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Heterogeneous catalysts for hydroamination reactions: structure–activity relationship

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Abstract

The catalytic activity of ion-exchanged zeolite BEA for hydroamination reactions, such as the cyclization of 6-aminohex-1-yne and 3aminopropylvinyl ether and the intermolecular addition of aniline to phenylacetylene, was studied. The most active catalysts were Cu(I)/H-BEA, Rh(I)/H-BEA, and Zn/H-BEA. These catalysts were fully characterized and the oxidation state and the local environment of copper, in particular, were explored with XANES and EPR spectroscopy. For Zn/H-BEA zeolites the catalytic activity of the material was related to the local structure around the zinc cations.

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1. Introduction

New C–N bond forming processes are highly interesting for both organic syntheses and industrial processes due to the importance of nitrogen-containing molecules as building blocks and in industrial applications. Commercially valuable products include amines, amides, ammonium and alkylammonium salts, ureas, carbamates, isocyanates, and amino acids [1].

Conceptually, the direct addition of an amine functionality to a CC multiple bond—hydroamination—is one of the most interesting approaches to synthesize amines, enamines, and imines [2,3]. The reaction utilizes readily available and inexpensive starting materials and has an optimal atom efficiency. Hence, considerable interest exists in developing new and more effective catalysts to accomplish this organic transformation. In commercial applications zeolites in the protonic form are typically employed as, e.g., in the synthesis of *tert*-butylamine from ammonia and 2-methylpropene [4,5]. However, the drawback of these solid acid catalysts

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Against this background, late-transition-metal-based heterogeneous catalysts, and in particular zeolite catalysts, were explored for the hydroamination of alkynes. Zeolites show Brønsted acidic properties, which are beneficial for coordination of metal cations at well-defined positions (ionexchange sites). Zeolite BEA has been chosen, because it showed exceptionally high catalytic activity in preliminary experiments [8]. The high activity of ion-exchanged BEA could be a result of either structural properties or the particular environment of metal cations in the pore system. In this respect, it is known that the outer surface of BEA zeolite exhibits acidic properties [9]. This enables the adsorption of basic molecules on the outer surface, which leads to an increase in the local concentration inside the zeolite pores. Additionally, it is known that the lattice of BEA zeolite is highly flexible [10], which stabilizes metal cations in specific cation-exchange positions and favors the access of the reactants.

In this study, the catalytic properties of ion-exchanged BEA zeolites for hydroamination reactions were studied. Characterization of the heterogeneous catalysts provided a detailed knowledge of the coordination geometry of the metal cations and, for the first time, allowed us to relate the

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catalytic activity of the material in hydroamination reactions with the local environment of the metal cations.

2. Experimental

2.1. Materials and methods

All reactions involving air- and/or water-sensitive compounds were performed using standard Schlenk techniques. Dry solvents were obtained from Aldrich; 6-aminohex-1-yne, 2-methyl-1,2-dehydropiperidine, and tetrahydro-2methyl-1,3-oxazine were prepared as described in [11,12]. Catalysts and other chemicals not described in the experimental section were purchased from Aldrich, Fluka, or Strem and used as received.

2.2. Physical and analytical methods

¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker AM 400 instrument and referenced in ppm relative to tetramethylsilane using the solvent shift as internal standard [13]. IR spectra were obtained on a Perkin-Elmer FT-IR 2000 spectrometer as KBr pellets. Mass spectroscopic analyses were performed on a Finnigan MAT 311A mass spectrometer by chemical ionization (CI). GC analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a crosslinked 5% diphenyl–95% dimethylpolysiloxane column (30 m, Restek GmbH, Rtx-5 Amine) and a flame ionization detector. GC-MS analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with an identical column and a massselective detector HP 5971A.

2.3. Synthesis and characterization of phenyl-(1-phenylethylidene)amine

Aniline (9.1 cm³, 0.1 mol) and the catalyst $Zn(CF_3SO_3)_2$ (3.6 g, 0.01 mmol) were dissolved in toluene (180 cm³) and the mixture was heated to reflux temperature. The reaction was started by addition of phenylacetylene (4.4 cm³, 0.04 mol) and the mixture refluxed overnight. Quantitative conversion of phenylacetylene was indicated by GC analysis. The product was separated by column chromatography using silica gel 60 as stationary phase and hexane/ethyl acetate 50/30 as eluent. The volatiles were removed and the single product was characterized by NMR, MS (CI), GC-MS, and IR analyses which confirmed the product to be phenyl-(1-phenyl-ethylidene)-amine.

Yield: 1.3 g, 16.7%. ¹H NMR (CDCl₃): δ 6.7–8 (m, 10H, Ph), 2.2 (s, 3H, CH₃) ppm. ¹³C{¹H} NMR (CDCl₃): δ 164.5 (C=N), 151.7 (N–C), 139.5 (Ph), 130.5 (Ph), 129.0 (Ph), 128.4 (Ph), 127.2 (Ph), 123.3 (Ph), 119.4 (Ph), 115.1 (Ph), 18.0 (Me) ppm. IR: 3054 (m), 1630 (vs), 1591 (vs), 1446 (s), 1214 (s), 761 (s), 693 (vs), 572 (w), 528 (w) cm⁻¹. GC-MS: m/z 180 (M⁺–CH₃). MS (CI) m/z 195 (M⁺).

A sample of phenyl-(1-phenylethylidene)amine was synthesized as reference by the acid-catalyzed (CF₃SO₃H, 0.03 g, 0.2 mmol) condensation of aniline (27.3 cm³, 0.3 mol) with acetophenone (29.2 cm³, 0.25 mol) in toluene (50 cm³) at reflux temperature (111 °C, 12 h). The reaction mixture was dried over MgSO₄ and distilled (product fraction: 110 °C, 30 mm). The product was recrystallized from hexane and analyzed using IR and NMR spectroscopy. The spectra for phenyl-(1-phenylethylidene)amine were identical with those for the product of the reaction between phenylacetylene and aniline.

