Immobilized nickel catalysts for cyclotrimerizations of acetylenes: enhancement of activities, stabilities, and lifetimes

Simone Reinhard,[a] Klaus D. Behringer[b] and Janet Blümel*[a]

[a] *Department of Organic Chemistry, University of Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. E-mail: J.Bluemel@urz.uni-heidelberg.de; Fax: +49 62 2154 4904; Tel: +49 62 2154 8470*

[b] *Department of Inorganic Chemistry, Technical University of Munich, 85747 Garching, Germany*

L e t t e r

Solid-state ^{31}P NMR is used to optimize the stability and minimize leaching of nickel catalysts for alkyne cyclotrimerization immobilized by mono- and bidentate phosphine linkers on silica.

There has been enormous recent interest in homogeneous catalysts being heterogenized by tethering them to solid supports *via* linkers.[1,2] Most popular are phosphine linkers, such as $Ph_2P(CH_2)_3Si(OEt)_3$ (**1**) or $Ph_2P(p\text{-}C_6H_4)Si(OEt)_3$ (**2**) for immobilization on oxidic supports. They have, for example, been successfully used to immobilize carbonyl nickel[3] or rhodium[2] catalysts. The materials are best characterized by classical solid-state NMR,[2,3] or under more realistic conditions, ^{31}P suspension NMR[4,5] spectroscopy. The main drawback of immobilized catalysts is their limited lifetime, due to leaching. As we have investigated previously, there are several origins of leaching. First, the ethoxysilane group might not be bound covalently to the support, but only adsorbed weakly, which leads to the catalyst being washed off along with the linker later.[6] With the wrong support, such as TiO_2 or acidic Al_2O_3, in spite of initial covalent bonding, the linkers are quickly detached from the surface also.[4] Silica is the optimal oxidic support.[4] Another problem, namely the oxidation of the phosphines by the combined action of ethoxysilanes and silica surface, can be avoided by the proper immobilization conditions.[7] Furthermore, it could be demonstrated that two monodentate phosphine linkers at one metal center do not necessarily both bind to the surface, thus forming a strong chelate complex, but that rather they establish a double layer.[8]

Here, using ^{31}P solid-state NMR we present direct evidence for yet another form of leaching, the detachment of the metal moiety from the surface-bound linkers. We will also present possible solutions for this problem and demonstrate that record turnover numbers (TON) can be achieved by quite simple measures.

For our studies we first used the carbonyl nickel catalysts $(CO)_2Ni[Ph_2P(p\text{-}C_6H_4)Si(O\text{–}SiO_2)_3]_2$ (**3**) and $(CO)_2Ni[Ph_2P(CH_2)_3Si(O\text{–}SiO_2)_3]_2$ (**4**), as described earlier.[3] Silica (Merck 40) with an average pore diameter of 40 Å and a specific surface area of 750 m^2 g^{-1} was used after drying at 600 °C *in vacuo* for 8 h. The surface coverage with catalyst was determined by weighing back the surplus catalyst in the supernatant solution after removal of the solvent. The result was checked by weighing the washed and dried loaded silica. As the catalytic reaction we chose the cyclotrimerization of acetylenes, because of its importance for synthetic chemistry.[9] PhC≡CH (**5**) turned out to be the optimal substrate, because it allows the determination of overall yield and selectivity with respect to the two

