Catalysis Letters 70 (2000) 61–65

The effect of flexible lattice aluminium in zeolite beta during the nitration of toluene with nitric acid and acetic anhydride

Mohamed Haouas, Andreas Kogelbauer [*] and Roel Prins [**]

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology (ETH), CH-8092 Zurich, Switzerland
E-mail: prins@tech.chem.ethz.ch

Received 6 June 2000; accepted 24 August 2000

The nitration of toluene with nitric acid and acetic anhydride using zeolite H-beta as catalyst was studied with multi-nuclear solid-state NMR spectroscopy in order to investigate the causes for the observed enhanced *para*-selectivity. The reversible transformation of framework aluminium from a tetrahedral into an octahedral environment was observed by ^{27}Al NMR upon interaction of the zeolite with the different components of the nitrating system. The octahedral co-ordination complex between lattice aluminium and acetylnitrate might explain the surface-catalysed *para*-selective nitration reaction and suggests that the lattice flexibility plays an important role in determining the regio-selectivity of the nitration catalysed by zeolites.

Keywords: flexible lattice aluminium, zeolite beta, nitration, regio-control, *para*-selectivity, toluene, NMR

1. Introduction

One of the key issues in aromatic nitration is achieving greater flexibility with respect to the product composition of substituted aromatics. Generally, *para*-substituted products are more desired but the products of mixed-acid nitrations usually contain a higher fraction of *ortho*-substituted products. A substantial research effort has been devoted to overcome this limitation [1] and zeolites have been given special attention due to their success in other shape-selective reactions [2]. Of particular interest is zeolite beta, which was recently reported to be a highly *para*-selective catalyst for the nitration of a broad range of substituted aromatics. The high *para*-selectivity was initially demonstrated for the acetylnitrate/beta system in the liquid phase [3]. We have shown that it also applies when the reaction is carried out only with 65% nitric acid in the vapour phase and even for deactivated aromatics such as 2-nitrotoluene (2-NT) in the liquid phase with simultaneous removal of the water formed during the reaction by distillation [4]. Similar observations were made by other groups for the nitration of fluorobenzene in the vapour phase [5] and toluene with azeotropic distillation [6].

The enhanced *para*-selectivity occurring with beta is far from being understood since classical shape-selectivity concepts do not apply. The well-known irreversibility of the reaction, which is evidenced by the lack of isomerisation of 2-NT into 4-NT or 3-NT excludes possible product shape-selectivity. In a recent study of the nitration of toluene and 2-NT we demonstrated by examining the dimensions of the transition states that classical transition-state selectivity cannot be the cause for the enhanced *para*-selectivity [7]. Our results, however, were consistent with the hypothesis that upon adsorption of the reactant on a rigid surface such as the zeolite framework steric hindrance would direct the orientation of the aromatic in the adsorbed state in a way that the substituent on the aromatic ring points toward the zeolite cavity where the least repulsion would be expected. This would give preference to the formation of the Wheeland intermediate leading to the *para*-substituted product. Such a hypothesis should apply in principle to all zeolitic materials but only H-beta with some minor exceptions has consistently proven to be *para*-selective. Clearly, a spectroscopic study was in demand to reveal the nature of the adsorbed species and provide more detailed insight into the molecular aspects of the zeolite-catalysed aromatic nitration. NMR spectroscopy was the preferred method for this study. It permits to avoid the interference of water that would be detrimental to IR investigations and furthermore allows the handling of the corrosive reaction medium in inert zirconia rotors. There are several examples in the literature demonstrating that *in situ* solid state NMR is a powerful method to understand reaction mechanisms based on the study of the nature, dynamics and reactivity of surface intermediates and active sites in zeolite-catalysed systems [8,9].

2. Experimental

Beta zeolite (Si/Al = 13) was obtained in the ammonium form from PQ Corporation. In order to ensure complete removal of sodium, the zeolite was subjected to another ammonium-exchange using a 1 M aqueous NH_4NO_3 solution. The material was calcined overnight at 500 °C

---

[*] Present address: Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London SW7 2BY, UK.

