol-type compound as a plasticizer or lubricating agent can impede aluminum migration—caused by the interaction between the hydroxyl groups in the polyols and aluminum species, which hinders migration and depletes the mobile aluminum species from the binder. The procedure results in catalyst bodies with densities of Brønsted acid sites nearly matching those expected from simple dilution by the binder.[28] Significantly, the use of a plasticizer with a peptizer can facilitate aluminum penetration, leading to the formation of new Brønsted acid sites, not only at the zeolite-binder interface but also within the zeolite framework. Thus, the decomposition products of methylcellulose, for example (in the presence of an acidic peptizer and adsorbed water), induce a higher degree of dealumination, creating additional silanol nests within the zeolite framework that are available for aluminum insertion.[28] We emphasize that it is important that aluminum migration from the alumina binder and dealumination within zeolites have contrasting effects on the acidities of zeolite catalysts. The well-documented increase in Brønsted acid site density and total acidity resulting from aluminum migration from the alumina binder is the outcome of a less pronounced simultaneous dealumination process within the zeolite. However, we emphasize that severe dealumination can result in a loss of acidity, even when alumina is used as the binder, as illustrated in Fig. 2, notably in the case of an outlier shown in the figure at coordinates (0.13,

0.09).[34] Dealumination entails the conversion of some tetrahedral aluminum into extra-framework aluminum species. This transformation results in catalysts with higher concentrations of Lewis acid sites than would be expected from alumina dilution alone. Some migrated aluminum may also reside in the pores or channels of zeolites as extra-framework species and Lewis acid sites. There is, however, an exception to this increase in the density of Lewis acid sites when a strong acid, such as nitric acid, is used as the peptizer. In this case, the strong acid has the capacity to dissolve extra-framework aluminum species, effectively leaching them out. Consequently, the catalyst body exhibits Lewis acid site concentrations that align with the predicted values.[28]

Clays

The influence of clays on the acidity of zeolite catalysts depends on the composition and structure of the clay. Clays, whether natural or synthetic, consist of planar or non-planar phyllosilicates. These phyllosilicates exhibit a plastic nature at appropriate water contents and solidify upon drying or firing.[57]

Ideal phyllosilicate structures comprise continuous tetrahedral (T) and octahedral (O) sheets that are condensed in either a 1:1 or 2:1 ratio, giving rise to an anisotropic repetition of TO or TOT layers.[11] The 1:1 layer structure consists of a repetition of sheets, with one having tetrahedral coordination and the next having octahedral coordination, whereas the 2:1 layer has one octahedral sheet sandwiched between two tetrahedral sheets. Within a tetrahedral sheet, each tetrahedron is connected to adjacent tetrahedra by sharing oxygen ions at three corners, forming a semi-infinite hexagonal mesh. In a sheet with octahedrally coordinated cations, the octahedra are interconnected by sharing edges consisting of neighboring oxygen ions. The edge-shared octahedra can be combined into two types of structures: a closely connected sheet with all six octahedral sites occupied, referred to as a trioctahedral sheet, or a loosely connected sheet with four of the six octahedral sites occupied, known as a dioctahedral sheet. The terms tri- or di-octahedral are based on the half unit-cell content, which indicates the number of occupied octahedral sites. Fig. 4 illustrates the representative constituent sheets and layer structures of clay materials. The representation here is conventional, showing the connections between the tetrahedra.

The clay structures can be either neutral or negatively charged (the latter requiring charge-compensating cations), depending on the cations in the sheets. Neutral layers occur when (a) the octahedral sheet comprises trivalent cations (*e.g.*, Al^{3+} and Fe^{3+}) in two octahedral sites with a vacant third octahedral site, or (b) when these cations are divalent (*e.g.*, Mg^{2+}, Fe^{2+}, Mn^{2+}) and occupy all three octahedral sites, or (c) when the sheet containing the tetrahedrally coordinated cations has Si^{4+} in each of the tetrahedra. Negatively charged layers are formed by (1) the substitution of Si^{4+} for Al^{3+} in tetrahedral sites, (2) the substitution of Al^{3+} or Mg^{2+} for cations with lower charges in octahedral sites, and (3) the presence of cation vacancies. In 1:1 phyllosilicates, the layers are nearly neutral; in 2:1 phyllosilicates, the layer charges are different and balanced with cations in the interlayer spaces. The variability in layer charge has significant implications for how clay binders influence the acidity of zeolite catalysts.

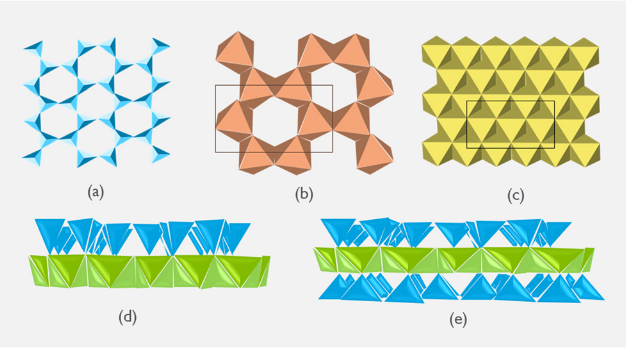

Fig. 4 Schematic representation of clay layer structures: (a) tetrahedral sheet (corner sharing); (b) dioctahedral sheet (edge sharing); (c) trioctahedral sheet (edge sharing); (d) 1:1 layer (TO); (e) 2:1 layer (TOT). Black rectangular frames in (b) and (c) denote unit cells.

Three types of clays are commonly used as binders for shaping zeolite catalysts, and we present details of each, as follows:

A. Kaolin group. Kaolin clays (those containing kaolinite) have dioctahedral 1:1 layer structures, and kaolinite, a representative polytype, is characterized by neutral layers with limited acidity associated with the absence of layer charges. The layers are connected by hydrogen bonds between siloxane and adjacent hydroxyl groups. When used as an additive in zeolite catalyst formulations (*e.g.*, in FCC catalysts), kaolin's role in modifying acidity is minor. The primary influence on the acidic matrix arises from the zeolite-binder interactions.[28,58] Kaolin is essentially inert, primarily filling large pores (and referred to as a "filler") and serving to create catalyst particles with desired density and attrition resistance. Upon heating, kaolinite undergoes a phase change that results in the formation of an impenetrable outer layer consisting of a dense phase with negligible pore volume, impeding access of reactants to interior zeolite acidic sites or metals.[26,35] Thus, zeolite catalysts made with kaolinite as the sole binder have little mesoporosity and low activities,[35,58] and they find few if any applications. On the other hand, kaolin is an ideal clay as a filler, facilitating the formation of densely packed and smooth spray-dried particles. This property is attributed to kaolin's hydrophilicity and the plate-like structure of its crystals, resulting in a high-solid content in sprayable slurries for fluid catalytic cracking applications.[41,59]

B. Smectite group. This group encompasses 2:1 phyllosilicates characterized by negatively charged layers with exchangeable cations in the interlayer spaces. Bentonite is one of these clays, and it consists mostly of montmorillonite. It is widely used as a binder in zeolite catalysts. Bentonite has a triple-layer structure, including a central sheet of AlO_6–

MgO_6 octahedra flanked by two sheets incorporating tetrahedrally coordinated silicon. To balance the negatively charged layers, cations such as Na^+ and Ca^{2+} are present in the interlayer spaces, along with adsorbed water.

When zeolites are agglomerated with bentonite, a notable reduction in the density of acid sites in zeolite catalysts is typically observed, because the Brønsted acid sites initially present in the zeolite are neutralized as they are replaced by the interlayer cations.[60] Zeolites with relatively high acid site densities may facilitate the ion-exchange of mobile cations.[31] Importantly, acid-site loss can be restored *via* subsequent ion-exchange (in other words, the ion-exchange reactions are reversible). Consequently, catalyst performance can be tuned by optimizing the degree of neutralization of acid sites in zeolites that are shaped by clay minerals incorporating exchangeable cations. The contents of the exchangeable metals can be reduced by ion-exchange with solutions of ammonium salts or mineral acids such as HCl or HNO_3.[31,61–63] Ion-exchange is a standard procedure for reactivating catalysts when acidity is desired. During reactivation, efforts should be made to minimize zeolite dealumination to maintain zeolite catalytic activity. Considering that neutralization and reactivation of acidic sites are reversible processes, severe loss of acidity (indicative of high neutralization efficiency) when clays are agglomerated is an indicator of efficient reactivation under suitable ion-exchange conditions. As an alternative to post-shaping modification, pre-shaping acid treatment of the clay binder is also effective in eliminating exchangeable cations. However, the acid-treated clay may exhibit slightly reduced binding capability.[27,64]

