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Nanostructured Nickel-Clusters as Catalysts in [3+2]Cycloaddition Reactions

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Abstract: Preformed Ni-clusters stabilized by tetraoctyl- or tetradodecylammonium bromide are readily available by electrochemical fabrication, the average size of the particles being 2.5 nm. Colloidal solutions of such clusters effectively catalyze the [3+2]cycloaddition of methylenecyclopropane to methyl acrylate. The preformed clusters can also be immobilized on solid supports, resulting in heterogeneous catalysts which also catalyze the cycloaddition reaction.

INTRODUCTION

Studies directed toward the fabrication of nanostructured transition metal clusters or colloids are currently attracting a great deal of attention.[1] Whereas such problems as efficiency of preparation, ease of isolation, size selectivity and characterization by physical methods are the primary points of interest, the potential use of such materials as colloidal solutions or as surface bound materials in the catalysis of organic reactions has not been studied in a systematic manner. In most cases efforts have been restricted to the investigation of catalytic properties in simple model reactions such as the hydrogenation of cyclohexene, if at all.[1,2] Thus, the potential advantages of preformed transition metal clusters relative to the use of traditional homogeneous or heterogeneous catalysts are mostly undefined. In fact, C-C bond forming reactions, although at the heart of organic chemistry, have hardly been explored using colloidal solutions of preformed clusters as catalysts. The first examples were reported in 1996 and pertain to R_4NX-stabilized Pd-clusters and Pd/Ni bimetallic clusters as catalysts in Heck[3,4] and Suzuki[3] reactions. Solvent stabilized transition metal clusters, e.g., nanostructured Pd-clusters stabilized by propylene carbonate are also capable of catalyzing Heck reactions.[5]

In this paper we present the results of a study concerning the use of R_4NX-stabilized Ni-clusters in the catalysis of the [3+2]cycloaddition of methylenecyclopropane **1** to methyl acrylate **2** with formation of the carbocyclic product **3**.

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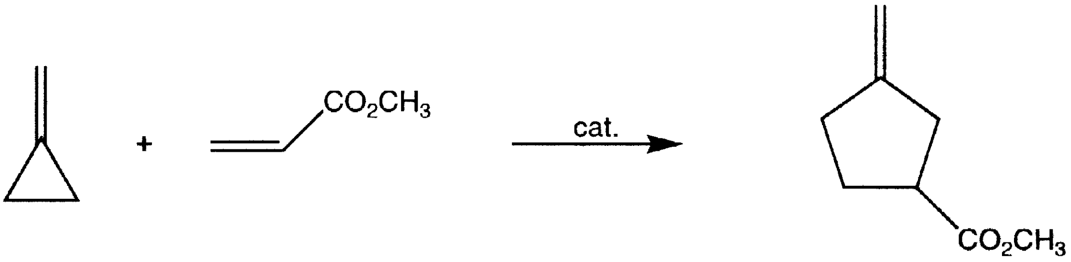

1 **2** **3**

Cycloaddition reactions of this kind were first reported by Noyori[6] and extensively studied by Binger,[7] who showed, inter alia, that the nickel complex $Ni(COD)_2$ is an ideal homogeneous catalyst for the particular transformation **1** + **2** → **3**. In other cases Pd-catalysts are better suited. These reactions are related to Trost's work on the Pd-catalyzed [3+2]cycloaddition of such precursors as $CH_2{=}C(CH_2SiMe_3)CH_2OAc$.[8]

The initial role of the nickel catalyst in the above reaction is that of C-C activation, metallacycles being involved in the catalytic cycle.[7] It is interesting to note that the Ni-catalyzed hydrogenolysis of cyclopropane is also believed to occur via C-C activation.[9] Indeed, C-C activation of cyclopropane by nickel atoms is not improbable, as shown by quantum mechanical calculations.[10] Thus, it was of particular interest to see if colloidal solutions of R_4NX-stabilized Ni-clusters catalyze the above reaction under mild conditions.

