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Efficient Transformation of Anisole into Methylated Phenols over High-Silica HY Zeolites under Mild Conditions

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Transformation of anisole (methoxybenzene), a typical component of bio-oil, into phenol and methylated phenols was studied over HY zeolites with framework Si/Al ratios of 5, 15, 25, and 35. It was demonstrated that the amounts of Brønsted acid and Lewis acid sites, the ratio of Lewis acid and Brønsted acid sites, and the textural properties of the zeolites were all crucial parameters that influenced the catalytic performance. The Brønsted acid and Lewis acid sites of the zeolites catalyzed the reaction cooperatively and efficiently promoted the transmethylation. The hierarchical channel system with fully open micropore–mesopore connectivity was favorable to reduce the amount of coke generated.

Pollution problems associated with the use of fossil fuels and the dwindling reserves of these fuels have resulted in increased attention on alternative sources. Biomass is an important renewable carbon resource for fuels and chemicals.[1] Among the various components of biomass, the transformation of lignin has attracted much attention in recent years. Lignin is considered to be the major aromatic resource of bio-based economy.[2] Some lignin structural linkage units are shown in Figure 1.[3] The direct use of bio-oil as a liquid fuel is currently not feasible owing to its high oxygen content and instability.[4] The transformation of methoxyphenols into liquid alkanes for bio-oil upgrading by cracking or hydrolysis, catalytic reduction, and catalytic oxidation has been extensively studied. Unfortunately, current upgrading process are usually accompanied by the generation of CH_4,[5] CH_3OH,[5,6] or other highly volatile products by demethylation or demethoxylation of the methoxy groups, which approximately account for 10–25% of lignin.[7] Transmethylation offers an atom-economic way to prevent carbon from being lost as a high-volatile product, and the methylated phenolic products can be further transformed into high-octane fuels by hydrodeoxygenation, and they are also fundamental raw materials of organic chemicals.[8]

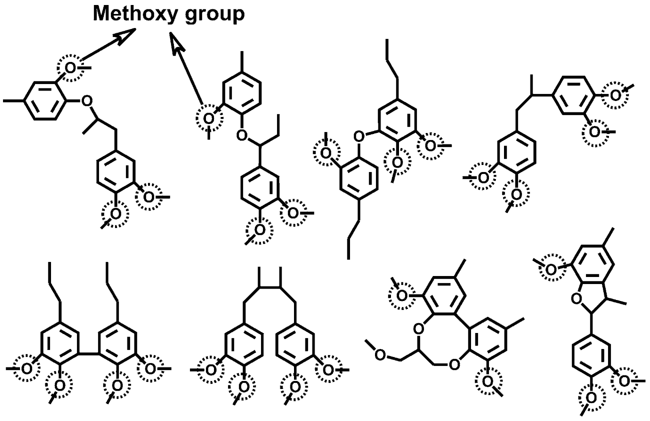

Figure 1. Methoxy group in the common lignin linkages adapted from Huber et al.[3]

Zeolites are widely used to catalyze various kinds of reactions. They have also been used in the transmethylation of anisole (methoxybenzene), which is a typical component of bio-oil.[9a] For example, Zhu et al. studied the transmethylation of anisole over HZSM-5 zeolite at approximately 200–550 °C.[9a] It was shown that the reaction temperature had a significant impact on the yields of the methylated products. At 250 °C, only 23% conversion of anisole was achieved, and the yields of the methylated products cresol and 2,4-xylenol were approximately 6 and 1%, respectively. By contrast, 95% conversion was achieved to provide cresol in 36% yield and 2,4-xylenol in 12% yield at 450 °C. They also reported the bifunctional transmethylation and hydrodeoxygenation of anisole over a Pt/HBeta catalyst at 400 °C.[9b] Wang et al. investigated the selective synthesis of *para*-cresol by conversion of anisole on HZSM-5 zeolites at 450 °C.[10a] The selectivity for *para*-cresol increased significantly by silylation and steaming treatments. Prasomsri et al. investigated the conversion of pure anisole and its mixtures with tetralin over HY and HZSM-5 zeolites at 400 °C.[10b] The dominant reaction of pure anisole was transalkylation, which produced phenol, methylated phenols, and methylanisoles as the main products, with significant catalyst deactivation. Co-feeding tetralin had a beneficial effect on anisole conversion and reduced coke formation. In general, reactions over zeolites have been studied under harsh reaction conditions, and the effects of the properties of zeolites on the transmethylation need to be studied further.

