



# Metallation of functional resins with copper acetate: control of metal speciation and catalytic activity in C–N coupling reactions

A. Biffis<sup>a</sup>, F. Filippi<sup>a</sup>, G. Palma<sup>b</sup>, S. Lora<sup>c</sup>, C. Maccà<sup>a</sup>, B. Corain<sup>a,d,\*</sup>

<sup>a</sup> Dipartimento di Chimica Inorganica Metallorganica ed Analitica, Università di Padova, Via Marzolo 1, I-35131 Padova, Italy

<sup>b</sup> Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, I-35131 Padova, Italy

<sup>c</sup> Istituto per la Sintesi Organica e la Fotoreattività—Sezione di Legnaro, C.N.R., Via Romea 4, I-35020 Legnaro, Italy

<sup>d</sup> Istituto di Scienze e Tecnologie Molecolari, C.N.R., Via Marzolo 1, I-35131 Padova, Italy

Received 23 November 2002; accepted 4 April 2003

## Abstract

Moderately cross-linked gel-type acidic ion-exchangers (0.8–1.0 meq. H<sup>+</sup>/g) obtained upon copolymerization of dimethylacrylamide (DMAA), methylenebisacrylamide (MBAA) and methacrylic acid (MAA) or sulfoethyl methacrylate (SEMA) were reacted with Cu(OAc)<sub>2</sub> under different initial H<sup>+</sup>/Cu(II) molar ratios. The metal speciation inside the polymer networks was characterized on the basis of analytical and spectroscopic data. Depending on the kind of ion-exchanger and reaction conditions employed, different species were identified. The kind of metal speciation appears to have a profound influence on the catalytic activity of the resulting resin-supported copper species in C–N coupling reactions. Use of a resin containing the proper copper species results in a catalytic performance superior to that of unsupported copper acetate.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Gel-type (microporous) ion-exchangers; Copper acetate; Polymer-supported catalysts; C–N coupling reactions

## 1. Introduction

Supported metal catalysis is well established in modern chemical technology, especially in the area of commodity synthesis [1–4]. A gradual extension of the application of supported metal catalysis to the realm of fine chemistry has become apparent in recent years [5–8], also in connection with the fulfillment of more and more strict environmental requirements that promote the replacement of conventional stoichiometric synthetic routes with catalytic ones. It is worth noting that the traditional supports employed so far

are high-surface inorganic materials and amorphous carbon from various sources [1,9].

Functional resins are currently employed in industrial processes as ion-exchangers, as acid catalysts in a variety of circumstances [10] and in a few instances also as supports of palladium metal catalysts [11–15]. Synthetic resins appear to be quite promising supports for metal catalysts, offering yet scarcely explored potentiality in the development of innovative catalysts for the fine chemical industry [5–8]. For example, they can be easily functionalized with reactive groups designed to modulate or to complement the action of given metal centers [16].

In recent years, we have developed various protocols for the dispersion of “metal ions” within gel-type resin supports and the subsequent production

\* Corresponding author. Tel.: +39-049-8275211;

fax: +39-049-8275223.

E-mail address: [corain@chin.unipd.it](mailto:corain@chin.unipd.it) (B. Corain).

of size-controlled metal nanoparticles with a pre-determined distribution throughout the body of the resin particles [16]. In order to understand the processes leading to the generation of metal nanoparticles within the resins and to gain control over them, an exact knowledge of the speciation of the metal ion precursor in these materials is advantageous. Indeed, different kinds of metal species may lead after reduction to metal nanoparticles possessing different properties (for a recent example, see [17]). Furthermore, such polymer-bound metal complexes can also be advantageously used as catalysts in their own right (“hybrid phase” catalysis). Recently, we have preliminarily reported on the successful dispersion of Pd(II), Ni(II), Cu(II) inside acidic gel-type resins based on the reaction with metal acetates and concomitant release of acetic acid, seemingly able to drive to completion metal ion implantation [18]. Herein, we wish to report on the different kinds of resin-bound copper species that can be obtained by suitable changes of the functional monomer in the resin and of the reaction conditions. Interestingly enough, copper(II) is a versatile metal center for the catalysis of useful organic transformations [19]. In particular, efficient protocols involving copper(II) species for C-heteroatom coupling reactions have been disclosed in recent years [20,21]. Therefore, we have performed a preliminary evaluation of our resin-supported copper species as catalysts of C–N coupling reactions.

