DOI: 10.1002/cctc.201402007



Annulation of Phenols: Catalytic Behavior of Conventional and 2D Zeolites

Maksym V. Opanasenko,^[a, b] Mariya V. Shamzhy,^[a, b] Changbum Jo,^[c] Ryong Ryoo,^[c, d] and Jiří Čejka*^[a]

Catalytic behavior of MFI zeolites differing in thickness of nanosheets and ordering was studied in annulation of phenols, and compared with 3D zeolites BEA and MFI containing large or medium pores as well as with micro/mesoporous zeolite USY. The highest conversions of phenols studied were achieved over ordered hexagonally mesostructured zeolite with 1.7 nm wall size, followed by materials possessing 2.1 and 2.7 nm of nanosheets thickness. This corresponds to decreasing surface area of materials studied. The preferences of materials with zeolitic layers and high surface areas over bulky zeolites BEA and especially MFI in annulation of phenols is more prominent for substrates with larger kinetic diameters [phenol (0.66 nm) < 1-naphthol (0.80 nm) < 2-naphthol (0.89 nm)]. USY zeolite exhibited higher conversions (32, 6, 25% for phenol, 1and 2-naphthol, respectively, after 300 min time on stream) than BEA (23, 6, 8%) and MFI (13, 0, 0%) not overcoming hexagonally mesostructured MFI (45, 36, 55%).

Introduction

Porous solid acids with predictable and well developed textural properties such as zeolites and metal-organic frameworks have been under most intensive investigations in catalysis in recent years. One of the reasons consists in their advantages and prospects as heterogeneous catalysts having numerous applications in petrochemistry, fine-chemical productions, and environmental protection.^[1] Among the advantages of zeolites, we can stress their high thermal and mechanical stability, relatively high adsorption capacity, and narrow pore-size distribution (leading sometimes to shape selectivity), and the possibility to control concentration, type, and strength of acid sites.^[2] However, zeolites generally suffer from intracrystalline diffusion limitations owing to the molecular dimensions of micropores. The size of zeolite pores (0.3–0.8 nm) also limits the accessibility of the active sites located in the channels for bulky reac-

[a]	Dr. M. V. Opanasenko, Dr. M. V. Shamzhy, Prof. J. Čejka
	Department of synthesis and catalysis
	J. Heyrovský Institute of Physical Chemistry
	Academy of Sciences of Czech Republic
	v.v.i Dolejškova 3, 182 23 Prague 8 (Czech Republic)
	Fax: (+ 420) 28658 2307
	E-mail: jiri.cejka@jh-inst.cas.cz
[b]	Dr. M. V. Opanasenko, Dr. M. V. Shamzhy

- Department of porous materials L.V. Pisarzhevskiy Institute of Physical Chemistry National Academy of Sciences of Ukraine pr. Nauky 31, 03028 Kiev (Ukraine)
- [c] Dr. C. Jo, Prof. R. Ryoo Center for Nanomaterials and Chemical Reactions Institute for Basic Science Daejeon 305-701 (Korea)
- [d] Prof. R. Ryoo Department of Chemistry KAIST, Daejeon 305-701 (Korea)

tants,^[1] which may negatively impact their catalytic performance for transformation of large molecules.

To avoid this disadvantage, synthesis of zeolites with extralarge micropores can be performed.^[3] However, this way is limited by the usual hydrothermal lability of such zeolites and complexity of their formation.

Another possibility to prepare effective catalysts for transformation of bulky molecules is increasing the external surface of zeolites. Such procedure is applicable if shape selectivity is not important for the reactions under consideration. Different methods to increase the external surface of zeolites have been studied recently. They include i) fabrication of micro-mesoporous materials with developed surface owing to mesoporosity,^[4] ii) decreasing the size of zeolite crystals to the nanoscale,^[5] iii) formation of thin zeolitic layers exhibiting large external surface areas.^[6]

Mesopores can be introduced in zeolite materials by use of solid templating (in the presence of a solid material that is eventually removed to generate porosity),^[7] supramolecular templating (by using an assembly of surfactants as porogen),^[8] synthesis with organosilanes^[9] and postsynthetic treatments (particularly, demetalation).^[10]

Nanocrystalline zeolites with crystal sizes of less than 100 nm have improved characteristics (increased surface area and decreased diffusion path lengths) in comparison with bulky zeolites.^[5] Incorporation of active sites onto the external surface results in high surface reactivity leading to zeolites with improved catalytic properties.^[5] However, in fabrication of nanocrystalline zeolites, the conditions have to be controlled very delicately and the synthesis often should be stopped at a very low yield. Thus, synthesis of zeolite nanoparticles for catalytic applications seems to be not suitable at the moment. To significantly increase the accessibility of acid sites for substrate molecules, delamination methods for fabrication of thin zeolitic layers were essayed particularly for MCM-22 precursor^[11] and respective derivatives.^[12] Recently, Čejka and coworkers reported the use of UTL zeolite for the synthesis of a 2D precursor with its further manipulation including swelling, delamination, pillaring, or even formation of new zeolites.^[13]

Ryoo and co-workers discovered and developed fundamentally different approaches for the synthesis of 2D zeolites.^[14] The method employs designed multiammonium surfactants combining both zeolite structure-directing agents (SDAs) and long alkyl chains as mesoporogens. Such surfactant molecules (gemini-type organic surfactants) can form micelles functioning as SDA in mesostructure (tails) and zeolitic level (multiammonium head groups). Mesophase materials with different zeolite framework topologies (MFI, MTW, BEA, MRE) were prepared by using this surfactant-directed synthesis route.[15] However, most of such mesophase materials do not contain individual layers of zeolites, their walls are constructed from very thin crystalline component with zeolitic structure. Thus, the mentioned materials may be considered as 2D zeolitic materials with mesoscale arrangement of the crystalline domains. Such 2D zeolites can exhibit not only excellent textural characteristics, but also promising catalytic properties in acid-catalyzed and oxidative reactions,^[16] sometimes superior to those of conventional zeolites.

