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Anchoring Metal Species on a Thiourea-Functionalized Silica Xerogel. In Situ Production of Colloidal Palladium Particles

Corrado Ferrari, Giovanni Predieri,* and
Antonio Tiripicchio

Istituto di Chimica Generale ed Inorganica
Università di Parma
Viale delle Scienze 78, I-43100 Parma, Italy

Mirco Costa

Istituto di Chimica Organica
Università di Parma
Viale delle Scienze 78, I-43100 Parma, Italy

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The production of new supporting materials is an important branch of metal catalysts design. In some instances, the nature and the structural features of the support may decisively improve activity, selectivity, and lifetime of the catalytic metal species. Recently, the use in catalysis of materials, particularly silica xerogels, obtained by hydrolysis and polycondensation of a silicon alkoxide, followed by drying under ambient atmosphere (the sol–gel process[1]), has attracted increasing attention.

Both anchored transition-metal complexes with catalytic activity[2] and supported small metal particles[3] can be conveniently prepared by the sol–gel process. In the former, a donor-ligand-functionalized support is required. This can be easily obtained by the incorporation of the suitable molecular fragment into the siloxane polymer. This synthetic procedure provides robust materials with a higher content of available ligand groups than their silica-immobilized counterparts.[4] In the latter, metal particles incorporation into ceramic oxides, derived from the sol–gel process, normally involves calcination and reduction at relatively high temperatures. However, this treatment destroys the permeability of the original xerogel. Alternatively, a new method for the deposition of palladium(0) into an intact silica xerogel has been developed, affording a catalyst with remarkable hydrogenation activity.[5]

In addition, new functionalized materials with sulfur donor ligands are possibly capable of selective binding of soft metal species. In this context, we attempted the synthesis of a thiourea-functionalized silica gel. Here we describe its characterization and some selected metal-anchoring reactions. Furthermore, the production of nanoscale palladium particles obtained by in situ reduction of the immobilized thiourea/palladium(II) complexes is described. Notable interest in this system is due to the specific catalytic properties of the thiourea/PdX_2 complexes, which were found to be efficient in catalyzing carbonylation of alkynes[6] and in inducing ring-closure processes of diynes.[7] Recently, composite materials con-

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(1) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

(2) (a) Schubert, U.; Rose, K.; Schmidt, H. *J. Non-Cryst. Solids* **1988**, *105*, 165. (b) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330. (c) Parish, R. V.; Habibi, D.; Mohammadi, V. *J. Organomet. Chem.* **1989**, *369*, 17. (d) Hilal, H. S.; Rabah, A.; Khatib, I. S.; Schreiner, A. F. *J. Mol. Catal.* **1990**, *61*, 1.

(3) (a) Tamagawa, H.; Oyama, K.; Yamaguchi, T.; Tanaka, H.; Tsuiki, H.; Ueno, A. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3189. (b) Schubert, U.; Amberg-Schwab, S.; Breitscheidel B. *Chem. Mater.* **1989**, *1*, 576. (c) Lopez, T.; Bosch, P.; Gomez, R. *React. Kinet. Catal. Lett.* **1990**, *41*, 217. (d) Lopez, T.; Lopez-Gaona, A.; Gomez, R. *Langmuir* **1990**, *6*, 1343.

(4) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* **1989**, *369*, 9.

(5) (a) Tour, J. M.; Pendalwar, S. L.; Cooper, J. P. *Chem. Mater.* **1990**, *2*, 647. (b) Tour, J. M.; Pendalwar, S. L. *Tetrahedron Lett.* **1990**, *31*, 4719. (c) Tour, J. M.; Cooper, J. P.; Pendalwar, S. L. *J. Org. Chem.* **1990**, *55*, 3452.

(6) Chiusoli, G. P.; Costa, M.; Pergreffi, P.; Reverberi, S.; Salerno, G. *Gazz. Chim. Ital.* **1985**, *115*, 691.

(7) Chiusoli, G. P.; Costa, M.; Masarati, E.; Salerno, G. *J. Organomet. Chem.* **1983**, *255*, C35.