2.4. Preparation of ion exchanged zeolites

Zeolite BEA in the acidic form was used as the parent material (diameter of the crystals 0.1-0.3 µm, Si/Al 11.6, BET surface area 537 m²/g). Transition-metal-based zeolite catalysts with Rh^+ , Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^+ , Cu^{2+} , and Zn^{2+} were prepared by ion exchange, for details, see Tables 1 and 2; for the oxidation state of the metal see Ref. [11]); La³⁺ was introduced by solid-state ion exchange. Except for Cu⁺ and Rh⁺ the ion exchange was performed by suspending the parent zeolite in an aqueous solution of the corresponding metal salt (80 °C). The zeolite was separated by centrifugation (5000 rpm, 20 min) and, to obtain a particular ion-exchange degree, the procedure repeated. The material was then calcined in a flow of air (100 ml/min). Prior to use, the Ni²⁺-exchanged zeolite was reduced in hydrogen to obtain a Ni⁰-containing catalyst (see [11]). Further, a series of zinc-exchanged BEA zeolites was prepared varying in the zinc loading [14]. The full characterization of this series of Zn/H-BEA zeolites is described elsewhere [15].

Copper(I) and rhodium(I) salts are susceptible to oxidation and/or disproportionation. Therefore, the ion exchange was carried out in anhydrous solvent (CH₃CN) under an inert conditions. The parent H-BEA zeolite was activated at 150 °C in vacuum (10 mbar). The zeolite was then suspended in a solution of the complexes [Cu(CH₃CN)₄]PF₆ or [Rh(NOR)₂]ClO₄ (NOR, norbornadiene) in CH₃CN (82 °C; for details, see Table 1). The solvent was removed under vacuum and the sample subsequently handled in an inert atmosphere. In case of lanthanum exchange, the parent material was ground with LaCl₃ × 7H₂O in an agate ball mill for 30 min. The mixture was heated in a stream of air (100 ml/min, RT–120 °C, 2 °C/min; 120 °C 2 h; 120–500 °C, 2 °C/min), washed with distilled water, and dried at 100 °C.

2.5. Catalytic experiments

The metal-exchanged zeolites (corresponding to 5.3×10^{-3} mmol M^{*n*+}, if not stated otherwise) were activated (12 h at 10 mbar, 200 °C). The zeolites Cu(I)/H-BEA and Rh(I)/H-BEA and the homogeneous catalysts were used in an inert atmosphere without activation. Dry toluene (15 cm³) was added, the mixture heated to reflux temperature (111 °C), and the catalytic reaction started by addition

Table 1	
Experimental conditions for the ion exchange of zeolite BE	έA

Sample	Metal salt	Concentration (mol/l)	Solution/zeolite (ml/g)	Number of repetitions	Total time of ion exchange (h)	Calcination method
H-BEA	_	_	_	_	_	_
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.01	5	1	93	А
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.02	5	1	14	А
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.03	5	1	14	А
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.06	5	1	45	В
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.06	5	2	69	В
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.06	5	3	163	В
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.06	5	4	189	В
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.38	5	4	131	В
Zn/H-BEA	$Zn(CH_3CO_2)_2$	0.55	7	4	96	А
Cu(I)/H-BEA	[Cu(CH ₃ CN) ₄]PF ₆	0.09 ^a	14 ^b	4	167	-
Cu(II)/H-BEA	$Cu(CH_3CO_2)_2$	0.01	70	1	12	А
Cu(II)/H-BEA	$Cu(CH_3CO_2)_2$	0.02	70	1	12	А
Rh(I)/H-BEA	[Rh(NOR)2]ClO4	0.01 ^a	13 ^b	1	60	-
Pd/H-BEA	PdCl ₂	0.06	5	3	63	А
Pt/H-BEA	$[Pt(NH_3)_4](OH)_2$	0.004	83 ^b	1	12	А
Ni/H-BEA	$Ni(CH_3CO_2)_2$	0.03	30	4	14	А
La/H-BEA	LaCl ₃ 7H ₂ O	0.35 ^c	_	1	0.5	С

Calcination method (A) RT–120 °C, 0.5 °C/min; 120 °C, 3 h; 120–500 °C, 1 °C/min; 500 °C, 2 h. (B) RT–500 °C, 5 °C/min; 500 °C, 5 h. (C) RT–120 °C, 2 °C/min; 120 °C, 2 h; 120–500 °C, 2 °C/min.

^a Solvent CH₃CN.

^b Wet impregnation.

^c In mmol/g zeolite.

Table 2

Chemical composition	(determined b	y AAS)) and surface area	of the	materials	used in t	this study
	`						

Sample	M ⁿ⁺ contents (mmol/g)	M^{n+}/Al	Al contents (mmol/g)	Si/Al	M^{n+} per unit cell	BET surface area (m ² /g)	Micropore surface area (m ² /g)
H-BEA	-	-	1.36	11.6	-	536.5	137.8
Zn/H-BEA	0.03	0.02	1.37	11.4	0.1	526.9	200.8
Zn/H-BEA	0.06	0.04	1.27	12.6	0.2	545.3	108.4
Zn/H-BEA	0.11	0.08	1.47	10.7	0.4	509.9	141.3
Zn/H-BEA	0.20	0.15	1.37	11.3	0.8	518.1	147.6
Zn/H-BEA	0.31	0.26	1.18	13.4	1.2	526.2	148.5
Zn/H-BEA	0.49	0.40	1.21	12.7	1.9	493.9	_
Zn/H-BEA	0.54	0.46	1.18	12.7	2.2	549.4	129.2
Zn/H-BEA	0.66	0.53	1.24	12.0	2.6	460.1	96.4
Zn/H-BEA	0.86	0.77	1.12	12.1	3.8	516.9	151.0
Cu(I)/H-BEA	0.47	0.61	0.76	20	1.9	_	_
Cu(II)/H-BEA	0.45	0.38	1.18	(12.5)	1.9	_	-
Cu(II)/H-BEA	0.67	0.60	1.12	(12.5)	3.2	_	_
Rh/H-BEA	0.15	0.12	1.26	(12.5)	0.6	_	_
Pd/H-BEA	0.40	0.32	1.26	(12.5)	1.5	_	_
Pt/H-BEA	0.29	0.23	1.26	(12.5)	1.1	_	-
Ni/H-BEA	0.88	0.78	0.76	13.6	3.4	_	_
La/H-BEA	0.27	0.21	1.26	(12.5)	1.0	-	-

of the substrate (0.53 mmol, if not stated otherwise). During the reaction, samples were taken for GC analysis. Samples containing heterogeneous catalyst were centrifuged for 10 min at 14,000 rpm before analysis.