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Table 1. Textural and acid properties of the HY and OHY zeolites.

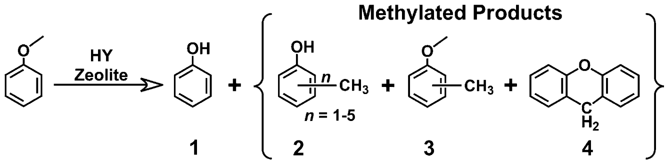
Entry	Catalyst	Si/Al_F[a]	Surface area $[m^2 g^{-1}]$		Pore volume $[cm^3 g^{-1}]$		Total amount $[\mu mol\, g^{-1}$, 200 °C] and distribution of acid sites[f]			
			S_{micro}[b]	S_{meso}[c]	V_{micro}[d]	V_{meso}[e]	Brønsted	Lewis	B+L[g]	L/B[h]
1	HY_5	4.97	665	154	0.275	0.090	1125	239	1364	0.21
2	HY_{15}	14.1	467	355	0.185	0.162	355	96	451	0.27
3	HY_{25}	23.4	382	423	0.156	0.192	229	125	354	0.55
4	HY_{35}	34.3	319	483	0.121	0.226	157	60	217	0.38
5	OHY_{25}	23.4	380	445	0.155	0.204	206	21	227	0.10

[a] Si/Al_F denotes the framework Si/Al_F ratio of the HY zeolite obtained by XRD. [b] The t-plot micropore surface area. [c] The t-plot mesopore surface area. [d] The t-plot micropore volume. [e] BJH mesopore volume. [f] The total amount of acid sites in the samples was calculated according to equations in Ref. [15] [g] "B+L" represents the sum of the amounts of Brønsted acid and Lewis acid sites. [h] "L/B" denotes the ratio of the amounts of Lewis acid and Brønsted acid sites.

In this work, we studied the transmethylation of anisole over HY zeolites with different properties under mild conditions. It was found that the acidic and textural properties of the zeolites influenced the reaction significantly. HY zeolites with larger Si/Al_F ratios (framework Si/Al ratio, mol) showed excellent transmethylation performance because of suitable textural properties and the cooperative effects of the Brønsted acid and Lewis acid sites in the catalysis.

The HY zeolites used were characterized by pyridine-adsorbed Fourier transformed infrared spectroscopy (Py-FTIR), X-ray diffraction (XRD), magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, N_2 adsorption/desorption, and transmission electron microscopy (TEM). Details are discussed in the Supporting Information (Figures S1–S6 and Tables S1 and S2). Table 1 presents their Si/Al_F ratios and their textural and acid properties.

The transformation of anisole over different zeolites was studied, as shown in Scheme 1 and Table 2. The conversions of anisole on the HY catalysts (HY_5, HY_{15}, HY_{25}, and HY_{35}; subscripts denote the Si/Al ratios) were all very high under the experimental conditions. However, the product distribution depended considerably on the properties of the zeolites used. A comparative experiment was conducted by using HZSM-5 zeolite as the catalyst (Table 2, entry 6). The conversion of anisole and yields of methylated phenols over the HZSM-5 zeolite were much lower than those on the high-silica HY zeolites at 240 °C. Taking into account the topology of the zeolite, the framework of HZSM-5 zeolite contains two perpendicularly intersecting channel systems composed of straight channels with dimensions of 0.51×0.54 nm and zigzag channels with free dimensions of 0.54×0.56 nm and only one type of framework hydroxy groups, which are probably located near the channel intersections.[11a–c] A high temperature is required to overcome the diffusional resistance of anisole from the pore openings to the intersections, where the transmethylation can be catalyzed on the Brønsted acid sites.[11d] However, the faujasite structure of the HY zeolites has a 3D channel system with supercages (1.3 nm) connected tetrahedrally through 12-membered silicate ring openings that are 0.74 nm in diameter.[11e] The hierarchical channel system with fully open micropore–mesopore connectivity of the HY zeolites is better for the diffusion of reactant and product.