[**] To whom correspondence should be addressed.

in air prior to further use. For the nitration studies using *in situ* NMR spectroscopy, the zeolite was impregnated first with a 90 wt% aqueous nitric acid solution, then with acetic anhydride and finally with toluene while NMR spectra were recorded after each impregnation step. This sequence of addition has been shown to give the highest *para*-selectivity [10] and was also applied in our earlier catalytic studies [11]. Typically 6–8 mmol of ^{15}N-enriched (7.6%) nitric acid per 1 g of zeolite were used. The amount of acetic anhydride employed was in excess based on the nitric acid present in order to compensate for its conversion into acetic acid by the water present in the mixture. Independent experiments confirmed that the conversion of water and acetic anhydride into acetic acid was quantitative and complete under our reaction conditions. The ratio of toluene to nitric acid was fixed to one. Samples were prepared at room temperature in air and were then directly transferred into the NMR rotor and sealed.

Solid state MAS NMR measurements were carried out on a Bruker AMX 400 spectrometer at 9.40 T, which corresponds to 40.54 and 104.26 MHz for the ^{15}N and ^{27}Al frequencies, respectively. ^{15}N spectra were collected using a 6.3 μs pulse (flip angle approximately 45°), and recycle delays of 30 s; 2880 transients were averaged for each spectrum. ^{27}Al spectra were recorded with a short 0.8 μs pulse (corresponding to a flip angle smaller than 15°) allowing quantitative measurements. Chemical shifts were referenced to ^{15}N-labelled glycine, as a secondary reference at -347.6 ppm with respect to neat liquid nitromethane [12], and to a 1 M $Al(NO_3)_3$ solution for ^{15}N and ^{27}Al, respectively.

3. Results and discussion

Figure 1 shows ^{27}Al MAS NMR spectra of the parent H-beta zeolite and the zeolite after successive impregnation with nitric acid, acetic anhydride and toluene. The signals centred at 53.2, 28.6 and -1.1 ppm in the spectrum of the parent zeolite (figure 1(a)) are attributed to tetrahedrally co-ordinated, distorted tetrahedrally co-ordinated or pentaco-ordinated and octahedrally co-ordinated aluminium species, respectively [13]. A very sharp signal at 0.4 ppm was observed after nitric acid was added to the zeolite, as shown in figure 1(b). This intense signal, which we will show not to originate from extra-framework aluminium, overlaps with a shoulder at -1.6 ppm, which probably corresponds to the initial extra-framework aluminium. Deconvolution of the spectrum using the Win-Fit program indicates that the area of the peak at -1.6 ppm corresponds to 33% of the total aluminium. This is somewhat higher than the value of 22% observed in the parent material before nitric acid impregnation suggesting that dealumination has taken place to a limited extent. In parallel, the intensity of the tetrahedral framework aluminium signal was drastically reduced to about 2% of the total aluminium. It should be pointed out that all aluminium was visible by NMR which was ascertained using an external quantitative reference compound [14].

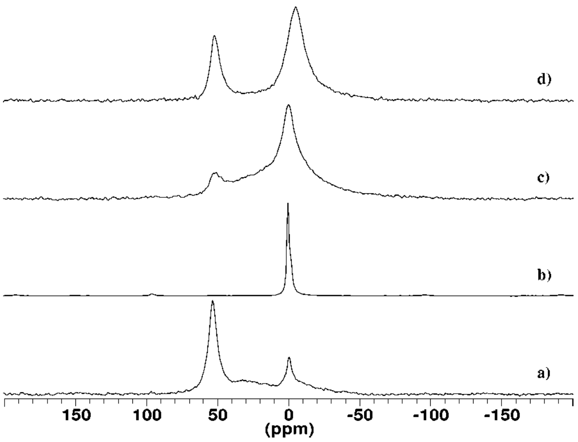

Figure 1. ^{27}Al MAS NMR spectra of zeolite beta; parent zeolite before impregnation (a), and after impregnation with 90 wt% HNO_3 (b), 90 wt% HNO_3 and Ac_2O (c) and 90 wt% HNO_3, Ac_2O and toluene (d). Loading 6–8 mmol-HNO_3/g-zeolite, $HNO_3/Ac_2O = 0.5$–1.1, HNO_3/toluene $= 1.1$.

The effect of nitric acid on the aluminium environment in the zeolite lattice is clearly established by these observations and it shows that nitric acid transforms tetrahedrally co-ordinated aluminium into octahedral geometry. This is not surprising since mineral acids are commonly used for dealumination of zeolites and it is known that leaching of zeolitic materials with nitric acid removes extra-framework aluminium species most likely by a co-ordination/dissolution mechanism [15]. The co-ordination complexes characterised by the signal at 0.4 ppm, however, are not due to extra-framework species. The extremely narrow signal at 0.4 ppm suggests that the electric field gradient surrounding the aluminium atom is very small. The octahedral aluminium species formed should therefore be of particularly high symmetry.

