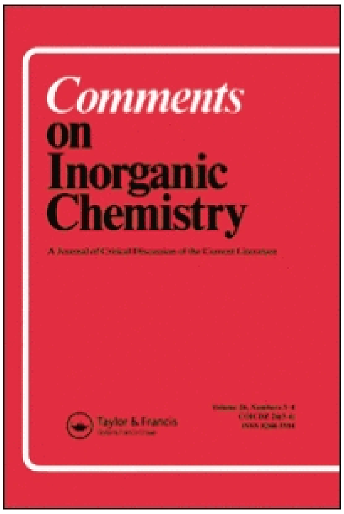

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SURFACE MODIFICATION BY DEPOSITION AND THERMAL DECOMPOSITION OF TRANSITION METAL CLUSTER HALIDES

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The surface modification of various materials with small particles of sizes down to the nano scale is technologically very important. In this article we report about the use of metal-rich niobium halide cluster compounds to modify surfaces. In a deposition and subsequent decomposition procedure, small metallic particles of the refractory high-melting metal niobium are produced. These particles offer several potential areas of applications, like in heterogeneous catalysis or as hard-surface coating materials. Overall, a new, easy-to-use method for surface modifications is described.

Keywords: cluster, halide, niobium, surface improvement

1. INTRODUCTION

As long as humans have inhabited the earth various methods for surface modification have been of extreme importance, like hardening, corrosion protection or wear protection, not to forget painting and coloring.[1] In recent years, significant amount of research effort in materials science and in other related fields has been focused on nano scaled materials, principally due to their difference in behavior compared to the bulk

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materials. As expected, nano scaled materials have also found their application in the field of surface improvement and surface modification. As examples, the well-known Lotus Effect[2,3] or several sorts of commercialized hardening car paintings[4] should be mentioned.

In this context, group 5 transition metals are an especially interesting group of materials. These metals, called refractory metals due to their high melting points and high tensile strengths and also some of their compounds, show interesting material properties, used, for example, in catalysis[5,6] or as wear and thermal coatings.[7,8]

From a chemical point of view, an interesting property of most of the refractory metals (among other early transition elements) is their ability to form cluster compounds. In terms of atoms and molecules we will refer to cluster compounds as aggregates of at least two metal atoms with strong metal-metal bonds, which have their coordination spheres saturated by non-metal ligand atoms.[9] The metal atoms in clusters are usually ordered in geometrical motives. A very common motive is an octahedron with 6 metal atoms.[10–12] Choices for ligands are quite often halogenido of chalcogenido moieties. Two possible arrangements exist for the ligand atoms (X) around an octahedron of the metal atoms (M). On the one hand, the metals of the group 4 and 5 of the periodic chart tend to form clusters with ligands bridging two M atoms over the octahedral edges ($[M_6X_{12}]$ type). On the other hand, the clusters coming from the elements in group 6 and 7 tend to have ligands bridging three M atoms over the faces ($[M_6X_8]$ type). These bridging ligands are called *inner* ligands, X^{i}.[13–23] In addition to the *inner* ligands, every octahedral M_6 cluster has further ligands bonded exo to the M atoms. These are called *outer* ligand atoms X^{a} $[M_6X^{\mathrm{i}}_{12}X^{\mathrm{a}}_6]$ *or* $[M_6X^{\mathrm{i}}_8X^{\mathrm{a}}_6]$, respectively, according to the notation of Schäfer et al.[24] Compounds with these cluster structures have found some very interesting applications; for example, in catalysis[25,26] or in the design of magnetic or luminescent materials.[27]

We report here a novel use of niobium cluster halides as precursors to obtain metallic niobium particles on metallic and non-metallic surfaces. Thanks to its refractory metal character, this niobium coating is intended to modify the properties of the bulk material used as substrate, especially their mechanical properties (hardening coatings) and thermal properties (thermo barrier coatings).

2. PROCEDURE TO MODIFY SURFACES BY CLUSTER DEPOSITION AND THERMAL DECOMPOSITION

The modification of selected metallic surfaces or glass takes place in three steps. The first step is the preparation of the coating precursor. This is a metal-rich niobium halide cluster compound soluble in polar solvents. In the second step, the substrate surface is treated with a solution of the niobium cluster precursor in order to achieve deposition of solid cluster material on the surface. Finally, in the third step, the clusters are decomposed in order to obtain elemental metal particles on the surface. The cluster decomposition is achieved by heating the cluster coated substrate. After the second and third step, EDX (Energy Dispersive X-ray spectroscopy) and SEM (Scanning Electron Microscopy) analyses are performed to monitor the homogeneity, distribution, and size of the formed particles.