2.6. EPR spectroscopy

The EPR spectra were recorded on a Jeol RE2X at Xband frequency at a temperature between 130 and 343 K, microwave frequency about 9.4 GHz, microwave power 5 mW, modulation frequency 100 kHz. The g values were determined with a NMR magnetometer and Mn^{2+}/MgO as g marker. The intensity of the spectra was obtained by numerical double integration of the sample and reference (Mg²⁺/MgO, known number of spins) spectra using the software ESPRIT-360 (JEOL). In the in situ EPR experiments the activated solid catalyst Cu(II)-BEA (65 mg, 0.03 mmol Cu²⁺) was suspended in toluene (600 mg) in the EPR tube under inert conditions. 6-Aminohex-1-yne (0.3 mmol, 34 µl) was added and the reaction mixture heated

to $70 \,^{\circ}$ C in the EPR cavity using the variable temperature unit. Spectra were taken for several hours at this temperature.

2.7. X-ray absorption spectroscopy

X-ray absorption spectra were collected at beamline X1 at HASYLAB, DESY Hamburg. A Si (111) monochromator was used and the intensity of incident and transmitted X-rays was recorded using ionization chambers. The energy was calibrated relative to a copper or zinc foil, located between the second and third ionization chamber. The measurements were performed on self-supporting wavers placed in a sample holder inside a stainless-steel reactor equipped with Kapton windows and a gas inlet and outlet system. The Cu(II)/H-BEA was activated for 0.5 h at 450 °C (heating rate 10°C/min, N₂ flow 65 ml/min). All absorption spectra were recorded at liquid nitrogen temperature. The XANES of Cu, Cu₂O, CuO, Zn, and ZnO were used as references. The spectra were analyzed with WinXas (Version 2.0) [16]. The energies of all spectra were aligned to the inflection point of the K-edge from the simultaneously measured metal foil. The normalized background was corrected by fitting the preedge region with a second order polynom and the section above the edge by a polynomial spline with seven nodes. The oscillations were weighted with k^2 and Fourier-transformed in the range $k = 2.1-16 \text{ Å}^{-1}$. The local environment of the metal atoms was determined from the EXAFS using phase-shift and amplitude functions for multiple-scattering processes (FEFF Version 8.10) [17,18].

3. Results and discussion

3.1. Catalytic measurements

For exploring the potential of ion-exchanged BEA as catalyst for hydroamination reactions we decided to focus on the intramolecular catalytic cyclization of molecules containing an amine and alkyne/alkene group. Specifically, the cyclization of 6-aminohex-1-yne (6AHI) and 3-aminopropylvinyl ether (3APE) were studied. The cyclization of 6-aminohex-1-yne first generated the enamine 2-methylenepiperidine, which isomerized to the corresponding imine 2-methyl-1,2-dehydropiperidine:

$$H = (CH_2)_4 NH_2 \xrightarrow{Cat.} \begin{bmatrix} H_2 C & H_3 \\ H_2 C & N \end{bmatrix} \rightarrow H_3 C & N$$
(1)

The cyclization of 3-aminopropylvinyl ether gave the *N*,*O*-acetal tetrahydro-2-methyl-1,3-oxazine:

$$H_2C = CH - O - (CH_2)_3 NH_2 \xrightarrow{Cat.} H_3C \xrightarrow{H} O$$
(2)



Fig. 1. Time-concentration profile for the cyclization of 6AHI with transition-metal-exchanged BEA zeolites.

To test the suitability of ion-exchanged BEA as catalyst for intermolecular reactions the hydroamination between phenylacetylene (PAE) and aniline (AIL) to phenyl-(1-phenylethylidene)amine was examined:

$$\begin{array}{c} H_2 N - Ph \\ + & \stackrel{\text{Cat.}}{\to} \\ Ph - - - H \end{array} \qquad \left[\begin{array}{c} HN \\ Ph \\ Ph \end{array} \right] \xrightarrow{Ph} \\ Ph \\ CH_2 \end{array} \right] \xrightarrow{N \\ Ph \\ CH_3}$$
(3)

All reactions were highly regioselective; only the product of the preferred Markownikow addition of the amine to the CC multiple bond was observed.

In order to identify the most suitable metals for hydroamination reactions, the catalytic activity of zeolite BEA ionexchanged with La^{3+} , Rh^+ , Pd^{2+} , Pt^{2+} , Cu^+ , Cu^{2+} , or Zn^{2+} or loaded with Ni⁰ was compared. These metal cations were chosen as corresponding d8 and d10 complexes had shown a high catalytic activity as homogeneous catalysts in the cyclization of 6AHI [11,19,20]. For the cyclization of 6AHI, the heterogeneous catalysts Cu(I)/H-BEA, Rh(I)/H-BEA, and Zn/H-BEA showed exceptional catalytic activity (Fig. 1). In contrast, La/H-BEA, Ni/H-BEA, and Pt/H-BEA had an activity that was only slightly higher than that of the parent H-BEA. The activity of Pd/H-BEA was intermediate between the activity of Pt/H-BEA and Zn/H-BEA.

