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Activity and selectivity differences of external Brønsted acid sites of single-unit-cell thick and conventional MFI and MWW zeolites

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ABSTRACT

A comparison of activity and selectivity of external Brønsted acid sites in catalytic conversion of benzyl alcohol in mesitylene over unit-cell thick zeolite materials (MCM36 or pillared MWW, pillared MFI, and self-pillared pentasil (SPP)) showed that the external surface of MWW and MFI zeolites influences drastically the activity and selectivity of the parallel alkylation and etherification reactions. Pillared MWW, containing independent (not-interconnected) micropores and mesopores, catalyzed both of the parallel reactions only in the mesopores as evidenced by complete loss of the activity upon 2,6-di-tert-butylpyridine (DTBP) titration. Pillared MFI and SPP, consisting of highly interconnected micropores and mesopores, catalyzed both of the parallel reactions in the mesopores. Pillared MFI and SPP catalyzed only the etherification reaction in the micropores as illustrated by the complete suppression of alkylation and retention of residual etherification activity after DTBP titration. Moreover, it was found that the external surface of MWW zeolites favors the alkylation reaction, while the etherification reaction takes place with similar reaction rates on MFI and MWW external surfaces. The evidence shown here for the assessment of external acid sites in catalyzing parallel reactions extends the scope of observed catalytic performances in these materials beyond those reflecting transport effects and accessibility of acid sites and highlights the importance of external surface structure.

It is a great pleasure to provide a contribution honoring the 60th birthday of Professor Thomas Bein on a subject where he has made inspiring contributions.

Meso-/microporous zeolites attempt to combine the catalytic features of microporous confinement with the improved mass transport provided by mesoporosity in a single material [1–7]. In certain cases, they can overcome mass-transfer constraints, a major drawback in reactions involving bulky molecules in conventional microporous zeolites [8–10]. A variety of zeolites containing structured porosity on micro- and mesopore levels have been created in the past decade [11–17] and catalytic tests showed that for certain reactions the meso-/microporous zeolites can exhibit higher apparent reaction rates, selectivity and improved stability to deactivation in comparison with their microporous-only zeolite analogues [18–20].

Earlier, in an effort to develop quantitative descriptions of catalytic properties of meso-/microporous zeolites, we reported on the acid site location and intrinsic catalytic behavior of three meso-/microporous zeolites (pillared MWW [12], pillared MFI [21] and three-dimensionally ordered mesoporous imprinted (3DOm-i) MFI [15] zeolites). Pillared MWW (or MCM-36), derived by swelling and pillaring of MCM-22(P), is the first pillared zeolite material with microporous layers and mesoporous interlayer spaces [22–25]. We have reported that a mild swelling of MCM-22(P) preserves the MWW layer structure and composition better compared to earlier methods involving aggressive treatments [12]. Pillared MFI can be created by direct pillaring (no need for swelling) of multilamellar MFI nanosheets [21]. 3DOm-i MFI zeolites were prepared by a confined growth of zeolite within 3DOm carbon template [15]. The Brønsted acid sites of these three meso-/microporous zeolites were determined by a series of titration experiments with dimethyl ether (DME) and 2,6-ditert butyl pyridine (DTBP) organic base, showing that a certain portion of Brønsted acid sites is accessible from the mesoporous environment in meso-/microporous MWW or MFI zeolites, while another portion is only accessible through the micropores. In addition, the presence of mesopores in the zeolites increases the accessibility

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of bulky reactant molecules to the active sites in catalytic reactions. The intrinsic catalytic behavior of pillared MWW [12], pillared MFI [16] and 3DOm-i MFI [15] using small alcohol and alkane activation reactions was examined under strict kinetic control in the absence of diffusion limitations. The catalytic results showed that for these reactions the Brønsted acid sites confined in meso- and micropores in MWW and MFI zeolites behave identically to those found in zeolites consisting exclusively of microporosity [26].

Later, we extended our effort to address the catalytic behavior of meso-/microporous MFI, including pillared MFI, 3DOm-i MFI and the more recently introduced self-pillared pentasil zeolite (SPP) [27], in space-demanding catalytic reactions. By deactivating the external surface acid sites by the organic base DTBP, we were able to probe the catalytic activity of acid sites located in the micropores and attribute (using a reaction/diffusion model) the 3–4 orders of magnitude variation in observed reaction rates between MFI zeolites with different crystal dimensions (from several micrometers to few nanometers) to diffusion limitations [27].

As the characteristic length of the micropore domains shrinks at the single- or near single-unit-cell level for MFI and MWW (nanosheets in multilamellar MFI are 1.5 unit cell thick [16,28,29] and 1 unit cell thick in SPP [27], pillared MWW [22] and delaminated MWW [30]) and, as a consequence, the fraction of external zeolite surface area becomes comparable to micropore surface area, the catalytic properties of the former (if not deactivated) become important or dominant contributors. Although the textural properties of these layered ultra-thin zeolite structures and their potential applications have been reviewed in several publications [31–35] and activities of traditional microporous MCM-22 and bulk MFI zeolites in catalytic reactions have been well studied [36], studies focusing on quantitative comparisons of reaction rates per active site at external surfaces are not available.

