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Highly active hydrotreatment catalysts prepared with chelating agents

Takehiro Shimizu*, Kazutaka Hiroshima, Takehide Honma,
Takeo Mochizuki, Muneyoshi Yamada

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University Aoba, Aramaki, Aoba-ku, Sendai 980-77, Japan

Abstract

Hydrotreatment catalysts (Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3 and Ni–W/Al_2O_3) were prepared by an impregnation method using an aqueous solution containing a chelating agent (nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) or *trans*-1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA)). Co–Mo/Al_2O_3 and Ni–W/Al_2O_3 prepared with the chelating agents showed higher hydrodesulfurization (HDS) activity as well as hydrogenation (HYD) activity under high pressure (5.1 MPa) than those prepared without the chelating agents. Co–Mo/Al_2O_3 prepared with CyDTA showed ca. 70% higher HDS activity for benzothiophene (BT) than that prepared without it. HYD activity of Ni–W/Al_2O_3 for *o*-xylene was promoted about 65% by the addition of CyDTA. FT-IR of nitric oxide (NO) adsorbed on the sulfided Co–Mo/Al_2O_3's suggested that Co was highly dispersed over the catalyst surface when the catalysts were prepared with the chelating agents.

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Keywords: Hydrotreatment catalysts; Chelating agents; NTA; EDTA; CyDTA; Hydrodesulfurization; Hydrogenation

1. Introduction

Co–Mo/Al_2O_3 and Ni–W/Al_2O_3 catalysts, which are active in sulfided form, are currently used for hydrotreatment. The former is used for its high hydrodesulfurization (HDS) activity and high sulfur tolerance, and the latter is employed when higher hydrogenation (HYD) activity is required. It is well known that Co or Ni has promoting effect, i.e., a small amount of Co or Ni increases catalytic activity (HDS as well as HYD) of Mo/Al_2O_3 or W/Al_2O_3 catalysts. This is the major reason why the catalyst system has been the subject to be investigated for this several decades. Many efforts have been devoted to the clarification of the structural or chemical form over the catalysts and to the specification of the practical active phase.

Topsøe et al. have proposed so called "Co–Mo–S model" in which Co is located at edge sites of MoS_2-like crystallites and that the specific phase is catalytically active [1]. On the other hand, Delmon et al. have proposed a model termed "remote control model" in which hydrogen molecules dissociate on cobalt sulfides and spill over and then reaction occurs on MoS_2 or Co–Mo–S phase [2]. These two models might be compatible, but they have not reached general agreement on the type of structures present in the active catalysts and the origin of promotion.

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*Corresponding author.

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Confusion has arisen from the variety of species exist on the catalysts, and has made it difficult to discuss the role of individual species.

Recently, an important development has been made as to the Co–Mo–S structure by van Veen et al. [3]. In the study expecting to understand "a real support effect", they have found that Co–Mo–S phase is selectively formed using nitrilotriacetic acid (NTA) in impregnating solution by means of Mössbauer emission spectroscopy. They have also found that the catalysts prepared with NTA have higher activity than conventionally prepared one for gas-phase thiophene HDS under ambient pressure. The preparing method has been originally invented by Thompson of Shell group for SiO_2 supported hydrotreatment catalysts [4]. The preparing method has been applied to the study of extended X-ray absorption fine structure (EXAFS) measurement, and it was suggested that Co is located at the edge site of MoS_2 structure and is coordinated with five or six sulfurs [5,6]. In these studies, the promoting effect of NTA for thiophene HDS activity of Co–Mo catalyst was again reported. They have further applied the catalysts, i.e., Co(Ni)–Mo/Al_2O_3 prepared with NTA, to dibenzothiophene (DBT) HDS under 3.5 MPa, and have reported negative effect of NTA [7].

On the basis of the works quoted above, we have investigated the effects of several chelating agents on activity and surface structure of hydrotreatment catalysts, and have tried to give an answer for the requirement of environmentally benign "green fuel". In the present work, we will show that Co–Mo/Al_2O_3 and Ni–W/Al_2O_3 catalysts can be promoted in their original functions, when the appropriate chelating agent is used during their preparation. Considering the practical conditions, we have adopted high pressure when it was feasible.