Scheme 1. Transformation of anisole on the HY zeolites.

Table 2. Transformation of anisole on different zeolite catalysts.[a]

Entry	Catalyst	Conversion [wt %]	Yield [wt %] 1	2	3	4	coke[b]
1	HY_5	94.3	22.8	40.4	2.5	3.3	18.3
2	HY_{15}	96.3	31.0	45.2	2.0	3.6	10.5
3	HY_{25}	96.6	31.7	51.5	1.9	4.1	5.3
4	HY_{35}	94.6	36.2	48.0	2.7	2.8	3.9
5	OHY_{25}	68.0	25.9	19.0	8.4	2.7	5.5
6	HZSM-5	40.3	17.2	5.3	5.4	0.8	7.5

[a] Reactions conditions: Anisole (0.010 mol), catalyst (0.1 g), N_2 (0.5 MPa), 240 °C, 3 h. [b] Equation (3) was used to calculate the coke yield.

Besides the textural structure, the properties of the acid sites are also important parameters for the transmethylation reaction. At a given Si/Al_F ratio, differences in the zeolite acidity between various sites and frameworks is generally due to differences in both the local structures and crystal potentials.[12a] As reported previously, the framework Si–O–Al bond angle in the local structure of the bridging OH group, which depends on the zeolite structure type, always affects the acid strength of the Brønsted acidic hydroxy protons.[12b] In HZSM-5 zeolite, the Si–O–Al bond angles vary from 137 to 177°, whereas hydroxy protons are preferably bound to the more accessible bridging oxygen atoms of the double six-membered ring (O1 positions) in zeolite HY, which limits the range of Si–O–Al bond angles from 138 to 147°, and this makes the O(1)H sites of high-silica HY zeolite more acidic than the "regular" acidic sites in HZSM-5 at lower temperatures.[12] So, the high-silica HY zeolite exhibits much better performance than HZSM-5 under mild conditions. The HY_{25} zeolite with a Lewis acid/Brønsted acid ratio of 0.55 (Table 1, entry 3) exhibited the highest yields of the methylated phenols (Table 2, entry 3), although HY_5 had the maximum total amount of Lewis acids and Brønsted acids. This suggests that Brønsted acids and Lewis acids cooperatively promote the transmethylation. Recently, the Gates group compared the activity of Pt/Al_2O_3 and Pt/HY catalysts in the hydrodeoxygenation of anisole and guaiacol.[13,14] Their results showed that the transalkylation activity of the catalysts was significantly affected by the type of acidic sites. Zhu et al. further confirmed the effect of acidic sites on transalkylation activity in the hydrodeoxygenation of anisole.[9b]