## 2. Results and discussion

We have prepared two gel-type resin supports (MPI and SPI) by batch polymerization of a monomer mixture containing (a) dimethylacrylamide (DMAA) as the major comonomer; (b) a functional monomer (sulfoethyl methacrylate (SEMA) or methacrylic acid (MAA)), useful for anchoring the copper(II) species; (c) a cross-linker, namely methylenebis(acrylamide) (Fig. 1). The compositions of the individual resins are reported in Table 1. The polymerization is initiated in all cases by  $\gamma$ -rays irradiation from a  $^{60}\text{Co}$  source and quantitative conversion of the monomers is achieved [22]. The supports are obtained as stiff rods, which are crushed and sieved to a particle size 180–400  $\mu\text{m}$ . SEM analyses of the obtained powders shows for all

Table 1  
Radiation-induced synthesis of resins MPI and SPI

Resin	Composition <sup>a</sup> (mol%)	H <sup>+</sup> <sup>b</sup> (mmol/g)	Yield (%)
MPI	MAA 12.1, DMAA 84.1, MBAA 3.8	1.00	99.6
SPI	SEMA 9.9, DMAA 86.1, MBAA 4.0	0.80	98.9

<sup>a</sup> Based on the initial composition of the monomer mixture.

<sup>b</sup> Experimental values.

materials the expected glassy morphology in the dry state.

The H<sup>+</sup> exchange capacity of the resins is determined by acid–base titration performed with a pH-static technique (see Section 3) and is found to match the acidic monomer content in the monomer mixture. The nature of the major comonomer and the nominal 4% cross-linking degree is chosen in order to ensure reasonable mechanical robustness and good swellability, i.e. molecular accessibility, of the resulting resins in dipolar aprotic solvents such as dichloromethane, which are the reaction media of choice for the target reaction to be catalyzed [20,21].

Resins MPI and SPI exhibit a quite appreciable swelling in polar media such as dichloromethane, methanol and water with specific swelling values ranging from 0.8 ml/g (MPI in dichloromethane) to 8.8 ml/g (SPI in water) (Table 2). Remarkably, the SPI resin does swell much more than the MPI resin in spite of the fully comparable cross-linking degree. This is probably the consequence of additional noncovalent cross-linking in the MPI resin due to strong hydrogen bonds between pendant carboxylic acid groups.

We have performed metallation reactions of our tailor-made resins with copper(II) acetate in methanol, using different ratios of the copper(II) species to the functional groups present within the polymer. In principle, the mode of binding of the copper to the resin

Table 2  
Swelling behavior of resins MPI and SPI in various media

Resin	Solvent	Expanded volume (ml/g)
MPI	Dichloromethane	0.8
	Methanol	2.6
	Water	3.4
SPI	Methanol	7.6
	Water	8.8

