Communications

Selective Carbonylation of Nitrobenzene over a Mixed Pd–Mo Cluster Derived Catalyst

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Summary: A mixed metal cluster derived (MMCD) catalyst has been used for the first time in the selective carbonylation of aromatic nitro derivatives to give isocyanates. The MMCD technique offers the potential of precisely defining the size and composition of the metallic particles deposited on the catalyst support.

The carbonylation of aromatic nitro derivatives (eq 1) is a reaction of great industrial relevance, since it represents a way to aromatic isocyanates.[1]

$$Ar–NO_2 + 3CO \rightarrow Ar–NCO + 2CO_2 \qquad (1)$$
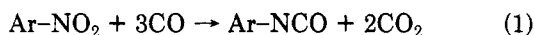
This reaction is also of academic interest since the detailed reaction mechanism(s) is (are) not yet well understood.[2] Various homogeneous[3] and heterogeneous[4] catalysts have been reported for this reaction, but improvements are still highly desirable. Palladium-based catalysts appear to be the most selective, and the combination $PdCl_2$/pyridine has been extensively studied.[1,3] It also has been determined that addition of, e.g., MoO_3, V_2O_5, or $FeCl_3$ greatly increases the yield of isocyanates,[1b,5] but MoO_3 alone, for example, has a high activity but poor selectivity (see Table I, experiment 2).

These heterogeneous catalysts usually are dispersed on highly divided inorganic oxides, and it is well recognized that in such systems an exact knowledge of both size and composition of the metallic particles is not easily gained.[6]

Furthermore, difficulties are sometimes encountered in reproducing such catalysts.

These observations have led us to prepare and investigate a "mixed metal cluster derived" (MMCD) catalyst. In this way, we hoped to improve the catalytic properties by synergic interactions between adjacent metal centers[7] and to improve our control of the size and composition of the metallic particles. These would be obtained by impregnation of a known molecular mixed-metal cluster onto an inorganic support and subsequent thermal removal of the ligands under carefully controlled conditions. Ideally, the reduction of supported molecular MMC could produce metal aggregates of precisely defined composition. This clearly cannot be done by reductive deposition from homogeneous solutions of two or more metal compounds.

In view of the interesting results disclosed mainly in the patent literature[1b,8] concerning catalysts prepared by simultaneous deposition of palladium and molybdenum, we chose as the MMCD catalyst precursor the easily prepared and stable heterotetrametallic $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6$-$(PPh_3)_2$ cluster.[9] To the best of our knowledge, this represents the first utilization of a mixed-metal cluster containing palladium as catalyst or catalyst precursor. We summarize in Table I the results obtained with this MMCD catalyst for the carbonylation of nitro derivatives. It offers the advantages of high activity and high yield of isocyanate under conditions sufficiently mild to preclude decomposition, and it thus could be of potential commercial significance.

For our initial investigations, two types of MMCD catalyst preparations were examined: (i) $\gamma\text{-}Al_2O_3$ was poured under nitrogen into a CH_2Cl_2 solution of the cluster, the mixture stirred, and the solvent removed under vacuo (experiments 6 and 7); (ii) $\gamma\text{-}Al_2O_3$ was placed in a rotating evaporator and the CH_2Cl_2 solution of the cluster continuously sprayed over under constant agitation, evaporation of the solvent occurring simultaneously in vacuo (experiment 8). In both cases, the impregnated support, once dried, was heated at increasing temperature (2 °C/min) under nitrogen. After 16 h at 300 °C, the catalyst was treated with H_2 and then placed under nitrogen. The catalyst then was transferred into the reactor. The quantities used in each experiment are given in Table I. For comparison, these same modes of impregnation, i.e., immersion (i) or spray (ii), were applied to "conventional" heterogeneous catalysts which were prepared from equimolar ratios of palladium acetate and ammonium molybdate in H_2O/NH_4OH solutions (experiments 4 and 5) and treated as above. In all our experiments, the mixed cat-

(1) (a) U.S. Patent 3576835; *Chem. Abstr.* **1969**, *71*, 80911; German Patent DE1815517. (b) U.S. Patent 3719699; *Chem. Abstr.* **1972**, *77*, 114022; German Patent DE2165355. (c) U.S. Patent 3737445; *Chem. Abstr.* **1969**, *71*, 123894; German Patent DE1901202.