La/H-BEA had to be activated at high temperatures to achieve a moderate catalytic activity. The initial rate of reaction increased from 0.9 to 2.7 mmol/(gh) when the activation temperature was increased from 200 to 450 °C. It is speculated that the concentration of water and hydroxide ligands coordinating to lanthanum has to be reduced by the temperature treatment [21] rendering the metal centers more Lewis acidic.

A plot of the intrinsic rate of reaction per metal center vs the ratio of charge [22] and ionic radius (e/r) resulted in a "volcano curve"-type correlation (Fig. 2). The rate of reaction was highest for metal cations with an intermediate ratio e/r (Rh⁺, Cu⁺, Zn²⁺), whereas it was low for Ni⁰ (e/r =0 Å⁻¹) and for Pd²⁺, Pt²⁺, and La³⁺ $(e/r \ge 2.5$ Å⁻¹). The ratio e/r is an approximate measure for the (hard) Lewis



Fig. 2. Rate of the cyclization of 6AHI for ion-exchanged BEA zeolites related to the ratio of charge and radius of the metal cation.

acidity of a metal cation [23]. Hence, it can be suggested that there is an optimum Lewis acidity needed for transition metal cations to catalyze the reaction, especially for those catalysts which work via activation of the alkyne moiety [24]. If the metal cation is a very weak Lewis acid, the catalyst–substrate complex is speculated to be to unstable to form. On the other hand, if the metal cation is very acidic, the catalyst–substrate complex is too stable to undergo further reaction. Therefore, metal cations with intermediate Lewis acidity provide the highest catalytic activity.

The small, but nonnegligible activity of the parent H-BEA zeolite in the cyclization of 6AHI (see Fig. 1) can be explained similarly. It has been shown that Brønsted acids, such as CF₃SO₃H, could not catalyze the cyclization of 6AHI. A test on leaching performed with Zn/H-BEA (0.53 Zn/Al) showed that the aluminum content decreased from 1.24 to 1.04 mmol/g indicating partial extraction of aluminum into the toluene solution, while the zinc content remained constant. When reusing the carefully separated toluene solution in the cyclization of 6AHI, a similar reaction rate was observed as for H-BEA. This indicates that Lewis acidic Al³⁺ species extracted from the zeolite were responsible for the activity of H-BEA. However, due to their high Lewis acidity Al³⁺ cations (e/r = 0.06 Å⁻¹) are unable to catalyze the cyclization of 6AHI efficiently (see Fig. 2).

3.2. Relation between oxidation state and catalytic performance—copper-based catalysts

In a more detailed study the nature of the catalytic sites was explored for two of the most active zeolites (Cu/H-BEA and Zn/H-BEA). In case of copper, the main question was focused on the oxidation state of the copper cations during catalysis as this has significant mechanistic implications. Cu(II)-exchanged zeolites are known to be unstable upon temperature treatment and reduction of Cu(II) to Cu(I) was reported even in inert atmosphere (Cu-BEA [25], Cu/H-ZSM-5 [26]). Recently, it was proposed that the Cu(I) species have their origin in $[Cu^{II}-OH]^+$ cations, which are



Fig. 3. Activity of copper catalysts in the cyclization of 6AHI in dependent of ligand sphere and oxidation state.

first dehydrated to $[Cu-O-Cu]^{2+}$ [27,28] and then reduced to Cu(I) according to

$$[\operatorname{Cu-O-Cu}]^{2+} \xrightarrow{200-400\,^{\circ}\mathrm{C}} 2\operatorname{Cu}^{+} + \frac{1}{2}\operatorname{O}_2 \tag{4}$$

The catalytic activities of Cu(II)-exchanged BEA zeolites (0.38 and 0.60 Cu/Al) were examined independent of the activation procedure. Prior to the catalytic reaction Cu(II)/H-BEA was dried (at 100 °C in air or 200 °C at 10^{-1} mbar) or calcined (at 450 °C in a stream of He or N₂). For comparison, genuine samples of Cu(I)/H-BEA (0.61 Cu/Al) and Cu(I)/H-BEA prepared in situ from H-BEA and [Cu(CH₃CN)₄]PF₆ were tested for their catalytic activities. Surprisingly, all materials displayed the same activity in the cyclization of 6AHI independent of the pretreatment and the metal loading. Note, that in all experiments the same amount of copper cations was employed. This observation indicates that—despite the different preparation of the material—the nature and quantity of the catalytically active sites were similar during catalysis.

The catalytic activity of Cu/H-BEA was compared with corresponding homogeneous catalysts (Fig. 3). The copper(I) complex $[(C_6H_6)(Cu(CF_3SO_3))_2]$ displayed an exceptionally high catalytic activity which was comparable to Cu(I)/H-BEA. [Cu(CH₃CN)₄]PF₆ which has a strongly coordinating acetonitrile ligand showed a significantly lower activity whereas the very stable complex [CuH(PPh₃)]₆ showed little catalytic activity. The copper(II) salts Cu(CF₃SO₃)₂ and Cu(BF₄)₂ displayed an intermediate catalytic activity. Closer inspection of the reaction kinetics showed that both copper(II) salts had an induction period, which was short for Cu(CF₃SO₃)₂ (ca. 5 min) and more pronounced for Cu(BF₄)₂ (ca. 2 h). This indicates either slow dissolution of the salts in the reaction mixture or, more likely, slow reduction of Cu(II) to the catalytically active copper(I). In line with this conclusion all copper(I) complexes showed an approximate first-order kinetics.