In this contribution, we aimed to compare the catalytic behavior of conventional 3D zeolites (MFI, BEA), micro-mesoporous ultrastable zeolite Y (USY), and novel 2D zeolites obtained by using multiammonium surfactants in annulation reaction between 2-methyl-3-buten-2-ol (MBO) and phenols (Scheme 1).



Scheme 1. Annulation of phenol with MBO.

The selected reaction provides chromanes (dihydrobenzopyranes), which represent (with their unsaturated derivatives-chromenes) a widely distributed and biologically active class of natural products.^[17]

2D zeolites may overcome limitations of conventional bulky zeolites having smaller pores. Therefore, materials consisting of thin zeolitic layers appear as promising solid catalysts for liquid-phase reactions. Comparison of the performance of 2D and 3D zeolites in annulation reaction is of high interest aiming to show the potential of layered materials in acid-catalyzed processes.

Results and Discussion

Structure, textural, and acidic properties of the catalysts

Hiererchical zeolites prepared in this work are depicted as N_n xd, for which N_n corresponds to the type of structure-directing agent used: $C_{18}H_{37}-N^+(Me)_2-\{C_6H_{12}-N^+(Me)_2\}_{n-2}-C_6H_{12}-N^+$ $(Me)_2-C_{18}H_{37}][Br^-]_n$ (n = 3, 4, and 5); and x is the duration of the synthesis (x = 1, 5, 9 d).

XRD patterns and TEM images of synthesized material (Figure 1 a,b) reveal that N_3 -1d sample exhibits MCM-41-like hexag-



Figure 1. a) XRD patterns and TEM images of b,c) $N_3\mbox{-}1d;\ d,e)\ N_3\mbox{-}5d;\ and f,g)\ N_3\mbox{-}9d.$

onal structure (with low-angle diffraction lines at 1.9, 3.2, and $3.8^{\circ} 2\theta$) containing noncrystalline mesopore walls. In the case of the N₃-5d sample, well resolved diffraction lines in the low-angle region of the XRD pattern are also present (Figure 1a). These lines correspond to a hexagonal mesostructure similar to that of the N₃-1d material but with slightly expanded lattice in comparison with the sample obtained after 1 d. The structure of N₃-5d sample was previously reported as hexagonally ordered mesoporous MFI zeolite.^[6] XRD patterns and TEM images of the sample N₃-5d (Figure 1a,d,e) evidenced the transformation of original mesopore walls (Figure 1b) to a crystalline rous zeolitic structure with the prolongation of bydro

microporous zeolitic structure with the prolongation of hydrothermal treatment up to 5 d.

The N₃-5d sample possessed relatively high surface area and pore volume (Table 1) in contrast to the sample obtained after 1 d. N₃-5d exhibited a type-IV adsorption isotherm with poresize distribution having maxima related to pore diameters $D_{\text{micro}} = 0.55 \text{ nm}$ and $D_{\text{meso}} = 3.3 \text{ nm}$.^[18] The pore diameter of 0.55 nm corresponds to the 10-ring channels in the zeolite framework. Thus, the architecture of N₃-5d can be described as mesoporous structure with the walls composed of the microporous zeolitic framework, probably similar to that of MFI.

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Textural properties of the materials under investigation.										
Sample	Description	Si/Al ^[a]	D _{micro} [nm]	D _{meso} [nm]	S_{BET} [m ² g ⁻¹]	S_{ext} [m ² g ⁻¹] ^[c]	V_{total} [cm ³ g ⁻¹]	d _{wall} [nm]		
N₃-1d	hexagonally mesostructured amorphous MCM-41-like framework	20.2	n.d. ^[b]	2.4	221	220	0.16	1.5 ^[d]		
N₃-5d	ordered hexagonally mesostructure, 10-ring zeolite	30.2	0.55	3.3	1090	990	1.40	1.7 ^[d]		
N₃-9d	1.5 nm thick MFI nanosheet	38.4	0.55	3.0	693	555	1.01	1.5 ^[e]		
N ₄ -5d	disordered mesostructure, 10-ring zeolite of 2.1 nm thickness	28.2	0.55	3.4	970	805	1.52	2.1		
N₅-5d	disordered mesostructure, 10-ring zeolite of 2.7 nm thickness	27.3	0.55	5.1	810	622	1.53	2.7		
MFI	3D pore system of intersecting sinusoidal and straight 10-ring channels	11.5	0.54	-	305	n.d. ^[b]	0.16	-		
BEA	3D pore system of intersecting 12-ring channels	12.5	0.66	-	670	n.d. ^[b]	0.2	-		
USY	3D pore system of interconnected supercages and mesopores with wide range diameters	15	0.74	n.d. ^[b]	770	335				
[a] Evaluated from the FTIR measurements. [b] Not defined. [c] Evaluated from the t-plot method. [d] Wall thickness was determined from D _{meso} and hexag- onal lattice parameter (XRD). [e] Wall thickness was measured from the TEM image.										