A very broad band appeared in the range of octahedral aluminium after addition of acetic anhydride to the nitric acid–zeolite system replacing the narrow signal at 0.4 ppm (figure 1(c)). Also, some of the intensity of the peak of tetrahedral aluminium was regenerated. These results are a strong indication that the octahedral aluminium species formed under the effect of nitric acid are still part of the zeolite framework. This is in agreement with earlier reports concluding that the octahedral aluminium in zeolite beta must be regarded as an inherent part of the framework [16,17]. The appearance of the much broader signal in the spectral range of octahedral aluminium is attributed to the formation of different types of adsorbed species like acetylnitrate and/or acetic acid on the aluminium sites. The interactions of these species would be weaker than those of nitric acid giving more distorted complexes.

After addition of toluene, the spectrum (figure 1(d)) showed an even more intense tetrahedral aluminium signal and a very broad signal at an apparent chemical shift of -5 ppm. This result confirms the reversibility of the symmetry transformation of the aluminium co-ordination in the

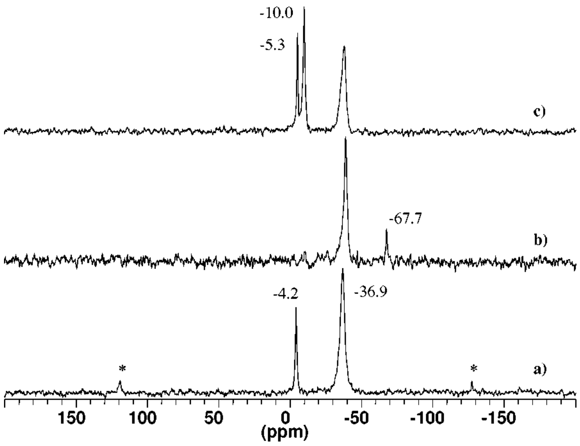

Figure 2. ^{15}N MAS NMR spectra of zeolite beta impregnated with 90 wt% HNO_3 (a), 90 wt% HNO_3 and Ac_2O (b) and 90 wt% HNO_3, Ac_2O and toluene (c). Loading 6–8 mmol-HNO_3/g-zeolite, $HNO_3/Ac_2O = 0.5$–1.1, HNO_3/toluene $= 1.1$.

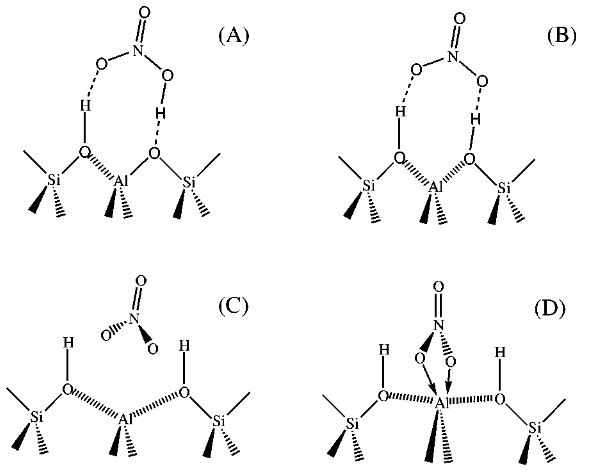

Figure 3. Proposed structures of nitric acid species interacting with the H-beta zeolite framework.

solid from tetrahedral to octahedral and *vice versa* since the consumption of the adsorbed reactive species, acetylnitrate, led to the recovery of more tetrahedral aluminium sites. A very similar spectrum was obtained when the zeolite was impregnated with acetic acid only (not shown) which suggests that the very broad signal observed in the ^{27}Al NMR spectrum after nitration at -5 ppm may be due to the interaction of the framework aluminium with the by-product acetic acid. This would lead to acetic acid adsorbing more competitively with ongoing reaction thereby lowering the activity of the surface-catalysed nitration, as observed in earlier studies of the liquid phase nitration of toluene using this nitration system [11].