2. Experimental

All the catalysts were prepared by incipient wetness method. The catalysts were prepared with a chelating agent as follows [8,9]: γ-Al_2O_3 was impregnated with an aqueous solution containing a chelating agent, cobalt nitrate (or nickel nitrate) and ammonium paramolybdate (or ammonium metatungstate), then dried at 393 K in air. The molar ratio of a chelating agent to Mo (or W) was 1.2 for NTA, and 0.6 in the cases of ethylenediaminetetraacetic acid (EDTA) and *trans*-1,2-cyclohexanediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (CyDTA). These catalysts are denoted hereinafter as "chelating agent"–"combination of metals", e.g., NTA–CoMo. The catalysts prepared without the chelating agents were used as the reference, and are denoted as "combination of metals", e.g., CoMo. γ-Al_2O_3 (Nippon Ketjen Co., LTD., 333 m^2/g), calcined at 793 K for 12 h, was used as a support. Cobalt nitrate, nickel nitrate, ammonium paramolybdate (Wako Pure Chemical Industry LTD.), ammonium metatungstate (Fluka) were used as metal sources. NTA, EDTA and CyDTA were guaranteed reagents purchased from Tokyo Chemical Industry Co., LTD. These chemicals were utilized as received.

The catalysts were sulfided in situ in the stream of 5% H_2S/H_2 under 1.1 MPa at 673 K, and individually supplied for activity tests or surface characterization with NO as a probe. Activity tests were carried out with a conventional fixed bed flow reactor. The conditions of HDS reactions were as follows: 5 mol% benzothiophene (BT) in *n*-dodecane (or 2.5 mol% DBT in decalin), 543 (or 573) K, 5.1 MPa, LHSV 300 h^{-1}, in H_2 stream (300 ml/min), H_2/feed 1000 v/v. The conditions of HYD reactions were as follows: *o*-xylene (or 1-methylnaphthalene (1-MN)), 673 K, 5.1 MPa, LHSV 6 (or 75) h^{-1}, in H_2 stream (300 ml/min), H_2/feed 1000 v/v. Products were analyzed by GC (FID) and/or GC-MS. The details of the apparatus and the procedure have been described in our preceding papers [10,11]. NO adsorption measurements and FT-IR of adsorbed NO were carried out as mentioned in our previous reports [9,12–14]. The NO adsorption measurements were carried out by pulse method. The amount of NO passed through catalyst bed was determined with GC (TCD) and the amount of NO adsorbed on the catalyst was calculated. In the FT-IR of adsorbed NO measured by diffuse reflectance spectroscopy (DRS), specially designed in situ cell was used [15]. The catalysts were sulfided at high pressure (1.1 MPa) as mentioned above, and NO was adsorbed on them to be saturated at ambient conditions in 10% NO/He flow.

3. Results and discussion

HDS activity for BT was estimated by ethylbenzene (EB) yield per metal contained in the used catalyst.

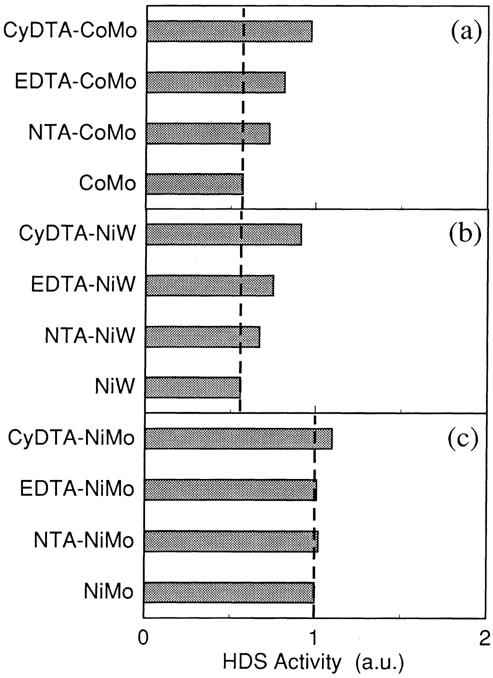


Fig. 1. Relative activity of the catalysts prepared with a chelating agent: Hydrodesulfurization (HDS) of benzothiophene. Pretreatment: in 5% H_2S/H_2, 673 K, 1.1 MPa. Reaction: 5 mol% benzothiophene/*n*-dodecane, in H_2, 543 K, 5.1 MPa, LHSV 300 h^{-1}.