resulting isomers, 1,2,4- and 1,3,5-triphenylbenzene (**6** and **7**), in a single run. The yield and product ratio can easily be determined by GC after peak assignment by ^{13}C NMR, using the characteristic *ipso* carbon resonances of the central benzene ring at 142.4 (**6**) and 142.3 (**7**) ppm. After catalysis, the volatile **5** can be removed *in vacuo* if necessary. In a typical catalytic run, at 80 °C in *n*-heptane, with a molar ratio of immobilized catalyst **3** to substrate **5** of 1 to 800, and a substrate concentration of 0.67 mol l^{-1}, after 70 h reaction time, an overall yield of 77.9%, corresponding to a TON of 623, with a **6**:**7** ratio of 14.6:1.0, can be obtained. The TON is comparable to the one found for $(CO)_2Ni(PPh_3)_2$ as the homogeneous catalyst under otherwise identical conditions. However, when catalyst **3** was recycled in a batchwise manner, the yields dropped quickly with every run, and were down to about 10% yield in the fourth cycle. Therefore, we studied the catalyst by solid-state NMR, as shown in Fig. 1, and recorded the ^{31}P spectra after the indicated times of catalytic reaction. In order to get quantitatively reliable signals, we used simple high-power proton decoupling with a long relaxation time at 4 kHz rotational speed rather than more sophisticated approaches with cross polarization (CP) at fast spinning (MAS).[10]
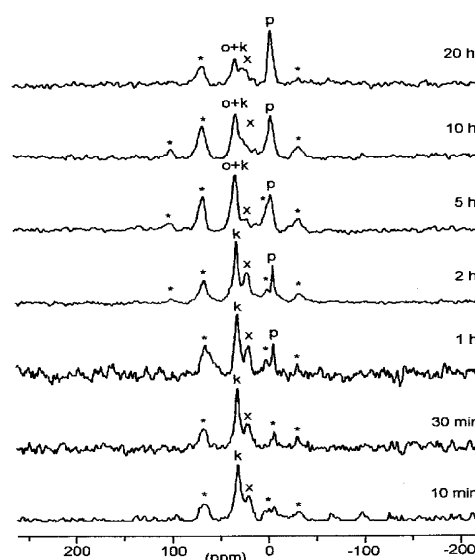

Fig. 1 121.5 MHz ^{31}P{^{1}H} MAS spectra of immobilized catalyst **3** after the indicated times of catalytic reaction with phenylacetylene **5**: 4 kHz rotational speed; asterisks denote spinning sidebands, k the signal of **3**, p the one of surface-bound **2**, and x an inert impurity.[7]
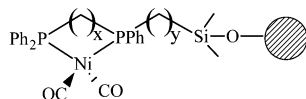
As displayed in Fig. 1, after 10 min. reaction time the signal of the catalyst[3] (labelled k, 32.3 ppm) still predominates. The traces of sideproduct[7] (peak x, 22.8 ppm) are unchanged throughout the whole reaction time and therefore cannot be responsible for any loss of catalytic activity. However, with time, the signal at −4.3 ppm, which belongs to uncomplexed, but still surface-bound phosphine, grows. Correspondingly, the k signal intensity decreases and, towards the end, even phosphine oxide (34.4 ppm, overlapping partly with signal k) can be identified by its large chemical shift anisotropy (CSA).[7] These spectra are direct evidence that in the case of carbonyl nickel catalysts the prevailing mechanism of leaching is the detachment of the metal moiety from the phosphine linkers, which remain surface-bound, as checked also carefully with ^{31}P NMR of the supernatant solution. This result is corroborated by earlier experiments by Basset and Maitlis,[11] who could prove the loss of the metal fragment and formation of Ni^0 deposits on the surface indirectly by reactivating the catalyst with CO. Furthermore, even after catalytic runs, we never found catalytic activity in any of the supernatant solutions.

To solve this leaching problem, we explored several options: (*i*) one can improve the reaction conditions further in order to enhance the lifetime of the catalyst; (*ii*) the metal center can be bound more firmly by using a genuine chelating phosphine linker, and (*iii*) a continuous approach can be pursued in order to check whether the catalyst is disturbed by cooling down and opening the reaction vessel between the cycles. Surprisingly, even approach (*i*) brought substantial improvements. Using cyclooctane as the solvent, for example, increased the yield, even in the case of **4**, up to 100% within 20 h (155 °C, 0.5 mol % **4**, 0.5 mol l^{-1} of **5**). Interestingly, all catalysts do not perform as well in *n*-octane. Analogous to the case of Wilkinson-type catalysts,[12] the lifetime of the immobilized catalysts can also be prolonged by reducing the surface coverage. While the densest possible surface coverage with **8** (Scheme 1, about 16 metal centers per 100 nm^2) leads to a maximal TON of 4810, dilution of the surface species to one fourth (4 per 100 nm^2) gives a TON of 7616.