To analyze the local environment of the Cu^{2+} cations in the material, an EPR study was performed. Both parent materials, Cu(I)/H-BEA (0.61 Cu/Al) and Cu(II)/H-BEA (0.60 Cu/Al), showed EPR spectra typical of Cu^{2+} species

bound to the zeolite lattice. They can be best described by a spin Hamiltonian of axial symmetry ($3d^9$, S = 1/2). The spectra are characterized by the hyperfine structure due to anisotropic interactions of the unpaired electron with the nuclear spin of 63,65 Cu (I = 3/2), which is well resolved for orientations of the magnetic field parallel to the z-axis, A_{\parallel} , while A_{\perp} is not resolved. The EPR parameters g and $A(^{63,65}Cu)$ of the Cu(II)-zeolite species after activation of Cu(II)/H-BEA (200°C, vacuum) are indicative of Cu(II) in a distorted square-planar or square-pyramidal coordination environment of oxygen atoms ($g_{\perp} = 2.079, g_{\parallel} = 2.323$, A_{\parallel} (^{63,65}Cu) = 15.7 mT) [29,30]. Even in the case of nonactivated Cu(I)-exchanged zeolites well-resolved EPR signals of Cu(II) were found demonstrating the high sensitivity of the method. The spectra have very low intensity (less than 5% of the Cu(II)-exchanged zeolite of similar copper loading as derived from double integration) and altered spectral parameters indicating a different coordination environment $(g_{\parallel} = 2.115, g_{\parallel} = 2.381, A_{\parallel} (^{63,65}Cu) = 10.8 \text{ mT}).$

The Cu(II)-zeolite species had a different coordination environment when the material was suspended in a solvent, which is reflected by the change in their EPR parameters. In toluene two species were present $(g_{\perp 1} = 2.092, g_{\parallel 1} =$ $2.377, A_{\parallel 1}$ (^{63,65}Cu) = 12.1 mT; $g_{\perp 2} = 2.092, g_{\parallel 2} = 2.338,$ $A_{\parallel 2}$ (^{63,65}Cu) = 14.2 mT), which differ in their EPR parameters from the species described above and from those in acetonitrile solution ($g_{\perp} = 2.095, g_{\parallel} = 2.351, A_{\parallel}$ (^{63,65}Cu) = 13.6 mT). However, in all cases the presence of anisotropic g and hyperfine structures in the EPR spectra indicate that the Cu(II) species were still bound rigidly to the zeolite lattice (no tumbling, no leaching).

In addition, in situ EPR experiments close to reaction conditions were performed. The activated solid catalyst Cu(II)/H-BEA was suspended in toluene and 6-aminohex-1yne added under inert conditions. The reaction mixture was heated to 70 °C in the EPR cavity and spectra were taken during several hours. The spectral parameters of the Cu(II) species ($g_{\perp} = 2.073$, $g_{\parallel} = 2.272$, A_{\parallel} (^{63,65}Cu) = 15.4 mT) clearly differ from those of the activated Cu(II)/H-BEA catalyst under argon and in pure toluene. Double integration of the spectra shows that the concentration of the copper(II) species was reduced by 30-40% within the first minutes. After 2 h only half of the original Cu(II) signal intensity was found (Fig. 4). This supports the above assumption that Cu(II) was reduced under reaction conditions to Cu(I), which is inferred to be the catalytically active species. In line with this conclusion, a 10 times lower catalytic activity for Cu(II) compared to Cu(I) is predicted from the ratio of charge to ionic ratio (e/r = 2.8 and 1.0 Å^{-1} , respectively).

To determine the oxidation state and local environment of the copper ions during catalysis X-ray absorption studies were performed. The excitation of Cu 1s electrons causes a sharp increase in X-ray absorption spectra near 8977 eV (Cu-K edge). The exact energy of the absorption edge is dependent on the electron density of the absorber atom. Conceptually, decreasing electron density leads to a shift of the



Fig. 4. X-band EPR spectra of a reaction mixture of the catalyst Cu(II)-BEA suspended in a toluene solution of 6-aminohex-1-yne at a reaction temperature of 70 °C. The spectra with decreasing intensity were taken after 0, 10, 20, and 120 min, respectively. (The superimposed sextet of sharp lines at B = 300-350 mT is due to the Mn²⁺/MgO standard.)

Table 3 Position of the Cu-K edge for Cu/H-BEA and reference materials

Sample	Metal content (mmol/g)	Edge energy (eV)	Oxidation state	Sample treatment
Cu	_	8977.0	0	
Cu ₂ O	_	8980.9	+I	
CuO	_	8984.3	+II	
Cu(II)/H-BEA	0.45	8986.8	+II	Before activation
Cu(II)/H-BEA	0.45	9982.1	+I ^a	Activation at 450 °C
Cu(I)/H-BEA	0.47	8980.6	+I	No activation ^b

^a See text.

^b Handled in inert atmosphere.

edge to higher energies [31]. Therefore, a comparison of the edge positions of the copper-exchanged zeolites with reference compounds (i.e., metallic copper, Cu₂O, and CuO) allows estimation of the average charge of the incorporated copper relative to those compounds (Table 3).

The energies of the Cu-K edge in metallic copper, Cu_2O , and CuO were 8977.0, 8980.9, and 8984.3 eV, respectively. Thus, a change of the oxidation state from 0 to +I and +II leads to a shift in edge energy toward higher energies $(\Delta E_{edge} = 3.9 \text{ and } 7.3 \text{ eV}, \text{ respectively}).$ For Cu(II) introduced in zeolite BEA an even larger shift in edge energy $(\Delta E_{edge} = 9.8 \text{ eV})$ relative to metallic copper was observed. This indicates that copper cations, when coordinated to zeolite framework atoms, have a lower electron density than in CuO, which might be related to the distorted coordination geometry of the copper cations in the zeolite matrix. Further, the oxidation state +II of copper is indicated by the presence of a small peak with maximum at ca. 8976 eV, due to a (forbidden) $1s \rightarrow 3d$ transition. In case of copper in the oxidation states 0 or +I this transition is not possible because of the fully occupied 3d orbital. However, for Cu(I) a preedge peak with maximum at 8982 eV is frequently observed which results from the $1s \rightarrow 4p_{x,y}$ electric-dipole allowed transition. Activation of Cu(II)-exchanged BEA ze-



Fig. 5. XANES spectra of $[Cu(CH_3CN)_4]PF_6$ dissolved in CH₃CN before and after the addition of 6AHI. Indicated are the edge positions of metallic copper, Cu₂O, and CuO.

olite in an inert atmosphere led to a shift of 4.7 eV to lower energies (from 8986.8 to 8982.1 eV). In parallel, the peak at 8976 eV decreased in intensity. These observations indicate partial reduction of the copper atoms and a change in the oxidation state from +II to +I. The difference in edge energy of 1.5 eV relative to the Cu(I)-exchanged BEA zeolite is probably related to a distinct local environment of the copper cations. In summary, the results indicate that the identical catalytic activities of BEA zeolites ion exchanged with Cu(I) and Cu(II) salts can be attributed to the generation of a similar Cu(I) species during catalysis.