C. Palygorskite–sepiolite group. Palygorskite and sepiolite are non-planar phyllosilicates, each consisting of continuous two-dimensional sheets of linked tetrahedra, along with discontinuous octahedral sheets organized in a similar 2 : 1 phyllosilicate structure. The discontinuous octahedral strips are linked to the tetrahedral sheets through Si–O–Si bonds, with an average width of two linked pyroxene-like single chains in palygorskite and three linked chains in sepiolite (attapulgite is commonly used as a synonym for palygorskite). These clays find extensive use in a wide range of industrial applications.[65] Sepiolite is a magnesium phyllosilicate with trioctahedral sheet strips and minimal structural substitution, whereas palygorskite is a magnesium aluminum phyllosilicate with mixed dioctahedral and trioctahedral strips (incorporating Mg^{2+}, Al^{3+}, and/or Fe^{3+}). Palygorskite and sepiolite have some cation exchange capacity, although it is generally lower than that of smectite-group minerals. The chain structure in non-planar phyllosilicates results in a fibrous texture of particles, with channels (microporosity) aligned parallel to the fiber axis. All phyllosilicates have pores of varying sizes and shapes, and fibrous palygorskite and sepiolite have high surface areas and microporosity. The water-mediated exchange of cations, from the attapulgite binder to the zeolite, has been demonstrated in experiments showing that Mg^{2+} exchange occurs when the attapulgite and the zeolite are physically separated from each other in the presence of water.[27]

In summary, the diverse compositions and structures of clay minerals provide opportunities for fine-tuning the acidity of catalyst bodies to suit various applications. Some examples of zeolite-clay combinations that make good catalysts are the following: clays from the palygorskite–sepiolite group are used in formulating catalysts with moderately reduced acidities; thus, attapulgite and sepiolite enhance the zeolite-catalyzed alkene cycle in methanol-to-olefin (MTO) and methanol-to-hydrocarbon (MTH) reactions.[27,41] When additional Brønsted acid sites in the zeolite are advantageous, matrices with added kaolin are effective and used for the direct catalytic cracking of crude oil and for catalysis of the aromatic cycle in MTO reactions – the inert kaolin does not hinder the formation of new Brønsted acid sites *via* aluminum migration from the binder to the zeolite.[41,59] In cases of significant acid-site neutralization, non-activated zeolite-bentonite catalysts exhibit favorable selectivity for isomerization over cracking in contrast to the activated H-form zeolite.[29] Owing to the nature of the Lewis acid sites associated with the metal ions, clay-bound technological catalysts can still exhibit total densities of acid sites similar to those of the zeolite component alone, even when the numbers of Brønsted acid sites are significantly reduced (Fig. 2).

Silica

In contrast to the influences of alumina and clay binders, the influence of silica as a binder on catalyst acidity is complex and characterized by inconsistent reports. Most reports have indicated significant reductions in the Brønsted acid site density of silica-bound catalysts, and these reductions cannot be attributed just to the zeolite-silica compositions.[27,33,36,43] But there are other examples indicating that the total number of such sites is that predicted by the compositions of the binder and catalyst (Fig. 2).[44,45] There is a lack of systematic investigations of these combinations and much yet to be understood about how silica binders affect the acidities of zeolite catalysts.

When silica sols are prepared from sodium silicate by partial neutralization with acids or acidic aluminates, sodium ions are introduced. These residual cations may neutralize strong zeolite acid sites, but this effect is minimized when an acidic silica binder is employed. Reported data show that the total acidity of silica-bound zeolite coatings decreases in the following order when various silica sols are used: acidic silica-bound materials > neutral silica-bound materials > basic silica-bound materials; this result implies that the basic silica decreases the total acidity most.[66] Significantly, some reports indicate the emergence of new Brønsted acid sites in silica-bound zeolite catalysts; this result, which at first may appear counterintuitive, is attributed to the formation of new Si–O–Al bonds resulting from reactions between the silica binder and extra-framework aluminum species generated during dealumination. These reactions convert some Lewis acid sites into Brønsted acid sites at the zeolite-matrix interfaces.[67–69] Further, mobile silicon-containing species can fill defect sites (*e.g.*, silanol nests), enhancing the hydrothermal stability of zeolites.[67]

Influence of binder/matrix on porosity

A shaped zeolite catalyst is typically characterized by microporosity inherent to the zeolite framework and meso-/macro-porosity introduced by the formation of the matrix and the aggregation of zeolite and matrix particles. In an ideal shaping process, the binder material should hold the catalyst particles together, without significantly obstructing the access of reactants to the zeolite by structural changes to the microporosity occurring during calcination. The influence of the binder on microporosity is often represented by changes in micropore volumes (V_{mic}) determined by inert gas physisorption measurements characterizing the formed catalysts and the zeolites themselves. An important result is that, with a few exceptions (*e.g.*, microporous γ-Al_2O_3 derived from nanocrystalline boehmite or the fibrous palygorskite–sepiolite group clay minerals), the incorporation of a binder generally results in a matrix that makes only a limited contribution to the microporosity of a technological catalyst. Hence, assessments of the porosity should prominently include consideration of the dilution effect of the binder.

Fig. 5 presents a compilation of V_{mic} data from the literature characterizing calcined catalyst bodies, along with predicted values that account for the binder dilution. This data set includes results characterizing catalyst bodies shaped with various techniques (*e.g.*, extrusion, spray drying, and three-dimensional printing) and including various types of zeolites.[26,27,29,33,36,37,39,41–47,52,58,70–85] The experimental V_{mic} values generally align with the values predicted by the assumption of a simple binder dilution. Consequently, these physisorption results point to the lack of significant micropore blocking in the calcined zeolite catalysts. We emphasize that the characterization of porosity in standard physisorption experiments represents a quasi-equilibrium approach that may not fully capture changes in sorption rates when pores are accessible. Therefore, it is advisable to complement equilibrium sorption measurements with measurements of diffusivities of relevant sorbates to better assess the effect of the matrix on microporosity and diffusion in zeolites.[86]

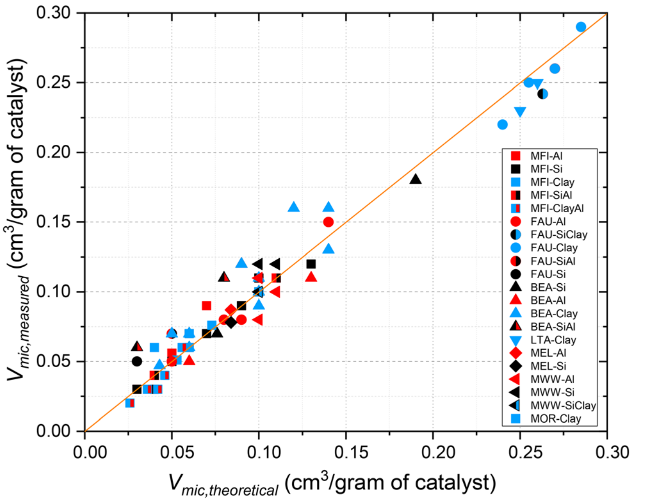

Fig. 5 Relationship between experimentally measured and theoretical V_{mic} by accounting for the binder dilution effect. The original data are collected from ref. 26, 27, 29, 33, 36, 37, 39, 41–47, 52, 58 and 70–85.

In technological catalysts, meso/macro pores arise primarily in the porous particulate matrices, which are typically derived from binders such as alumina or silica. In the petroleum refining industry, a porous acidic alumina matrix has become increasingly essential for designing catalysts used in cracking applications. The pores are needed for the pre-cracking of larger (heavier) hydrocarbons present in the oil feedstock. Among the various known transition aluminas, γ-Al_2O_3 stands out as the most widely used matrix, owing to its high surface area and acidic surface properties. When shaping zeolite catalysts, a colloidal boehmite binder is commonly used as a precursor to create the γ-Al_2O_3 matrix, which is formed by the high-temperature dehydration. The goal is to ensure a favorable dispersion of zeolite crystallites within a well-controlled porous matrix.

The colloidal boehmite is prepared by acid peptization using mineral acids. The acid peptizer's role is to deagglomerate alumina by adjusting the pH of the zeolite-binder paste to a value below the point of zero charge of boehmite, resulting in the creation of positively charged particles that repel each other. This process reduces the size of γ-Al_2O_3 aggregates and leads to a more uniformly dispersed alumina phase than would arise without it.

The quantity and strength of the acids used in this process affect the particle size distribution of γ-Al_2O_3. For example, employing a peptizer with a strong acid (*e.g.*, nitric acid) results in a higher degree of alumina de-agglomeration than otherwise, leading to smaller particles, which results in more mesopore volume and less macropore volume. The reduced macropore volume is advantageous for facilitating the diffusion in the pores by reducing so-called "macropore resistance" (*e.g.*, partially blocked, or isolated macropores, narrow macropores, irregular geometry, *etc.*)[87] while maintaining the mechanical strength of the catalyst body.