(2) Weigert, F. J. *J. Org. Chem.* **1973**, *38*, 1316.

(3) (a) U.S. Patent 3636028; *Chem. Abstr.* **1970**, *72*, 21477; German Patent DE1909190. (b) U.S. Patent 3637786; *Chem. Abstr.* **1970**, *73*, 109478; German Patent DE2005811. (c) French Patent 2017317; *Chem. Abstr.* **1970**, *72*, 132289; German Patent DE1944747. (d) French Patent 2222363 *Chem. Abstr.* **1975**, *82*, 3958; German Patent DE2413962.

(4) (a) Hardy, W. B.; Bennett, R. P. *Tetrahedron Lett.* **1967**, 961. (b) Patent 1257932; *Chem. Abstr.* **1970**, *72*, 66595; German Patent DE1932211.

(5) Nefedov, B. K.; Manov-Yuvenskii, V. I.; Chimishkyan, A. L.; Englin, V. M. *Kinet. Katal.* **1978**, *19*, 1065.

(6) Whyman, R. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 8.

(7) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15; *Science (Washington, D.C.)* **1977**, *195*, 641.

(8) (a) U.S. Patent 3823174; *Chem. Abstr.* **1975**, *82*, 4750. (b) U.S. Patent 4207212; *Chem. Abstr.* **1980**, *93*, 150873.

(9) This cluster is analogous to $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PEt_3)_2$: Bender, R.; Braunstein, P.; Dusausoy, Y.; Protas, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 596; and was prepared in a similar way, using Pd-$(PPh_3)_2Cl_2$ instead of $Pd(PEt_3)_2Cl_2$.

Table I. Catalytic Conversion of PhNO₂ in PhNCO

expt	catalyst descriptn[a]	py, g	PhNO₂, g	catalyst, g			molar ratios		react conditns[b]		conversn,[c] %	selectivity,[c] %	remarks
				total	Pd	Mo	PhNO₂/Pd	PhNO₂/Mo	temp, °C	react time, h			
1	Pd/Al₂O₃[d]	1	10	1.66	0.083	...	104	...	240	1.2	0	0	after long induction period, low activity was noted
2	MoO₃[e]	1	10	0.13	...	0.087	...	90	240	0.3	100	19	degradation of the products in the reactor
3	Pd/Al₂O₃[d] + MoO₃[e]	1	10	1.7 + 0.13	0.083	... 0.087	104	... 90	240	0.4	100	49	
4	(Pd–Mo)[f]/Al₂O₃[g] impregn (i)[a]	1	10	1.8	0.054	0.054	150	144	240	0.8	100	62	
5	(Pd–Mo)[f]/Al₂O₃[g] impregn (ii)[a]	1	9	1.6	0.048	0.048	160	145	240	1.0	100	67	
6	(Pd₄Mo₂ cluster)[h]/Al₂O₃[g] impregn (i)[a]	1	10	1.8	0.059	0.053	147	147	240	1.2	100	71	
7	same as in expt 6	5	10	1.9	0.062	0.056	139	139	220	4.0 (1 h induction)	100	80	azobenzene, 0; diphenylurea, 1.7%
8	(Pd₄Mo₂ cluster)[h]/Al₂O₃[g] impregn (ii)	1	10	1.8	0.059	0.053	147	147	240	1.2	100	71.5	
8a	catalyst from expt 8 recycled[i]	0.77	7.8	1.4	0.046	0.041	148	148	240	1.0	100	71	
9	PdCl₂ + py + MoO₃[e]	1	10	0.14 0.126	0.084	0.084	103	93	240	0.3	100	81.5	"soluble catalyst"; after test, the liquid was transferred and distilled, affording 1.5 g of solid residue containing 1.2% Pd and 5.3% Mo
9a	PdCl₂ + py + MoO₃[e]	1	10	0.083 + 0.075	0.05	0.05	174	156	240	0.7	100	79	
10	blank following expt 9	1	10	...	...	...	...	...	240	1.1	100	73	