(8) Ulrich, D. R. *Chem. Eng. News* **1990**, *68* (1), 28.

(9) (a) Bradley, J. S.; Hill, E.; Leonowicz, M. E.; Witzke, H. *J. Mol. Catal.* **1987**, *41*, 59. (b) Wang, Y.; Liu, H.; Jiang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1878.

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Table I. Catalytic Activity[a] of Pd/XGSILTU[b] for the Hydrogenation of Alkynes. Comparison with the Lindlar Catalyst[16]

catalyst	substrate	product	time, min	conversion,[c] %	yield,[c] %
Pd/XGSILTU	$PhC{\equiv}CH$	$PhCH{=}CH_2$	80	97.0	88[d]
Lindlar cat.	$PhC{\equiv}CH$	$PhCH{=}CH_2$	80	92.0	82[e]
Pd/XGSILTU	$PhC{\equiv}CH$	$PhCH_2CH_3$	150	100	100
Pd/XGSILTU	$PhC{\equiv}CPh$	*Z*-$PhCH{=}CHPh$	160	92.2	87.5[f]
Pd/XGSILTU	$HOMe_2CC{\equiv}CH$[g]	$HOMe_2CCH{=}CH_2$	35	97.5	97.5

[a] Experimental conditions: temperature, 25 °C; solvent, methanol, 15 mL; total pressure, 1 atm; Pd, 0.015 mmol; alkyne, 4.5 mmol. [b] From $[PdCl_4]^{2-}$; Pd, 3%; surface area 270 $m^2\ g^{-1}$. [c] Determined by internal standard method. [d] $PhCH_2CH_3$, 9%. [e] $PhCH_2CH_3$, 10%. [f] *E*-$PhCH{=}CHPh$, 4.6%. [g] Dimethylpropargyl alcohol.

taining colloidal metal particles have attracted much attention for use in ceramic modification[8] and for the study of dispersed metal catalysts.[9]

In the first stage of our investigations, we prepared the substituted thiourea $(EtO)_3Si(CH_2)_3NHC({=}S)NHPh$ (SILTU), by the reaction of $(EtO)_3Si(CH_2)_3NH_2$ with a slight excess of PhNCS in absolute ethanol. After refluxing for 15 min, the solvent and the excess PhNCS have been removed under reduced pressure, affording a colorless oily product analyzed by FTIR, ^1H and ^{13}C NMR, and mass spectroscopies.[10]

The corresponding thiourea-functionalized xerogel (XGSILTU) was easily prepared by hydrolysis and polycondensation of SILTU and tetraethoxysilane (1:10 volume ratio) in a water–ethanol mixture at reflux for a few hours. The obtained xerogel, after crushing, washing, and drying in vacuo, exhibited a surface area of 380 $m^2\ g^{-1}$ (BET method). Elemental analysis provided the following results: C 8.3, H 1.6, N 2.0, S 1.9. The IR spectrum showed the characteristic bands of the thiourea fragment at 1556, 1502, 1454, and 697 cm^{-1}.

Encouraging results were obtained by testing this organic–inorganic hybrid material in anchoring reactions with different metal species, namely, Pd^{2+} complexes, $(cp')Mn(CO)_3$ (cp′ = MeC_5H_4), and $M(CO)_6$ (M = Cr or Mo). XGSILTU was able to bind palladium(II) by simply mixing it in aqueous $[PdCl_4]^{2-}$ or alcoholic $Pd(PhCN)_2Cl_2$ solutions at room temperature. The suspended xerogel quickly turned brownish-orange and was easily filtered, washed, and dried without loss of metal. The unfunctionalized xerogel, derived from $Si(OEt)_4$ alone, was unable to bind the same palladium species, under identical conditions.