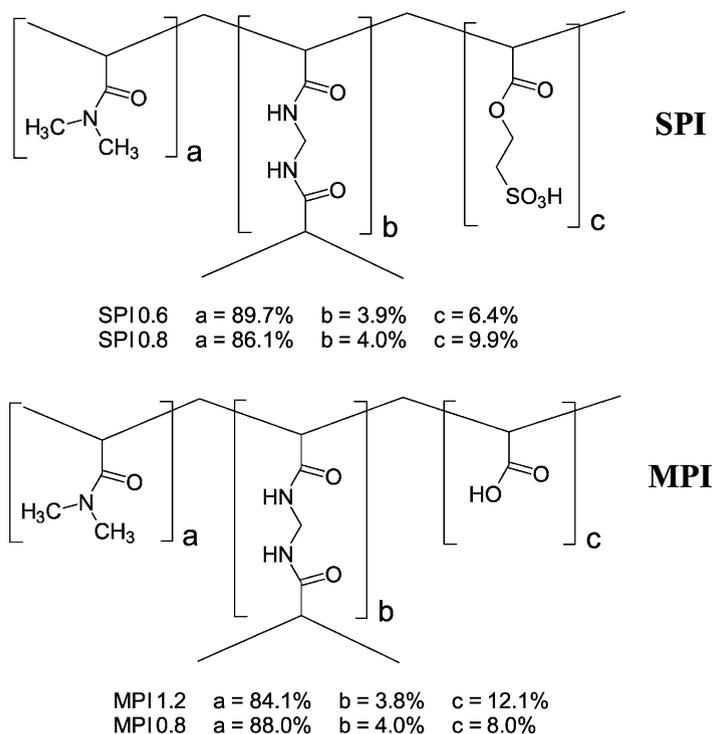


Fig. 1. Sketch of the structure of resins MPI and SPI and theoretical molar composition of resins MPI and SPI based on the assumption of 100% polymerization yield (see text).

can be two-fold (Scheme 1), i.e. the acidic groups present in the resin can substitute one (A) or both (B) of the original acetate ligands in the starting copper(II) complex. Situation A is expectedly promoted by an overall functional group/Cu(II) ratio equal to 1.0 while situation B should be favored by a functional group/Cu(II) ratio equal to 2.0. The experimen-

tal outcome of the metallation reactions is outlined in Table 3.

The addition of blue solutions of  $\text{Cu}(\text{OAc})_2$  to the appropriate amount of pre-swollen resin under moderate stirring leads to the immediate color uptake by the reacting resin. In the case of entries 1 and 3, colorless solutions are obtained while residual blue color in the

Table 3  
Metallation of resins SPI and MPI in MeOH at 2:1 and 1:1  $-\text{OH}/\text{Cu}(\text{II})$  initial molar ratios

Entry	Resin	$\text{H}^{\text{a}}$ (mmol)	$\text{Cu}(\text{OAc})_2^{\text{b}}$ (mmol)	$\text{Cu}(\text{II})$ incorporated <sup>c</sup> (mmol)	% Incorporated <sup>d</sup>	$\text{H}^{\text{+e}}$ (mmol)	Bonding situation <sup>f</sup>
1	SPI	0.80	0.44	0.43	97	0.82	B
2	SPI	0.80	0.82	0.66	80	1.10	A + B
3	MPI	1.00	0.50	0.48	96	0.64	A + B
4	MPI	1.00	1.00	0.74	74	0.84	A + B

<sup>a</sup>  $\text{H}^{\text{+}}$  content in the resin sample.

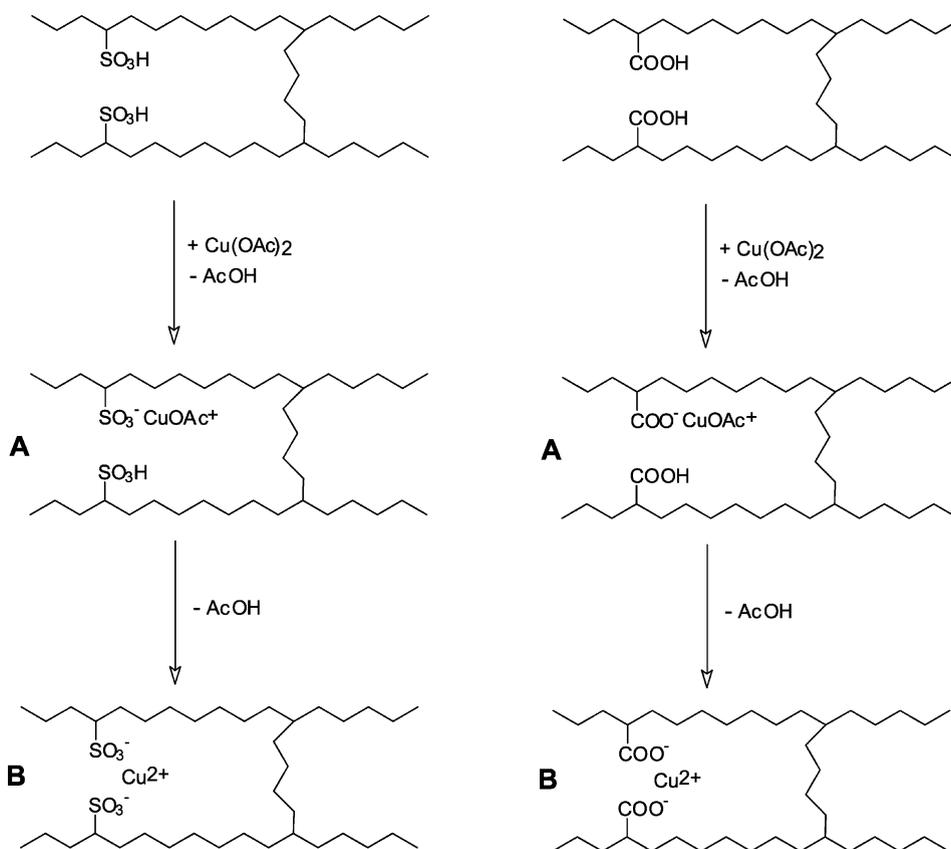
<sup>b</sup>  $\text{Cu}(\text{II})$  made available.