[a] The impregnation methods by immersion (i) or spray (ii) are described in the text. [b] The solvent used was o-dichlorobenzene, in quantities such as total volume = 100 mL. Initial CO pressure was typically 200 atm. We used a 50-mL Hastelloy C reactor with magnetic stirring. [c] The conversion is defined as the ratio [PhNO₂] reacted/[PhNO₂] introduced, and was determined by GC (Perkin-Elmer silicones D.C. columns, l = 2 m, 110 °C). PhNCO was chemically titrated by dibutylamine. The selectivity is defined as the ratio [PhNCO] produced/[PhNO₂] reacted. [d] Commercial catalyst Engelhard 5% Pd ($S(Al_2O_3) > 300$ m²/g). [e] Introduced as molybdic acid (92% MoO_3). [f] Prepared from palladium acetate and ammonium molybdate in equimolar ratio. [g] γ-Al_2O_3 from Condea Chemie, 250 m²/g, pulverized and sifted to 200–600 μm. [h] See text for preparation of the MMCD catalyst. Typically, 5.3 g of catalyst was prepared from 5 g of γ-Al_2O_3[g] and 1 g of cluster. [i] The quantities of reactants were adjusted so as to give the same molar ratios as in experiment 8.

alyst contained between 2.5 and 3% Pd and Mo. Pyridine was added in all our experiments in view of its favorable role in this reaction.[10]

Supported palladium was found to be inactive for 1.2 h (experiment 1), whereas MoO_3 (in the form of molybdic acid) displayed high activity but low selectivity (experiment 2). Addition of MoO_3 to supported Pd gives a catalyst of high activity and medium yield (experiment 3). In contrast, *simultaneous* deposition of Pd and Mo on the support improves the yield and maintains the high activity (experiments 4 and 5). But the best results were obtained with the MMCD catalyst (experiments 6–8). Improved yields were generally observed when the spray impregnation method (ii) was used, probably because of better dispersion of the catalyst precursor.[11] Both the activity and the selectivity of our catalyst are retained on repeated usage (experiment 8a).

For comparison we have also run the reaction with the well-known $PdCl_2$/pyridine/MoO_3 catalyst (experiment 9).[1b,3,8] With this high-yield system, catalyst recovery is very difficult since everything appears soluble after the reaction, though $PdCl_2$ and MoO_3 were insoluble before the reaction. With this catalyst system we have made the important observation that when the reactor is emptied of its contents and recharged with reactants but no catalyst, catalytic activity if found (experiment 10). This implies that metal-containing materials were deposited on the walls of the reactor during experiment 9 and that, in fact, this so-called "homogeneous" catalyst[12] may well have an heterogeneous component.[13] Only 25–50% of the palladium introduced was found in the solution. However, it is not separable from the polymeric reaction byproducts which represent ca. 20% of the selectivity, and thus, it cannot be recycled. By contrast, with the MMCD catalyst no detectable quantities of metals appear in the product solution or on the walls of the reactor. As a result, essentially all the MMCD catalyst is easily recoverable.

Our MMCD catalyst overcomes the usual inverse relationship between catalytic activity and selectivity. The use of a neutral MMC such as $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6\text{-}(PPh_3)_2$ soluble in organic solvents and containing metals in low oxidation states should be of general interest since (i) they avoid the dramatic redox processes which are expected to take place during cluster deposition and activation (processes which might lead to undesirable molecular or particle rearrangements, or support modifications) and (ii) cleaner water- and halide-free[14] catalysts become available. We believe that comparative studies, under similar reaction conditions, between "conventional" and MMCD catalysts will improve our knowledge of bimetallic catalysis in general and reveal some unique features of carefully prepared MMCD catalysts. Such further studies are in progress.

(10) (a) U.S. Patent 3 903 125; *Chem. Abstr.* **1975**, *82*, 72629; Japanese Patent Kok. 74/92 041. (b) Nefedov, B. K.; Manov-Yuvenskii, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2597.