The properties of the Brønsted acids or Lewis acids in the HY zeolites is generally related to the location of the aluminum atoms within the zeolites.[16] With an increase in the Si/Al_F ratio, the number of Al atoms per unit cell ($N_{Al/UC}$, Table S1) and the relative content of the $Si(OAl)_n(OSi)_{4-n}$ units (Table S2, $n=1$, 2 and 3) in the HY zeolites decreases; this correlates with a gradual decrease in the Brønsted acid sites of the HY zeolites and proves the function of framework aluminum (FAl) species as the predominant source of Brønsted acid sites.[17] Besides, it is generally accepted that framework Al species in the microporous skeleton are also the suppliers for the Lewis acid sites.[18] The content of extra-framework oxoaluminum (EFAl) is only 0.6 %, and the amount of Lewis acid can still reach 239 $\mu mol\,g^{-1}$ for HY_5 zeolite (Table 1). In contrast to the HY_5 and HY_{15} zeolites, HY_{25} possesses a lower content of FAl species but a higher EFAl/FAl ratio (0.28, Table S2), which indicates that six-coordinated EFAl, such as AlO^+, $Al(OH)_2^+$, and $AlOH^{2+}$, or some neutral species, AlOOH and $Al(OH)_3$ resonating in the ^{27}Al MAS NMR spectrum of HY_{25} zeolite at $\delta \approx 0$ ppm (Figure S4),[19] should be responsible for the larger Lewis acid quantity.[20] According to a previous study on electrophilic aromatic substitution reactions, Lewis acids can activate the benzene ring, which tends to make one of the carbon atoms of the benzene ring highly nucleophilic, and this facilitates electrophilic aromatic substitution.[21] Lewis acidic EFAl species in the HY_{25} zeolite can be considered as more effective activators of the aromatic ring, owing to their readily accessible deposition in the voids of the zeolite.[21c–d]

In the catalysis of the high-silica HY zeolites, the cooperative effect between the Brønsted acid and Lewis acid sites contributes significantly to the high yield of the desired product. The cooperative mechanism of the Brønsted acids and Lewis acids is shown in Figure 2. First, the methoxy group is transferred to the Brønsted acid site of the HY zeolite to form a methyl carbocation, and then the benzene ring is attacked to form the product through an electrophilic substitution reaction.[22] It is the Lewis acid sites that promote the aromatic electrophilic substitution reaction. To further demonstrate the contribution of the Lewis acid sites, HY_{25} zeolite was treated with oxalic acid (defined as OHY_{25}, entry 5 of Table 1) to decrease the Lewis acid quantity.[23] Compared with HY_{25}, the conversion of anisole and yield of methylated phenols were clearly lower over OHY_{25} zeolite (Table 2, entry 5). The results convincingly demonstrate that Lewis acid sites, especially the Lewis acidic EFAl positions, contribute to activating the aromatic ring and are indispensable to highly effective methylation.

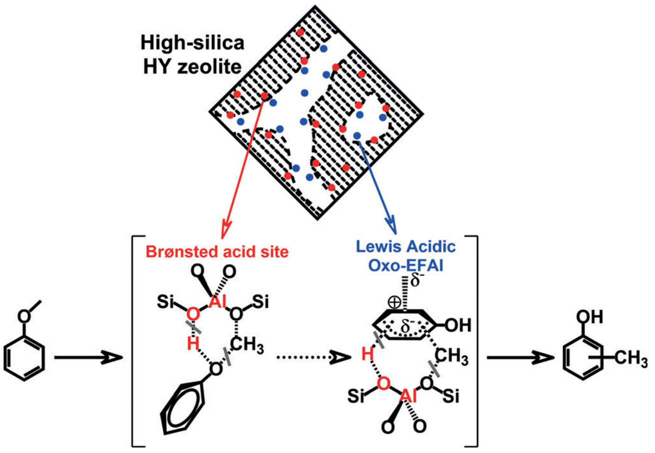


Figure 2. Proposed catalytic mechanism for the transmethylation of anisole over high-silica HY zeolite.