Only slight changes in the XANES spectra were observed when the homogeneous catalyst $[Cu(CH_3CN)_4]PF_6$ was dissolved in CH₃CN. This indicates that the metal cation had a similar electron density and coordination sphere in solution and in the solid state. Apparently, neither the geometry nor the number of CH₃CN molecules coordinating to Cu(I) changed. In contrast, when the heterogeneous catalyst Cu(I)/H-BEA (0.61 Cu/Al) was suspended in CH₃CN the edge energy was shifted by 0.30 eV to higher energies. Conceptually, this indicates a lower electron density on copper caused by coordination of CH₃CN.

After addition of 6AHI to the solution/suspension of [Cu(CH₃CN)₄]PF₆ or Cu(I)/H-BEA in CH₃CN, the shape of the XANES spectra changed significantly (Fig. 5, for [Cu(CH₃CN)₄]PF₆). For both homogeneous and heterogeneous catalysts, the white line decreased in intensity. For [Cu(CH₃CN)₄]PF₆ the edge energy had shifted to lower energies ($\Delta E_{edge} = -0.16 \text{ eV}$), indicating a higher electron density on copper. In contrast, for Cu(I)/H-BEA, a higher edge energy was observed ($\Delta E_{edge} = +0.20 \text{ eV}$). However, the changes in edge energy were small in comparison to the shift caused by different oxidation states $(\Delta E_{edge} = \pm 4.0 \text{ eV})$. This clearly indicates that copper is mainly present in the oxidation state +I during catalysis. This conclusion is supported by the presence of the preedge transition at 8982 eV, which is characteristic for copper in the oxidation state +I.

Table 4 Number and distances of nearest neighbors in Cu/H-BEA and Zn/H-BEA

Sample	Shell	Ν	r (Å)	$\Delta\sigma\;(\text{\AA})\times10^{-3}$	ΔE_0
Cu(I)/H-BEA	Cu–O	3.1	1.924	8.6	1.6
	Cu–O	3.4	3.13/	2.5	-10.0
in CH ₃ CN	Cu–O Cu–O	3.1 3.1	1.932 3.150	6.2 2.0	-10.7
-	Cu–N	1.0	2.565	8.2	0.024
Cu(I)/H-BEA	Cu–O	3.9	1.975	5.9	-0.3
+ 6AHI in CH ₃ CN	Cu-N(C)	1.1	2.574	3.8	-0.4
Zn/H-BEA	Zn–O Zn–O	4.3 1.9	2.045 2.974	7.1 2.3	-0.3 -7.1
Zn/H-BEA	Zn–O	4.3	2.097	12.3	-1.3
in CH ₃ CN	Zn–O Zn–N	1.8 1.3	3.466 2.248	21.3 12.9	0.1
Zn/H-BEA	Zn-O	4.4	2.096	27.0	-0.2
+ 6AHI in CH ₃ CN	Zn–N	1.5	2.359	10.4	0.1

Detailed analysis of the EXAFS revealed the presence of three oxygen neighbors at 1.92 Å and three oxygen neighbors at 3.14 Å (Table 4). This strongly suggests that the copper cations are coordinated to six-membered rings of oxygen atoms. Displacement relative to the center of the ring provides three oxygen atoms at a shorter distance and three at a longer distance. For Cu(I)/H-BEA suspended in acetonitrile, coordination of one acetonitrile molecule to the copper cations at a distance d(Cu-N) = 2.57 Å is accompanied by a slight lengthening of the Cu–O distances to 1.93 and 3.15 Å. This indicates that the copper cations remain at their original position. In contrast, after addition of 6AHI four nearest oxygen neighbors are found at 1.98 Å and an additional nitrogen or carbon neighbor at 2.57 Å. This indicates that the copper cations have moved to the center of the six-membered ring of oxygen atoms. Note that due to a similar phase shift and amplitude functions it cannot be distinguished if the neighbor is a N or C atom.

For $[Cu(CH_3CN)_4]PF_6$ dissolved in acetonitrile, the radial distribution function is dominated by the first-shell Cu–N contributions at 1.99 Å. The peak reflects the contribution of the four nearest nitrogen neighbors. At further distance, a peak at 3.17 Å can be ascribed to the backscattering carbon atoms in the second shell. After addition of 6AHI, the first shell contribution was at 2.05 Å in the Fourier transformation. This indicates coordination of an atom at a larger distance to the metal center or the formation of a second coordination sphere around copper. This would be consistent with the formation of an intermediate complex.

3.3. Relation between oxidation state and catalytic performance—zinc-based catalysts

Corresponding X-ray absorption experiments were also performed for heterogeneous and homogeneous zinc catalysts (Zn/H-BEA, 0.08 Zn/Al, or 0.53 Zn/Al and Zn(CF₃SO₃)₂). In a first step, the XANES of the solid catalysts were compared to those of the catalysts dispersed/dis-



Fig. 6. XANES spectra of Zn/H-BEA (0.08 Zn/Al) dispersed in CH_3CN before and after the addition of 6AHI.

solved in acetonitrile. The addition of CH₃CN to Zn²⁺based catalysts led to an increase in the white line area. This is attributed to adsorption of the polar acetonitrile molecules on the Zn²⁺ cations. The XANES signal changed significantly at energies higher than 15 eV above of the edge, which indicates that the coordination sphere around zinc is altered. In case of Zn(CF₃SO₃)₂ the Zn-K edge was shifted by 1.18 eV to lower energies. It is known that CH₃CN coordinates more strongly to transition metals than CF₃SO₃⁻ [32]. Replacement of the two CF₃SO₃⁻ anions by the stronger electron-donating CH₃CN molecules leads to the significant increase in electron density at zinc.