Furthermore, the use of a plasticizer can be beneficial for porosity modification. Plasticizers such as methylcellulose and polyols enhance the rheological properties of the paste and also contribute to the improved dispersion of alumina particles. Well-chosen combinations of peptizer and plasticizer can typically be expected to result in the formation of a matrix with a desirable pore size distribution.[28]

A recent noteworthy advance and an alternative to the regulation of porosity involves minimizing the silica component in the matrix to create binder-free zeolite catalysts.[43–45,70–74] The term binder-free zeolites implies the creation of monolithic zeolite catalysts in a crystallization process that transforms binder/matrix components into zeolites without compromising the overall catalyst structure. This zeolite formation is typically accomplished in the presence of organic structure-directing agents (OSDAs) under hydrothermal or dry-gel conversion conditions. In this procedure, the silica binders are partially dissolved, either in alkaline OSDA solutions or when exposed to OSDA and steam vapors, before undergoing crystallization to form the desired zeolite phase. The resulting catalysts exhibit significantly greater mechanical strength than catalysts with binder agglomerates, owing to stronger intercrystalline interactions and ordering of the material.

The newly formed zeolites are often silicon-rich and therefore hydrophobic, making them well-suited as catalysts for hydrocarbon conversion. Furthermore, when the concentration of alkaline solutions or organic-steam vapors is sufficiently high, intracrystalline mesopores are generated within the original zeolite phase by desilication. This treatment results in binder-free catalysts that are characterized by a wide range of porosities, including micro/meso porosity in the zeolites and meso/macro porosities originating from the agglomeration of the silica matrix and zeolites prior to binder conversion.

Influence of binders on metal–acid-group proximity

In the contemporary petroleum refining and petrochemical industries, the role of metal–acid bifunctional catalysis has become increasingly pivotal in a range of large-scale processes.[88] The roles of the noble metal nanoparticles are dehydrogenation of alkane reactants to give alkene intermediates and hydrogenation of isomerized and/or cracked alkene intermediates to give alkane products (and hydrogenation of coke precursors); in contrast, the acid sites of the zeolite catalyze isomerization (often a desired reaction) and cracking (often undesired) of the alkene intermediates. In metal–acid bifunctional catalysis, the nanoscale spatial arrangement of the metal nanoparticles, which can be localized either on the binder or the zeolite as a support, and the zeolite acid sites profoundly influence the activity and selectivity of the catalysis. Indeed, binders, as alternative supports for the metal nanoparticles, introduce an additional layer of complexity to the structure–property relationships when incorporated into a metal/zeolite bifunctional catalyst. Assuming minimal mobility of the metal species during catalysis, intimate metal–acid proximity is achieved when metal nanoparticles are deposited within zeolite pore channels (metal-in-zeolite). In this configuration, reaction intermediates traverse the micropores between metal and acid sites, over diffusion lengths ranging from several to several dozens of nanometers, up to half the crystal size. Alternatively, metal nanoparticles can be deposited on the binder (metal-on-binder), resulting in a relatively longer diffusion path between the metal and acid sites that are now on different support particles. This configuration providing a separation between metal and zeolite acid sites serves two crucial purposes: (1) preventing micropore blockage by metal clusters and (2) enhancing the accessibility (degree of openness) and therefore the utilization of the metal sites.

To investigate the impact of binders on metal–acid proximity, we focus on a key application—the hydroisomerization of linear alkanes with bifunctional catalysts (whereby hydrocracking is a less desired competitive reaction). A widely investigated class of industrial catalyst comprises a noble metal (*e.g.*, platinum) paired with a solid acid (*e.g.*, a zeolite) and γ-alumina as the binder. In platinum-acid bifunctional catalysis, the activity and selectivity in alkane hydroisomerization hinge on the balance of metal–acid sites and the proximity of these sites. The metal–acid site balance is quantified by the ratio of accessible platinum atoms to acid sites ($C_{\mathrm{Pt}}/C_{\mathrm{Acid}}$ or $C_{\mathrm{Pt}}/C_{\mathrm{H+}}$), with the ideal being a "well-balanced" catalyst achieved at sufficiently high metal loadings.[89] This balance may ensure an optimal utilization of the acidic groups in the zeolite, without excessive adsorption of alkene intermediates on these sites, which leads to consecutive isomerization and cracking.[90] Generally, for linear alkanes, the isomerization is considered to be rate limiting, with hydrogenation/dehydrogenation reactions at the metal sites being quasi-equilibrated, even when the metal loading is as low as 0.01–0.05 wt%.[2,91] As described below, the nanoscale spatial arrangement, or metal–acid site proximity, can profoundly influence the activity and selectivity of the bifunctional catalysts.

Contrary to the classical intimacy criterion favoring closer proximity, recent investigations have led to the proposed concept termed "nanoscale intimacy" with an optimal metal–acid distance of several hundred nanometers required in certain instances for maintaining high isomerization selectivity and activity.[2,39,91,92] Achieving nanoscale intimacy is more likely with zeolites of sub-micron particle sizes when metal nanoparticles are placed on the alumina binder in intimate contact with the zeolite.

For example, the deposition of platinum on a γ-Al_2O_3 binder (for nanoscale intimacy) rather than on the Y zeolite was investigated with catalysts used for hydroisomerization of normal and branched C_{10}–C_{19} alkanes.[92] With *n*-C_{10} as the reactant, higher activity was observed for platinum on the alumina rather than for platinum on the zeolite. Numerous related data for a less sterically bulky *n*-C_7 alkane as the reactant are also in line with this previous observation, spanning a variety of zeolite framework structures.[2,91] In contrast, when the reactant was pristane (a multiply branched C_{19} alkane), the opposite trend was observed (the comparison catalysts each consisted of the same amounts of Pt/Y zeolite/γ-Al_2O_3 binder). Comparable results characterizing the *n*-C_{19} reactant – a linear alkane that is in between *n*-C_{10} and pristane in steric bulk – showed that it was also in the middle in terms of its reactivity preferences, favoring neither platinum placement on the zeolite nor on the alumina (*i.e.,* both catalysts were the same). Yet, contrary to the trends described above, the selectivity trends for the *n*-C_{19} alkane reactant were different from those observed for *n*-C_{10} and pristane reactants, for which the limiting selectivities at a low conversion were both unaffected by platinum location. The contrasting patterns characterizing catalytic activities and selectivities are not simply explained, with the data pointing to quite some degree of complexity of the reaction kinetics/transport phenomena.[91,92]

Experiments characterizing the influence of transport were done with *n*-C_7 as the reactant and with HMOR as the zeolite, chosen to be small particles (200 nm) on the one hand and micron-sized crystallites on the other, and, again, γ-Al_2O_3 was the binder.[91] The data demonstrate the activity/conversion advantage to placing platinum within the zeolite when there are strong intrazeolite diffusion limitations, in order to minimize the distance needed to travel between metal and acid sites; but such close proximity between platinum and acid sites is detrimental for the isomer selectivity because of the undesired cracking reactions (Fig. 6a and b). Additional results providing evidence of intraparticle transport limitations were obtained with catalysts containing large USY zeolite aggregates (~20 μm); the corresponding large average metal–acid distance negatively affected the catalyst performance when the platinum was present in the binder compared with when it was located in the zeolite.[93]

In some examples, however, the intraparticle transport limitations were negligible in the hydroconversion of ethylcyclohexane, and so the activity and selectivity of hydroconversion were unaffected by the metal–acid site distances, fulfilling the intimacy criterion up to a 1 μm distance.[94] The same outcome was observed for *n*-C_7 conversion with a medium-pored zeolite, HZSM-5, presenting such high diffusional barriers that there was a complete lack of control of catalyst performance with the separation distance between the platinum and zeolite acid sites, even when bulk physical mixtures of γ-Al_2O_3 binder and HZSM-5 were used.[39]

Yet transport limitations are not sufficient to elucidate the phenomena in this bifunctional catalysis, as illustrated by the example below, which emphasizes the importance of catalyst materials properties. When a low platinum loading of only 0.01 wt% was used, platinum in HMCM-22 zeolite was much more active than the alternative of a catalyst with platinum localized on the alumina binder, with the latter catalyst giving more cracking and less hydroisomerization products (Fig. 6c). The catalytic results were explained by metallic platinum nanoparticles residing at the pore mouths of the zeolite. Such a location for platinum was preferred over the alumina binder, which at such a low loading resulted in a more nearly atomically dispersed platinum, which is cationic and less active for hydrogenation/dehydrogenation than the nanoparticles.[2]