Due to sulfur coordination,[10] the IR spectrum of the composite material Pd(II)/XGSILTU showed the thiourea bands (1559, 1498, 1442, and 695 cm^{-1}) slightly shifted with respect to XGSILTU. Although elemental analysis data have provided a S/Pd atomic ratio close to 2, it is possible that different complexes are present on the xerogel surface. In fact, though only the 4:1 thiourea/Pd complexes can be easily separated in the solid state,[11,12] there is spectroscopic evidence that other species are present in solution, depending on the thiourea/Pd molar ratio.[13] Nevertheless, once these anchored species are obtained, regardless of the prevailing superficial complexes, they are inert toward the most common regents, excluding alkaline hydroxides, which destroy the siloxane framework.

Furthermore, to obtain additional insight into the actual capacity of the C=S donor groups to form metal complexes, XGSILTU was reacted with the above-mentioned metal carbonyls by photochemical activation according to

$$L_nM(CO)_m \xrightarrow[\text{THF, XGSILTU}]{h\nu\ (366\ \text{nm}),\ \text{room temp}} L_nM(CO)_{m-1}(\text{XGSILTU}) \qquad [M]/[S] \gg 1$$

The freshly obtained anchored complexes $(cp')Mn(CO)_2(XGSILTU)$ (light brown) and $M(CO)_5(XGSILTU)$ (M = Cr or Mo, both yellow) showed the expected CO stretching bands at 2020, 1953 (Mn) 2065 w, 1985 sh, 1938 s, 1884 sh (Cr) 2074 w, 1990 sh, 1944 s, and 1886 sh (Mo) cm^{-1}, due to the anchored monosubstituted carbonyl species.[14] A S/Mn atomic ratio close to 1 was achieved with manganese, suggesting that almost all the sulfur donor groups were available for coordinative interactions.

In addition, from treatment of an ethanol suspension of Pd(II)/XGSILTU with dihydrogen and an excess of phenylacetylene, ethylbenzene is quantitatively produced in 48 h at room temperature and atmospheric pressure. When recovered by filtration, the gel appeared deep brown. After this initial slow hydrogenation cycle, the catalytic activity increased drastically. The catalyst was quite active in the hydrogenation of double and triple carbon–carbon bonds at room temperature and atmospheric pressure for several runs, without any apparent drop in activity. It also appears to be selective in converting alkynes to the corresponding alkenes. As shown in Table I, hydrogenation of styrene practically did not start until phenylacetylene was present, due to the stronger ligating properties of the latter. Moreover, this catalyst exhibits a good stereoselectivity in converting diphenylacethylene to the corresponding *Z*-alkene.[15] Very recently, a similar catalytic system containing reduced palladium supported on an unfunctionalized siloxane framework has been found to possess a superb stereoselectivity over dialkylacetylenes,[5b,c] providing an effective alternative to the Lindlar reduction catalyst.[16] Additional experimental work is in progress

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(10) SILTU, ^1H NMR ($CDCl_3$, TMS), δ/ppm: 0.57 (m, 2 H, $SiCH_2$), 1.15 (t, 9 H, CH_3, *J* = 7 Hz), 1.61 (m, 2 H, CH_2), 3.58 (m, 2 H, CH_2N), 3.73 (q, 6 H, CH_2O *J* = 7 Hz), 6.3 (br s, 1 H, NH), 7.1–7.5 (m, 5 H, Ph), 8.5 (br s, 1 H, HNPh). ^{13}C NMR ($CDCl_3$, TMS), δ/ppm: 7.17 ($SiCH_2$), 17.8 (CH_3), 21.9 (CH_2), 46.6 (CH_2N), 57.9 (CH_2O), 124.2, 125.6, 129.0, 137.2 (Ph), 179.7 (CS). MS, *m/z* (%): 356 (80), 163 (100), 151 (78), 135 (53), 93 (90). IR, cm^{-1}: 1597 m, 1539 s, 1497 s, 1102 vs, 1080 vs, 696 m.

(11) (a) Yamaguchi, A.; Penland, R. B.; Mizushima, S.; Lane, T. J.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc* **1958**, *80*, 527. (b) Lane, T. J.; Yamaguchi, A.; Quagliano, J. V.; Ryan, J. A.; Mizushima, S. *J. Am. Chem. Soc.* **1959**, *81*, 3824.