<sup>c</sup> Incorporated  $\text{Cu}(\text{II})$ .

<sup>d</sup> Percentage  $\text{Cu}(\text{II})$  incorporated.

<sup>e</sup>  $\text{H}^{\text{+}}$  released upon metallation.

<sup>f</sup> See Scheme 1.



Scheme 1. Schematic representation of possible bonding situations involving a solvated “ $\text{Cu}^{2+}$ ” ion and the ligating groups of acidic functional resins.

supernatant solutions is observed in the case of entries 2 and 4. The acetic acid which is liberated through the metallation reaction can be quantitatively estimated by pH-static potentiometric titration. The amount of incorporated copper as well as of liberated acetic acid clearly indicate the existence of different bonding situations of the metal within the resins. Thus, it may be appreciated that a change in the stoichiometry provides resin-bound complexes of different nature.

XRMA carried out on equatorial sections of metallated resin particles reveals that the Cu dispersion is essentially homogeneous throughout the body of the resin particles. Interestingly, the metallation of the polymer network is accompanied by quite perceivable consequences in the swelling behavior. Thus, in both resins SPI–Cu(II) (2:1) and SPI–Cu(II) (1:1) the specific swelling volume in methanol drops from 7.6 to 1.2 and 1.4 ml/g respectively. However, a far less

marked contraction is observed for resins MPI–Cu(II) (from 2.6 to 1.4 and 1.8 ml/g respectively). The marked shrinking effect observed in the case of SPI resins appears to be compatible with “ $\text{Cu}^{2+}$ ” acting in fact as an effective cross-linking agent among macromolecular chains. The effect is smaller with MPI resins, since in the metal-free state the resin is already crosslinked via hydrogen bonds between pendant carboxylic acid groups (see above). Furthermore, the slight increase in the swelling volume of both kinds of resin on going from a 2:1 to a 1:1 stoichiometry may reflect an increase of the importance of bonding situation A in respect to situation B (Scheme 1).

In addition to elementary stoichiometric arguments, the evaluation of the metal speciation inside our resins rests on the solid state electronic spectra of the materials recorded in the visible region (Table 4). From the data of Table 3, it is apparent that an unambiguous

Table 4

Solid state electronic spectra of metallated resins in the visible region compared to those of  $\text{Cu}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$  and of  $\text{Cu}(\text{OAc})_2$  recorded in methanol

Entry	Sample species	Solvent <sup>a</sup>	Chromophore	$\lambda_{\text{max}}$ (nm)	$\mu$ (BM)
1	$\text{Cu}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$	MeOH	$[\text{Cu}(\text{MeOH})_6]^{2+}$	821.0	
2	$\text{Cu}(\text{OAc})_2$	MeOH	$[\text{Cu}(\text{MeOH})_x(\text{OAc})_y]^b$	700.0	
3	SPI–Cu (2:1)	MeOH	$[\text{Cu}(\text{MeOH})_6]^{2+}$	821.0	1.7
4	SPI–Cu (1:1)	MeOH	Mixture of species	757.3	
5	MPI–Cu (2:1)	MeOH	$[\text{Cu}(\text{MeOH})_x(\text{carboxylate})_y]^b$	707.0	1.7
6	MPI–Cu (1:1)	MeOH	$[\text{Cu}(\text{MeOH})_x(\text{carboxylate})_y]^b$	707.0	

Some observed magnetic moments.