PREPARATION OF Ni-CLUSTERS

We have previously shown that certain R_4NX-stabilized transition metal clusters are readily accessible electrochemically, two options being possible.[11] Accordingly, transition metal salts MX_n dissolved in an organic solvent are reduced at the cathode in a simple electrochemical cell, R_4NOAc serving as the electrolyte, stabilizer and chemical species necessary for a mild oxidation process at the anode (Kolbe electrolysis). Another strategy makes use of a sacrificial anode as the metal source (e.g., a Pd-sheet). In this case the metal dissolves anodically and is then reduced back to the zero-valent form at the cathode. In both methods the adsorbed atoms (ad-atoms) generated at the cathode form clusters which are effectively trapped and stabilized by the ammonium salts, thereby preventing undesired metal precipitation. The surfactant forms a monomolecular layer around the metal atoms, as shown by a recent combined TEM/STM study.[12] It should be noted that R_4NX-stabilized metal clusters are normally prepared by chemical means.[13] The advantages of the electrochemical process include clean preparation (no need to separate from the reducing agent), easy isolation and the possibility of size-selectivity. The latter has been achieved by variation of the nature of the solvent,[14] temperature[14] and current density.[11]

In this study we chose the second method. Thus, a nickel sheet was incorporated as the sacrificial anode in a simple electrolysis cell, $(C_{12}H_{25})_4NBr$ serving as the electrolyte and stabilizer:

$$\begin{array}{llllllll}
\text{Anode:} & & & & & Ni_{bulk} & \longrightarrow & Ni^{2+} + 2\,e^- \\
\text{Cathode:} & Ni^{2+} & + & 2\,e^- & + & \text{stabilizer} & \longrightarrow & Ni_{coll}/\text{stabilizer} \\
\hline
\text{Sum:} & & & Ni_{bulk} & + & \text{stabilizer} & \longrightarrow & Ni_{coll}/\text{stabilizer}
\end{array}$$

Figure 1 summarizes the electrochemical process schematically.