2.1. Preparation of the Coating Precursor

Niobium halide cluster compounds of the type A^I_4 [Nb_6Cl_{18}] (A^I = Na, K, or Rb) are used for the experiments, which are prepared in the form of dark green powders. Starting materials are elemental niobium powder, $NbCl_5$ and carefully dried A^ICl. The chemical reaction is carried out following a high-temperature solid-state chemistry procedure similar to the one described by Fleming et al.[15] summarized in the already known reaction shown in (1).

$$20\ A^I\mathrm{Cl} + 14\ \mathrm{NbCl_5} + 16\ \mathrm{Nb} \xrightarrow{\Delta} 5\ A^I_4[\mathrm{Nb_6Cl_{18}}] \qquad (A^I = \mathrm{Na, K, Rb}) \tag{1}$$

In order to be able to evenly distribute the cluster materials on the substrate surfaces, the solid powder of the cluster compound is dissolved in methanol. Consequently, the cluster powder and methanol are sealed in glass ampoules, which are heated in a sand bath at 110°C. After 24 hours a dark green solution is obtained. Undissolved material is filtered off.

2.2. Deposition of the Coating Precursor

For our investigations the chosen substrates include the metals aluminum and copper, as well as glass. In order to have clean as well as grease-free substrate surfaces and to achieve a homogeneous distribution of the cluster solution, the surfaces are cleaned with acetone. For the purpose of obtaining uniformly distributed cluster material on the substrate surfaces, two different techniques were tested, the *cluster solution spreading* and *substrate submerging* technique. In the *cluster solution spreading* technique the cluster solution is evenly distributed on the cleaned surface and the solvent is slowly evaporated at room temperature. In the *substrate submerging* technique the previously cleaned substrate is placed in the cluster solution and left there up to 15 days without evaporation of the solvent. The parameters that have been varied are the cluster concentration in the solution, the temperature of the solution and of the substrate, the time of exposure (or submerging), and the type of counter cation present in the precursor material. Our experiments have shown that direct spreading of the cluster solution on the surfaces produces better results regarding the homogeneity on the distribution of cluster particles. This is in accordance with the results of Prokopuk and Shriver in their work on niobium clusters on gold substrates.[28] The graphs on the left side of Figure 1 show results of the direct spreading of a solution of $K_4[Nb_6Cl_{18}]$ in methanol on a copper substrate. Graph A1 is a SEM picture ($100 \times 100\,\mu m$) of the particles of $K_4[Nb_6Cl_{18}]$, formed during evaporation of the methanol solvent. Graphs A2 to A5 in Figure 1 show EDX scans along the line in Graph A1. These EDX data prove that the cluster composition does not change during the treatment with the solvent. The counting rates in the range of the background in A5 indicate the absence of oxygen. It is necessary to check the deposited cluster material for oxygen because the halogenido ligands of the cluster in solution can be easily substituted against oxygen-containing ligands, like methanol,[29] water, or hydroxide ions, if exposed to moist air.

Different growth behaviors can be observed on the samples, depending mainly on the deposition time and the substrate. The observed growth behavior of the cluster particles is consistent with that described in the literature[30,31] for the growth of metallic particles from ligand-free clusters. The observations on the SEM pictures suggest that the formation of ligand-based cluster particles follows the same steps as the formation of ligand-free cluster assemblies. A sketch of the different steps of the particle growth process is shown in Figure 2. Starting from the *initial* surface, the stages include *formation, early stage growth*, and *late stage growth*.