In contrast to the mentioned samples, N_3 -9d exhibited no low-angle reflections in XRD pattern (Figure 1a). At the same time, the high-angle diffraction peaks were better resolved than those of N_3 -5d and they can be attributed to the (*hOL*) reflections corresponding to the MFI zeolite structure. The absence of the reflections with *k*-indices distinct from zero (along the *b*-axis) indicates that the zeolite morphology could be extremely thin in this direction not providing interlayer connections.

TEM images (Figure 1 f,g) confirmed that N_3 -9d possess zeolitic 2D nanosheet morphology. Each nanosheet is composed of a single "layer" of micropores corresponding to 1.5 nm thickness and 3/4 of the *b* lattice parameter of the MFI unit cell. Thus, N_3 -9d can be described as 2D nanomorphic MFI zeolite with disordered assembly of the zeolitic nanosheets. Despite the absence of ordering, the nanosheets maintain relatively high interparticle porosity (Table 1).

The structural and textural properties of N₄-5d and N₅-5d samples are considerably similar to those of N₃-5d material as deduced from XRD and sorption data (Figure 2 a, Table 1). Both N₄-5d and N₅-5d exhibit a reflection in the low-angle region (the less distinct peak for N₅-5d may be attributed to the thicker walls of mesopores and their lower structural coherence) and three broad diffraction lines in the wide-angle region in the XRD pattern. Based on the results of Ar adsorption, the presence of 10-ring channels similar to those in N₃-5d can be assumed for N₄-5d and N₅-5d samples.^[18]

The TEM images of these materials (Figure 2b–e) evidenced the disordered interconnection of zeolitic layers. It was found that the thicknesses of the zeolite layers (forming mesopore walls) increased with the increasing number of quaternary N atoms in used SDA (number of ammonium groups). In this way, the thicknesses of the mesopore walls in N₃-5d, N₄-5d, and N₅-5d samples were equal to 1.7, 2.1, and 2.7 nm, respectively (Table 1).

Zeolite MFI is characterized by a sinusoidal pore system of intersecting 10-ring channels with sizes of 0.51×0.55 and 0.53×0.56 nm (Figure 3 a). Zeolite BEA (Figure 3 b) possesses a 3D pore system of intersecting 12-ring channels (0.64×0.76 and 0.56×0.56 nm), whereas ultrastable zeolite Y (Figure 3 c) belongs to the large-pore zeolites that have quasispherical su-

percages of 1.22 nm in diameter interconnected tetrahedrally through windows of 0.74 nm in diameter. Zeolite USY also contains mesopores with broad pore size distribution.



Figure 2. a) XRD patterns and TEM images of b,c) N_4 -5d and d,e) N_5 -5d.

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 3. Frameworks of a) MFI, b) BEA, c) FAU, and d) XRD patterns of the corresponding zeolites.

The X-ray diffraction patterns of all 3D zeolites under study (Figure 3d) match well with those reported in the literature.^[19] Zeolites BEA and MFI show a type I isotherm, typical for microporous solids, and the adsorption isotherm for USY zeolite is a combination of types I and IV with hysteresis loop created by capillary condensation in the mesopores within the pore systems of FAU. The textural properties of all 3D zeolites are summarized in Table 1.

To evaluate the total concentrations of acid sites in the catalysts under investigation FTIR spectroscopy of adsorbed pyridine was used. The concentrations of Brønsted and Lewis acid sites calculated from the integral intensities of the bands at 1546 and 1454 cm⁻¹ by using extinction coefficients^[20] are given in Table 2.

Notably, all 3D zeolites under investigation possess significantly higher amounts of Brønsted acid centers (0.200– 0.619 mmolg⁻¹) than prepared N_n-xd materials (0.03– 0.072 mmolg⁻¹). At the same time, the fraction of Lewis acid centers in N_n-xd samples (71–89%) notably exceeds that characteristic for 3D zeolites (25–63%). It is an expected result, regarding the missing connectivities in the third dimension of N_n-xd materials resulted in an increased concentration of defects. The surface acidity of N_n-xd samples was studied by FTIR

Table 2. Concentrations of acid sites in N _n -xd samples and conventional zeolites measured by pyridine and 2,6-DTBP adsorption.										
Sample	c(Lewis) [mmol g ⁻¹]	Pyri c(Brønsted) [mmol g ⁻¹]	dine c(Lewis)/c(Lewis+Brønsted) [%]	2,6-DTBP c(Brønsted) [mmol g ⁻¹]						
N₃-1d	0.007	0	100	0.008						
N₃-5d	0.252	0.030	89	0.068						
N₃-9d	0.179	0.072	71	0.028						
N ₄ -5d	0.261	0.048	84	0.067						
N₅-5d	0.269	0.050	84	0.066						
MFI	0.201	0.619	25	0.005						
BEA	0.280	0.311	47	0.281						
USY	0.340	0.200	63	0.202						