As previously reported, solid acid catalyzed alkylation is always accompanied with coke formation.[24] A comparison of coke yield at nearly the same conversion of anisole is given in Table 2. The amount of coke produced over the zeolites follows the order $HY_5 > HY_{15} > HY_{25} > HY_{35}$. As shown in Figure S5 a, the uptake of nitrogen at a relative pressure (P/P_0) exceeding 0.8 is justifiably attributed to the occurrence of a wide pore-size distribution,[25] which is clearly evidenced by the mesopores with another broad distribution centered at approximately 20 nm in the HY_n ($n=15$, 25, and 35) zeolites. The TEM images (Figure S6) also reveal that as the Si/Al_F ratio of the HY zeolites increases, the integrity and angular shape of the crystals get progressively worse and ill defined, respectively, which coincides with the XRD analysis (Figure S2, Table S1). Especially noteworthy is that the structures of HY_{15}, HY_{25}, and HY_{35} are more mesoporous than that of HY_5 zeolite (Figure S6). Concretely, as the Si/Al_F ratio of the HY zeolite increases from 5 to 35, the microporous surface area and volume decrease from 665 to 319 $m^2\,g^{-1}$ and from 0.275 to 0.121 $cm^3\,g^{-1}$, respectively (Table 1). Furthermore, the mesoporous surface area and volume of HY_{35} are almost 3.1 and 2.5 times higher than those of the HY_5 zeolite, respectively (Table 1). Therefore, it can be deduced that the hierarchical porous HY_{25} and HY_{35} zeolites with more mesopores and fully open micropore–mesopore connectivity could provide more diffusional paths for the fast diffusion of phenol and methylated phenols formed on the acid sites located in the micropores and mesopores, and this, therefore, retards coke formation.[26] In contrast, the amount of coke was very large if the HY_5 zeolite was used as the catalyst. The main reason may be that it has very large amounts of FAl-derived Brønsted acid sites in the long and narrow micropores but a small ratio of Lewis acid and Brønsted acid sites. Consequently, the primary products generated on the FAl-derived acid sites within the HY_5 zeolite are subjected to deep reactions and the formation of coke precursors through a transalkylation route owing to diffusion limitations of the micropores.[27] Subsequently, oligomerization of the coke precursors trapped inside the micropores results in a higher coke yield and lowers the yields of phenol and methylated phenols.[28]

The above results indicate that HY_{25} is the best catalyst for the transmethylation reaction among the zeolites tested owing to its hierarchical channel system and suitable ratio of Brønsted acid sites and Lewis acid sites. Therefore, we studied the effects of reaction temperature and time on the reaction performance of HY_{25} zeolite. The conversion of anisole and the yields of the products as a function of temperature are plotted in Figure 3a. It can be seen that the conversion of anisole increased from 45.7 to 99.6% as the temperature was changed from 180 to 280 °C. In this temperature range, the yield of methylanisole began to decrease at 200 °C. By contrast, the yields of phenol, cresol, and xylenols kept increasing with temperature from 180 to 240 °C. The amount of coke increased markedly at temperatures above 220 °C, because oligomerization of the coke precursors became more severe. The results in Figure 3a show that the optimum temperature for the transformation of anisole is 240 °C. The effect of reaction time on the reaction at 240 °C is illustrated in Figure 3b. The yield of methylanisole increased in the time range of 0 to 20 min and then decreased, and the yield of the phenolic products such as phenol, cresol, and xylenols increased with time until 180 min. The yields of phenol and methylated phenols decreased slightly after 180 min, because the side reactions that produce byproducts (e.g., xanthene and coke) became more pronounced.