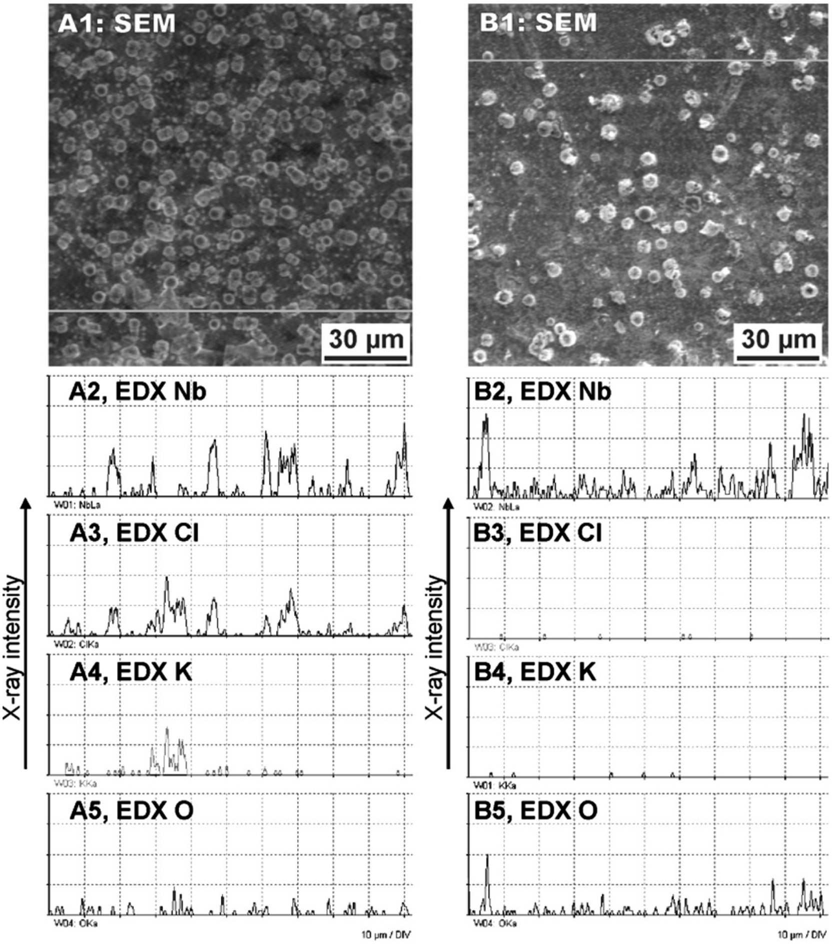


Figure 1. **A1** to **A5**: SEM micrograph and EDX line scan graphs for $K_4[Nb_6Cl_{18}]$ on a copper substrate, deposited using the *spreading* technique; **B1** to **B5**: SEM micrographs and EDX line scan graphs of the niobium particles obtained after cluster decomposition (1 hr at 900°C).

As soon as the precursor cluster compound is in contact with the *initial* surface the *formation* phase begins, with random *nucleation* and *spinodal decomposition* as the two dominating processes. In both cases the particles reach diameters up to 1 µm. Following this phase, the system evolves to the *early stage growth*, where *coalescence, diffusive growth*, and the *break-up of the spinodal structures* are the distinguishable