Regarding approach (*ii*), a variety of chelating phosphines[5] with different bite angles and spacer lengths leads to catalysts **8**–**11** (Scheme 1), all of which give similar catalytic activity and selectivity. In every case, the initial product ratio **6**:**7** of about 4.5:1 changes gradually within the course of 6 cycles to about 1:1, which persists as the final ratio. This change in selectivity was investigated in a parallel project recently.[13] Overall, with this type of flexible ligand,[5] the bite angle or the distance to the support surface do not make a significant difference. However, with such chelating ligands the lifetimes of all immobilized catalysts are prolonged substantially, and even after 12 cycles the yields are still relatively high, as displayed in Fig. 2 for **9**. In contrast to **4** under non-ideal conditions (Fig. 1), which shows the ^{31}P solid-state NMR signals of uncomplexed phosphine already in the first run, catalysts **8**–**11** do so only after several runs. Compared to **9**, catalyst **4** with monodentate phosphine ligands gives up to about 10% less conversion especially in later cycles (Fig. 3) under otherwise identical (optimal) conditions. Similar success of the chelate ligands[5] has been demonstrated for immobilized Wilkinson-type rhodium hydrogenation catalysts.[12]

Following strategy (*iii*) we made a first step towards continuous catalysis. The silica-supported catalyst **4** was filled into the porous cup of a soxhlet extractor, and wetted with cyclooc-
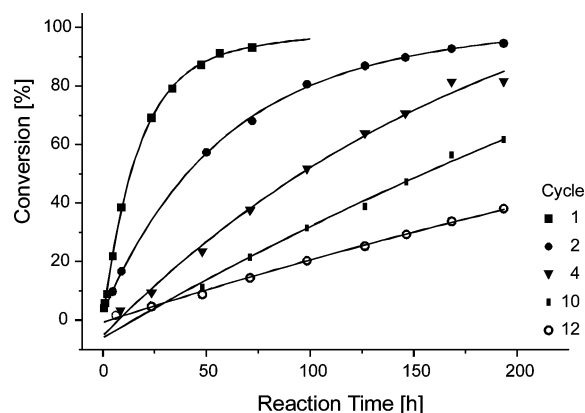

Fig. 2 Substrate conversion *versus* reaction time in batchwise repeated cyclotrimerization of **5** with catalyst **9** at 155 °C. The ratio **9**:**5** is 1:200; 0.5 mol l^{-1} **5** in cyclooctane. The curves of cycles 3, 5–9, and 11 have been omitted for clarity.
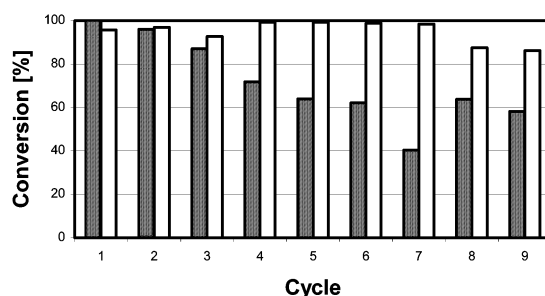

Fig. 3 Comparison of the performance of catalyst **4** in 9 batchwise (hatched) and continuous runs (see text). For reaction conditions see Fig. 2 caption and text.

tane. Then the phenylacetylene was distilled up to the cup as an azeotropic mixture with the solvent (ratio **5**:cyclooctane is about 1:3). The non-volatile products **6** and **7** were washed down into the bottom flask by the solvent and thus were continuously removed from the catalyst. Fresh **5** was added to the bottom flask as soon as the previous portion was used up, without otherwise disturbing the system. As shown in Fig. 3, the performance of **4** is much better, if the runs are done in a pseudo-continuous, as compared to a batchwise, manner.

Comparing the ^{31}P{^{1}H} MAS spectrum of fresh catalyst **4** with the one of **4** after 9 runs in the soxhlet extractor (Fig. 4) shows that there is no major decomposition of the catalyst, but only slightly more phosphine oxide, which most probably stems from the batchwise addition of **5**.