© 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

spectroscopy of adsorbed 2,6-di-tert-butylpyridine (2,6-DTBP) from the integral intensity of the band at 1531 cm^{-1} (Table 2). The kinetic diameter of the 2,6-DTBP molecule is approximately 0.79 nm,^[21] which is larger than the size of pores in 10-ring zeolites under investigation, which makes accessible only acid centers on the outer surface of N_n -xd and MFI samples. At the same time, in the case of 3D 12-ring systems, such as BEA and FAU (USY) zeolites, an easy penetration of 2,6-DTBP into their pore network was demonstrated in Ref. [21]. In agreement with Ref. [21], the most Brønsted acid centers in BEA and USY zeolites are accessible for interaction with 2,6-DTBP molecules (Table 2), however, it does not guarantee the accessibility of internal sites for bulky substrates (such as naphthols) during reaction. In contrast, only 10% of Brønsted acid centers in 3D MFI zeolite interact with bulky 2,6-DTBP molecules. The fraction of surface acid sites in prepared 2D 10-ring zeolites (e.g., 39% for N₃-9d) significantly exceeds the value for conventional 3D MFI zeolite. However, the contribution of surface silanol groups with increased acidity, as a result of the interaction with the nearest AI Lewis acid sites,^[22] to the intensity of absorption band at 1531 cm⁻¹ cannot be excluded for N_n-xd (x =5), which is characterized by highly developed surface Lewis acidity.

Thus, the increased 1) specific pore volume (V_{total}), 2) external surface area, 3) fraction of Lewis acid centers, and 4) surface Brønsted acid sites are found to be the features distinguishing 2D zeolites from 3D MFI analogue.

Catalytic investigations

The annulation reaction includes two acid-catalyzed reaction steps (Scheme 1): 1) isoprenylation of phenols with MBO resulting in formation of isoprenylphenol followed by 2) its intramolecular cyclization with the formation of target derivatives of 3,4-dihydro-2*H*-1-benzopyran (chroman).^[23] Phenols differing in size (i.e., phenol, 1-naphthol, 2-naphthol) were used as substrates to establish the influence of structure, textural, and acidic properties of catalysts on their efficiency in annulation reaction. The kinetic diameters of phenol, 1-naphthol, and 2-naphthol total 0.66, 0.80, and 0.89 nm, respectively (values were obtained by using HyperChem Molecular Modeling System, release 8.0.8).

In all cases (phenol, 1-naphthol, 2-naphthol), we observed in the reaction mixture the formation of intermediate prenylphenols (PP, Figure 4a), targeting 2,2-dimethylbenzopyranes (DMBP, Figure 4b), and the products of their thermal rearrangement,^[24] 2,2,3trimethylbenzofuranes (TMBF, Figure 4c). Moreover, the side product of MBO oxidative dimerization was detected (Figure 4d).

The conversion of phenol was found to increase in the following order: $MFI < N_3-1d < N_3-9d < BEA < USY < N_5-5d < N_4-5d < N_3-5d$ (Figure 5 a). It should be pointed out, that the highest conversions (38–46% after 300 min time on stream, TOS) were achieved over N₃₋₅-5d samples characterized by the largest external surface area, the highest pore volume



Figure 4. Isomeric products formed during annulation reaction of phenol: a) PP, b) DMBP, c) TMBF, d) 1-(2-methylbut-3-en-2-yloxy)-3-methylbutane-2,3diol.



Figure 5. a) Conversion of phenol and b) selectivities to TMBF and DMBP at 30% conversion (or at maximal conversion if 30% is unachievable) over 2D and conventional zeolites.

(Table 1), and the amount of accessible acid centers (Table 2). At the same time, significantly lower conversions reached over zeolites BEA (23% after 300 min TOS) and especially MFI (13% after 300 min TOS) may be caused by slower diffusion of reac-

tants in pore system of 3 D zeolites in comparison with the diffusion in N_n -xd materials. N_3 -1d sample, possessing the lowest concentration of acid sites at reasonable porosity, provided slightly higher conversion than MFI zeolite (19% versus 13% at 300 min TOS).

Relatively low conversion over N_3 -9d sample having considerable porosity may be caused by low concentration of surface acid sites (Table 2). The overall selectivities to substituted DMBP/TMBF over all catalysts under investigation were in the range of 60–85%, but the regioselectivities differed significantly (Figure 5b). Notably, the catalysts giving the lowest conversion (MFI, N_3 -1d, N_3 -9d) exhibited higher selectivity to TMBF (59–66% in DMBP/TMBF fraction) than more active catalysts (6–39%). This can be explained by thermally induced rearrangement of the DMBP derivative to the corresponding TMBF, which is assumed to play a significant role in the case of low-active catalysts as a result of the relatively low rate of annulation to DMBP relative to that of thermally induced rearrangement consuming this product.

The differences in conversions of bulkier 1-naphthol over 3 D and 2 D zeolites are more dramatic (Figure 6 a). N_{3-5} -5d samples exhibited 30–35% conversion after 300 min of the reaction time whereas conventional zeolites, mesostructured amorphous N_3 -1d, and N_3 -9d samples with relatively low external acidity showed conversions < 10%.