<sup>a</sup> Solvent for entries 1 and 2, metallation medium for entries 3–6.

<sup>b</sup> Net charge not indicated.

assignment of metal speciation is possible only for SPI resin when a  $2\text{H}^+ : 1\text{Cu}(\text{OAc})_2$  molar ratio is employed. In this case, in fact, the species evenly dispersed inside the polymer network appear to be  $[\text{Cu}(\text{solvent})_6]^{2+}$ . Thus, SPI–Cu obtained from methanol exhibits an electronic spectrum identical to that displayed by solid  $\text{Cu}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$  dissolved in methanol where the quantitative formation of  $[\text{Cu}(\text{MeOH})_6]^{2+}$  can be safely predicted. When the SPI resin is let to react with  $\text{Cu}(\text{OAc})_2$  under a  $1\text{H}^+ : 1\text{Cu}(\text{OAc})_2$  molar ratio, the resulting 757 nm band turns out to be located between 821 nm  $[\text{Cu}(\text{MeOH})_6]^{2+}$  and 700 nm that corresponds to the mixture of chromophores expected to form upon dissolving  $\text{Cu}(\text{OAc})_2$  in methanol (entry 4, Table 4). The resin-bound chromophores can be tentatively proposed as a mixture of acetate-free and acetate-coordinated species. In the case of MPI resins, under both  $2\text{H}^+ : 1\text{Cu}(\text{OAc})_2$  and  $1\text{H}^+ : 1\text{Cu}(\text{OAc})_2$  conditions similar mixed coordination sphere chromophores appear to be formed, quite similar to those observed in methanol solutions of  $\text{Cu}(\text{OAc})_2$ .

The observed magnetic moments (corrected for the diamagnetic contribution calculated on the basis of the “molecular formula” of the resin stemming from elementary analysis data) are not particularly helpful in this connection. However, although the observed  $\mu$  values (just slightly lower than those expected for an octahedral copper(II) species) do not offer specific suggestions about the metal speciation, they do rule out the existence inside the metallated resins of dimeric copper(II) carboxylate species featured by a significant Cu(II)–Cu(II) magnetic exchange able to strongly quench the individual paramagnetic contributions, at least at room temperature [23].

The resin-supported copper species have been employed to promote the C–N coupling reaction of *p*-toluidine with phenylboronic acid. This reaction was discovered a few years ago [20] and recently made catalytic in copper by running it under an oxygen atmosphere [21].

Initially, we have utilized the standard reaction conditions proposed by Jadhav and co-workers [21(c)], that is, 10 mol% copper acetate in the presence of powdered 4 Å molecular sieves and excess triethylamine, which is reported to have a beneficial effect on the reaction. The reaction time is set constant at 24 h and was not further optimized. The results are reported in Table 5.

We have soon recognized that triethylamine acts in fact as an inhibitor of this reaction, probably because it occupies all the free coordination sites at the copper centers, and that much higher conversions of toluidine could be obtained without the amine base (compare in Table 5, entries 1 and 7 with entries 2 and 6, respectively). However, in the absence of triethylamine the selectivity for the desired product is lower, which is found to be mainly due to the parallel formation of a boronic acid monoamide adduct 2, which is not further converted to the desired product. The byproduct can be detected and identified by GC–MS in all the tests run without the amine base. Interestingly enough, this adduct is not formed in the absence of copper catalyst. We suppose that when using more basic amines as substrates, the formation of this byproduct may become predominant. In this case, the presence of a tertiary amine base such as triethylamine, able to coordinate to the boronic acid moiety without forming the monoamide, becomes



Table 7  
C–N coupling reaction of different aromatic amines with catalyst MPI–Cu (1:1)

Entry	Aromatic amine	Conversion (%)	Yield (%) <sup>a</sup>
1	4-Toluidine	65	53
2	4-Anisidine	69	65
3	Aniline	60	32
4	4-Bromoaniline	24	19
5	3-Chloroaniline	20	19
6	3-Nitroaniline	0	0

Reaction conditions: 1 mmol amine, 1 mmol phenylboronic acid, 0.1 mmol copper catalyst, 10 ml dichloromethane, 1 atm O<sub>2</sub>, RT, 24 h.

<sup>a</sup> Yields referred to 100% conversion.