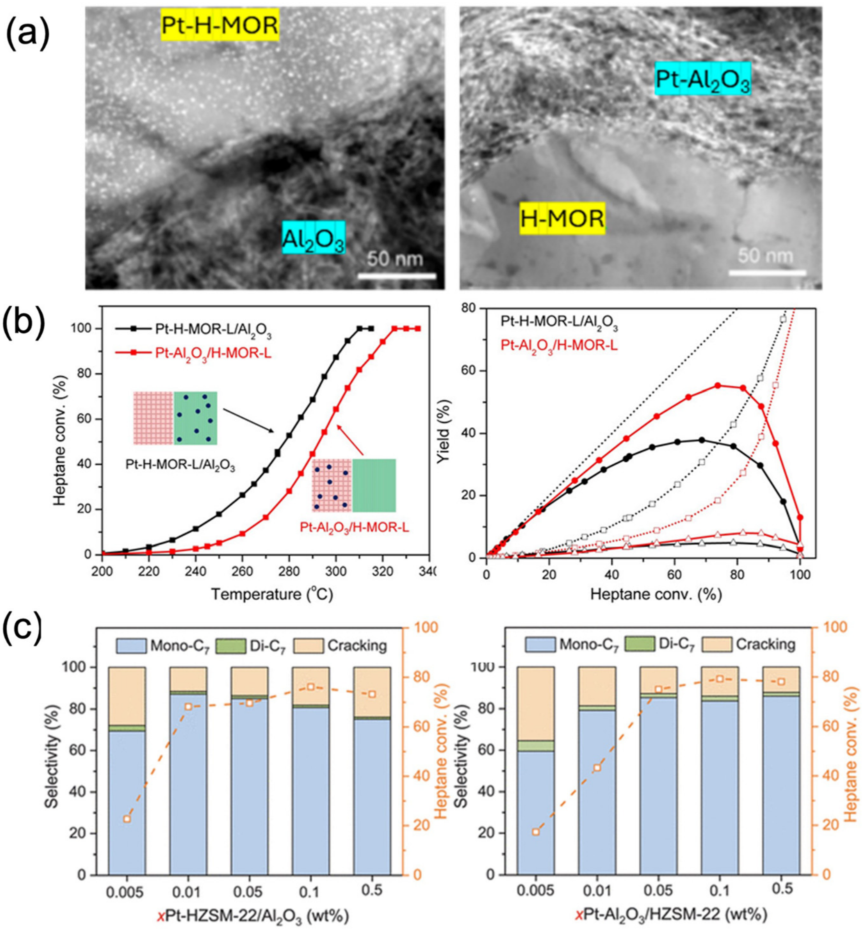

Fig. 6 (a) Deposition of platinum on either the zeolite phase (Pt-HMOR) or the alumina support (Pt–Al_2O_3). (b) Effect of the platinum placed on the alumina (Al_2O_3) or the micron-sized mordenite zeolite (HMOR-L) on *n*-heptane hydroconversion: conversion *vs.* reaction temperature or total isomer yields. Fig. 6(a) and (b) are adapted from ref. 91 with permission. Copyright 2020 Wiley-VCH Verlag GmbH & Co. (c) Effect of platinum locations and loadings on *n*-heptane hydroconversion on Pt-zeolite bifunctional catalysts: Pt-HZSM-22/Al_2O_3 (Pt on the HZSM-22 zeolite); Pt–Al_2O_3/HZSM-22 (Pt on the alumina binder). Adapted from ref. 2. Copyright 2022 American Association for the Advancement of Science.

The data summarized above point to complex interplays of transport and reaction that involve combinations of pore-mouth catalysis, intrapore transport, surface diffusion barriers,[95–100] and speciation of metals on various surfaces at various loadings for various reactions. These reactions include syngas conversions to alkenes, gasoline, and aromatics through metal oxide-zeolite tandem catalysis *via* methanol. We posit that there are significant opportunities for further elucidating and optimizing of the roles of nanoscale separation (and related metal localization on zeolites *vs.* binders) in bifunctional catalysts, with potential ramifications even to biological catalysts, which are thought to exhibit reactant channeling.[101] For example, in syngas to aromatics reactions, effective removal of adsorbed hydrogen species from the last dehydrogenation step is crucial, which is accomplished by generating gaseous hydrogen on metal oxide sites to prevent the hydrogenation of alkene intermediates. Therefore, closely organized functional sites are imperative, facilitating a synergistic tandem route involving the transfer of intermediate species,[102] and this type of system may also exhibit rich nanoscale proximity effects involving the binder and location of metal sites.

Aluminum phosphate binder/matrix

Aluminum phosphate ($AlPO_4$) is used as a binder to improve strength and reduce porosity in ceramic coatings used in refractory ceramics.[103] $AlPO_4$ is also used as a binder in zeolite catalysts, imparting the following valuable characteristics:[48]

1. The $AlPO_4$ binder creates a dense matrix affixed to zeolite crystallites, exhibiting minimal surface area. The porosity of the matrix depends on the dimensions of embedded zeolite particles.

2. In contrast to an Al_2O_3 binder, the $AlPO_4$ binder is not a source of aluminum migration into the zeolite.

3. The $AlPO_4$ matrix lacks catalytic activity, distinguishing it from active Al_2O_3 matrices (*e.g.*, γ-Al_2O_3).

$AlPO_4$ matrices can be derived from commercial $AlPO_4$ binders or in various syntheses, including sol–gel syntheses or boehmite peptization with phosphorous acid. Post-synthetic modifications involving phosphorus-containing species or direct synthesis contribute to the formation of $AlPO_4$ matrices.

The modification of Al_2O_3-bound zeolite catalysts with phosphorus-containing species, such as H_3PO_4 or $NH_4H_2PO_4$, is characterized by interactions between phosphorus and both the zeolite and Al_2O_3 binder phases.[84,104,105] In shaped catalysts incorporating high-silica zeolites, the predominant phosphorus–aluminum interaction occurs between phosphorus-containing species and binder aluminum, resulting in a reduction in the number of Lewis acid sites. Reported results also show a decrease in the density of Brønsted acid sites in zeolites following phosphorus incorporation as a result of the condensation of bridging hydroxyl groups with POH groups, partially neutralizing the original Brønsted acid sites; this loss is reversible and can be restored by steaming or repetitive ion-exchange steps.[106,107] The reduction in the density of zeolite Brønsted acid sites and the reversibility of phosphorus–aluminum interactions align with documented effects of phosphorus modification on acidity in powder zeolites.[108] Consequently, the phosphate-containing matrix typically leads to a decrease in total acidity and the ratio of strong to weak acid sites.

These alterations are advantageous for weak-acid-catalyzed reactions, such as methanol conversion to light alkenes. The catalytic outcomes include enhanced methanol conversion, increased yields of light alkenes and improved resistance to coking. Moreover, the bonding between phosphorus and zeolite framework aluminum enhances the hydrothermal stability of zeolites against steaming-induced dealumination.[48,83,104,109]

Significant distinctions in both the textural and acidic properties contrasting Al_2O_3 and $AlPO_4$ matrices become apparent when phosphoric acid is used for boehmite peptization.[110] Phosphorus interacts with aluminum species in the boehmite binder, inducing a transformation in the morphology of alumina crystallites. This change results in the formation of an amorphous aluminophosphate gel, which is subsequently converted into a crystalline $AlPO_4$ matrix (containing cristobalite and tridymite) through the condensation of OH groups during calcination. The crystallization of $AlPO_4$ is a densification process, leading to a notable reduction in the surface area and porosity of the matrix. With an increase in the aluminum content in the zeolite, the interaction between phosphorus and aluminum in zeolites becomes more pronounced. This point is exemplified by a USY zeolite/$AlPO_4$ catalyst, wherein the phase transformation temperature of $AlPO_4$ is altered, suppressing its crystallization under severe steaming conditions (800 °C). The retention of an amorphous $AlPO_4$ phase contributes to the porous nature of the resulting USY zeolite/$AlPO_4$ catalyst, along with well-documented advantages such as enhanced framework aluminum retention post-steaming.[107] It appears that the energetic favorability of the bonding involving zeolite aluminum and phosphate oxygen groups surpasses that of the condensation of hydroxyl groups, which typically induces crystallization and densification of the matrix.

P–OH self-condensation in $AlPO_4$ matrices and phosphorus–zeolite interactions may allow tuning of the porosity of the matrix and thereby the rates of transport of key species such as catalytic reaction intermediates. A proposed mechanism for migration of amorphous aluminophosphate species into zeolite silanol nest defects for alumination[84] may be responsible for the formation of Brønsted acid sites that were observed after phosphorus modification of an alumina-bound zeolite Beta catalyst, with a remarkable 58% increase in the density of these acid sites. There is more to learn about the chemistry of zeolite catalysts incorporating $AlPO_4$ matrices, and, although no aluminum migration from the matrix to the zeolite crystallites evidently occurs, it would be worthwhile to do further work to elucidate the nature of any migrating species and their effect on total Brønsted acid site density (even including weak Brønsted acid sites arising from aluminophosphate species), as the surface of aluminum phosphate can exhibit acidity.[48,106,107]

Concluding remarks & future outlook

Binders are present in most industrial zeolite catalysts, playing pivotal roles in shaping the structure and porosity of the catalyst particles and influencing their activity, selectivity, and mechanical strength. Important binders used in zeolite catalysts include clays and alumina, along with silica and $AlPO_4$. The binders influence the acidity and porosity, which affect the catalytic properties; and metals such as platinum in the catalysts can reside on the binder or within the zeolite pores, with the contrasting distances for transport of reaction intermediates between the metal and acid sites being important in influencing catalyst performance.

