Pergamon

Tetrahedron 56 (2000) 4765–4768

TETRAHEDRON

Synergistic Effect in Bimetallic Ni–Al Clusters. Application to Efficient Catalytic Reductive Dehalogenation of Polychlorinated Arenes

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Received 24 February 2000; accepted 8 May 2000

Abstract—Subnanometric Ni–Al clusters, in situ prepared by reduction of equimolar amounts of $Ni(OAc)_2$ and $Al(Acac)_3$ induced by alkoxide activated sodium hydride, exhibit a high catalytic activity for efficient reductive dehalogenation of aliphatic and aromatic halides and polychlorinated arenes. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Organic halides, especially polychlorinated aromatic ones (PCBs), are important industrial chemicals but represent also a major environmental problem because they are quite difficult to degrade either by reductive or oxidative enzymatic pathways.[1] Therefore a variety of dehalogenation reagents have been developed during the last few years including transition metal catalysed hydrogenation[2] or reduction,[3] metal hydride reduction,[4,5] hydride or Grignard reagents combined with transition metal salts[6,7] or, as reported recently, by activation of Ni(II) using an arene-catalysed lithiation process.[8] In recent years, many reports have been made concerning the combination of organometallic reagents with Ni(II) salts for performing useful organic reactions.[6a,b,8]

However, many of the proposed methods suffered from some limitations and the development of new and efficient dehalogenation procedures continues to be of current interest. In the course of our studies dealing with low temperature synthesis of new polymetallic nanomaterials, we found that subnanometrical Ni–Al clusters can be easily prepared by simultaneous reduction of Al(III) and Ni(II) salts by activated NaH.[9] In this paper, we would like to report a remarkable synergistic effect on the catalytic properties of these materials allowing reductive dehalogenation of alkyl and aryl (poly)halides.

Results and Discussion

Transmission electron microscopy (TEM) of the non-pyrophoric colloidal Ni–Al black suspensions, obtained from in situ reduction of a [1:1] $Ni(OAc)_2$–$Al(Acac)_3$ mixture by *t*-BuONa-activated NaH, revealed a homogeneous distribution of uniformly sized and amorphous very small particles (<0.5 nm). In addition, Energy-Dispersive-X-ray-Spectroscopy (EDXS) showed a good preservation (up to 96%) of the initial metal ratios in the Ni–Al materials. The amount of hydrogen evolved indicated that, at the end of the preparation, both salts were totally reduced by alkoxide activated NaH. However, because aluminium is a very oxophilic metal, it was not possible to prove unambiguously the existence of oxide-free Ni–Al nano-intermetallics in these experiments. In fact, by Electron-Energy-Loss-Spectroscopy (EELS), we could identify the materials in the Ni(0) and Al(III) oxidation states. The selected area electron diffraction patterns showed only a very broad diffraction halo indicating the absence of conventional crystalline phases. Ni atoms appeared to be aggregated in very small isolated clusters of a few tenths the size of atoms. In comparison to our previously described nanometric Ni clusters,[10,11] it may be assumed that a nanometric aluminium oxide matrix is spontaneously formed in the presence of traces of oxygen contained in the reaction solvent indicating that a high dispersion of Ni species in this matrix is obtained for our Ni–Al clusters. Therefore, we thought that such a dispersion may have an influence on the catalytic activity and we decided to investigate this in the dehalogenation of representative (poly)halogenated compounds.

We first studied the Ni–Al catalysed reduction of representative alkyl or aryl halides. The results reported in Table 1

Keywords: reductive dehalogenation; nickel catalyst; bimetallic clusters.