That of CoMo and NiW was promoted by being prepared with the chelating agents (Fig. 1(a), (b)). In both cases, the degree of promotion appeared in the following order: CyDTA > EDTA > NTA > none. CyDTA-CoMo and CyDTA-NiW have attained about 70% and 65% higher HDS activity than those prepared without it, respectively. On the other hand, NiMo was not affected with the chelating agents (Fig. 1(c)). We believe that the chelating agents have a role of promoting to form highly active sites. If the active sites have been already completely formed, the addition of the chelating agents could not increase the catalytic activity. NiMo originally has high activity for the reaction, so there might be little space to be promoted. The effects of these additives were further examined in HDS of DBT. In this reaction, biphenyl (BP) and cyclohexylbenzene (CHB) were obtained as main products in the condition adopted here. The sum of BP and CHB yield per metal contained in the used catalyst was evaluated as HDS activity of each catalyst. The activities of CoMo and NiW were also promoted by being prepared with the chelating agents (Fig. 2(a), (b)). Also in these cases, the extent of promotion appeared in the order: CyDTA > EDTA > NTA > none. The promotion ratio of CoMo with CyDTA was ca. 25%, but only a little with NTA. Van Veen et al. have reported negative results as to HDS of DBT on NTA-modified Co(Ni)-Mo/Al_2O_3 [7]. At this time, we cannot explain this contradiction. HDS activity for DBT was much more promoted in Ni–W/Al_2O_3 than in Co–Mo/Al_2O_3 with the chelating agent addition. We can say that HDS activity of Ni–W/Al_2O_3 is more susceptible to the preparation method than that of Co–Mo/Al_2O_3. For HDS of DBT's, especially 4- and/or 6-alkyl-substituted DBT, it is known that HYD activity is important [16,17]. So we have examined HYD activities of the catalysts.

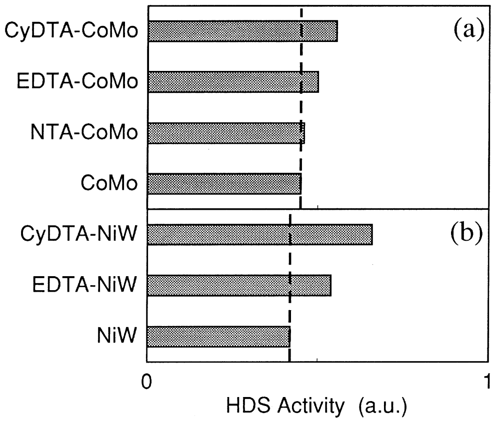


Fig. 2. Relative activity of the catalysts prepared with a chelating agent: Hydrodesulfurization (HDS) of dibenzothiophene. Pretreatment: in 5% H_2S/H_2, 673 K, 1.1 MPa. Reaction: 2.5 mol% dibenzothiophene/decalin, in H_2, 573 K, 5.1 MPa, LHSV 300 h^{-1}.

HYD activities for *o*-xylene (the sum yield of 1,2-dimethylcyclohexane and other cycloaliphatic compounds per metal contained in the used catalyst) of CoMo and NiW were promoted about 40% and 65% by the addition of CyDTA, respectively Fig. 3(a), (b)). In the case of Co–Mo/Al_2O_3, the degree of promotion was almost same in the three additives. HYD activity for 1-MN (the sum yield of 1-methyltetralin and 5-methyltetralin per metal contained in the used catalyst) of NiW was promoted about 40% by the addition of CyDTA, but that of CoMo was not so much promoted (Fig. 4(a), (b)).

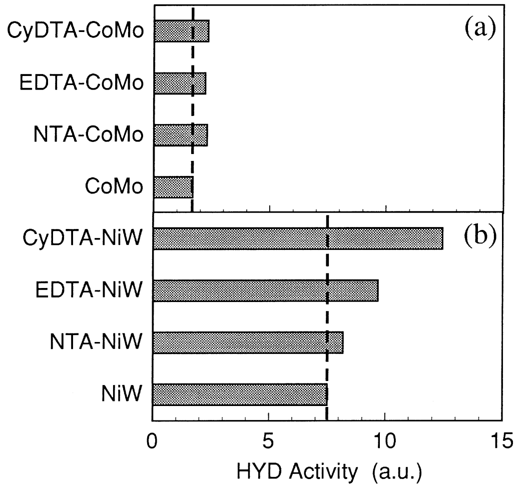


Fig. 3. Relative activity of the catalysts prepared with a chelating agent: Hydrogenation (HYD) of *o*-xylene. Pretreatment: in 5% H_2S/H_2, 673 K, 1.1 MPa. Reaction: *o*-xylene (neat), in H_2, 673 K, 5.1 MPa, LHSV 6 h^{-1}.

