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Probing the active catalytic sites of zeolites with benzyl chloride

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Abstract—Zeolites contain numerous catalytic sites. In order to conduct organic chemistry properly, it is necessary to know which site catalyzes the reaction. The conversion of benzyl chloride was tested as a probe reaction. Different products are obtained when the reaction is catalyzed by a Brønsted acidic site instead of a Lewis acidic site. Basic catalysis, water content and coke formation complicate the probe reaction. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Zeolites have become very popular as hosts, wherein a rich variety of organic reactions can be conducted.[1–3] These minerals are, however, much more than simple inorganic hosts. Molecular sieves contain many different catalytic sites, which have to be taken into account when studying an organic reaction within zeolites.

Zeolites contain both Brønsted- and Lewis acidic sites.[4–6] The nature of the Lewis acidic sites is still subject of speculation. Coordinatively unsaturated aluminum[7] and silicon,[8–9] different extra-framework aluminum species,[10–13] metal impurities,[14] and counter cations affiliated with the tetrahedrally coordinated aluminum[15] have all been suggested to be Lewis acidic sites.

In contrast, the nature of the Brønsted acidic sites is well understood.[16] Zeolites are made up of tetrahedra, with oxygen atoms as apices and silicon or aluminum in their center. Each oxygen anion shares two lattice cations, thus connecting the corners of the tetrahedra. The $SiO_{4/2}$ tetrahedra are neutral, but the $(AlO_{4/2})^-$ tetrahedra bear a negative charge. When the cation compensating this negative charge is a proton, a Brønsted acidic site is obtained (see Fig. 1). The zeolite lattice oxygen atoms are the complementary bases.

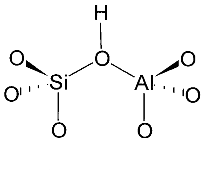


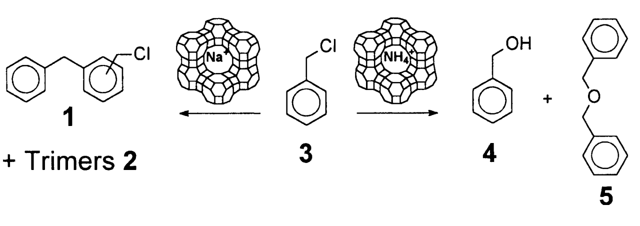
Figure 1. Zeolitic Brønsted acidic site.

The acidic sites of zeolites can be determined with a wide variety of analytical methods, such as temperature programmed desorption, IR and NMR spectroscopy. Unfortunately, none of these methods is perfect. Each method has its specific advantages and disadvantages.[17]

Knowing all catalytic sites that are all available within a zeolite does not, however, answer all questions. It is often still uncertain *which* catalytic site or which reaction pathway is responsible for a specific organic transformation. Silasesquioxanes, small well-defined silica building blocks, have successfully been used as homogeneous[18] and heterogeneous[19–20] models for catalytic sites. An organic model reaction which allows to distinguish Brønsted and Lewis acidity, however, fails. As this information is of paramount importance to conduct organic reactions as properly as possible, an attempt has been made to present such a reaction.

Benzyl chloride promises to be an ideal molecule for such a probe reaction, because it undergoes different reactions in the presence of a conventional Brønsted acid as in the presence of a Lewis acid (see Scheme 1).

In the presence of a Brønsted acid, benzyl chloride is converted in benzyl alcohol.[21–22] Under the Brønsted acidic conditions applied, benzyl alcohol reacts further to dibenzyl ether.[23] Catalysis by a common Lewis acid, like $AlCl_3$, leads to fast polymerization.[24] Within the confinement of the



Scheme 1. The model reaction.

Keywords: zeolite; catalytic sites; benzyl chloride.

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Table 1. IR spectra of pyridine absorbed on the zeolite probes

Entry	Zeolite[a]	Surface area (AU)		Ratio of Lewis/Brønsted
		1540 cm^{-1}	1450, 1440 cm^{-1}	
1	NaY	0.46	8.22	17.87
2	NH_4Y	3.76	0.20	0.05
3	HY	8.84	6.98	0.79
4	CaY	2.83	1.26	0.45
5	NaX	0.06	9.99	166.5

Difference spectra of zeolite with and without pyridine, pyridine absorption at 150°C, 5×10^{-2} mbar pyridine.