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PII: S0040-4020(00)00383-5

Table 1. Ni–Al clusters catalysed dehalogenation of monohalogenated compounds (typical reaction conditions: *t*-BuOH (8 mmol), $Ni(OAc)_2$ (4 mmol), $Al(Acac)_3$ (4 mmol, for Ni–Al Catalyst), NaH (108 mmol), organic halide (40 mmol), THF, reflux)

Entry	Starting material	Ni catalyst			Ni–Al catalyst		
		Time[a] (h)	Conv.[a] (%)	Yield[a] (%)	Time[a] (h)	Conv[a] (%)	Yield[a] (%)
1	1-Bromodecane	2	100	Quant.	0.25	100	Quant.
2	1-Chlorodecane	5	100	98	1.25	100	Quant.
3	1-Chloroadamantane	48	95	95	1.0	100	Quant.
4	Bromobenzene	1	100	Quant.	0.5	100	Quant.
5	Chlorobenzene	60	100	Quant.	0.75	100	Quant.
6	1-Chloro-4-(trifluoro methyl) benzene	–	–	–	1	100	98[b]
7	4-Chloroanisole	–	–	–	2	95	91
8	1-Chloronaphthalene	90	100	92[c]	2.5	98	90[d]
9	4-Chlorophenol	–	–	–	0.25	100	Quant.
10	Octyl 4-methyl-1-benzene sulfonate	–	–	–	4	100	80
11	4-Tolyl benzenesulfonate	8	95	92	2	100	97

[a] Unless otherwise noted, determined by GC.
[b] Isolated yield.
[c] 1,1′-binaphthyl was isolated in 5% yield.
[d] 1,1′-binaphthyl was isolated in 4% yield.

were compared with those obtained for Ni-catalysed reactions.[12]

We found that the reduction of 1-bromo, 1-chlorodecane and 1-chloroadamantane in the presence of 10 mol% Ni–Al clusters in refluxing THF led to the corresponding alkanes as the sole reaction products (Table 1, entries 1–3). Ni–Al clusters were found to be much more efficient than the monometallic Ni ones (Table 1) since reaction times were strongly decreased. The same behaviour was observed for the reduction of haloarenes. Bromo and chlorobenzene were quantitatively converted into benzene in less than 1 h under Ni–Al catalysis (entries 4 and 5). As expected, the presence of electron donating groups on the aromatic ring decreased the reduction rate (compare entries 5 and 7) while electron-withdrawing ones had a weak effect (entry 6). Chloronaphthalene gave the expected reduction product (naphthalene) in 90% yield. In this case, the reduction was accompanied by the homocoupling of the starting material leading to 1,1′-binaphthyl as already observed with Ni containing reducing reagent.[13] On the other hand, the presence of a hydroxyl group on the aromatic ring markedly enhanced the reaction rate (entry 9). This result may be interpreted as a consequence of the chelating properties of the in situ generated phenoxide. Entries 10 and 11 showed that tosylates could also be reduced by our reagent. Finally, it must be noted that all these reactions may be conducted in the presence of 5 mol% of Ni–Al for an extended reaction time (2–12 h).

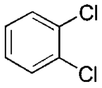
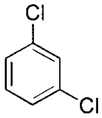
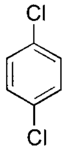
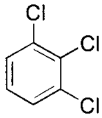
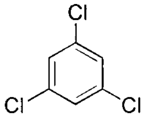
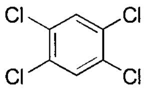
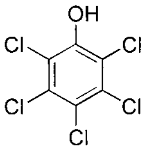
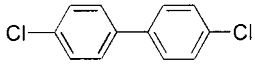
The interpretation of the synergistic effect obtained in Ni–Al induced reactions remains unclear however, the obtained results may provide some clues. At first, a pure S_N2 mechanism as well as an elimination-reduction pathway is ruled out since 1-chloroadamantane is rapidly and quantitatively reduced into adamantane. An elimination-reduction pathway may also be excluded for 1-bromodecane. Indeed, no elimination product was detected by GC during the Ni–Al catalysed reduction when 1-decene slowly produced decane under the same reaction conditions.[14] This result was also confirmed by reacting octyl 4-methyl-1-benzenesulfonate, a substrate more sensitive to elimination, with Ni–Al clusters (entry 10). Octane (80%) was obtained as the major product besides octene (20%) resulting from a fast elimination observed at the beginning of the reaction. Note that the amount of octene remained constant during all the experiment. In addition, the high yield of octane obtained after 4 h reaction time allowed us to reject a classical free-radical mechanism based on a pure single electron transfer (SET) pathway.