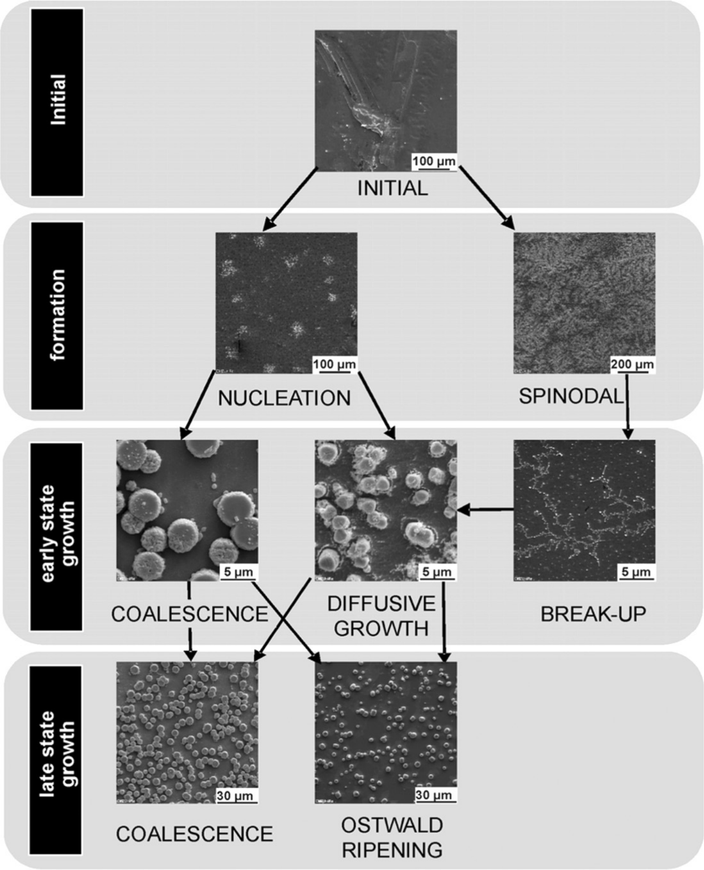
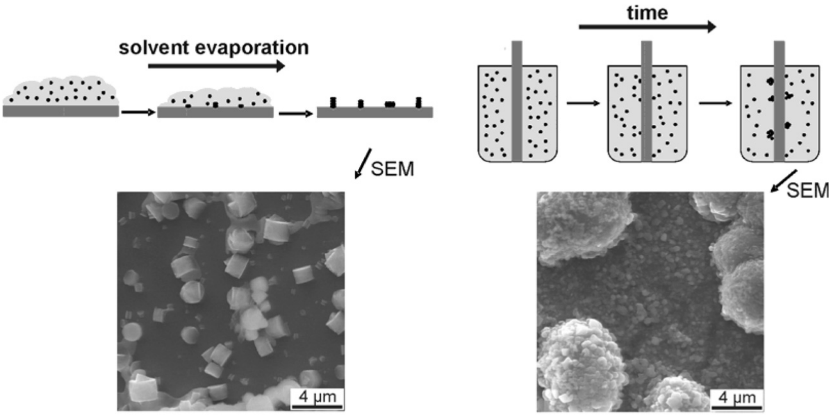


Figure 2. Overview of the particle formation stages of A^{I}_4 [Nb_6Cl_{18}] (A^{I} = Na, K, Rb) on different surfaces, adapted from the work of Zinke-Allmang et al.[30] SEM images of the different growth stages. The used substrates were aluminum *(spinodal)*, copper (*initial* and *diffusive growth*), glass (*coalescence, break-up* and *Ostwald ripening*), and zirconium (*nucleation*).

processes (see Figure 2). In this phase the particles reach diameters up to 4 µm. Finally, in the *late stage growth direct ripening* is the leading process, but *coalescence* can also take place in this part of the process. In this step the particle sizes enlarge up to 5 µm in diameter. However, the particle size can widely vary depending on the substrate and Nb cluster precursor. Nevertheless, the diameter of the cluster particles is found in the range from 100 nm to 5 µm for the deposition using the *spreading* technique and from 200 nm to 3.2 µm for the *submersion* technique.



(a) **Cluster solution spreading** (b) **Substrate submerging**

Figure 3. Growth modes of the cluster particles on surfaces. (a) Formation of cylindrical particles of $K_4[Nb_6Cl_{18}]$ on a chromium substrate obtained by the solution *spreading* technique. (b) Spherical particles of $Na_4[Nb_6Cl_{18}]$ on a copper substrate, obtained by the *substrate submerging* technique.

Interestingly, the shape of the cluster particles that are deposited on the substrate surfaces differs for the *cluster solution spreading* and the *substrate submerging* technique. The direct deposition of the cluster solution on the substrate surface has been found to lead mainly to the formation of cylindrical particles, as shown in Figure 3a. The submersion of the substrates in the cluster solution has been found to lead mainly to the formation of spherical particles (Fig. 3b). In this last case, the size of the particles is also dependant on the deposition time.

2.3. Cluster Decomposition – Metallic Nb Particles

The third step of the process to produce metallic niobium particles on substrate surfaces is to decompose the niobium cluster material. By heating niobium cluster compounds to high temperature, the chemical reaction represented in (2) takes place, according to Simon et al.[32]

$$2\ A^I[\mathrm{Nb_6Cl_{18}}]_{(s)} \xrightarrow{\Delta} 8\ A^I\mathrm{Cl}_{(g)} + 7\ \mathrm{NbCl}_{4(g)} + 5\ \mathrm{Nb}_{(s)} \qquad (2)$$