[a] Activation: 10°C/min to 200°C, 90 min at 200°C.

reaction space available in a zeolite, however, polymerization is considerably reduced and dimers and trimers are obtained.[25]

Therefore, it is expected that if a zeolite is used as catalyst for benzyl chloride reactions, the Brønsted acidic sites should yield benzyl alcohol and dibenzyl ether. Lewis acidic sites, in contrast, will afford dimers and trimers. Thus, the conversion of benzyl chloride could be a powerful probe reaction for analyzing both types of acidic sites.

2. Results and discussion

Different faujasite type zeolites were investigated. They were activated under mild conditions (at 200°C).

In order to be able to evaluate the results of the probe reaction, the ratio between the Lewis and Brønsted acidic sites of the zeolites studied were determined by IR spectroscopy using pyridine as a surface probe (see Table 1).[26] The peak at 1540 cm^{-1} corresponds to a pyridinium ion (resulting from protonation by a Brønsted acidic site), whereas the bands at 1450, 1440 cm^{-1} originate from pyridine adsorbed on Lewis acidic sites.[26]

Under the mild activation conditions applied, the zeolite lost most of its lattice water, but there were still enough water molecules available for the substitution reaction of benzyl chloride to benzyl alcohol. Even when zeolite X or Y is activated at 400°C, at least one water molecule remains within each sodalite cage.[27] The results of the probe reaction are summarized in Table 2. The main product extracted from zeolite Y with Na^+ as counter cation, was benzylbenzyl chloride (**1**) (see Table 2, entries 1 and 2), which is expected to originate from Lewis acidic catalysis. Also the secondary products, trimers **2**, were present in a relative yield of 10–23%. The products derived from catalysis by Brønsted acidic sites, benzyl alcohol (**4**) and dibenzyl ether (**5**) were also found, but they were not the dominating products. Thus, zeolite NaY acts primarily as a Lewis acidic catalyst in the reaction of **3**. This corresponds perfectly to the dominant Lewis acidic character of NaY (see Table 1, entry 1).

Not only NaY was tested, but also zeolite NH_4Y. The ammonium ions residing within zeolites are strongly H-bonded to the basic oxygens of the lattice.[28] Upon activation some NH_4^+ ions were converted into H^+ with concomitant loss of NH_3 gas and Brønsted acidic sites, as depicted in Fig. 1, were generated. Furthermore, it has been proven by NMR spectroscopy that also the NH_4^+ ions residing within the zeolites are Brønsted acidic.[29]

Indeed, when the probe reaction was conducted within NH_4Y, the products formed by the Brønsted acidic reaction, **4** and **5** clearly dominated (see Table 2, entries 3 and 4). The more Brønsted acidic NH_4Y steered the reaction in another direction than the more Lewis acidic NaY. The 'Lewis/Brønsted' ratio was even completely reversed! For example,

Table 2. Relative product ratios from the reaction of **3** conducted within faujasite type zeolites

Entry	Zeolite[a]	Time[b] (h)	Uptake[c]	Recovered[d] (%)	**1**[e]	**2**[f]	**4**	**5**	Other[g]
1	NaY	2	2.1	73	63	10	16	11	<1
2	NaY	24	2.1	64	74	23	1	1	1
3	NH_4Y[h]	2	1.6	75	6	0	31	58	4
4	NH_4Y[h]	24	1.6	66	7	0	16	72	5
5	HY	2	1.6	6	67	33	0	0	0
6	HY	24	1.6	9	47	20	0	0	33
7	CaY	24	1.5	<1	Trace	0	0	0	Trace
8	NaX	24	1.7	89	<1	0	53	47	0
9	NaX[i]	24	1.8	49	2	<1	65	20	13

[a] Zeolite activated at 200°C.

[b] Time starts as soon as the BnCl solution is added to the zeolite; extraction time not included.

[c] Uptake in mmol of **3**/g activated zeolite.

[d] Recovered material.

[e] Three isomers, ratios as described in Ref. 25.

[f] Fifteen isomers possible.

[g] Benzaldehyde, toluene, BnBnOH, benzal chloride, benzotrichloride and more.

[h] NH_4^+ cations partly converted into H^+ upon activation.