Finally, a preliminary screening of the reactivity of various aromatic amines under these reaction conditions has been performed (Table 7). Interestingly, electron-donating substituents on the aromatic ring appear to increase the reactivity of the amine, whereas electron-withdrawing substituents decrease it. No reaction is observed with strongly electron-withdrawing substituents such as nitro groups.

In conclusion, we have succeeded in preparing resin-supported copper catalysts with a precise control of metal speciation inside the resin support. These materials are active catalysts in C–N coupling reactions with aromatic amine. We are currently working at the optimization of the catalytic performance as well as at the extension of our investigations to other reactions of practical interest, such as C–N couplings with other nitrogen-containing compounds and C–O coupling reactions.

### 3. Experimental

#### 3.1. Resin preparation

Polymerizations were carried out with standard protocols set up in these laboratories [25]. The monomers were combined in the appropriate ratios (Table 1) and the resulting clear monomer mixtures were put in screw-cap vials and exposed to the  $\gamma$ -rays from a <sup>60</sup>Co source at 0.12 Gy s<sup>-1</sup> at room temperature and at a distance of 22 cm for 24 h. The resulting clear transparent rods were crushed, extensively washed with methanol, vacuum dried and sieved to a particle size of 400–180  $\mu$ m.

#### 3.2. Determination of resin acidity

The total exchange capacity (acidic functionality) of the resins was determined by pH-metric back titration of the residual alkalinity of known volumes of sodium hydroxide standard solution after standing in contact with weighed amounts of resin for 24 h [26]. The titrations were performed by means of a pH-static technique [27,28], which allowed to operate with small volumes of standard base (less than 1 cm<sup>3</sup>) contacted with very small amounts of resins, as well as with the traditional procedure when possible.

#### 3.3. Resin metallation

One gram resin was pre-swollen in 10 ml methanol, then 10 ml of a methanol solution of Cu(OAc)<sub>2</sub> at the appropriate concentration (Table 3) were added. The mixture was gently stirred at room temperature for 30 min, after which the resin was separated by filtration, washed three times with methanol and dried at 50 °C under vacuum to constant weight.

#### 3.4. Determination of incorporated Cu(II)

The exchange capacity towards copper(II) (Table 3, column 5) was determined after equilibration of the resin in the hydrogen form with 0.05–0.15 M copper(II) acetate solution for 24 h. In the presence of excess copper(II), the copper intake could not be accurately determined by simple pH-metric titration of the acetic acid formed by the exchange reaction. Thus, complexometric titration of residual copper in the conditioning solution was performed. The pH-static technique [29,30] was advantageous also for this purpose. The titrant chelating agent (EDTA) was added by simultaneously keeping the pH of the titrated copper(II) solution at constant pH (4.00) by addition of sodium hydroxide solution [30]. A sharp slope change of the volume of base plotted against the volume of EDTA solution yielded the equivalence volume of the titrant solution.

#### 3.5. Catalytic tests

Typical procedure: 0.107 g (1.0 mmol) *p*-toluidine and 0.122 g (1.0 mmol) phenylboronic acid were put in a three-necked 100 ml round-bottomed flask equipped

with a magnetic stirring bar and a septum inlet. Copper catalyst (10 mol%) were then added: the flask was closed, evacuated for a few minutes and then filled with dioxygen. Solvent (10 ml) as well as 50  $\mu$ l hexadecane as internal standard were then added and the mixture was vigorously stirred for 24 h. Conversions and yields were estimated by gas chromatography, and in selected cases the chromatographic result was confirmed by isolating the reaction product by column chromatography on silica (eluent—hexane:ethyl acetate (20:1)).

### Acknowledgements

We gratefully acknowledge the skillful assistance of G. Marcolongo (solid state UV-Vis spectra), F. De Zuane (magnetic susceptibility measurements) and L. Soldà (titrations). This work was partially supported by MIUR (PRIN 2001–2003, Project number 2001038991).