Alumina binders offer catalytic activity complementing that of the zeolite and, with their relatively large pores, may facilitate pre-cracking of hydrocarbon molecules that are too large to fit into the zeolite micropores; the alumina may also serve to trap compounds that act as poisons of zeolites.[25] Clays are finding increasing applications in zeolite catalysts as versatile matrices/fillers, offering structural diversity and adjustable acidity. Besides serving as binders, silica matrices are used to create binder-free catalysts with enhanced mechanical strength. Some authors have suggested that reactions of amorphous silica with zeolite crystallites may counteract zeolite pore-blocking by binders, but equilibrium physisorption results suggest no apparent micropore blocking.[43,70,72–74] Work employing dynamic (as opposed to equilibrated) adsorption is needed to clarify these points.

In evaluating the properties of zeolite catalysts that incorporate binders, it is prudent to make thorough comparisons that account not only for the physical and catalytic properties of the formed particles, but also to characterize the properties of the zeolite and binder components in the materials and in the individual components alone that have undergone identical treatments. This approach allows for the exploration of structural transformations that binders can undergo during calcination. In catalyst performance evaluations, it is essential to establish benchmarks that facilitate the assessment of the catalytic roles of the matrices. Equilibrium adsorption measurements characterizing the shaped catalysts are essential—bolstered by rate measurements—to provide insights into their potential influences of transport phenomena in catalysis.

The locations of metals in bifunctional metal–zeolite catalysts incorporating binders influence the performance of some catalysts. As summarized above, the issues are complex and not fully resolved, and require a deeper understanding of surface barriers to mass transport in zeolites.[95–100] A further goal is to elucidate the migration of metal species within the catalysts, especially when the catalysts undergo cycles of reaction in reducing atmospheres and regeneration by coke burning in oxidizing atmospheres—during these cycles, the metals may undergo changes in oxidation state, degree of aggregation, and location. For example, platinum in zeolite catalysts migrates as platinum nanoparticles or clusters are oxidatively fragmented and then reduced to again become aggregated.[111] During high-temperature oxidizing regeneration, platinum cluster/nanoparticle fragmentation occurs, leading to the formation and stabilization of atomically dispersed Pt^{2+} ions in close proximity to paired aluminum sites within the zeolite; reduction leads to platinum migration and cluster/nanoparticle formation.[112] When metal oxides are present (*e.g.*, as binders), they may affect the metal mobility and its various locations, thereby affecting the transport limitations that may influence catalyst performance. Further, mobile metal ions neutralize acid sites in zeolites, thereby altering catalyst performance.[113] The consequences of the metal migration, and especially the neutralization of Brønsted acid sites in zeolites, may often be essentially irreversible. Therefore, stabilizing the performance of metal oxide/zeolite catalysts may involve strategies such as replacing mobile elements, spatially separating reactive sites, or immobilizing reactive components through compounding.[114]

These issues are ripe for further investigation, and the evolving challenges present focal points for future research, particularly when the zeolite catalysts incorporate binder matrices. Separately, advances in catalyst characterization techniques have made it possible to visualize single catalyst particles with high resolution and sensitivity.[115] This progress, coupled with advanced spectroscopic methods, is expected to provide continuing new insights into the composition, nature, location, and distribution of active sites in zeolites and catalyst matrices, all to the benefit of the tailoring and design of commercial zeolite catalysts.[116–120]

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this article.

Author contributions

Conceptualization, K. Z.; investigation, K. Z.; writing – original draft, K. Z., X. J., M. J. F., A. K; writing – review & editing, M. S., M. AA., M. AA., M. AJ., E. AS., W. AS., B. C. G., and A. K.

Conflicts of interest

The authors declare no competing interests.

Acknowledgements

AK and BCG gratefully acknowledge funding from the CeRCaS National Science Foundation IUCRC.

References

1 T. W. van Deelen, C. Hernández Mejía and K. P. de Jong, Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity, *Nat. Catal.*, 2019, **2**(11), 955–970.

2 K. Cheng, L. C. Smulders, L. I. van der Wal, J. Oenema, J. D. Meeldijk, N. L. Visser, G. Sunley, T. Roberts, Z. Xu and E. Doskocil, Maximizing noble metal utilization in solid catalysts by control of nanoparticle location, *Science*, 2022, **377**(6602), 204–208.

3 B. A. Mehrabadi, S. Eskandari, U. Khan, R. D. White and J. R. Regalbuto, A review of preparation methods for supported metal catalysts, *Adv. Catal.*, 2017, **61**, 1–35.

4 F. Pinna, Supported metal catalysts preparation, *Catal. Today*, 1998, **41**(1–3), 129–137.

5 B. E. Koel and J. Kim, Promoters and Poisons, in *Handbook of Heterogeneous Catalysis*, 2008, pp. 1593–1624.

6 Z. Asgar Pour, M. M. Abduljawad, Y. A. Alassmy, L. Cardon, P. H. M. Van Steenberge and K. O. Sebakhy, A Comparative Review of Binder-Containing Extrusion and Alternative Shaping Techniques for Structuring of Zeolites into Different Geometrical Bodies, *Catalysts*, 2023, **13**(4), 656.

7 K. Yang, D. Zhang, M. Zou, L. Yu and S. Huang, The Known and Overlooked Sides of Zeolite-Extrudate Catalysts, *ChemCatChem*, 2021, **13**(6), 1414–1423.

8 J. Hargreaves and A. Munnoch, A survey of the influence of binders in zeolite catalysis, *Catal. Sci. Technol.*, 2013, **3**(5), 1165–1171.

9 S. Mitchell, N.-L. Michels and J. Pérez-Ramírez, From powder to technical body: the undervalued science of catalyst scale up, *Chem. Soc. Rev.*, 2013, **42**(14), 6094–6112.

10 R. Bingre, B. Louis and P. Nguyen, An overview on zeolite shaping technology and solutions to overcome diffusion limitations, *Catalysts*, 2018, **8**(4), 163.

11 F. Bergaya and G. Lagaly, General introduction: clays, clay minerals, and clay science, in *Developments in Clay Science*, Elsevier, 2013, vol. 5, pp. 1–19.

12 F. Rascón, R. Wischert and C. Copéret, Molecular nature of support effects in single-site heterogeneous catalysts: silica vs. alumina, *Chem. Sci.*, 2011, **2**(8), 1449–1456.

13 T. Pu, H. Tian, M. E. Ford, S. Rangarajan and I. E. Wachs, Overview of Selective Oxidation of Ethylene to Ethylene Oxide by Ag Catalysts, *ACS Catal.*, 2019, **9**(12), 10727–10750.

14 E. T. Vogt, G. T. Whiting, A. D. Chowdhury and B. M. Weckhuysen, Zeolites and zeotypes for oil and gas conversion, *Adv. Catal.*, 2015, **58**, 143–314.

15 A. Primo and H. Garcia, Zeolites as catalysts in oil refining, *Chem. Soc. Rev.*, 2014, **43**(22), 7548–7561.

16 W. Vermeiren and J.-P. Gilson, Impact of zeolites on the petroleum and petrochemical industry, *Top. Catal.*, 2009, **52**(9), 1131–1161.

17 M. E. Davis and R. F. Lobo, Zeolite and molecular sieve synthesis, *Chem. Mater.*, 1992, **4**(4), 756–768.

18 C. S. Cundy and P. A. Cox, The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time, *Chem. Rev.*, 2003, **103**(3), 663–702.

19 B. M. Weckhuysen and J. Yu, Recent advances in zeolite chemistry and catalysis, *Chem. Soc. Rev.*, 2015, **44**(20), 7022–7024.

20 M. Moliner, F. Rey and A. Corma, Towards the rational design of efficient organic structure-directing agents for zeolite synthesis, *Angew. Chem., Int. Ed.*, 2013, **52**(52), 13880–13889.

21 A. J. Jones, R. T. Carr, S. I. Zones and E. Iglesia, Acid strength and solvation in catalysis by MFI zeolites and effects of the identity, concentration and location of framework heteroatoms, *J. Catal.*, 2014, **312**, 58–68.

22 M. L. Sarazen, E. Doskocil and E. Iglesia, Catalysis on solid acids: Mechanism and catalyst descriptors in oligomerization reactions of light alkenes, *J. Catal.*, 2016, **344**, 553–569.

23 R. Gounder and E. Iglesia, The roles of entropy and enthalpy in stabilizing ion-pairs at transition states in zeolite acid catalysis, *Acc. Chem. Res.*, 2012, **45**(2), 229–238.

24 A. J. Jones, S. I. Zones and E. Iglesia, Implications of transition state confinement within small voids for acid catalysis, *J. Phys. Chem. C*, 2014, **118**(31), 17787–17800.

25 E. T. Vogt and B. M. Weckhuysen, Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis, *Chem. Soc. Rev.*, 2015, **44**(20), 7342–7370.