[i] Activated overnight at 500°C.

at reaction times of 24 h this ratio was 97:2 when catalyzed by NaY (see Table 2, entry 2), whereas the ratio was 7:88 upon catalysis by NH_4Y (see Table 2, entry 4). Thus, the reaction of benzyl chloride seems to be a valuable probe reaction (see Scheme 1).

Unfortunately, entries 5–9 of Table 2 demonstrate that the probe reaction is not as simple as it may seem, and that more effects than only those based on the acidity of the zeolite play a role.

The reaction of **3** within HY was also examined (see Table 2, entries 5 and 6). This zeolite was prepared by calcination of NH_4Y at 500°C. By doing so, most of the ammonium ions were transformed into protons under concomitant loss of NH_3. Then, the zeolite was allowed to cool down in order to become saturated with water molecules. Afterwards, the HY obtained was mildly activated at 200°C. HY contains mainly Brønsted acidic sites and less Lewis acidic sites, as determined by IR spectroscopy of adsorbed pyridine (see Table 1, entry 3).

First of all, the total amount recovered from the strong Brønsted acidic HY is minimal. Secondly, and quite surprisingly, this small amount did not consist of the expected ‘Brønsted products’, but is composed of ‘Lewis products’. This could be due to the fact that the Brønsted products are less stable within the zeolite than the Lewis products. Furthermore, the relative amount of Lewis products increased with increasing reaction time. The Lewis/Brønsted ratio rises from 73:27 after 2 h (see Table 2, entry 1) to 97:2 after 24 h (see Table 2, entry 2). Of course, the zeolite did not contain any more Lewis acidic sites after a prolonged reaction time. There are two possible explanations for this phenomenon. First of all, the water content is decreasing in time. Secondly, Brønsted products were consumed by secondary reactions to inextractable products faster than the Lewis products.

This was also demonstrated by the reaction of **3** within CaY (See Table 2, entry 7). Zeolite CaY is also strongly Brønsted acidic,[30] because lattice water is reacting with Ca^{2+} to give $Ca(OH)^+$ and H^+. As a result, the reaction products of **3** reacted further to coke and only traces of products were obtained. Thus, the probe reaction is not adequate for zeolites containing strong Brønsted acidic sites.

Beside zeolite Y the synthetic zeolite X has been tested with the probe reaction (see Table 2, entries 8 and 9). Just like zeolite Y, zeolite X possesses the faujasite framework. The difference is, that zeolite X contains more aluminum. Thus, the framework is more negatively charged and, therefore, the protons are stronger bound. Calculations[31] and experimental observations[32–33] have shown that the intrinsic acidity per Brønsted site decreases with decreasing lattice Si/Al ratio. As determined by IR spectroscopy of adsorbed pyridine, NaX is foremost Lewis acidic (see Table 1, entry 5).

But, although the Brønsted acidic sites are weaker, the Brønsted products clearly dominated. This shows another limitation of the probe reaction. The ‘Brønsted reaction’ $\mathbf{3}+H_2O\rightarrow\mathbf{4}+HCl$ is a reaction in which zeolitic lattice water is involved, whereas this is not the case in the ‘Lewis reaction’ $\mathbf{3}+\mathbf{3}\rightarrow\mathbf{1}$. The reaction rate of the Brønsted reaction depends on the water concentration, while this does not hold true for the Lewis reaction. Because the lattice of zeolite X is more ionic than the lattice of Y, it lost less water (−15 mass%) than zeolite Y (−21 mass%) upon activation. Thus, the water concentration was higher in zeolite X, and the Brønsted reaction was more favored for this reason. In order to obtain more evidence for this concept, zeolite X was also activated at 500°C (see Table 2, entry 9). At this activation temperature, the zeolite lost 18 mass% of lattice water. Indeed, with less water molecules available, the relative share of Brønsted products decreased.

Moreover, it is also known that bases are better catalysts for the conversion of $\mathbf{3}\rightarrow\mathbf{4}$ than Brønsted acids.[21,22] The higher aluminum content of NaX compared to NaY results in an enhanced basicity strength of the framework oxygen atoms. Thus, also basic catalysis was probably participating in the formation of benzyl alcohol.