The corresponding ^{15}N MAS NMR spectra of H-beta zeolite impregnated progressively with nitric acid, acetic anhydride and toluene are shown in figure 2. After impregnation with nitric acid two signals were observed, one at -36.9 ppm corresponding to hydrated nitric acid of ca. 90 wt% [12], and another at -4.2 ppm. According to its chemical shift the latter signal at lower field could be due to the nitrosonium ion [18] or to nitrate species [12]. A quantitative analysis of the spectrum showed that the amount of nitrogen corresponding to this peak was about 1.8 ± 0.2 mmol/g-zeolite which is close to the aluminium content of the solid (1.2 mmol/g). It is therefore concluded that the species characteristic of the signal at -4.2 ppm is interacting with the aluminium–oxygen lattice tetrahedra and forms an octahedral co-ordination complex with the aluminium. This is only possible for a nitrate anion which can co-ordinate to the aluminium due to its nucleophilic character, in contrast to the nitrosonium ion which is a strong electrophile. Some CP-MAS experiments (not shown) were carried out in order to probe species in the vicinity of protons. No CP-MAS signals were obtained supporting that the species due to the -4.2 ppm signal does not contain protons. The inefficiency of cross polarisation for the signal of free nitric acid is presumably due to the high mobility of these species. The formation of the nitronium species on the solid acid catalyst [19] which is characterised by a signal around -132 ppm [18] was not observed. We cannot entirely discard the possibility that nitronium ions are fixed to the oxide matrix of the zeolite on the Brønsted acid site becoming a nitrate-like moiety, as was proposed for sulfated zirconia [20], but it seems unlikely since this type of interaction is not expected to lead to a change in the co-ordination symmetry. A scheme of the proposed sequence for the formation of the octahedral lattice-aluminium/nitrate species is shown in figure 3.

Addition of acetic anhydride to the nitric acid H-beta system led to the disappearance of the peak at -4.2 ppm and to the appearance of the signal characteristic of acetylnitrate at -67.7 ppm (figure 2(b)). From this it was concluded that the surface-bonded nitrate, schematically represented in structure (D) of figure 3, was transformed into adsorbed acetylnitrate upon addition of acetic anhydride. The lower symmetry of the new adsorption complex, evidenced by the much broader peak in the corresponding ^{27}Al NMR spectrum, suggests a weaker interaction and consequently a more reactive species. Note, that the surface-bonded nitrate does not react to nitrotoluene upon addition of toluene, as was verified independently. Figure 4 shows a scheme for the proposed formation of this surface complex and possible adsorption states.

Nitration of toluene over the H-beta/HNO_3/Ac_2O zeolite was subsequently monitored by solid state ^{15}N MAS NMR and the expected nitration products, *ortho*- and *para*-nitrotoluene, were observed at -5.3 and -10.0 ppm, respectively (figure 2(c)). The conversion was estimated at 50% based on integration of the signal of unreacted nitric acid. A substantial increase of the *para*-isomer product selectivity was observed which does not occur in homogeneous nitration [11]. The *para*-to-*ortho* ratio was equal to 2.5 in agreement with our earlier work on the liquid phase batch nitration using this system [11].

Based on these observations we conclude that surface-bonded acetylnitrate, more likely structure H in figure 4, is the active nitrating species. Acetylnitrate co-ordinates to lattice aluminium forming an adsorption complex of distorted octahedral geometry. The formation of this adsorption complex is directly linked to flexible framework aluminium species which are abundantly available in H-beta zeolite. Van der Waal et al. invoked an inversion of the aluminium–oxygen tetrahedron with simultaneous breakage of one Si–O–Al bond which was induced by the co-ordination of water to explain their results of the Meerwein–Pondorf–Verley reduction of ketones [21]. A similar inversion-bond breaking may occur in the case of nitric acid interaction which should be assisted by the weakening of the second Si–O–Al bond due to the proton transfer from nitric acid. This proposal would certainly account for the formation of a highly symmetric octahedral adsorption complex on the lattice aluminium with nitrate anions.

It is furthermore inferred that the reason for the high *para*-selectivity is the presence of a surface-bonded nitrating species which forms the sterically less demanding Wheeland intermediate in which the methyl group points towards the main channel. A proposal along the same lines was made by Nagy et al. for the nitration of substituted aromatics over H-ZSM-11 [22] without specifying the nature of the active site that could cause such action.