Dispersion of Zn/H-BEA (0.08 Zn/Al) in CH₃CN led to a shift in edge energy by 0.98 eV to higher energy whereas at a high zinc loading (0.53 Zn/Al) the zinc K edge was shifted to lower energies ($\Delta E_{edge} = -0.17 \text{ eV}$). This can be explained by the presence of different zinc sites in this material as described previously [15]. At a low zinc loading, most zinc cations are coordinated to six-membered rings of oxygen atoms. These rings are distorted leading to four nearest and two distant oxygen neighbors. Adsorption of CH₃CN molecules on such zinc cations leads to a framework relaxation [33] and a more preferred tetrahedral geometry of ligands around zinc. At high zinc loading two further zinc phases are formed in the material. For Zn/H-BEA (0.53 Zn/Al) around 60% of the zinc cations are present as highly dispersed ZnO. XANES are not in the position to differentiate between these zinc phases, as the energy of the excitation of 1 s electrons is not sufficiently separated.

The addition of 6AHI to Zn(CF₃SO₃)₂ and Zn/H-BEA (0.08 Zn/Al) dissolved (dispersed) in CH₃CN led to a shift of the edge to lower energies and a decrease in the intensity of the white line (Fig. 6). This clearly indicates a higher electron density on zinc during catalysis, although the changes in edge energy were small ($\Delta E_{edge} = -0.51$ and -1.34 eV) in comparison to the shift in edge energy caused by changes in the oxidation state ($\Delta E = \pm 2.80$ eV). Thus, we conclude that strongly electron donating ligands are bound to the Zn²⁺ cation during catalysis. Additionally, upon the addition of

6AHI, the shape of the XANES signal changed slightly at energies higher than 15 eV above of the edge. Thus, the coordination sphere around the Zn^{2+} cation during catalysis is significantly different from the local environment in pure CH₃CN.

Analysis of the EXAFS of Zn/H-BEA (0.08 Zn/Al) revealed the presence of four oxygen neighbors at 2.05 Å and two oxygen neighbors at 2.97 Å (Table 4). This suggests that the zinc cations are coordinated to six-membered rings of oxygen atoms and located on a straight line passing through the center of the six-membered ring. For Zn/H-BEA suspended in acetonitrile, coordination of one acetonitrile molecule to the Zn^{2+} cations at a distance d(Zn-N) = 2.25 Å leads to elongation of the Zn–O distances to 2.10 and 3.47 Å, respectively. This indicates that the zinc cations are shifted away from the center of the six-membered ring along the perpendicular line. After addition of 6AHI, the four nearest oxygen neighbors remain at a distance d(Zn-O) = 2.10 Å and an additional nitrogen or carbon neighbor is located at 2.36 Å. This indicates substitution of acetonitrile by a nitrogen or carbon ligand. These observations and conclusions are in line with those for copper indicating thatduring catalysis-similar reaction steps occur on both metal cations.

3.4. Role of the cation concentration on the catalytic properties of Zn/H-BEA

The correlation between the cation concentration and the catalytic activity of the material was explored for Zn/H-BEA with zinc concentrations up to 0.86 mmol/g (0.77 Zn/Al). The cyclization of 6AHI and 3APE and the reaction between aniline and phenylacetylene were studied. For all reactions, the product was formed according to approximate first-order kinetics, although deactivation of the catalyst was observed for 3APE at prolonged reaction times. In case of the cyclization of 6AHI a linear increase of the catalytic activity was observed up to 0.15 Zn/Al (Fig. 7). The activity increased further in the range 0.15-0.26 Zn/Al, although the increase was less pronounced. For Zn²⁺ concentrations above 0.26 Zn/Al, the activity approached a constant level. Note that the same amount of Zn²⁺-exchanged zeolite was employed in each reaction and consequently the total amount of Zn²⁺ in the reaction mixtures varied. A similar correlation between the catalytic activity and the zinc loading was also observed for the other two reactions. In case of the cyclization of 3APE the initial reaction rates were comparable to 6AHI (Fig. 8), while the intermolecular reaction between aniline and phenylacetylene was around 100 times slower (Fig. 9). Nevertheless, also in this case the trend in the initial reaction rates was similar to the cyclization of 6AHI and 3APE. By correlating the initial reaction rates with the nature of the zinc sites in the material, the intrinsic catalytic activity of each site can be estimated.

Characterization of the zinc-exchanged BEA zeolites had shown that, depending on the metal content, up to three dif-



Fig. 7. Initial rates for the cyclization of 6AHI with Zn/H-BEA zeolites varying in the Zn^{2+} concentration.



Fig. 8. Initial rates for the cyclization of 3APE with Zn/H-BEA zeolites varying in the Zn^{2+} concentration.



Fig. 9. Initial rates for the addition of aniline to phenylacetylene with Zn/H-BEA zeolites varying in the Zn^{2+} concentration.

ferent zinc sites are present [15]. In the range 0-0.26 Zn/Al protons associated with Brønsted acid sites are exchanged by zinc cations (Fig. 10). Within this range two zinc sites were found differing in the location of charge balancing oxygen atoms. The zinc cations are best stabilized when the divalent charge is directly balanced by two framework Si-O-Al



Fig. 10. Possible zinc sites in Zn/H-BEA; (O) framework oxygen atom.

groups. This requires that the two aluminum atoms are in vicinity (zinc site A). In the most stable arrangement, the zinc cations are coordinated to 6-membered rings of oxygen atoms. This site is preferentially formed at low zinc concentrations (< 0.15 Zn/Al). The second site consists of [Zn–O–Zn]²⁺ cations charge balanced by two framework Si–O⁻–Al groups (zinc site B). In this case, the two aluminum atoms can be further apart (up to 1.2 nm). This site is preferentially formed at zinc concentrations between 0.15 and 0.26 Zn/Al. Both zinc sites A and B are located in the 12-ring channels of zeolite BEA, where the sites are readily accessible for reactants. At zinc loadings above 0.26 Zn/Al zinc is incorporated as ZnO (zinc site C).