(12) Berta, D. A.; Spofford, W. A.; Boldrini, P.; Amma, E. L. *Inorg. Chem.* **1970**, *9*, 136.

(13) (a) Patil, S. P.; Shinde, V. M. *Mikrochim. Acta* **1974**, 853. (b) Morelli, B. *Anal. Lett.* **1984**, *17*, 2267.

(14) (a) Fischer, E. O.; Herberhold, M. *Experientia, Suppl.* **1964**, *9*, 259. (b) Tripathi, S. C.; Srivastava, S. C.; Pandey, R. D. *J. Inorg. Nucl. Chem.* **1973**, *35*, 457. (c) Granifo, J.; Costamagna, J.; Garrao, A.; Pieber, M. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1587.

(15) In the reduction of diphenylacetylene, there is evidence that *Z*-stilbene converts to *E* on the catalyst, as selectivity depends on the extent of the substrate conversion. When the conversion is only 87%, the selectivity is very high (97% of *Z* isomer); when the conversion reachs 99%, *Z* selectivity lowers to 92%.

(16) Lindlar, H.; Dubois, R. *Org. Synth.* **1973**, *5*, 880.

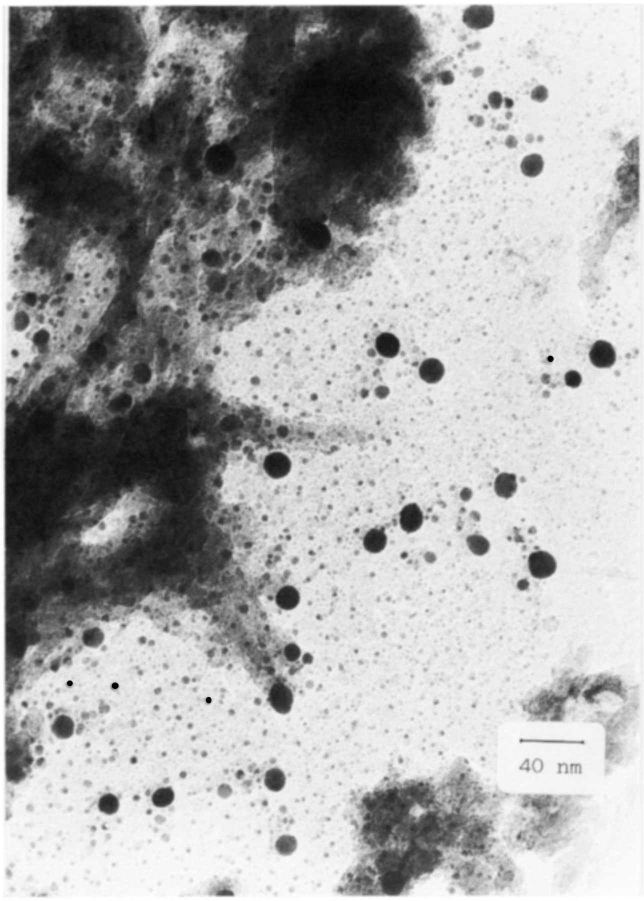

Figure 1. Bright field TEM micrograph of the catalyst.

in order to establish if Pd/XGSILTU and other related systems (obtained by different isocyanates) are able to stereoselectively reduce other selected alkynes.

As expected, TEM investigations carried out on Pd/XGSILTU after some catalytic runs have revealed the presence of nanoscale palladium particles, uniformly dispersed throughout the siloxane matrix. Figure 1 shows that these particles are spheroidal in shape, ranging in size from about 10 to 20 nm. The in situ formation of colloidal metal aggregates, responsible for the hydrogenating activity, does not exclude, however, the persistence of palladium(II) species, possibly protected by a suitable number of thiourea groups. XPS investigations have been planned, in order to clarify this point.

In conclusion, this catalyst exhibits an excellent hydrogenation activity, which is far from being fully exploited. The presence of sulfur donor groups (as in ref 9b) probably prevents the colloidal particles from further aggregation. Furthermore, the new xerogel XGSILTU could play the unprecedented double role of both an efficient recovery agent for palladium(II) from acidic wastes and an effective support for nanoscale palladium particles.