When zeolites are treated with high concentrations of mineral acids it is imperative to consider dealumination as the most likely outcome. From the modest intensity gain of the signal at -1.6 ppm in the ^{27}Al NMR spectrum of H-beta after nitric acid impregnation a limited extent of dealumination was already apparent. In order to check the stability of the H-beta structure during the course of multiple nitration reactions, successive nitration runs with intermediate regeneration steps at 550 °C were carried out. These nitration reactions were performed following the procedure used in our earlier work, i.e., using much higher loading (35 mmol of 90 wt% of natural abundance nitrogen nitric acid, 53 mmol of acetic acid and 35 mmol of toluene per gram of zeolite). After each run and before the calcination, the zeolite was extensively washed with methylene chloride in order to extract the organic products. Figure 5 shows the ^{27}Al NMR spectra of the H-beta zeolite before reaction, after one nitration run and after three consecutive nitration runs. The spectrum of the zeolite before use exhibited signals of the framework aluminium at 53.2 ppm with some extra-framework aluminium at -1.6 ppm. After one and three nitration runs there is no major change in the spectrum indicating that most of the aluminium is still incorporated in the framework in a tetrahedral environment. Practically no extra-framework aluminium was found after three nitration steps. Quantitative analysis revealed, however, that both the framework and extra-framework aluminium concentration decreased during the course of successive nitrations (table 1). The extent of dealumination observed after one nitration run, evidenced through the fraction of retained framework aluminium of 87%, is quantitatively in good agreement with the intensity gain of the peak attributed to extra-framework aluminium at -1.6 ppm in fig-

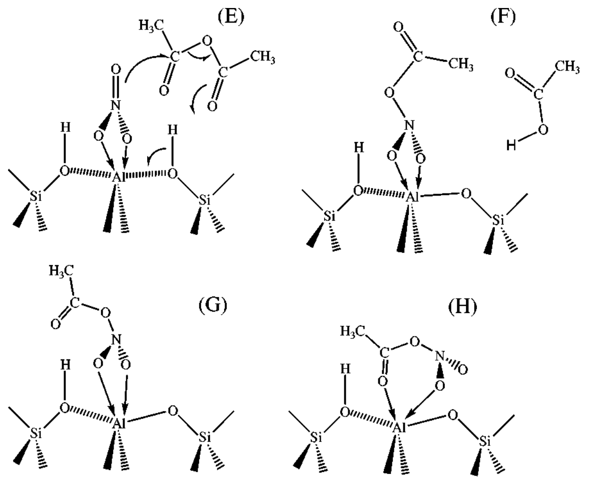

Figure 4. Proposed mechanism of acetylnitrate formation over the H-beta zeolite surface.

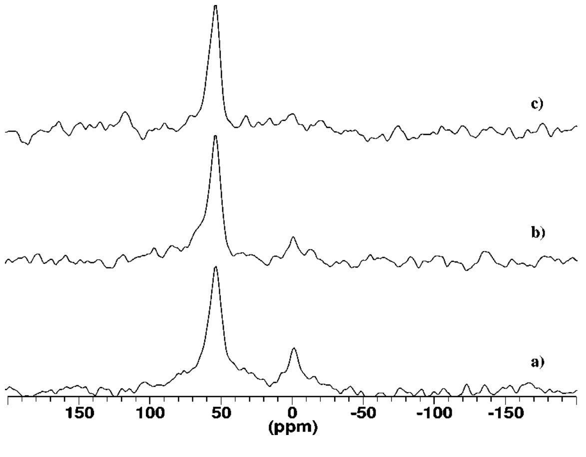

Figure 5. ^{27}Al MAS NMR spectra of zeolite beta before nitration (a), after one nitration run with subsequent regeneration at 550 °C during 10 h (b), and after three nitration runs with regeneration after each run (c).

Table 1
Aluminium content of H-beta zeolite before and after nitration (F – framework, EF – extra-framework) as determined by ^{27}Al solid state NMR.

	Before nitration	After 1 nitration	After 3 nitration
Al_F/Al_{bulk} (%)	81	89	100
Al_{EF}/Al_{bulk} (%)	19	11	0
$Al_F/Al_{F(before\ nitration)}$ (%)	100	87	64
$Al_{EF}/Al_{EF(before\ nitration)}$ (%)	100	50	0
$(Si/Al)_F$[a]	16	18	25

[a] From combination of elemental analysis (AAS) and ^{27}Al MAS NMR.

ure 1(b). This clearly shows that the peak at 0.4 ppm does not correspond to an extra-framework species because complete dealumination would have been expected in that case after only one nitration run. These results are consistent with the proposed reversibility of the change of aluminium co-ordination but also show that this transformation is not completely reversible.