The probe reaction suffers from even more complications by the fact that benzyl alcohol undergoes, as a secondary reaction, in small amounts disproportionation to benzaldehyde and toluene. This effect has been clearly observed on strong acidic sites at 78°C,[34] and was also found in the reactions in Table 2. Furthermore, it has been reported that dibenzyl ether can also be obtained from a direct reaction between benzyl chloride and benzyl alcohol within zeolite KY.[35]

3. Conclusions

The set of simple reactions described here clearly demonstrates the rich variety of zeolitic catalytic sites and their almost unlimited possibilities to direct reactions. Just by carefully choosing and tailoring the zeolite, the organic reaction can be steered towards the desired products.

Benzyl chloride reacts to benzyl alcohol and further towards dibenzyl ether when catalyzed by a Brønsted acid. The sum of these products amounts to 88% after 24 h upon catalysis by NH_4Y. With a Lewis acidic zeolite, however, benzyl chloride is converted into the dimer benzylbenzyl chloride (three isomers) and then further into the trimer (up to 15 isomers). After reacting benzyl chloride for 24 h in zeolite NaY, 97% of the extracted products consist of dimers and trimers.

Nevertheless, because of the reasons listed below, caution is warranted to use these reactions as a probe to distinguish between Brønsted and Lewis acidic sites:

- The ratio between ‘Lewis’ and ‘Brønsted’ products formed is not constant in time.
- Strong Brønsted acidic sites convert the reaction products into coke.
- The rate of the Brønsted reaction depends on the lattice water content, whereas the Lewis reaction does not.
- Basic sites also catalyze the conversion of benzyl chloride into benzyl alcohol.
- Dibenzyl ether can also be formed from a direct reaction between benzyl chloride and benzyl alcohol.

- Strong Brønsted acidic sites catalyze to a small amount the disproportionation of benzyl alcohol into benzaldehyde and toluene.

It is hoped that this work will stimulate further interest in the search towards simple model reactions. Carefully conducted, such a strategy has the potential to generate secure information that allows a detailed description of the catalytic characteristics of a zeolite.

4. Experimental

The following zeolites are commercially available: NaY (LZY-52, Aldrich 33,444-8), NH_4Y (LZY-62, Aldrich 33,441-3) and NaX (13-X, Acros 26925-5000). CaY was prepared from NaY by ion exchange: a solution of 10.0 g $CaCl_2$ in 75 mL of distilled water was refluxed for 24 h with 5.0 g of NaY. The zeolite was filtered off, added to a fresh $CaCl_2$ solution (10.0 g/75 mL) and the resulting mixture refluxed for an additional 24 h. After this time, the zeolite was filtered off, washed with warm distilled water (2×100 mL) and dried for 6 h at 75°C. By using this method, the initial Ca/Na molar ratio of the commercial NaY sample, that was originally between 1.5×10^{-3} and 50×10^{-3}, was increased to 1.6 ± 0.3.

4.1. General procedure

The zeolite (2.4 g) was activated in an evaporating dish in a muffle furnace (temperature program: 1 h to 100°C, 1 h at 100°C, 1 h to 200°C, 1 h at 200°C). After the activating period, the hot zeolite was immediately transferred into a dry flask filled with argon and the flask was sealed. As soon as the zeolite reached room temperature, the loading solution of 870 mg of **3** in 150 mL of pentane (dried over molecular sieves prior to use) was added. The suspension was magnetically stirred during the reaction time. A drying tube containing anhydrous $CaCl_2$ was mounted on the flask to keep out moisture. The guest uptake within the zeolite was monitored by UV analysis of aliquots from the supernatant solution. The signal ($\varepsilon_{260\ \mathrm{nm}}=202\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) decreased as more guest was taken up by the zeolite. The uptake was found to be rapid: for NaY 90% of the maximum loading was reached within only 5 min and complete uptake within 15 min. Abundant guest molecules remaining within pentane did not react. After the reaction time, the zeolite was filtered through a glass sinter (Por. 4) and washed several times with pentane. In order to retrieve the products, the zeolite was continuously extracted for 18 h with hot CH_2Cl_2 using a Soxhlet apparatus. The solution obtained was evaporated under reduced pressure and the recovered material weighed and analyzed. Ratios were determined by GC analysis and compared with standards of independently synthesized materials.

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