Notably, annulation of 1-naphthol practically did not proceed over 3D MFI zeolite, which may be connected with the low concentration of surface active sites and unaccessibility of internal acid centers through the pore system of the zeolite for bulky 1-naphthol molecules. As the mesophase and lamellar materials with MFI structure of zeolitic layers (having access to active sites from two sides) were reasonably active in annulation of 1-naphthol under the same reaction conditions, we can assume that the studied process requires a reaction space larger than the unilateral pore mouth of MFI.

Significantly higher conversion of phenol was achieved over USY zeolite than over BEA, both catalysts showed almost equal conversion of bulkier 1-naphthol. This result may be connected with partial blocking of the inner faujasite cavities (1.2 nm diameter) by bulky products (kinetic diameter of pyranyl isomer molecule is approximately 1.03 nm), whereas 1-naphthol (molecule size is 0.64×0.75 nm) can penetrate through 0.74 nm micropore windows in USY. The conversions of 1-naphthol over both N₃-1d and N₃-9d samples were similar (5-10%) but significantly lower than over N_{3-5} -5d materials (31–36%). We assume fundamentally different reasons for this. In the case of MCM-41-like solid, the amount of acid sites (of low acid strength) is very low for transformation of relatively inert 1-naphthol, and the diffusion limitation owing to the stacking of the layers and/or irregularity of interlayer pore system (Figure 1 e,f) might be the reason for the low conversion of the respective substrate.

In contrast to selectivities to phenol, selectivities to pyranyl/ furanyl derivatives of 1-naphthol were similar for all used catalysts (Figure 6b). However, the ratio of DMBP/TMBF formed over low-active catalysts was almost unchanged during the course of the reaction (0–1300 min, selectivities to furanyl

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 6. a) Conversion of 1-naphthol and b) selectivities to corresponding TMBF and DMBP isomers over solids under study.

(TMBF) isomer were in the range of 63–70%), but it slightly decreased with time in the case of more active N_{3-5} -5d materials (selectivities to TMBF changed from 65–70 to 58–59%). Observed differences in selectivities for more or less active catalysts can again be explained by competition between formation of pyranyl product and its rearrangement to furanyl isomer.

Further differentiation of 3D zeolites and materials containing thin crystalline layers was observed in the case of the most bulky substrate, 2-naphthol. Similarly to previously discussed phenols, N_{3-5} -5d materials exhibited the highest conversion of 2-naphthol (Figure 7a). Again, this correlates with the values of external surface area and agrees with the highest amount of surface acid sites. 3D materials with the narrower pores (MFI, BEA) and MCM-41-like sample with the lowest concentration of acid sites predictably showed minor conversion.

In contrast to the cases of phenol and 1-naphthol transformation, the ratio of DMBP/TMBF in the case of 2-naphthol transformation varied during the course of the reaction for all





Figure 7. a) Conversion of 2-naphthol and b) ratio between corresponding TMBF and DMBP isomers over N_n -xd and conventional materials under investigation.

catalysts under investigation. The ratio increased with time over 3D zeolites and MCM-41-like material whereas it decreased over all 2D zeolites studied (Figure 7 b). The dependence of DMBP/TMBF ratio on the reaction time indicates that in the case of bulky substrate (2-naphthol) local surrounding the acid site may govern the preferential formation of these isomeric products. Notably, in comparison with initial reaction periods, the absolute amount of TMBF (if it was minor component, over conventional solids and N₃-1d) has changed with time insignificantly. This means that such isomer formed at the beginning of the reaction and its concentration almost did not change further.

It was found that the nature of the used solvent strongly influences the yields in annulation reaction of 2-naphthol. In particular, conversion of 2-naphthol over N₃-5d catalyst dramatically decreased with increasing solvent polarity in the following sequence: *p*-xylene (relative polarity is 0.074) > chlorobenzene (0.188) > 1,2-dichloroethane (0.327) \geq dimethylsulfoxide (DMSO, 0.444, Figure 8a). Regarding the better stabilization of the polar intermediate complex in a more polar solvent, the result obtained indicates the competition between reactant and the solvent for interaction with active sites. At the same

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 8. a) Conversion of 2-naphthol and b) ratio between corresponding pyranyl/furanyl products over N₃-5d material in annulation reaction using different solvents (80 °C) and at different temperatures (60, 70, 80 °C; 1,2-dichloroethane as the solvent); c) change of conversion of 2-naphthol (solid lines) and 6/5-ring isomers ratio (dotted lines) after adding of catalyst or MBO after 240 min.

time, the selectivities significantly decreased with time for reactions performed in different solvents at $80 \,^{\circ}$ C (Figure 8b).

In contrast, the change of reaction temperature impacted the conversion of 2-naphthol insignificantly (Figure 8 a), influencing mainly the selectivity to the DMBP/TMBF isomeric products (Figure 8 b). The decreasing reaction temperature resulted in significant increase in the ratio DMBP/TMBF, which is obviously caused by deceleration of the thermal rearrangement of DMBP to corresponding TMBF.