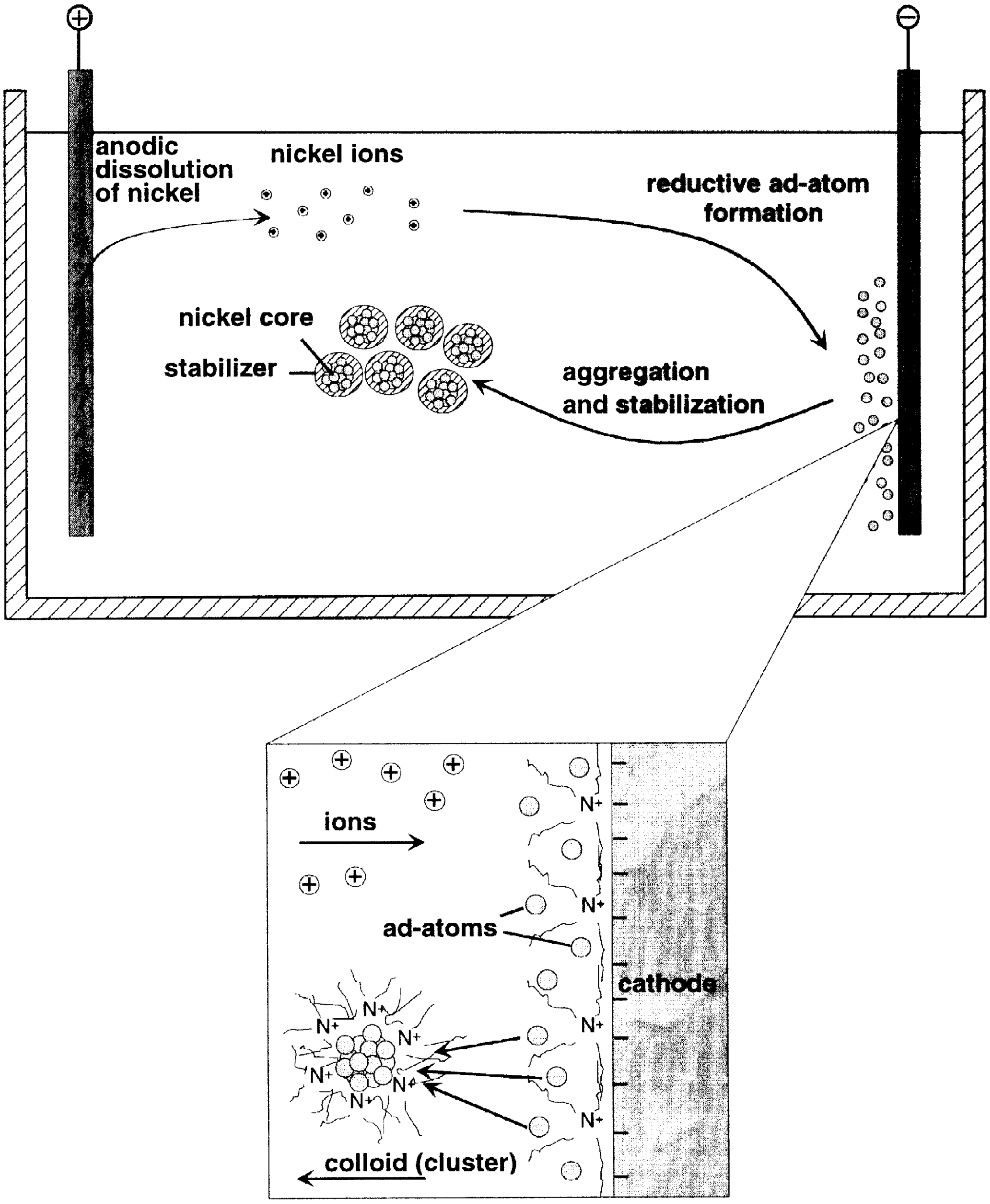

Fig. 1. Schematic representation of Ni-colloid formation (the bromide counterions have been omitted for reasons of brevity).

Upon applying a current density of 2.8 mA/cm^2, the Ni-anode dissolved. Concomitantly a black colloidal solution of $(C_{12}H_{25})_4NBr$-stabilized Ni-clusters was formed. Conventional TEM analysis showed the presence of 2.5 nm sized metal clusters (Figure 2). The preparation of the $(C_8H_{17})_4NBr$-stabilized clusters was performed in an analogous manner (ca. 2.5 nm particles).