Short reaction times associated with the high efficiency of our method led us to believe that a mechanism based on carbon halide hydrogenolysis appeared to be more probable. Indeed, molecular hydrogen (evolved during the preparation of our reagent and/or its regeneration by NaH) could be adsorbed on the surface of the Ni–Al catalyst yielding a nickel hydride species. Subsequent oxidative addition of the organic halide and reductive elimination led to the hydrocarbon and initial Ni species were regenerated by sodium hydride reduction. A hydrogenolysis based mechanism was supported by the fact that the addition of a stoichiometric amount relative to the aryl halide of a reactive ethylenic compound, such as styrene, induced a strong decrease in the reaction rate. For example, 1,4-dichlorobenzene was reduced in 18 h in the presence of styrene. Styrene was assumed in this example to act as a Ni(0) scavenger leading to a classical hydrogenation process. The enhanced catalytic activity of Ni–Al clusters compared to Ni ones may then be attributed to an increased dispersion of Ni species in a subnanometric aluminium matrix. Surprisingly, it appeared that the active site accessibility was not decreased.

We next studied the dehalogenation of polychlorinated benzenes. The results obtained using Ni–Al and Ni clusters as catalyst are reported in Table 2. A catalyst loading of 10 mol% Ni relative to each carbon–chlorine unit was used in these experiments.

In all cases the dechlorination of polychlorobenzenes was complete leading to benzene as the sole reaction product.

Table 2. Ni–Al clusters catalysed dehalogenation of polyhalogenated arenes (typical reaction conditions: a catalyst loading 10 mol% was used per C–Cl unit. Reactions on aryl di-, tri-, and tetrachlorides were performed on respectively 20, 13.3 and 10 mmol starting material using *t*-BuOH (8 mmol), $Ni(OAc)_2$ (4 mmol), $Al(Acac)_3$ (4 mmol), NaH (108 mmol). Dehalogenation of pentachlorophenol was performed on 8 mmol starting material, *t*-BuOH (8 mmol), $Ni(OAc)_2$ (4 mmol), $Al(Acac)_3$ (4 mmol) and NaH (116 mmol))

Entry	Starting material	Ni catalyst			Ni–Al catalyst		
		Time^a (h)	Conv.^{a} (%)	Yield^a (%)	Time^a (h)	Conv^a (%)	Yield^a (%)
1		11	100	Quant.	1.5	100	Quant.
2		–	–	–	1.5	100	Quant.
3		–	–	–	1.5	100	Quant.
4		25	100	Quant.	1.75	100	Quant.
5		–	–	–	1.75	100	Quant.
6		27	100	Quant.	8.0	100	Quant.
7		–	–	–	0.75	100	Quant.
8		110	93	Quant.	6.0	100	95^b

[a] Unless otherwise noted, determined by GC.

[b] Isolated yield by flash chromatography.

The higher efficiency of Ni–Al clusters compared to Ni ones was confirmed since completion of Ni–Al induced reactions were obtained in less than 8 h while Ni-catalysed ones needed 11 to 110 h. It is worthy to note that mono- or dihalogenated intermediates were only observed as traces during the reduction of di- and trihalogenated substrates respectively. In contrast, 1,2,4,5-tetrachlorobenzene was firstly and selectively reduced into 1,2,4-trichlorobenzene (90% yield after 1 h) which underwent a classical reductive dehalogenation into benzene. Compared to the methods reported in the literature,[15] these results are interesting since all dehalogenations were completed in short reaction times and under mild conditions. In addition, and as previously observed with 4-chlorophenol (Run 9, Table 1), the presence of a hydroxyl group on the aromatic ring allowed a rapid and efficient reduction process.