To investigate the catalytic performance of the most active N₃-5d catalyst in more detail, two additional experiments were performed: 1) adding of an extra amount of the MBO (4.5 mmol), and 2) addition of a fresh portion of the catalyst (50 mg) at 240 min TOS. Notably, doubling the amount of catalyst (Figure 8c, red line) had less effect (+11%) on the increasing substrate conversion related to the standard experiment (Figure 8c, black line) than addition of extra MBO (+18%, Figure 8c, blue line). The additional amount of the catalyst mainly triggered the isomerization process (indicated by decreasing DMBP/TMBF ratio, Figure 8c), whereas the increase in the MBO concentration led to the formation of DMBP (indicated by increasing relative content in the mixture of isomers, Figure 8c). Thus, as soon as conversion of 2-naphthol over N₃-5d catalyst reaches plateau, the DMBP-to-TMBF rearrangement becomes dominant over the annulation reaction. The obtained results indicate that reaching the plateau is caused by both partial deactivation of the catalyst and adsorption/desorption competition between reactants and products.

Conclusions

Catalytic properties of mesophase and lamellar materials composed of MFI nanosheets of different thickness were investigated in annulation of phenols differing in size of the molecules (i.e., phenol, 1-, and 2-naphthol).

The conversions of phenols under study decreased in the following sequence of materials: N_3 -5d > N_4 -5d > N_5 -5d > N_3 -9d, following the decreasing external surface area and concentration of surface acid sites. The preferences of 2D zeolites having improved textural characteristics (i.e., higher specific pore volume, external surface area) over bulky zeolites BEA and especially MFI in annulation of phenols become more prominent with increasing the size of substrates under investigation (phenol < 1-naphthol < 2-naphthol). The 2D material containing one pentasil layer (N₃-9d) surpasses not only medium-pore zeolite MFI and large-pore zeolite BEA, but also micro-/mesoporous USY zeolite, which seems to be caused by higher void volume within N₃-9d sufficient for a) the activation of substrates and b) the formation of bulky intermediates arising from its superior textural characteristics at reasonable acidity.

Increasing of the temperature and the decreasing of the relative polarity of the solvent used (in the order: DMSO > 1,2-dichloroethane > chlorobenzene > *p*-xylene) resulted in the increase of the yield of target products. The results of this study clearly demonstrate that the novel materials characterized by improved textural characteristics, compared with conventional 3D zeolites, can be regarded as promising acid catalysts of reactions involving more bulky substrates.

Experimental Section

Synthesis of zeolites

Zeolite synthesis was performed by using gemini-type multiquaternary ammonium surfactants having formulas [C₁₈H₃₇-N⁺(Me)₂- $\{C_6H_{12}\text{-}N^+(Me)_2\}_{n-2}\text{-}C_6H_{12}\text{-}N^+(Me)_2\text{-}C_{18}H_{37}][Br^-]_n \ (n=3,\ 4,\ \text{and}\ 5) \ \text{as}$ SDAs (denoted as 18-N_n-18). The synthesis of SDAs was performed as described elsewhere.^[25] The starting gel composition for zeolite synthesis was 30 SiO₂:0.5 Al₂O₃:(0.8–1.3) 18-N_n-18:6.6 Na₂O:1070 H₂O. The bromide form of 18-N_n-18 was dissolved in water solution of NaOH and NaAlO₂. Then, tetraethyl orthosilicate was added to prepared solution into a polypropylene bottle under vigorous stirring. After further mixing by using a mechanical stirrer for 6 h in an oven at 60°C, the resultant gel was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was tumbled with mixing baffles at 60 rpm in an oven at 140 $^\circ\text{C}.$ If 18-N₃-18 was used as SDA, the precipitated solid was sampled after 1, 5, and 9 d. In the case of $18-N_4-18$ and $18-N_5-18$, the synthesis was stopped after 5 d. The collected samples were filtered, washed with distilled water, dried at 100°C, and finally calcined in air at 580°C. The calcined samples were treated two times with 1 M aqueous solution of NH₄Cl at RT followed by profound washing in distilled water. The NH₄⁺ ion-exchanged samples were then calcined at 550 °C to convert zeolites to the H⁺ ionic form. Obtained samples were denoted as N_n -xd, for which *n* is the number of ammonium segments in SDA used, x is duration of hydrothermal synthesis (days). For comparison, commercially available H-forms of zeolites MFI, BEA, ultrastable FAU (USY) were used.

Characterization

XRD patterns were recorded with a Rigaku Multiflex diffractometer using Cu_{ka} radiation ($\lambda = 0.1541$ nm) at 30 kV and 40 mA.

Nitrogen adsorption-desorption isotherms were measured with a Micromeritics Tristar II volumetric adsorption analyzer at -196 °C after degassing the H⁺ form of samples for 6 h at 300 °C. The specific surface area was calculated from the adsorption branch in the range of $0.1 \le p/ps \le 0.3$ using the BET equation. The pore-size distribution was estimated by using the Barrett-Joyner-Halenda (BJH) algorithm. Ar adsorption-desorption isotherms were measured with Micromeritics ASAP 2020 at -186 °C. Micropore size distribution was estimated by using the Non-Localized Density Functional Theory calculation from the adsorption branch of Ar isotherm.

TEM images were obtained with a Philips F30 Tecnai with accelerating voltage of 300 kV. SEM images were taken by using a Hitachi S-4800 without a metal coating.