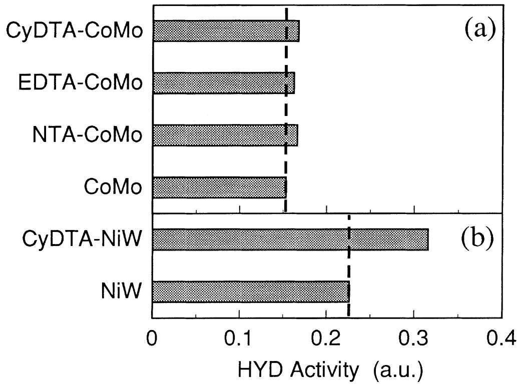


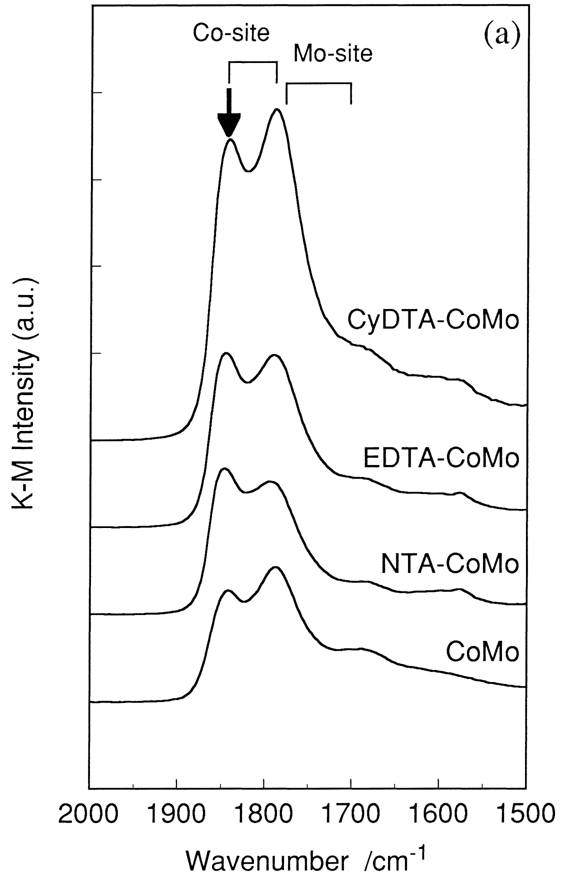
Fig. 4. Relative activity of the catalysts prepared with a chelating agent: Hydrogenation (HYD) of 1-methylnaphthalene. Pretreatment: in 5% H_2S/H_2, 673 K, 1.1 MPa. Reaction: 1-methylnaphthalene (neat), in H_2, 673 K, 5.1 MPa, LHSV 75 h^{-1}.

These promoting effects did not appear in each component system, i.e., Co/Al_2O_3, Mo/Al_2O_3, Ni/Al_2O_3 or W/Al_2O_3. It is obvious that the chelating agents improve the promoting effects of Co for CoMo and that of Ni for NiW. The chelating agents would have a role to promote formation of specific bimetal phase. It can be said that NTA does not necessarily fully promote the formation of highly active sites of Co–Mo/Al_2O_3 or Ni–W/Al_2O_3, because CyDTA apparently overcomes NTA in promoting effect. Van veen et al. have suggested that the role of NTA is to complex with both Co and Mo [3,6]. Interestingly, CyDTA does not chelate with Mo [18,19] or W [18] as observed by NMR. It seems that the chelating with Mo or W is not necessary to improve the promoting effect of Co or Ni.

Fig. 5 shows FT-IR/DRS around N–O stretching region of the sulfided catalysts on which NO was adsorbed. For Co–Mo/Al_2O_3, Kubelka-Munk (K-M) function intensity (corresponding to absorbance) of NO adsorbed on Co-site (ca. 1840 cm^{-1}) is apparently higher in the case the catalyst was prepared with the chelating agents in the following order: CyDTA > EDTA > NTA > none (Fig. 5(a)). This order is well consistent with the order of HDS activity. Also for Ni–W/Al_2O_3's, K-M intensity of NO adsorbed on Ni-site (ca. 1830 cm^{-1}) is higher for CyDTA-NiW than for NiW (Fig. 5(b)). It is suggested that Co (or Ni) is highly dispersed and much amount of Co-site (or Ni-site) to which NO can be adsorbed are generated over the surface, when the catalysts were prepared using the chelating agents, especially CyDTA.