26 M. E. Velthoen, A. L. Paioni, I. E. Teune, M. Baldus and B. M. Weckhuysen, Matrix Effects in a Fluid Catalytic Cracking Catalyst Particle: Influence on Structure, Acidity, and Accessibility, *Chem. – Eur. J.*, 2020, **26**(52), 11995.

27 N.-L. Michels, S. Mitchell and J. Perez-Ramirez, Effects of binders on the performance of shaped hierarchical MFI zeolites in methanol-to-hydrocarbons, *ACS Catal.*, 2014, **4**(8), 2409–2417.

28 G. T. Whiting, S.-H. Chung, D. Stosic, A. D. Chowdhury, L. I. Van Der Wal, D. Fu, J. Zecevic, A. Travert, K. Houben and M. Baldus, Multiscale mechanistic insights of shaped catalyst body formulations and their impact on catalytic properties, *ACS Catal.*, 2019, **9**(6), 4792–4803.

29 A. de Lucas, J. L. Valverde, P. Sánchez, F. Dorado and M. J. Ramos, Influence of the binder on the n-octane hydroisomerization over palladium-containing zeolite catalysts, *Ind. Eng. Chem. Res.*, 2004, **43**(26), 8217–8225.

30 A. de Lucas, J. L. Valverde, P. Sánchez, F. Dorado and M. J. Ramos, Hydroisomerization of n-octane over platinum catalysts with or without binder, *Appl. Catal., A*, 2005, **282**(1–2), 15–24.

31 F. Dorado, R. Romero and P. Cañizares, Hydroisomerization of n-butane over Pd/HZSM-5 and Pd/Hβ with and without binder, *Appl. Catal., A*, 2002, **236**(1–2), 235–243.

32 Y. Zhang, Y. Zhou, A. Qiu, Y. Wang, Y. Xu and P. Wu, Effect of alumina binder on catalytic performance of PtSnNa/ZSM-5 catalyst for propane dehydrogenation, *Ind. Eng. Chem. Res.*, 2006, **45**(7), 2213–2219.

33 K.-Y. Lee, H.-K. Lee and S.-K. Ihm, Influence of catalyst binders on the acidity and catalytic performance of HZSM-5 zeolites for methanol-to-propylene (MTP) process: single and binary binder system, *Top. Catal.*, 2010, **53**(3), 247–253.

34 N. Xue, R. Olindo and J. A. Lercher, Impact of forming and modification with phosphoric acid on the acid sites of HZSM-5, *J. Phys. Chem. C*, 2010, **114**(37), 15763–15770.

35 X. Du, X. Kong and L. Chen, Influence of binder on catalytic performance of Ni/HZSM-5 for hydrodeoxygenation of cyclohexanone, *Catal. Commun.*, 2014, **45**, 109–113.

36 I. Gerzeliev, V. Zhmylev, D. Khusaimova, A. Shkuropatov, E. Knyazeva, O. Ponomareva, I. Ivanova and A. Maksimov, Effect of binder on the properties of MWW zeolite catalysts in benzene alkylation with propylene, *Pet. Chem.*, 2019, **59**(7), 695–700.

37 O. Ponomareva, T. Bok, E. Andriako, A. Shkuropatov, E. Knyazeva, I. Dobryakova and I. Ivanova, Comparative study of catalysts based on zeolites BEA and MWW in benzene alkylation with propylene, *Pet. Chem.*, 2019, **59**(8), 918–924.

38 O. Ben Moussa, L. Tinat, X. Jin, W. Baaziz, O. Durupthy, C. Sayag and J. Blanchard, Heteroaggregation and selective deposition for the fine design of nanoarchitectured bifunctional catalysts: application to hydroisomerization, *ACS Catal.*, 2018, **8**(7), 6071–6078.

39 J. Oenema, J. Harmel, R. P. r. Vélez, M. J. Meijerink, W. Eijsvogel, A. Poursaeidesfahani, T. J. Vlugt, J. Zečević and K. P. De Jong, Influence of nanoscale intimacy and zeolite micropore size on the performance of bifunctional catalysts for n-heptane hydroisomerization, *ACS Catal.*, 2020, **10**(23), 14245–14257.

40 F. M. Almulla, S. A. Ali, M. R. Aldossary, E. I. Alnaimi, V. I. Zholobenko, A. bin Jumah and A. A. Garforth, On the influence of alumina as a binder on the performance of Pt-Beta catalyst during the transalkylation of toluene and 1, 2, 4-Trimethylbenzene, *Microporous Mesoporous Mater.*, 2021, **320**, 111095.

41 T. Shoinkhorova, A. Dikhtiarenko, A. Ramirez, A. Dutta Chowdhury, M. Caglayan, J. Vittenet, A. Bendjeriou-Sedjerari, O. S. Ali, I. Morales-Osorio and W. Xu, Shaping of ZSM-5-based catalysts via spray drying: effect on methanol-to-olefins performance, *ACS Appl. Mater. Interfaces*, 2019, **11**(47), 44133–44143.

42 W. Chu, S. Liu, W. Xin, Y. Wang, Z. Liu, C. Yang, Y. Wang, L. Xu, X. Li and X. Zhu, Effect of Binder Type on MWW-Based Catalysts for the Liquid-Phase Alkylation Reaction of Benzene with Ethylene, *Ind. Eng. Chem. Res.*, 2022, **61**(7), 2693–2700.

43 J. Liu, S. Li, Z. Zhang, N. Fusi, C. Liu, G. Xiong, G. Vilé and N. He, Structured Binder-Free Al-β Zeolite for Acid-Catalyzed Dehydration, *ACS Appl. Nano Mater.*, 2021, **4**(11), 11997–12005.

44 W. Zhang, S. Zhang, W. Xin, H. Liu, Y. Shang, X. Zhu, S. Liu and L. Xu, Shaped binderless ZSM-11 zeolite catalyst prepared via a dry-gel conversion method: Characterization and application for alkylation of benzene with dimethyl ether, *J. Energy Chem.*, 2017, **26**(3), 380–389.

45 W. Zhang, S. Gao, S. Xie, H. Liu, X. Zhu, Y. Shang, S. Liu, L. Xu and Y. Zhang, A shaped binderless ZSM-11 zeolite catalyst for direct amination of isobutene to tert-butylamine, *Chin. J. Catal.*, 2017, **38**(1), 168–175.

46 G. T. Whiting, F. Meirer, M. M. Mertens, A. J. Bons, B. M. Weiss, P. A. Stevens, E. de Smit and B. M. Weckhuysen, Binder Effects in SiO2-and Al2O3-Bound Zeolite ZSM-5-Based Extrudates as Studied by Microspectroscopy, *ChemCatChem*, 2015, **7**(8), 1312.

47 L. Lakiss, J.-P. Gilson, V. Valtchev, S. Mintova, A. Vicente, A. Vimont, R. Bedard, S. Abdo and J. Bricker, Zeolites in a good shape: Catalyst forming by extrusion modifies their performances, *Microporous Mesoporous Mater.*, 2020, **299**, 110114.

48 J. Freiding and B. Kraushaar-Czarnetzki, Novel extruded fixed-bed MTO catalysts with high olefin selectivity and high resistance against coke deactivation, *Appl. Catal., A*, 2011, **391**(1–2), 254–260.

49 D. S. Shihabi, W. E. Garwood, P. Chu, J. N. Miale and R. M. Lago, Aluminum insertion into high-silica zeolite frameworks. II: Binder activation of high-silica ZSM-5, *J. Catal.*, 1985, **93**(2), 471–474.

50 C. D. Chang, C. T. Chu, J. N. Miale, R. F. Bridger and R. B. Calvert, Aluminum insertion into high silica zeolite frameworks. 1. Reaction with aluminum halides, *J. Am. Chem. Soc.*, 1984, **106**(26), 8143–8146.

51 K. Yamagishi, S. Namba and T. Yashima, Preparation and acidic properties of aluminated ZSM-5 zeolites, *J. Catal.*, 1990, **121**(1), 47–55.

52 S. Zhou, C. Zhang, Y. Li, Y. Luo and X. Shu, Effect of Particle Size of Al_2O_3 Binders on Acidity and Isobutane–Butene Alkylation Performance of Zeolite Y-Based Catalysts, *Ind. Eng. Chem. Res.*, 2020, **59**(13), 5576–5582.

53 L. Xu, A. Okrut, T. Rea, K. Chaudhuri, J. Han, A. Kuperman and A. Katz, Control of Zeta Potential of Hierarchical Mesoporous Zeolite Y via Inorganic Surface Modification without Micropore Blockage and Phase Separation, *Cryst. Growth Des.*, 2023, **23**(8), 5601–5613.

54 J. R. Regalbuto, in *Catalyst Preparation: Science and Engineering*, ed. J. Regalbuto, CRC Press, 2016, ch.13, pp. 297–318.

55 V. R. Choudhary, P. Devadas, A. K. Kinage and M. Guisnet, Influence of binder on the acidity and performance of H-Gallosilicate (MFI) zeolite in propane aromatization, *Appl. Catal., A*, 1997, **162**(1–2), 223–233.