Concentration and type of acid sites were determined by adsorption of pyridine and 2,6-DTBP as probe molecules followed by FTIR spectroscopy (Nicolet 6700 FTIR with AEM module). Prior to the adsorption, self-supporting wafers of individual catalysts were activated in situ by evacuation at temperature 450 °C for 12 h. Details of measurement are described elsewhere.^[18]

Catalysis

Annulation reaction between MBO and phenols (phenol, 1-naphthol, 2-naphthol) was performed in a liquid phase under atmospheric pressure and temperatures of 60-100°C in a multiexperiment work station StarFish. Before the catalytic experiments, catalyst portions of 50 mg were activated at 450 °C for 90 min with a temperature heating rate of 10°C min⁻¹. Typically, phenol (3 mmol), mesitylene (0.4 g, internal standard), catalyst (50 mg), and 1,2-dichloroethane (10 mL, solvent) were added to the threenecked vessel, equipped with a condenser and thermometer, stirred, and heated. Then MBO (4.5 mmol) was added into the reaction vessel through a syringe as soon as the desired reaction temperature was reached. Volumes of 0.2 mL of the reaction mixture were sampled by means of a syringe with needle after 10, 30, 60, 120, 180, 300, and 1440 min. The reaction products were analyzed by gas chromatography (GC) using an Agilent 6850 with flame ionization detector equipped with a nonpolar HP1 column (diameter 0.25 mm, thickness 0.2 µm, and length 30 m). The reaction products were identified by using GC-MS analysis (ThermoFinnigan, FOCUS DSQ II Single Quadrupole GC/MS).

Acknowledgements

R.R. acknowledges support by Institute for Basic Science (IBS) [CA1301]. J.Č. acknowledges the Czech Science Foundation (P106/12/G015).

Keywords: acidity • annulation • arenes • nanostructures • zeolites

- a) A. Corma, *Chem. Rev.* **1997**, *97*, 2373–2419; b) A. Dhakshinamoorthy,
 M. Opanasenko, J. Čejka, H. Garcia, *Adv. Synth. Catal.* **2013**, *355*, 247–268; c) J. Čejka, G. Centi, J. Perez-Pariente, W. J. Roth, *Catal. Today* **2012**, *179*, 1–15.
- [2] a) D. P. Serrano, J. M. Escola, P. Pizarro, Chem. Soc. Rev. 2013, 42, 4004–4035; b) M. Bejblová, D. Prochazkova, J. Čejka, ChemSusChem 2009, 2, 486–499; c) M. E. Davis, Chem. Mater. 2014, 26, 239–245; d) E. Mahmoud, R. F. Lobo, Microporous Mesoporous Mater. 2014, 189, 97–106.
- [3] a) A. Corma, M. J. Diaz-Cabanas, J. Luis Jorda, C. Martinez, M. Moliner, Nature 2006, 443, 842–845; b) A. Corma, M. J. Diaz-Cabanas, F. Rey, S. Nicolooulas, K. Boulahya, Chem. Commun. 2004, 1356–1357; c) J. Jiang, J. Yu, A. Corma, Angew. Chem. Int. Ed. 2010, 49, 3120–3145; Angew. Chem. 2010, 122, 3186–3212; d) J. Sun, C. Bonneau, A. Cantin, A. Corma, M. J. Diaz-Cabanas, M. Moliner, D. Zhang, M. Li, X. Zou, Nature 2009, 458, 1154–U1190.
- [4] J.-B. Koo, N. Jiang, S. Saravanamurugan, M. Bejblova, Z. Musilova, J. Čejka, S.-E. Park, J. Catal. 2010, 276, 327–334.
- [5] a) L. Tosheva, V. P. Valtchev, Chem. Mater. 2005, 17, 2494-2513; b) S. C. Larsen, J. Phys. Chem. C 2007, 111, 18464-18474.
- [6] K. Na, C. Jo, J. Kim, K. Cho, J. Jung, Y. Seo, R. J. Messinger, B. F. Chmelka, R. Ryoo, *Science* **2011**, *333*, 328–332.
- [7] a) X. T. Wei, P. G. Smirniotis, *Microporous Mesoporous Mater.* 2006, *89*, 170–178; b) H. Chen, J. Wydra, X. Zhang, P.-S. Lee, Z. Wang, W. Fan, M. Tsapatsis, *J. Am. Chem. Soc.* 2011, *133*, 12390–12393.
- [8] a) L. Wang, Z. Zhang, C. Yin, Z. Shan, F.-S. Xiao, *Microporous Mesoporous Mater.* 2010, 131, 58–67; b) Y. Jin, Y. Li, S. Zhao, Z. Lv, Q. Wang, X. Liu, L. Wang, *Microporous Mesoporous Mater.* 2012, 147, 259–266; c) F. S. Xiao, L. F. Wang, C. Y. Yin, K. F. Lin, Y. Di, J. X. Li, R. R. Xu, D. S. Su, R. Schlogl, T. Yokoi, T. Tatsumi, *Angew. Chem. Int. Ed.* 2006, 45, 3090–3093; Angew. Chem. 2006, 118, 3162–3165.
- [9] H. Wang, T. J. Pinnavaia, Angew. Chem. Int. Ed. 2006, 45, 7603-7606; Angew. Chem. 2006, 118, 7765-7768.
- [10] a) Y. S. Tao, H. Kanoh, L. Abrams, K. Kaneko, *Chem. Rev.* 2006, *106*, 896–910; b) K. P. de Jong, J. Zecevic, H. Friedrich, P. E. de Jongh, M. Bulut, S. van Donk, R. Kenmogne, A. Finiels, V. Hulea, F. Fajula, *Angew. Chem. Int. Ed.* 2010, *49*, 10074–10078; *Angew. Chem.* 2010, *122*, 10272–10276.