For this purpose, the samples are placed in a silica tube and heated in a furnace for a few minutes at a temperature above 600°C. In order to eliminate the volatile $NbCl_4$ and the A^ICl, the tube is put under high vacuum. After the heating, no traces of chlorine or the respective counter ions A^I are found by EDX and EDX mapping. One example is given by the graphs on the right side of Figure 1. The SEM picture (graph B1) shows that the metallic niobium particles are of almost uniform size. The presence of niobium and the absence of chlorine and potassium are proven by the EDX line scans shown in graphs B2 to B4. The presence of small amounts of oxygen is indicated by the EDX scan shown in graph B5. The size of the niobium particles has also been found to be substrate and precursor dependent, with particles up to 5 µm in diameter being obtained using the *spreading* technique and up to 1 µm for those being obtained through the *submersion* method.

As stated above, further investigations were conducted to study the influence of temperature, heating time, and heating rate on the particle formation. Concerning the cluster decomposition temperature, it has been observed that the optimal temperature depends on the substrate being, for example, 900°C in the case of copper substrates or 600°C in the case of aluminum substrates. It has also been observed that, when increasing this temperature up to 1000°C, the niobium starts to crystallize in the form of needles. Concerning the heating time, short time periods of 5 minutes have been found to be sufficient to decompose the cluster material. When longer heating times are used the metallic particles grow larger, presumably through a sintering process. Finally, in terms of the heating rate from room temperature to the desired temperature, the ideal value is of 5°C/min, since it has been found that with a faster raise of temperature the particles become smaller, but less defined.

3. CONCLUSIONS

Our investigations have shown that small particles of metal-rich niobium halide clusters can be deposited on the surfaces of metallic substrates as well as on glass. The cluster compounds can be thermally decomposed to small metallic niobium particles, which cover the substrate surfaces. Several process parameters were systematically varied in order to investigate their influence on the particle size and morphology. Current evidence indicates that the size of the particles before and after the cluster decomposition depends on the type of substrate and the cation in the cluster compound used as precursor (A^I = Na, Rb, or K). It has been observed that smaller particles are formed when using the *submersion* technique as precursor deposition method. The shape of the particles has also been found to be dependent on the precursor deposition method. Predominantly cylindrically shaped particles are obtained when using *direct spreading* of the precursor solution and predominantly spherically shaped particles when using the *submersion* of the substrate in the precursor solution.

4. OUTLOOK

The ability to deposit metal-rich niobium cluster compounds as small particles on substrates as well as to produce layers of small metallic particles offers various opportunities for applications. Substrates covered with particles of metals or metal-rich compounds certainly can serve as catalysts for a multitude of chemical reactions. For example, Kamiguchi et al. have shown that crushed crystals of niobium halide cluster compounds are useful as heterogeneous catalysts.[33,34]

The small particles spread on solid substrates, which are produced by our method, should have large surface areas and could be even better heterogeneous catalysts. This subject is currently being pursued. Further work is directed towards the use of laser light as an alternative energy source to decompose the cluster compounds. Laser light would have the advantage of not significantly increasing the temperature of the substrate, so that substrates with low melting point, for example polymers, could be used. First promising results are that rather low beam intensities are sufficient for the decomposition of the clusters and that wave lengths around 800 nm produce acceptable cluster decomposition rates.