56 S. Zhou, C. Zhang, Y. Li, B. Shao, Y. Luo and X. Shu, A facile way to improve zeolite Y-based catalysts' properties and performance in the isobutane–butene alkylation reaction, *RSC Adv.*, 2020, **10**(49), 29068–29076.

57 S. Guggenheim and R. Martin, Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees, *Clays Clay Miner.*, 1995, **43**(2), 255–256.

58 G. T. Whiting, A. D. Chowdhury, R. Oord, P. Paalanen and B. M. Weckhuysen, The curious case of zeolite–clay/binder interactions and their consequences for catalyst preparation, *Faraday Discuss.*, 2016, **188**, 369–386.

59 M. Alabdullah, T. Shoinkhorova, A. Rodriguez-Gomez, A. Dikhtiarenko, J. Vittenet, O. S. Ali, I. Morales-Osorio, W. Xu and J. Gascon, Composition-performance Relationships in Catalysts Formulation for the Direct Conversion of Crude Oil to Chemicals, *ChemCatChem*, 2021, **13**(7), 1806–1813.

60 Z. Asgar Pour, R. Koelewijn, M. El Hariri El Nokab, P. C. van der Wel, K. O. Sebakhy and P. P. Pescarmona, Binder-free

Zeolite Beta Beads with Hierarchical Porosity: Synthesis and Application as Heterogeneous Catalysts for Anisole Acylation, *ChemCatChem*, 2022, **14**(19), e202200518.

61 K. Zhang, S. Fernandez, J. A. Lawrence III and M. L. Ostraat, Organotemplate-free β zeolites: From zeolite synthesis to hierarchical structure creation, *ACS Omega*, 2018, **3**(12), 18935–18942.

62 J. Scherzer, The preparation and characterization of aluminum-deficient zeolites, *ACS Symp. Ser.*, 1984, 157–200.

63 B. Yilmaz, U. Müller, M. Feyen, S. Maurer, H. Zhang, X. Meng, F.-S. Xiao, X. Bao, W. Zhang and H. Imai, A new catalyst platform: zeolite Beta from template-free synthesis, *Catal. Sci. Technol.*, 2013, **3**(10), 2580–2586.

64 M. Romero, J. Calles, A. Rodríguez and A. De Lucas, Acidity modification during the agglomeration of ZSM-5 with montmorillonite, *Microporous Mater.*, 1997, **9**(5–6), 221–228.

65 E. Galán, Properties and applications of palygorskite-sepiolite clays, *Clay Miner.*, 1996, **31**(4), 443–453.

66 G. Liu, J. Guo, F. Meng, X. Zhang and L. Wang, Effects of colloidal silica binder on catalytic activity and adhesion of HZSM-5 coatings for structured reactors, *Chin. J. Chem. Eng.*, 2014, **22**(8), 875–881.

67 N.-Y. Chen, M.-C. Liu, S.-C. Yang, H.-S. Sheu and J.-R. Chang, Impacts of binder-zeolite interactions on the structure and surface properties of NaY–SiO_2 extrudates, *Ind. Eng. Chem. Res.*, 2015, **54**(34), 8456–8468.

68 U. Etim, P. Bai, Y. Wang, F. Subhan, Y. Liu and Z. Yan, Mechanistic insights into structural and surface variations in Y-type zeolites upon interaction with binders, *Appl. Catal., A*, 2019, **571**, 137–149.

69 A. Corma, M. Grande, V. Fornes, S. Cartlidge and M. Shatlock, Interaction of zeolite alumina with matrix silica in catalytic cracking catalysts, *Appl. Catal.*, 1990, **66**(1), 45–57.

70 J. Zhou, J. Teng, L. Ren, Y. Wang, Z. Liu, W. Liu, W. Yang and Z. Xie, Full-crystalline hierarchical monolithic ZSM-5 zeolites as superiorly active and long-lived practical catalysts in methanol-to-hydrocarbons reaction, *J. Catal.*, 2016, **340**, 166–176.

71 Z. Shen, C. Ma, J. He, D. Wang, H. Sun, Z. Zhu and W. Yang, Preparation of a shaped core-shell structured binder-free ZSM-5 catalyst and its application for benzene alkylation with ethylene, *Appl. Catal., A*, 2019, **577**, 20–27.

72 Z. Li, X. Jiang, G. Xiong, B. Nie, C. Liu, N. He and J. Liu, Towards the preparation of binderless ZSM-5 zeolite catalysts: the crucial role of silanol nests, *Catal. Sci. Technol.*, 2020, **10**(23), 7829–7841.

73 W. Song, Y. Zuo, G. Xiong, X. Zhang, F. Jin, L. Liu and X. Wang, Transformation of SiO_2 in Titanium Silicalite-1/SiO_2 extrudates during tetrapropylammonium hydroxide treatment and improvement of catalytic properties for propylene epoxidation, *Chem. Eng. J.*, 2014, **253**, 464–471.

74 J. Yin, X. Jin, H. Xu, Y. Guan, R. Peng, L. Chen, J. Jiang and P. Wu, Structured binder-free MWW-type titanosilicate with Si-rich shell for selective and durable propylene epoxidation, *Chin. J. Catal.*, 2021, **42**(9), 1561–1575.

75 C. Shang, Z. Wu, W. D. Wu and X. D. Chen, Chemical crosslinking assembly of ZSM-5 nanozeolites into uniform and hierarchically porous microparticles for high-performance acid catalysis, *ACS Appl. Mater. Interfaces*, 2019, **11**(18), 16693–16703.

76 S. Lawson, K. Newport, Q. Al-Naddaf, A. E. Ameh, A. A. Rownaghi, L. F. Petrik and F. Rezaei, Binderless zeolite monoliths production with sacrificial biopolymers, *Chem. Eng. J.*, 2021, **407**, 128011.

77 H. Thakkar, S. Eastman, A. Hajari, A. A. Rownaghi, J. C. Knox and F. Rezaei, 3D-printed zeolite monoliths for CO_2 removal from enclosed environments, *ACS Appl. Mater. Interfaces*, 2016, **8**(41), 27753–27761.

78 S. Wang, P. Bai, M. Sun, W. Liu, D. Li, W. Wu, W. Yan, J. Shang and J. Yu, Fabricating Mechanically Robust Binder-Free Structured Zeolites by 3D Printing Coupled with Zeolite Soldering: A Superior Configuration for CO_2 Capture, *Adv. Sci.*, 2019, **6**(17), 1901317.

79 S. Couck, J. Lefevere, S. Mullens, L. Protasova, V. Meynen, G. Desmet, G. V. Baron and J. F. Denayer, CO_2, CH_4 and N_2 separation with a 3DFD-printed ZSM-5 monolith, *Chem. Eng. J.*, 2017, **308**, 719–726.

80 S. Couck, J. Cousin-Saint-Remi, S. Van der Perre, G. V. Baron, C. Minas, P. Ruch and J. F. Denayer, 3D-printed SAPO-34 monoliths for gas separation, *Microporous Mesoporous Mater.*, 2018, **255**, 185–191.

81 H. Zhang, P. Wang, H. Zhang, H. Yang, H. Wang and L. Zhang, Structured Zeolite Monoliths with Ultrathin Framework for Fast CO_2 Adsorption Enabled by 3D Printing, *Ind. Eng. Chem. Res.*, 2020, **59**(17), 8223–8229.

82 P. S. Mendes, J. M. Silva, M. F. Ribeiro, A. Daudin and C. Bouchy, From powder to extrudate zeolite-based bifunctional hydroisomerization catalysts: on preserving zeolite integrity and optimizing Pt location, *J. Ind. Eng. Chem.*, 2018, **62**, 72–83.

83 S. Zhang, Y. Gong, L. Zhang, Y. Liu, T. Dou, J. Xu and F. Deng, Hydrothermal treatment on ZSM-5 extrudates catalyst for methanol to propylene reaction: Finely tuning the acidic property, *Fuel Process. Technol.*, 2015, **129**, 130–138.

84 B. Wang, X. Yan and H. Zhang, Interaction between phosphorus and zeolite/binder: A realumination study on beta zeolites, *Microporous Mesoporous Mater.*, 2021, **312**, 110735.

85 N. Kubicek, F. Vaudry, B. Chiche, P. Hudec, F. Di Renzo, P. Schulz and F. Fajula, Stabilization of zeolite beta for fcc application by embedding in amorphous matrix, *Appl. Catal., A*, 1998, **175**(1–2), 159–171.

86 L. Gueudré, M. Milina, S. Mitchell and J. Pérez-Ramírez, Superior mass transfer properties of technical zeolite bodies with hierarchical porosity, *Adv. Funct. Mater.*, 2014, **24**(2), 209–219.

87 C. Chmelik and J. Kärger, In situ study on molecular diffusion phenomena in nanoporous catalytic solids, *Chem. Soc. Rev.*, 2010, **39**(12), 4864–4884.