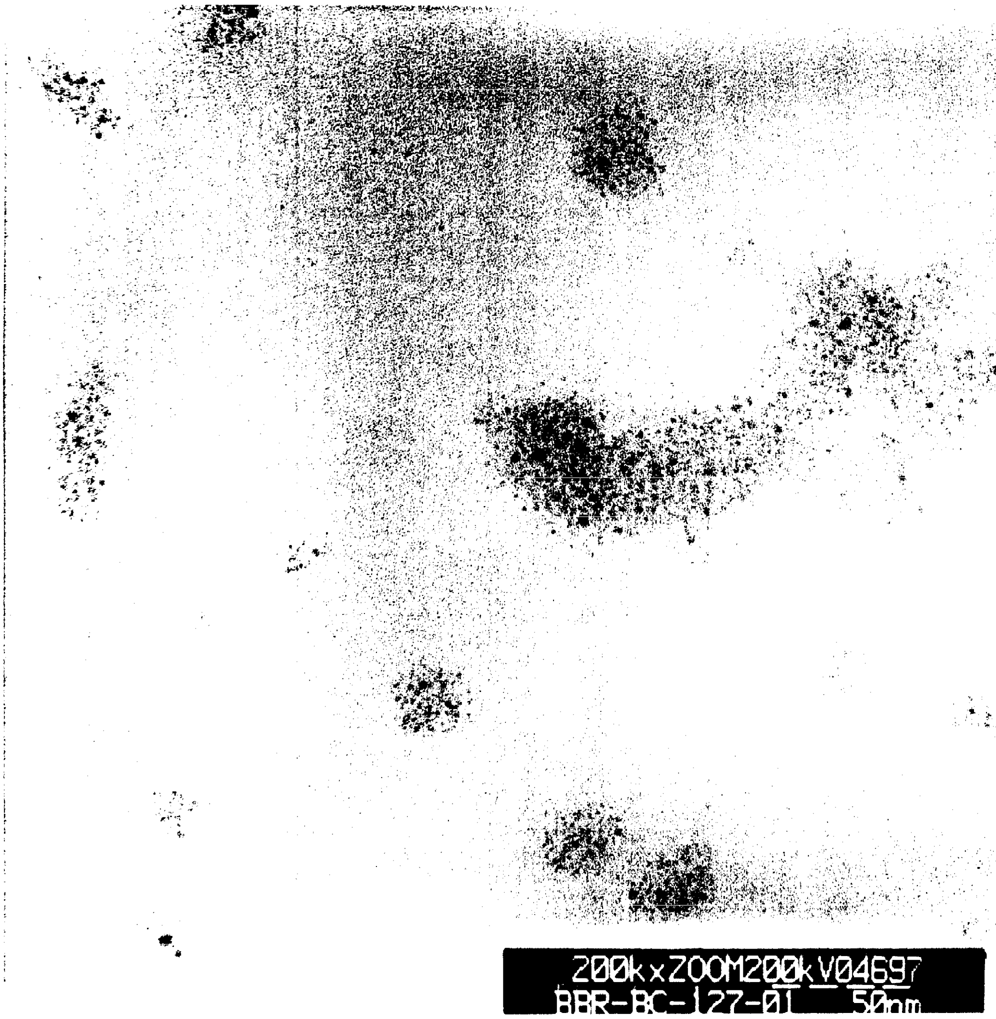

Fig. 2. Transmission electron micrograph (TEM) of $(C_{12}H_{25})_4NBr$-stabilized Ni-clusters.

IMMOBILIZATION

We have previously shown that preformed R_4NX-stabilized Pd-clusters can be immobilized on solid supports such as Al_2O_3.[15] Upon using Al_2O_3-pellets it was demonstrated that shell catalysts can be prepared readily without recourse to special techniques as in conventional methodologies based on the impregnation of metal salts.[16] In addition to this macroscopic property (100 - 300 µm thick shells can be detected by the human eye), the use of preformed nanostructured metal clusters also allows for morphological control at the microscopic level.[15] Accordingly, the R_4NX-stabilized clusters do not penetrate deeply into the pores of the inorganic support. Rather, they are deposited onto the surface of the Al_2O_3, forming so-called cortex catalysts, as shown by TEM analyses of microtomic slices.[15] Other types of preformed clusters have been immobilized on solid supports by other groups.[1,17]

In the present study colloidal solutions of $(C_8H_{17})_4NBr$-stabilized Ni-clusters were treated with solid supports such as Al_2O_3 or charcoal, as previously performed with the analogous Pd-clusters,[15] which resulted in the efficient immobilization of the Ni-containing particles. The material was washed several times with methanol and THF to remove most of the ammonium salt. A detailed investigation of the morphology of the heterogeneous catalyst was not carried out.

INVESTIGATION OF CATALYTIC PROPERTIES

Colloidal solutions of the $(C_{12}H_{25})_4NBr$-stabilized Ni-clusters as well as the immobilized forms were tested as potential catalysts in the [3+2]cycloaddition of **1** to **2**. Table 1 shows that catalysis is observed in all cases, but that the efficiency varies, depending upon which Ni-containing material is used. It appears that the colloidal solution of $(C_{12}H_{25})_4NBr$-stabilized Ni-clusters is optimal (entries 3 and 6). In a control experiment it was shown that in the absence of a Ni-catalyst no reaction occurs whatsoever (entry 1).

Table 1. Ni-catalyzed [3+2]cycloaddition.