### References

- [1] C.H. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, second ed., McGraw-Hill, New York, 1991.
- [2] J.M. Thomas, W.J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.
- [3] M. Twigg (Ed.), *Catalysis Handbook*, Manson Publishing, London, 1996.
- [4] R.A. Van Santen, P.W.N.M. Van Leeuwen, J.A. Moulijn, B.A. Averill (Eds.), *Catalysis: An Integrated Approach*, Elsevier, Amsterdam, 1999.
- [5] R.A. Sheldon, *J. Mol. Catal. A: Chem.* 107 (1996) 75.
- [6] R.A. Sheldon, *Chem. Ind. (London)* (1997) 12.
- [7] R.A. Sheldon, R.S. Downing, *Appl. Catal. A: Gen.* 189 (1999) 163.
- [8] H.-U. Blaser, M. Studer, *Appl. Catal. A: Gen.* 189 (1999) 191.
- [9] P. Albers, J. Pietsch, *J. Mol. Catal. A: Chem.* 173 (2001) 275 (and references therein).
- [10] M.A. Harmer, Q. Sun, *Appl. Catal. A: Gen.* 221 (2001) 45.
- [11] W. Neier, in: K. Dorfner (Ed.), *Ion Exchangers*, de Gruyter, Berlin, 1991, p. 982.
- [12] R. Wagner, P.M. Lange, *Erdöl, Erdgas, Kohle* 105 (1989) 414.
- [13] K. Weissermel, H.-P. Arpe, *Industrial Organic Chemistry*, third ed., VCH, Weinheim, 1997, Chapter 11, p. 281 (MIBK), Chapter 3, p. 71 (MTBE).
- [14] P.M. Lange, F. Martinola, S. Oeckel, *Hydrocarbon Processing*, December 1985, p. 51.
- [15] D.C. Sherrington, *Chem. Commun.* (1998) 2275.
- [16] B. Corain, M. Kralik, *J. Mol. Catal. A: Chem.* 159 (2000) 153.
- [17] A. Drelinkiewicz, M. Hasik, M. Kloc, *J. Catal.* 186 (1999) 123.
- [18] D. Belli Dell'Amico, S. Lora, A.A. D'Archivio, L. Galantini, A. Biffis, B. Corain, *J. Mol. Catal. A: Chem.* 157(2000) 173.
- [19] L.S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Sausalito, 1999.
- [20] (a) D.M.T. Chan, K.L. Monaco, R.-P. Wang, M.P. Winters, *Tetrahedron Lett.* 39 (1998) 2933;  
(b) D.A. Evans, J.L. Katz, T.R. West, *Tetrahedron Lett.* 39 (1998) 2937;  
(c) P.Y.S. Lam, C.G. Clark, S. Saubern, J. Adams, M.P. Winters, D.M.T. Chan, A. Combs, *Tetrahedron Lett.* 39 (1998) 2941;  
(d) D.J. Cundy, S.A. Forsyth, *Tetrahedron Lett.* 39 (1998) 7979.
- [21] (a) J.P. Collman, M. Zhong, *Org. Lett.* 2 (2000) 1233;  
(b) J.P. Collman, M. Zhong, *J. Org. Chem.* 66 (2001) 1528;  
(c) P.Y.S. Lam, G. Vincent, C.G. Clark, S. Deudon, P.K. Jadhav, *Tetrahedron Lett.* 42 (2001) 3415;  
(d) J.C. Antilla, S.L. Buchwald, *Org. Lett.* 3 (2001) 2077.
- [22] B. Corain, M. Zecca, F.O. Sam, G. Palma, S. Lora, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 384.
- [23] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, fifth ed., Wiley, New York, 1988, p. 772.
- [24] F.A. Cotton, G. Wilkinson *Advanced Inorganic Chemistry*, fifth ed., Wiley, New York, 1988, p. 758.
- [25] B. Corain, M. Kralik, *J. Mol. Catal. A: Chem.* 173 (2001) 99.
- [26] C.E. Harland, *Ion Exchange: Theory and Practice*, second ed., R.S.C., Cambridge, 1994.
- [27] C. Maccà, L. Soldà, *Electroanalysis* 14 (2002) 57.
- [28] C. Maccà, L. Soldà, *Electroanalysis* 14 (2002) 63.
- [29] C. Maccà, *Anal. Chim. Acta* 456 (2002) 313.
- [30] C. Maccà, L. Soldà, M. Zancato, *Anal. Chim. Acta* 470 (2002) 277.