88 J. I. Mirena, J. W. Thybaut, G. B. Marin, J. A. Martens and V. V. Galvita, Impact of the spatial distribution of active material on bifunctional hydrocracking, *Ind. Eng. Chem. Res.*, 2021, **60**(18), 6357–6378.

89 M. Guisnet, "Ideal" bifunctional catalysis over Pt-acid zeolites, *Catal. Today*, 2013, **218**, 123–134.

90 N. Batalha, L. Pinard, C. Bouchy, E. Guillon and M. Guisnet, n-Hexadecane hydroisomerization over Pt-HBEA catalysts. Quantification and effect of the intimacy between metal and protonic sites, *J. Catal.*, 2013, **307**, 122–131.

91 K. Cheng, L. I. van der Wal, H. Yoshida, J. Oenema, J. Harmel, Z. Zhang, G. Sunley, J. Zečević and K. P. de Jong, Impact of the spatial organization of bifunctional metal–zeolite catalysts on the hydroisomerization of light alkanes, *Angew. Chem.*, 2020, **132**(9), 3620–3628.

92 J. Zecevic, G. Vanbutsele, K. P. de Jong and J. A. Martens, Nanoscale intimacy in bifunctional catalysts for selective conversion of hydrocarbons, *Nature*, 2015, **528**(7581), 245–248.

93 P. S. Mendes, J. M. Silva, M. F. Ribeiro, A. Daudin and C. Bouchy, Bifunctional Intimacy and its Interplay with Metal-Acid Balance in Shaped Hydroisomerization Catalysts, *ChemCatChem*, 2020, **12**(18), 4582–4592.

94 E. Gutierrez-Acebo, C. Leroux, C. Chizallet, Y. Schuurman and C. Bouchy, Metal/acid bifunctional catalysis and intimacy criterion for ethylcyclohexane hydroconversion: when proximity does not matter, *ACS Catal.*, 2018, **8**(7), 6035–6046.

95 W. Fan, M. A. Snyder, S. Kumar, P.-S. Lee, W. C. Yoo, A. V. McCormick, R. Lee Penn, A. Stein and M. Tsapatsis, Hierarchical nanofabrication of microporous crystals with ordered mesoporosity, *Nat. Mater.*, 2008, **7**(12), 984–991.

96 X. Qi, V. Vattipalli, K. Zhang, P. Bai, P. J. Dauenhauer and W. Fan, Adsorptive nature of surface barriers in MFI nanocrystals, *Langmuir*, 2019, **35**(38), 12407–12417.

97 O. Gobin, S. Reitmeier, A. Jentys and J. Lercher, Role of the Surface Modification on the Transport of Hexane Isomers in ZSM-5, *J. Phys. Chem. C*, 2011, **115**(4), 1171–1179.

98 L. Zhang, C. Chmelik, A. N. van Laak, J. Kärger, P. E. de Jongh and K. P. de Jong, Direct assessment of molecular transport in mordenite: dominance of surface resistances, *Chem. Commun.*, 2009, 6424–6426.

99 S. Peng, M. Gao, H. Li, M. Yang, M. Ye and Z. Liu, Control of surface barriers in mass transfer to modulate methanol-to-olefins reaction over SAPO-34 zeolites, *Angew. Chem.*, 2020, **132**(49), 22129–22132.

100 S. J. Reitmeier, O. C. Gobin, A. Jentys and J. A. Lercher, Enhancement of sorption processes in the zeolite H-ZSM5 by postsynthetic surface modification, *Angew. Chem., Int. Ed.*, 2009, **48**(3), 533–538.

101 E. W. Miles, S. Rhee and D. R. Davies, The molecular basis of substrate channeling, *J. Biol. Chem.*, 1999, **274**(18), 12193–12196.

102 Y. Li, M. Wang, S. Liu, F. Wu, Q. Zhang, S. Zhang, K. Cheng and Y. Wang, Distance for communication between metal and acid sites for syngas conversion, *ACS Catal.*, 2022, **12**(15), 8793–8801.

103 M. Vippola, J. Keränen, X. Zou, S. Hovmöller, T. Lepistö and T. Mäntylä, Structural characterization of aluminum phosphate binder, *J. Am. Ceram. Soc.*, 2000, **83**(7), 1834–1836.

104 Y. Song, L.-l. Zhang, G.-d. Li, Y.-s. Shang, X.-m. Zhao, T. Ma, L.-m. Zhang, Y.-l. Zhai, Y.-j. Gong and J. Xu, ZSM-5 extrudates modified with phosphorus as a super effective MTP catalyst: Impact of the acidity on binder, *Fuel Process. Technol.*, 2017, **168**, 105–115.

105 C. P. Nicholas, L. T. Nemeth, W. M. Plencner, T. M. Mezza, C. L. Nicholas, S. Prabhakar and W. Sinkler, Elucidation of phosphorus interaction in dual component zeolite/matrix catalysts: Selectivity control in olefin oligomerization with MTW/Al_2O_3, *Appl. Catal., A*, 2017, **536**, 75–84.

106 J. Freiding, F.-C. Patcas and B. Kraushaar-Czarnetzki, Extrusion of zeolites: Properties of catalysts with a novel aluminium phosphate sintermatrix, *Appl. Catal., A*, 2007, **328**(2), 210–218.

107 E. C. de Souza, M. M. Pereira, Y. L. Lam, E. Morgado Jr and L. S. Chinelatto Jr, Aluminum phosphate as active matrix of fluid catalytic cracking catalysts: Y zeolite stabilization, *Appl. Catal., A*, 2021, **619**, 118156.

108 H. E. van der Bij and B. M. Weckhuysen, Phosphorus promotion and poisoning in zeolite-based materials: synthesis, characterisation and catalysis, *Chem. Soc. Rev.*, 2015, **44**(20), 7406–7428.

109 Y.-J. Lee, Y.-W. Kim, N. Viswanadham, K.-W. Jun and J. W. Bae, Novel aluminophosphate (AlPO) bound ZSM-5 extrudates with improved catalytic properties for methanol to propylene (MTP) reaction, *Appl. Catal., A*, 2010, **374**(1–2), 18–25.

110 X.-D. Chen, X.-G. Li, H. Li, J.-J. Han and W.-D. Xiao, Interaction between binder and high silica HZSM-5 zeolite for methanol to olefins reactions, *Chem. Eng. Sci.*, 2018, **192**, 1081–1090.

111 M. Moliner, J. E. Gabay, C. E. Kliewer, R. T. Carr, J. Guzman, G. L. Casty, P. Serna and A. Corma, Reversible transformation of Pt nanoparticles into single atoms inside high-silica chabazite zeolite, *J. Am. Chem. Soc.*, 2016, **138**(48), 15743–15750.

112 N. Felvey, J. Guo, R. Rana, L. Xu, S. R. Bare, B. C. Gates, A. Katz, A. R. Kulkarni, R. C. Runnebaum and C. X. Kronawitter, Interconversion of atomically dispersed platinum cations and platinum clusters in zeolite ZSM-5 and formation of platinum gem-dicarbonyls, *J. Am. Chem. Soc.*, 2022, **144**(30), 13874–13887.

113 Y. Ding, F. Jiao, X. Pan, Y. Ji, M. Li, R. Si, Y. Pan, G. Hou and X. Bao, Effects of proximity-dependent metal migration on bifunctional composites catalyzed syngas to olefins, *ACS Catal.*, 2021, **11**(15), 9729–9737.

114 Y. Wang, G. Wang, L. I. van der Wal, K. Cheng, Q. Zhang, K. P. de Jong and Y. Wang, Visualizing Element Migration over Bifunctional Metal-Zeolite Catalysts and its Impact on Catalysis, *Angew. Chem.*, 2021, **133**(32), 17876–17884.

115 I. L. Buurmans and B. M. Weckhuysen, Heterogeneities of individual catalyst particles in space and time as monitored by spectroscopy, *Nat. Chem.*, 2012, **4**(11), 873–886.

116 C. Vogt and B. M. Weckhuysen, The concept of active site in heterogeneous catalysis, *Nat. Rev. Chem.*, 2022, **6**(2), 89–111.

117 S. Bordiga, C. Lamberti, F. Bonino, A. Travert and F. Thibault-Starzyk, Probing zeolites by vibrational spectroscopies, *Chem. Soc. Rev.*, 2015, **44**(20), 7262–7341.

118 Y. Wei, T. E. Parmentier, K. P. de Jong and J. Zečević, Tailoring and visualizing the pore architecture of hierarchical zeolites, *Chem. Soc. Rev.*, 2015, **44**(20), 7234–7261.

119 Q. Zhang, S. Gao and J. Yu, Metal sites in zeolites: Synthesis, characterization, and catalysis, *Chem. Rev.*, 2022, **123**(9), 6039–6106.

120 M. Shamzhy, M. Opanasenko, P. Concepción and A. Martínez, New trends in tailoring active sites in zeolite-based catalysts, *Chem. Soc. Rev.*, 2019, **48**(4), 1095–1149.