Entry	Catalyst	Ni : Substrate Ratio	Temperature [°C]	Time[h]	Yield of **3**[a] [%]	TON[b]
1	no catalyst	-	140	48	0	0
2	Ni/Al_2O_3	1 : 256	130	24	3	7
3	Ni colloid	1 : 111	130	24	35	39
4	Ni/Al_2O_3	1 : 232	140	48	0.6	1
5	Ni/C	1 : 263	140	48	3	7
6	Ni colloid	1 : 103	140	48	28	29

[a] Determined by GC analysis with toluene as an internal standard and corrected by the response factors of the compounds. [b] Calculated from the yield and the total amount of Ni.

DISCUSSION

We have shown for the first time that colloidal solutions of ammonium salt stabilized Ni-clusters are capable of catalyzing the [3+2]cycloaddition of methylenecyclopropane (**1**) to an olefin (**2**). Although the catalytic activity and efficiency are not higher than in the case of traditional Ni-catalysts such as $Ni(COD)_2$, the results are nevertheless of considerable theoretical interest. Thus, it is now clear that colloidal solutions of transition metal clusters are catalytically active in a variety of unrelated C-C bond forming reactions, namely Heck reactions,[3,4] Suzuki couplings[3] and the present [3+2]cycloadditions. It is important to point out that although we use the term "colloidal solution", we do not mean homogeneous catalysis in the classical sense.[18] In fact, the processes that are described in this study are more related to heterogeneous catalysis. Thus, it is likely that the catalytically active sites occur at the steps, kinks or defects on the surface of the nanostructured cluster, similar to the mode of action of many heterogeneous catalysts.[19] More work is necessary to define the synthetic scope, the possibility of catalyst recyclability and the exact mode of action. The question of cluster size and catalytic activity also needs to be addressed.

EXPERIMENTAL SECTION

Electrochemical Preparation of a $(C_{12}H_{25})_4NBr$*-stabilized Ni colloid:*[20] A standard electrolysis cell (130 mL capacity) was constructed by using a Ni sheet (5 x 5 cm^2) as the anode and a Pt sheet (5 x 5 cm^2) as the inert cathode, approximately 3 mm apart. The cell was dried in an oven (1 h/70 °C) and flushed with argon. The electrolyte [0.1 M $(C_{12}H_{25})_4NBr$ solution in THF (130 mL)] was added and the electrolysis cell immersed in an ultrasonic cleaning bath, thermostated at 33 °C. A current density of 2.8 mA/cm^2 was applied and the whole cell was kept under a slight stream of argon. After 26.5 h (1.2 Ah) a deep black solution was formed. Analysis of the Ni anode by weight showed that 532 mg Ni had gone into solution corresponding a current yield of 40 %. TEM analysis showed the presence of 2.5 nm sized clusters.

For workup, the black solution was syphoned into a Schlenk flask, the solvent was removed under reduced pressure. The black, flaky solid was redissolved in anhydrous toluene. The resulting stock colloidal solution was used for catalysis.

In an analogous fashion $(C_8H_{17})_4NBr$-stabilized Ni-clusters were prepared; immobilization on Al_2O_3 or charcoal (Cabot Vulcan VXC 72) was performed using a previously described method.[15]

Representative procedure: An oven-dried 100 mL stainless steel autoclave was charged under argon with a stock solution of a $(C_{12}H_{25})_4NBr$-stabilized Ni colloid (1.36 mmol) in anhydrous toluene (14.8 g) and cooled in an ice bath. Then a -78 °C cold stock solution of methylenecyclopropane (151 mmol) and acrylic acid methyl ester (169 mmol) in anhydrous toluene (18.3 g, 199 mmol) was added. The reaction mixture was heated to 130 °C and stirred 24 h at that temperature. After cooling down to room temperature the crude mixture was distilled at 90 °C/10^{-2} mbar into a trap cooled with liquid nitrogen. The distillate was analyzed by GC (column: 30 m RPX 35, 0.25, DF 0.25) with toluene as an internal standard.

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20. The handling of Ni colloids requires scrupulous exclusion of oxygen and moisture. $(C_{12}H_{25})_4NBr$ (Fluka 87249) was dried by dissolving in anhydrous THF : toluene (1 : 1), evaporation of the solvents and drying the white powder in vacuo (oil pump) overnight.