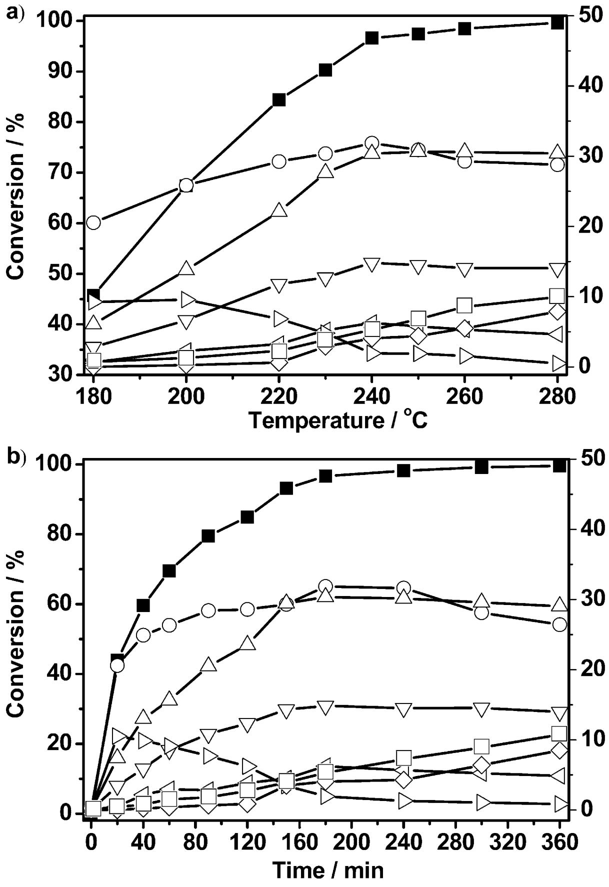


Figure 3. The effect of a) reaction temperature and b) time on the conversion of anisole (■) and on the yields of phenol (○), cresol (△), xylenols (▽), tri/tetra/pentamethylphenol (◁), methylanisole (▷), xanthene (◇) and coke (□). Reaction conditions for a) Anisole (0.010 mol), HY_{25} (0.1 g), N_2 (0.5 MPa), 180 min. Reaction conditions for b) Anisole (0.010 mol), HY_{25} (0.1 g), N_2 (0.5 MPa), 240 °C.

In conclusion, we studied the transformation of anisole into phenol and methylated phenols over HY zeolites. It was found that high-silica HY zeolites, such as HY_{25} and HY_{35}, are highly efficient for the transmethylation reaction under mild conditions. HY_{25} zeolite showed the best transmethylation performance, because it has both the proper ratio of Lewis acid sites and Brønsted acid sites and a suitable porous structure. The Brønsted acid and Lewis acid sites of the zeolites have an excellent cooperative effect in promoting the transmethylation reaction. The hierarchical channel system with fully open micropore–mesopore connectivity is favorable to reduce the amount of coke generated. We believe that high-silica HY zeolites have potential applications in atom-economic transmethylation and lignin transformations.

Experimental Section

Typical experimental procedure

Anisole (1.0813 g) and the catalyst (0.10 g) were charged into a 25 mL stainless-steel reactor. After flushing the reactor with N_2 (3×), it was placed in an air bath of the desired temperature and the stirrer was started. After a known time, the reactor was quenched in an ice-water bath, and the organic products were extracted with acetonitrile. Quantitative analysis of the mixture was performed by using gas chromatography (GC, HP 4890) with a flame ionization detector and a DB-5 capillary column (30 m× 250 μm). The products were also identified by GC–MS (Shimadzu QP 2010S) and by comparing the retention times of the standards in the GC traces. The conversion and selectivity were calculated from the GC data by using biphenyl as an internal standard.

The conversion was calculated by using Equation (1), the yield was calculated by using Equation (2), and the coke yield was calculated on the mass basis of the fresh and used catalysts [Eq. (3)]:[29]

$$\text{Conversion}\,[\text{wt}\,\%] = \frac{(\text{mass of converted raw material})}{(\text{total mass of raw material})} \times 100\,\% \tag{1}$$

$$\text{Yield}\,[\text{wt}\,\%] = \frac{(\text{mass of each product})}{(\text{total mass of raw material})} \times 100\,\% \tag{2}$$

$$\text{Coke yield}\,[\text{wt}\,\%] = \frac{(\text{mass of used catalyst} - \text{mass of fresh catalyst})}{(\text{mass of loaded anisole})} \times 100\,\% \tag{3}$$

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Keywords: Brønsted acids · Lewis acids · lignin · transmethylation · zeolites

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