In conclusion, we could demonstrate that in order to enhance the lifetime of immobilized catalysts (*i*) it pays
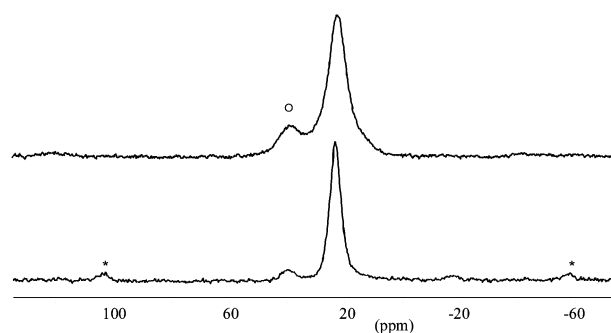
8: x=3, y=2
9: x=2, y=3
10: x=2, y=2
11: x=3, y=3

Scheme 1 Examples of carbonyl nickel catalysts with chelating ligands.

Fig. 4 162.0 MHz ^{31}P{^{1}H} MAS spectra of **4** prior to catalysis (lower trace), and after (upper trace) 9 runs of continuous catalysis (see text). Rotational speed 13 kHz, for other details of the measurement see ref. 10.

to optimize the reaction conditions even for seemingly well-known reactions, (*ii*) chelating phosphines as linkers give superior performance by preventing leaching of the metal moiety, and (*iii*) one should try to use continuous systems in order to avoid any interruption of the catalytic reaction. Parallel projects with immobilized rhodium catalysts show that these measures can be successfully applied to other systems and are thus of a general nature.

Acknowledgements

References

1   *Chiral Catalyst Immobilization and Recycling*, eds. D. E. DeVos, I. F. J. Vankelecom and P. A. Jacobs, Wiley-VCH, Weinheim, 2000; J. H. Clark, *Catalysis of Organic Reactions by Supported Inorganic Reagents*, VCH, Weinheim, 1994; J. H. Clark, A. P. Kybett and D. J. Macquarrie, *Supported Reagents*, VCH, Weinheim, 1992; H. Gao and R. J. Angelici, *Organometallics*, 1999, **18**, 989; Z. Lu, E. Lindner and H. A. Mayer, *Chem. Rev.*, 2002, **102**, 3543; J. A. Gladysz, *Pure Appl. Chem.*, 2001, **73**, 1319.

2   C. Merckle, S. Haubrich and J. Blümel, *J. Organomet. Chem.*, 2001, **627**, 44.

3   K. D. Behringer and J. Blümel, *Inorg. Chem.*, 1996, **35**, 1814.

4   C. Merckle and J. Blümel, *Chem. Mater.*, 2001, **13**, 3617.

5   G. Tsiavaliaris, S. Haubrich, C. Merckle and J. Blümel, *Synlett*, 2001, 391.

6   K. D. Behringer and J. Blümel, *J. Liquid Chromatogr.*, 1996, **19**, 2753; J. Blümel, *J. Am. Chem. Soc.*, 1995, **117**, 2112.

7   J. Blümel, *Inorg. Chem.*, 1994, **33**, 505.

8   K. D. Behringer and J. Blümel, *Chem. Commun.*, 1996, 653.

9   Recent examples: C. Müller, R. J. Lachicotte and W. D. Jones, *Organometallics*, 2002, **21**, 1975; M. A. Bennett, C. J. Cobley, A. D. Rae, E. Wenger and A. C. Willis, *Organometallics*, 2000, **19**, 1522; S. Saito, T. Kawasaki, N. Tsuboya and Y. Yamamoto, *J. Org. Chem.*, 2001, **66**, 796; N. Mori, S. Ikeda and K. Odashima, *Chem. Commun.*, 2001, 181.

10 S. Reinhard and J. Blümel, *Magn. Reson. Chem.*, 2003, **41**, in press.

11 A. K. Smith, J. M. Basset and P. M. Maitlis, *J. Mol. Catal.*, 1977, **2**, 223.

12 C. Merckle and J. Blümel, *Adv. Synth. Catal.*, 2003, **345**, 584.

13 S. Reinhard, P. Soba, F. Rominger and J. Blümel, *Adv. Synth. Catal.*, 2003, **345**, 589.