(11) Preliminary surface studies of the catalyst by scanning electron microscopy indicate indeed better dispersion for the MMCD than for the conventional catalyst. Microprobe examination of the MMCD and simultaneously impregnated catalysts reveals the presence of both Pd and Mo in the particles of each.

(12) Unverferth, K.; Höntsch, R.; Schwetlick, K. *J. Prakt. Chem.*, **1979**, *321*, 86.

(13) This observation is of particular importance when consecutive catalytic tests are carried out in the same reactor.

(14) Metal halides are notoriously corrosive, leading to short reactor lifetimes.

Synthesis, Structural Elucidation, and Stereochemistry of Five-Coordinate Organoarsenic Catecholates

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Summary: The synthesis of five-coordinate organoarsenic catecholates, with substitution of 3-CH_3, 4-CH_3OC(=O); 4,5-C_6H_4, and 3,3'-C(=O)$NH(CH_2)_4NHC$(=O) groups on the catechol ring and CH_3 or Ph on arsenic, was performed. These reactions provided new insight into the structures and stereochemistry of these organoarsenic compounds. In one case, 3-methylcatecholate of phenylarsonic acid, a single-crystal X-ray analysis provided unequivocal evidence for cis stereochemistry of the methyl groups on the catechol rings, an essentially rectangular-pyramidal configuration around arsenic, and a preferred conformation of the phenyl group in relation to the oxygens surrounding the arsenic atom.

Recently, we have been investigating the speciation or molecular characterization of organoarsenic compounds thought to be present in biogeochemical materials such as oil shale kerogen and the products of the pyrolysis of oil shale kerogen, those of the shale oils, and the retort waters.[1a,b] These studies led to the identification, for the first time, of methyl- and phenylarsonic acids in these precursors and products.

In view of these discoveries, we have initiated studies to find innovative methods for the removal of these compounds and other organometallics from fossil fuel products. In this regard, we have been experimenting with a method that utilizes substituted catechols as potential ligands that could be placed in a polymeric matrix for the future removal of organoarsenic compounds from the above-mentioned products.

Surprisingly, we found very few references on the reactions of catechols with alkyl- or arylarsonic acids[2a-f] and none on similar reactions with substituted catechols.[3] Thus, in this paper, we present our initial results on the synthesis, structural elucidation, and stereochemistry of the five-coordinate organoarsenic catecholates we prepared as model compounds for the above-mentioned purposes.

Chart I shows the catechols 1–4 we utilized in the reactions with methyl- or phenylarsonic acid, 5 or 6. Compound 1 reacts with either 5 or 6 to provide a mixture of cis and trans five-coordinate organoarsenic catecholates 7–10 (eq 1).

Compounds 7–10 were characterized by a combination of nuclear magnetic resonance spectroscopy (NMR), mass

(1) (a) Fish, R. H.; Brinckman, F. E.; Jewett, K. L. *Environ. Sci. Technol.* **1982**, *16*, 174. (b) Weiss, C. S.; Brinckman, F. E.; Fish, R. H., Proceedings on Environmental Speciation of Trace Metal-Containing Compounds in Energy-Related Processes, May 18–20, 1981, Gaithersburg, MD. *NBS Spec. Publ. (U.S.)* **1981**, *618*, 197.

(2) (a) Salmi, E. J.; Merivuori, K.; Laaksonen, E. *Kemistilehti Suomen* **1946**, *19B*, 102 (*Chem. Abstr.* **1946**, *41*, 5440a). (b) Bacher, J. H.; Van Oosten, R. P.; *Recl. Trav. Chim. Pays-Bas* **1940**, *59*, 41. (c) Englund, B. *Chem. Ber.* **1926**, *59*, 2669. (d) Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157. (e) Wieber, M.; Eichhorn, B.; Gotz, J. *Chem. Ber.* **1973**, *106*, 2738. (f) Maroni, P.; Holeman, M.; Wolf, J. G.; Richard, L.; Fischer, J. *Tetrahedron Lett.* **1976**, 1193.

(3) Fish, R. H.; Weitl, F. L., Proceeding of the Tenth International Conference on Organometallic Chemistry, Toronto, Canada, Aug 9–14, 1981, Abstract 1D12, p 62.