Finally, we examined the dehalogenation of 4,4′-dichlorobiphenyl (Table 2, entry 8), a well-known representative substrate of the PCB family.[16] We found that dehalogenation can be quantitatively obtained in 6 h leading to biphenyl as the sole reaction product. No trace of 4-chlorobiphenyl was detected. This last result underlines the particular efficiency of our catalyst.

Conclusion

The results obtained from the above experiments show that the non-pyrophoric bimetallic Ni–Al catalyst, obtained by simultaneous NaH induced reduction of Ni(II) and Al(III) salts under mild conditions, exhibit a remarkable synergistic effect for the reductive dehalogenation of aromatic and aliphatic (poly)chlorides and bromides. Work is in progress in order to define scope and limitations with functional halides.

Experimental

Materials

Tetrahydrofuran (THF) was distilled from benzophenone-sodium adduct and stored over sodium wire. Tertiary butyl alcohol (*t*-BuOH) (Aldrich) was distilled from sodium. Sodium hydride (NaH) (65% in mineral oil, Fluka) was used after three washings with 20 mL of THF under N_2 atmosphere. Nickel acetate [$Ni(CH_3COO)_2$] (Fluka) was dried under vacuum (20 mmHg) at 110°C during 12 h. Water content after drying was lower than 0.5 mol%. Aluminium acetylacetonate [$Al(CH_2COCH_2COCH_3)_3$] (97%, Acros) was use without further purification.

Preparation of Ni–Al clusters

t-BuOH (8.0 mmol) in THF (5 mL) was added dropwise at 63°C to a suspension of degreased NaH (108.0 mmol) in THF (35 mL) followed by $Al(Acac)_3$ (4.0 mmol) and $Ni(OAc)_2$ (4.0 mmol) and the mixture was stirred at reflux for 5 h under a nitrogen atmosphere. Gaseous hydrogen evolved and a non-pyrophoric black colloidal suspension was formed. Note that the same procedure was used without $Al(acac)_3$ for Ni clusters. The measure of the hydrogen evolution allowed us to verify the complete preparation of the catalysts; 18 mmol or 12 mmol of H_2 must be obtained for the preparation of Ni–Al or Ni catalyst, respectively.

Characterization of Ni–Al nanoparticles

Characterization of Ni–Al clusters was performed using Transmission Electron Microscopy (TEM). TEM specimens were prepared by placing a drop of the colloidal solution onto a holey-carbon-coated TEM grid and were studied using a Philips CM20 with an unsaturated LaB_6 cathode operating at 200 kV. EDX spectra were recorded by means of an EDXS spectrometer equipped with an ultrathin window X-ray detector. The analysis was carried out in nanoprobe mode with a diameter of the probe of 10 nm. The presence of the Al Ka peak at 1.486 keV and the Ni Ka peak at 7.47 keV can be observed.

Reductive dehalogenation procedure

A typical dehalogenation procedure is as follows: The alkyl or aryl monohalide (40 mmol) in THF (10 mL) was added to the obtained dark grey suspension of the Ni–Al clusters and the products were detected by GC. Reductions of di-, tri- and tetrachlorobenzenes were performed on respectively 20, 13.3 and 10 mmol using a 10 mol% catalyst loading relative to each chlorine function [*t*-BuOH (8 mmol), $Ni(OAc)_2$ (4 mmol), $Al(Acac)_3$ (4 mmol) and NaH (108 mmol)]. The reactions were monitored by GC analyses (HP1 column, 20 m×0.32 mm ID×0.25 μ) and GC-MS (EI) analyses of small aliquots using hydrocarbons (C_8–C_{14}) as internal standard. At the end of the reaction, 10 mL of water were added dropwise at 0°C. (Note that the low amount of residual hydride insured a safe hydrolysis step for completed reactions.) Except for benzene, products were then extracted by diethyl ether and purified either by distillation or by flash chromatography on silica gel. Their spectroscopic data are in accordance with those of authentic samples.

Acknowledgements

The authors wish to thank M. Bernard Reibel for his perfect technical assistance.

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16. For dehalogenation of chlorobiphenyls, see Refs. 4a,4c,6a.