The linear correlation between the activity and the zinc loading in the range 0-0.15 Zn/Al shows that a constant proportion of the zinc cations is available for catalysis. The further increase in activity in the range 0.15-0.26 Zn/Al confirms the increased number of catalytically active zinc cations in this range. The increasing activity of the material, thus, correlates with the increasing concentration of Zn^{2+} , which is incorporated as site A and site B, respectively. However, the Zn^{2+} cations in site B are catalytically only about half as active than those in site A. The high activity of Zn/H-BEA in hydroamination reactions seems, in part, related to the rigid coordination sphere of the zinc cations in zinc site A, which is far from the typical tetrahedral ligand sphere of zinc cations in solution. This coordination geometry is speculated to enhance the Lewis acidity of the zinc cations. The constant level of activity at loadings above 0.26 Zn/Al indicates that Zn^{2+} incorporated as ZnO (zinc site C) is catalytically inactive. The low activity is associated with the low Lewis acidity of ZnO that did not show any catalytic activity in hydroamination reactions [34]

3.5. On the different mechanism of hydroamination

Two different reaction sequences are proposed for hydroamination reactions catalyzed by late-transition-metal compounds [35–37]: (i) oxidative addition of the amine to the metal center, followed by insertion of the CC unsaturated moiety into the metal–nitrogen bond and (ii) a nucleophilic attack of the amine on a coordinated CC double or triple bond (Fig. 11).

• With respect to the oxidative addition route, the key step is the activation of the amine by oxidative addition to the metal center. This step requires two electrons



Fig. 11. Possible pathways of hydroamination reactions catalyzed by late-transition metals. Shown are the routes via oxidative addition (left) and nucleophilic attack (right) for the model substrate 6AHI. Formal [1,3]-hydrogen shifts are indicated with \pm H.

of the metal and is well established for electron-rich metal centers. Typical redox pairs for this reaction are Rh^+/Rh^{3+} , Ni^0/Ni^{2+} , and Pd^0/Pd^{2+} . A catalytic cycle for hydroamination can be realized, if the oxidative addition step can be coupled to an alkene/alkyne insertion process, followed by reductive elimination of the product.

 In nucleophilic addition, the activation of the alkene/ alkyne is generally accomplished by its coordination to a late-transition metal, which renders the π-system more susceptible to attack by exogenous amine nucleophiles. This gives an intermediate 2-aminoalkyl/alkenyl complex. Protonation of the carbon attached to the metal gives the hydroamination product.

If the reaction proceeds via oxidative addition, a significant decrease in electron density on the metal center is expected whereas for the route via nucleophilic attack an increase in electron density is expected.

The results on X-ray absorption clearly showed that the electron density at the metal cation (Cu⁺ and Zn²⁺) increased after addition of 6AHI. This strongly suggests that the reaction proceeds via an electron-rich intermediate similar to the 2-ammonioethenyl complex described for palla-

dium [24]. Thus, we conclude that a mechanistic route based on a nucleophilic attack on a coordinated alkyne/alkene group predominates for the Cu(I) and Zn(II) catalysts studied. The alternative route, oxidative addition, is intrinsically impossible for Zn(II) and appears unlikely for Cu(I), but is in principle possible for Rh(I). However, as Rh/H-BEA displays a very similar catalytic behaviour as the Cu(I) and Zn(II) catalysts it is speculated that the hydroamination reactions catalyzed by Rh/H-BEA also proceed via nucleophilic attack. A mechanistic route based on nucleophilic addition is also in line with the intermediate Lewis acidity of the metal cations (Rh⁺, Cu⁺, and Zn²⁺) which provided the highest rates in the cyclization of 6AHI.

4. Conclusions

The cyclization of 6-aminohex-1-yne and 3-aminopropylvinyl ether and as the reaction between phenylacetylene and aniline were studied as model reactions for the direct addition of amine N–H to CC multiple bonds (hydroamination). A particularly high catalytic activity for this type of reaction was observed for the heterogeneous catalysts Rh(I)/H-BEA, Cu/H-BEA, and Zn/H-BEA and the homogeneous catalyst $[(C_6H_6)(Cu(CF_3SO_3))_2].$

The key factor for a high catalytic activity seems to be the intermediate Lewis acidity of Rh^+ , Cu^+ , and Zn^{2+} cations. As a consequence, the propensity of the metal cation for coordination of either the amine or the alkyne functionality is balanced. This enables activation of the alkyne group in the presence of amines and a mechanistic route via coordination of the alkyne to the metal center and subsequent nucleophilic attack of the amine lone pair becomes viable.

Zinc ion-exchanged BEA zeolites were studied in particular detail. Zn^{2+} cations immobilized at ion-exchange positions prefer to coordinate to two vicinal Brønsted acid sites. In the most stable geometry, the zinc cations are coordinated in a square pyramidal fashion to four framework oxygen and two further oxygen at a longer distance. This distorted coordination geometry probably enhances the Lewis acidity of the zinc cations, leading to a much higher catalytic activity of Zn/H-BEA in hydroamination reactions compared to corresponding homogenous catalysts.

In summary, this study correlates the local environment of metal cations immobilized at ion-exchange positions of zeolite BEA with the catalytic activity of the material in hydroamination reactions. To further increase the catalytic activity, BEA zeolites with a lower Si/Al ratio are required. In this case a higher concentration of Lewis acidic metal cations at ion exchange positions becomes available.

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