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REFERENCES

1. Bach, F.-W., A. Laarmann, and T. Wenz. 2004. *Modern Surface Technology*, Wiley-VCH, Weinheim, Germany.
2. Cerman, Z., A. K. Stosch, and W. Barthlott. 2004. *Biol. Unserer Zeit.*, **34**: 290–296.
3. Oles, M., E. Nun, G. Dombacher, and B. Schleich. 2000. 1st Annual International IEEE-EMBS Special Topic Conference on Microtechnologies in Medicine & Biology Proceeding, 331–333.
4. Fröba, M., W. Scheld, C. Gath, and F. Hoffmann. 2004. *Chem. Unserer Zeit.*, **38**: 162–171.
5. Liang, G., J. Huot, S. Boily, A. Van Neste, and R. Schulz. 1999. *J. Alloys Comp.*, **292**: 247–252.
6. Breysse, M., G. Djega-Mariadassou, S. Pessayre, C. Geantet, M. Vrinat, G. Perot, and M. Lemaire. 2003. *Catal. Today.*, **84**: 129–138.
7. Gibson, I. P. 1981. *Thin Solid Films*, **83**: 27–36.
8. Padture, N. P., M. Gell, and E. H. Jordan. 2002. *Science*, **296**: 280–284.
9. The term "cluster" is used in various ways. In physics, it often refers to a small, ligand-free particle of solely metal atoms, see for example Meiwes-Broer, K.-H. 2000. *Metal Clusters at Surfaces*, Springer Verlag, Berlin-Heidelberg. In coordination chemistry "cluster" often means a multinuclear coordination compound without direct metal-metal bonds. See for example Abe, M., T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K. Uosaki, and Y. Sasaki. 2003. *Angew. Chem.*, **115**: 3018–3021.
10. Cotton, F. A. 1963. *Inorg. Chem.*, **2**: 1166–1171.
11. Cotton, F. A. 1964. *Inorg. Chem.*, **3**: 1217–1220.
12. Braunstein, P., L. A. Oro, and P. R. Raithby. 1999. *Metal Clusters in Chemistry, Vol. 1*, Wiley-VCH, Weinheim.
13. Simon, A., H. G. Schnering, H. Wöhrle, and H. Schäfer. 1965. *Z. Anorg. Allg. Chem.*, **339**: 155–170.
14. Kuhn, P. J. and R. E. McCarley. 1965. *Inorg. Chem.*, **4**: 1482–1486.
15. Fleming, P. B., L. A. Müller, and R. E. McCarley. 1967. *Inorg. Chem.*, **6**: 1–4.
16. Simon, A. 1988. *Angew. Chem., Int. Ed. Engl.*, **27**: 159–183.
17. Perrin, C. and M. Sergent. 1991. *Eur. J. Solid State Inorg. Chem.*, **28**: 933–948.
18. Perrin, C., S. Cordier, S. Ihmaine, and M. J. Sergent. 1995. *Alloys Comp.*, **229**: 123–133.
19. Hughbanks, T. 1995. *J. All. Comp.*, **229**: 40–53.
20. Corbett, J. D. 1996. *J. Chem. Soc., Dalton Trans.*, **5**: 575–587.
21. Meyer, G. 1998. *Chem. Rev.*, **88**: 93–107.
22. Propkopuk, N. and D. F. Shriver. 1999. *Adv. Inorg. Chem.*, **46**: 1–49.
23. Corbett, J. D. 2000. *J. Chem. Soc., Dalton Trans.*, **13**: 1961–1968.

24. Schäfer, H. and H. G. von Schnering. 1964. *Angew. Chem.*, **20**: 833–849.
25. Shephard, D. S., T. Maschmeyer, G. Sankar, J. M. Thomas, D. Ozkaya, B. F. G. Johnson, R. Raja, R. D. Oldroyd, and R. G. Bell. 1998. *Chem. Eur. J.*, **4**: 1214–1224.
26. Braunstein, P., L. A. Oro, and P. R. Raithby. 1999. *Metal Clusters in Chemistry, Vol. 2*, Wiley-VCH, Weinheim.
27. Cordier, S., F. Dorson, F. Grasset, Y. Molard, B. Farbre, H. Haneda, T. Sasaki, M. Mortier, S. Ababou-Girard, and C. Perrin. 2009. *J. Clust. Sci.*, **20**: 9–21.
28. Propkopuk, N. and D. F. Shriver. 1998. *Chem. Mater.*, **10**: 10–12.
29. Piedra-Garza, L. F. and M. Köckerling. 2006. *Inorg. Chem.*, **45**: 8829–8831.
30. Zinke-Allmang, M., L. C. Feldman, and M. H. Grabow. 1992. *Surf. Sci. Rep.*, **16**: 377–463.
31. Meiwes-Broer, K.-H. 2000. *Clusters at Surfaces*, Springer Verlag, Berlin-Heidelberg.
32. Simon, A., H.-G. von Schnering, and H. Z. Schäfer, 1968. *Naturf.*, **B361**: 235–248.
33. Kamiguchi, S., M. Watanabe, K. Kondo, M. Kodomari, and T. J. Chihara. *Molec. Cat.*, **203**: 153–163.
34. Kamiguchi, S., S. Takaku, M. Kodomari, and T. Chihara. 2006. *J. Molec. Cat. A*, **260**: 43–48.