ChemCatChem 0000, 00, 1 - 10

^{© 2014} Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

- [11] W. J. Roth, C. T. Kresge, J. C. Vartuli, M. E. Leonowicz, A. S. Fung, S. B. McCullen in *Stud. Surf. Sci. Catal.*, *Vol. 94* (Eds.: H. K. Beyer, H. G. Karge, I. Kiricsi, J. B. Nagy), **1995**, pp. 301–308.
- [12] a) A. Corma, U. Diaz, V. Fornes, J. M. Guil, J. Martinez-Triguero, E. J. Creyghton, J. Catal. 2000, 191, 218–224; b) W. J. Roth, in Stud. Surf. Sci. Catal., Vol. 158 (Eds.: J. Čejka, N. Zilkova, P. Nachtigall), 2005, pp. 19–26.
- [13] a) W. J. Roth, O. V. Shvets, M. Shamzhy, P. Chlubna, M. Kubu, P. Nachtigall, J. Čejka, *J. Am. Chem. Soc.* **2011**, *133*, 6130–6133; b) W. J. Roth, P. Nachtigall, R. E. Morris, P. S. Wheatley, V. R. Seymour, S. E. Ashbrook, P. Chlubna, L. Grajciar, M. Polozij, A. Zukal, O. Shvets, J. Čejka, *Nat. Chem.* **2013**, *5*, 628–633.
- [14] a) K. Na, W. Park, Y. Seo, R. Ryoo, *Chem. Mater.* 2011, *23*, 1273–1279;
 b) J. Kim, W. Park, R. Ryoo, *ACS Catal.* 2011, *1*, 337–341.
- [15] a) W. Park, D. Yu, K. Na, K. E. Jelfs, B. Slater, Y. Sakamoto, R. Ryoo, *Chem. Mater.* 2011, 23, 5131–5137; b) E. Verheyen, C. Jo, M. Kurttepeli, G. Vanbutsele, E. Gobechiya, T. I. Koranyi, S. Bals, G. Van Tendeloo, R. Ryoo, C. E. A. Kirschhock, J. A. Martens, *J. Catal.* 2013, 300, 70–80.
- [16] a) M. J. Climent, A. Corma, A. Velty, *Appl. Catal. A* 2004, *263*, 155–161;
 b) A. Corma, V. Fornes, J. M. Guil, S. Pergher, T. L. M. Maesen, J. G. Buglass, *Microporous Mesoporous Mater.* 2000, *38*, 301–309; c) A. Corma, U. Diaz, V. Fornes, J. L. Jorda, M. Domine, F. Rey, *Chem. Commun.* 1999, 779–780; d) A. Corma, U. Diaz, M. E. Domine, V. Fornes, *Chem. Commun.* 2000, 137–138; e) W. J. Roth, J. Čejka, *Catal. Sci. Technol.* 2011, *1*, 43–53.

- [17] D. Harel, D. Schepmann, H. Prinz, R. Brun, T. J. Schmidt, B. Wunsch, J. Med. Chem. 2013, 56, 7442-7448.
- [18] C. Jo, R. Ryoo, N. Zilkova, D. Vitvarova, J. Čejka, Catal. Sci. Technol. 2013, 3, 2119–2129.
- [19] M. M. J. Treacy, J. B. Higgins, Collection of Simulated XRD Powder Patterns for Zeolites, Elsevier, Amsterdam, 2007.
- [20] a) C. A. Emeis, J. Catal. **1993**, 141, 347–354; b) J. A. Lercher, A. Jentys, in Stud. Surf. Sci. Catal., Vol. 168 (Eds.: P. A. Jacobs, E. M. Flanigen, J. C. Jansen, H. van Bekkum), Elsevier, Amsterdam, **2007**, pp. 435–476.
- [21] A. Corma, V. Fornes, L. Forni, F. Marquez, J. Martinez-Triguero, D. Moscotti, J. Catal. 1998, 179, 451–458.
- [22] A. Ungureanu, T. V. Hoang, D. Trong On, E. Dumitriu, S. Kaliaguine, *Appl. Catal. A* 2005, 294, 92–105.
- [23] J. H. P. Tyman, Synthetic and natural phenols, Vol. 52, Elsevier, Amsterdam, 1996.
- [24] a) E. D. Weil, E. Leon, J. Linder, J. Org. Chem. 1961, 26, 5185-; b) D. N.
 Bobrov, A. S. Lyakhov, A. A. Govorova, V. I. Tyvorsky, Chem. Heterocycl. Compd. 2000, 36, 899-904.
- [25] J. Jung, C. Jo, K. Cho, R. Ryoo, J. Mater. Chem. 2012, 22, 4637-4640.

Received: February 4, 2014 Revised: April 3, 2014 Published online on ■■ ■, 0000

FULL PAPERS

M. V. Opanasenko, M. V. Shamzhy, C. Jo, R. Ryoo, J. Čejka*

Annulation of Phenols: Catalytic Behavior of Conventional and 2D Zeolites



Ideal for bulky substrates: Catalytic behavior of hierarchical MFI zeolites was investigated in annulation reaction of phenols differing in size with methylbutenol and compared with that of medium and large-pore zeolites MFI and BEA.