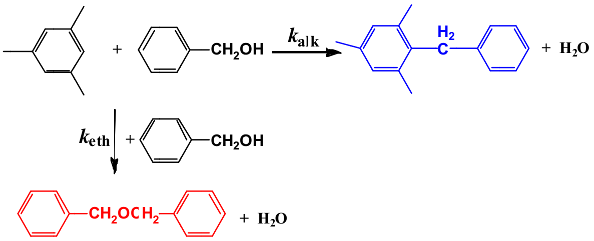

Fig. 1. Scheme for alkylation (k_{alk}) and etherification (k_{eth}) reactions of benzyl alcohol in mesitylene over MWW and MFI zeolite catalysts. In this scheme, the reaction converting the dibenzyl ether to 1,3,5-trimethyl-2-benzylbenzene is neglected.

Here, we make a comparison of external surface catalytic activity between MWW and MFI for a wide range of crystal sizes ranging from several microns to few nanometers (single-unit-cell), using the liquid phase parallel catalytic conversions of benzyl alcohol in mesitylene (*etherification to dibenzyl ether* and *alkylation to 1,3,5-trimethyl-2-benzylbenzene*) as probe reactions. We show that external surface structure can alter substantially the reaction rates and selectivity obtained from external Brønsted acid sites. Zeolyst MFI (CBV 8014), three synthesized conventional MFI zeolites with different particle sizes (17 μm MFI, 1.4 μm MFI, and 0.2 μm MFI, respectively), and conventional MCM-22 were studied for comparison purpose. For simplicity in nomenclature, MCM-22 and ZSM-5 are designated as MWW and MFI, respectively, in the remainder of this paper.

In the liquid phase catalytic conversions of benzyl alcohol in mesitylene (Fig. 1) the parallel reactions, alkylation and etherification, of benzyl alcohol produce 1,3,5-trimethyl-2-benzylbenzene and dibenzyl ether products, respectively. The apparent rate constants of the parallel alkylation and etherification reactions over the meso-/microporous MWW and MFI catalysts (Fig. 2) as well as several other conventional and mesoporous zeolites were evaluated at 343 K, with less than 10% conversion of benzyl alcohol, under rigorous agitation, and in excess amount of mesitylene (molar ratio of mesitylene to benzyl alcohol = 45:1) to eliminate the effect of catalyst deactivation, external mass transfer limitations, and limit the reaction converting dibenzyl ether to 1,3,5-trimethyl-2-benzylbenzene [37]. Details on the experimental method, scanning electron microscope (SEM) images, textural properties and acidity of the catalysts tested are included in the Supplementary Information.

Fig. 3 shows the conversion and selectivity of the parallel etherification and alkylation reactions over meso-/microporous and conventional MWW and MFI catalysts under conditions where all active sites of the zeolite catalysts were unperturbed and under conditions where 2,6-di-tertbutyl-pyridine (DTBP) had been added to the reaction mixture to selectively titrate acid sites located in the mesopores/external surface of the zeolite catalysts.

In the absence of the DTBP titrant, the meso-/microporous MWW and MFI zeolites had a higher conversion in comparison with their corresponding microporous-only zeolite analogues when examined under the same reaction conditions (Fig. 3(a) and (b)). This finding is consistent with previously reported higher conversion in benzylation reactions of benzene with benzyl alcohol over mesoporous mordenite [18], ZSM-5 [19] and zeolite-like SAPO [20] catalysts, and other aromatics alkylation reactions over meso-/microporous zeolite catalysts [38,39]. The selectivity towards each of the parallel reactions, shown in Fig. 3(c) and (d),

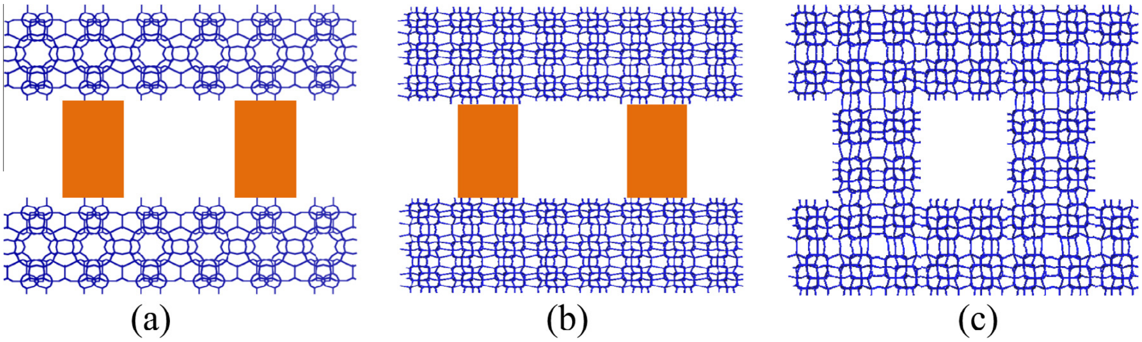

Fig. 2. Schematic illustration of some of the meso-/microporous zeolite structures investigated in this study: (a) pillared MWW, (b) pillared MFI, and (c) SPP catalysts. Pillared MWW viewed parallel to the microporous layer; pillared MFI and SPP viewed along the *c*-axis direction. Silica pillars are highlighted in orange in pillared MWW and pillared MFI zeolites. SEM images are shown in Supplementary Information, while TEM images have been reported earlier [12,16,27]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)