4. Conclusions

The framework aluminium in H-beta zeolite plays a critical role during the nitration reaction. We observed the reversible transformation of the co-ordination environment of the lattice aluminium into an octahedral co-ordination upon interaction with nitric acid, acetylnitrate and acetic acid. The ability of H-beta to accommodate such a co-ordination state transformation is consistent with the high degree of lattice flexibility of this zeolite and makes it unique for this type of reaction. The narrow width of the ^{27}Al NMR signal of the aluminium complexes formed when nitrate ions interact with the zeolite wall suggests strongly the necessity of the opening of the Si–O–Al bond in the lattice to accommodate a very high symmetry environment. The dynamic character of those aluminium atoms which are only partially connected to the framework appears to play the key role in the catalytic activity and selectivity. Nitration occurs through surface-bonded acetylnitrate as reactive nitrating species. Thus, since classical shape-selectivity concepts do not account for the observed selectivity patterns with this large pore zeolite, the product selectivity is dictated by steric hindrance during the formation of the Wheeland intermediate which is induced by adsorption on the zeolite surface.

Acknowledgement

We are indebted to D. Vassena for his assistance in batch nitration experiments. We acknowledge Zeolyst International for providing the zeolite.

References

[1] A. Kogelbauer and H.W. Kouwenhoven, in: *Fine Chemicals through Heterogeneous Catalysis*, eds. R.A. Sheldon and H. van Bekkum (Wiley–VCH, New York), in press.
[2] A. Corma and H. Garcia, Catal. Today 38 (1997) 257.
[3] K. Smith, A. Musson and G.A. DeBoos, J. Chem. Soc. Chem. Commun. (1996) 469.
[4] D. Vassena, A. Kogelbauer and R. Prins, Catal. Today, accepted.
[5] A. Germain, T. Akouz and F. Figueras, Appl. Catal. A 136 (1996) 57.
[6] B.M. Choudary, M. Sateesh, M.L. Kantam, K.K. Rao, K.V.R. Prasad, K.V. Raghavan and J.A.R.P. Sarma, J. Chem. Soc. Chem. Commun. (2000) 25.
[7] D. Vassena, A. Kogelbauer and R. Prins, in: *Proc. 12th Int. Congr. on Catalysis*, accepted.
[8] E.G. Derouane, H. He, S.B. Derouane-Abd Hamid and I.I. Ivanova, Catal. Lett. 58 (1999) 1.
[9] M. Hunger and T. Horvath, Catal. Lett. 49 (1997) 95.
[10] K. Smith, A. Mudsson and G.A. DeBoos, J. Org. Chem. 63 (1998) 8448.
[11] D. Vassena, A. Kogelbauer and R. Prins, Stud. Surf. Sci. Catal. 125 (1999) 501.
[12] M. Witanowski, L. Stefaniak and G.A. Webb, Annu. Rep. NMR Spectrosc. 25 (1993) 1.
[13] T.-H. Chen, B.H. Wouters and P.J. Grobet, Eur. J. Inorg. Chem. (2000) 281.
[14] M. Müller, G. Harvey and R. Prins, Micropor. Mesopor. Mater. 34 (2000) 281.
[15] L. Bertea, H.W. Kouwenhoven and R. Prins, Appl. Catal. A 129 (1995) 229.
[16] E. Bourgeat-Lami, P. Massiani, F. Di Renzo, P. Espiau, F. Fajula and T. Des Courieres, Appl. Catal. 72 (1991) 139.
[17] L.C. De Ménorval, W. Buckermann, F. Figueras and F. Fajula, J. Phys. Chem. 100 (1996) 465.
[18] G.A. Olah, B.G.B. Gupta and S.C. Narang, J. Am. Chem. Soc. 101 (1979) 5317.
[19] N.C. Marziano, C. Tortato, L. Ronchin, F. Martini and C. Bianchi, Catal. Lett. 58 (1999) 81.
[20] G.D. Yadav and J.J. Nair, Catal. Lett. 62 (1999) 49.
[21] J.C. van der Waal, E.J. Creyghton, P.J. Kunkeler, K. Tan and H. van Bekkum, Topics Catal. 4 (1997) 261.
[22] S.M. Nagy, K.A. Yarovoy, V.G. Shubin and L.A. Vostrikova, J. Phys. Org. Chem. 7 (1994) 385.