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Novel Quaternary Salts of Quinoline Oligomer as Metal Surface Protective Materials against Acid Corrosion

Long Y. Chiang,* J. W. Swirczewski,
T. A. Ramanarayanan, and J. D. Mumford

Corporate Research Laboratory
Exxon Research and Engineering Company
Annandale, New Jersey 08801

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The corrosion of metals at the solid–liquid interface by acids is a problem that is encountered in many industries. One preventive method to subside the corrosion rate of metal in the liquid media is the application of metal surface active organics as corrosion-inhibiting additives in the liquid phase. Some of aromatic heterocyclic organics have been used as corrosion inhibitors under various conditions and applications.[1] However, the use of aromatic heterocyclic polymers as corrosion inhibitors remains rare. They possess promising potential to improve the thermal and chemical stability of materials at elevated temperatures and under highly acidic conditions.

Recently we described a new phenomena of catalytic dehydrogenative polycondensation (CDHP) reaction for the synthesis of linear aromatic heterocyclic oligomers utilizing transition metal sulfides as catalysts as shown in Scheme I.[2–5] The reaction resulted in a catalytic conversion of 1,2,3,4-tetrahydroquinoline (THQ) directly to nonsubstituted quinoline oligomers (**1a** and **1b**)[6] in a one-step synthesis. Here we report that the transformation of these oligomers to their water-soluble quaternary salts makes them suitable for use as metal surface protective agents against acid corrosion.[7]

Due to the electron-accepting properties of oligomer **1**, as demonstrated in its cyclic voltammetry in acetonitrile displaying a reversible one-electron reduction wave with a reductive half-wave potential at −1.78 V vs SCE, the quaternarization reaction of **1** was carried out with reactive alkylation reagents such as dimethyl sulfate or trimethyloxonium salts. Thus oligomeric methylquinolinium methylsulfate **2a** and **2b** (MQO-$MeSO_4$, $x^- = MeSO_4^-$) mixtures were prepared in 80% yield by the reaction of the soluble fraction of corresponding oligomer **1a** and **1b** ($x = 3–11$) with dimethyl sulfate (excess) in dimethyl formamide at 110 °C. The crude products were precipitated from the reaction mixtures by an addition of diethyl ether. The purification process was carried out through a repeated reprecipitation of **2a** and **2b** by an addition of the product solution in a mixture of methanol and H_2O into vigorously stirred acetone. The degree of quaternarization in oligomer **2** was determined by the ^1H NMR spectroscopy. The chemical shift of two groups of methyl protons in DMSO-d_6 centered at 4.51 and 3.32 ppm, corresponding to quinolinium methyl protons and methyl

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(1) For review see: Hausler, R. H. Corrosion Chemistry; ACS Symposium Series 89; Brubaker, G. R., Phipps, P. B., Eds.; American Chemical Society: Washington, DC, 1979; pp 262–320.

(2) Chiang, L. Y.; Chianelli, R. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1461.

(3) Chiang, L. Y.; Chianelli, R. R. U.S. Patent 4,727,135, Feb 23, 1988.

(4) Chiang, L. Y.; Swirczewski, J. W.; Chianelli, R. R.; Stiefel, E. I. *Catal Lett.* **1988**, *1*, 177.

(5) Chiang, L. Y.; Swirczewski, J. W.; Passaretti, J. D.; Chianelli, R. R. *Solid State Ionics* **1989**, *32/33*, 988.

(6) Chiang, L. Y.; Swirczewski, J. W.; Kastrup, R.; Hsu, C. S.; Upasani, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 6574. Chiang, L. Y.; Kastrup, R. V.; Hsu, C. S.; Swirczewski, J. W. *Mater. Res. Soc. Symp. Proc.* **1989**, *134*, 101.

(7) Chiang, L. Y. U.S. Patent 4,880,907, Nov 14, 1989.