It was easily considered that there might be larger amount of active sites in more active catalysts. In general, the degree of coordinative unsaturation is associated with the amount of catalytically active sites, and NO would be selectively adsorbed on the coordinatively unsaturated sites (CUS). Accordingly, the amount of catalytically active sites could be estimated by means of NO adsorption measurement. In Table 1, NO uptakes of the sulfided catalysts are shown. It seems that there is no correlation between the value and the catalytic activity. That is, the relative activity cannot be explained only with the amount of CUS or the amount of catalytically active sites. Co–Mo/Al_2O_3's and Ni–W/Al_2O_3's prepared with the chelating agents should have highly active sites than those prepared without them.

From these results, the chelating agents, especially CyDTA, might have roles to disperse Co (or Ni) in effective phases, and the phases should be active sites. These active sites might come from utilizing the edge site of MoS_2- (or WS_2-) like structure formed on the sulfided catalysts as Topsøe et al. has suggested [1]. We have inferred that highly active sites are more



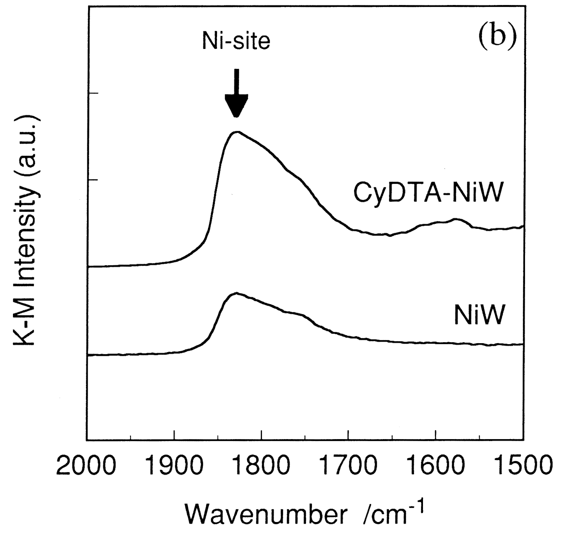


Fig. 5. FT-IR/DRS of NO adsorbed on the sulfided catalysts. Pretreatment: in 5% H_2S/H_2, 673 K, 1.1 MPa. NO adsorption: in 10% NO/He, ambient.

Table 1
NO uptake of the sulfided catalysts

Catalyst	NO uptake (mol/mol-metal)
CyDTA-CoMo	0.15
NTA-CoMo	0.14
CoMo	0.15
CyDTA-NiW	0.10
NTA-NiW	0.08
NiW	0.07
CyDTA-NiMo	0.16
NTA-NiMo	0.11
NiMo	0.13

Pretreatment: 5% H_2S/H_2, 673 K, 1.1 MPa.
Adsorption: 10% NO/He (by pulse), ambient.

selectively formed when Ni–W/Al_2O_3 as well as Co–Mo/Al_2O_3 are prepared with CyDTA than NTA.

4. Conclusion

In the present work, we have investigated performance of hydrotreatment catalysts (Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3 and Ni–W/Al_2O_3) prepared with a chelating agent (NTA, EDTA, or CyDTA) for HDS or HYD under high pressure (5.1 MPa), and have shown that Co–Mo/Al_2O_3 and Ni–W/Al_2O_3 catalysts can be promoted in their original functions, when the appropriate chelating agent is used during their preparation. The amount of NO adsorption suggested that the modified catalysts have comparable number of CUS to the conventional ones. FT-IR of adsorbed NO indicated that the modified catalysts have much more dispersive and exposed Co sites than the conventional one. From these results, we have considered that the addition of the chelating agents induced the formation of highly active sites, but not the increase in the number of CUS. And we have inferred that the higher activity of Co–Mo (or Ni–W)/Al_2O_3 modified with one of these chelating agent came from the higher dispersion of Co (or Ni), and that highly active sites are more selectively formed when Ni–W/Al_2O_3 as well as Co–Mo/Al_2O_3 are prepared with CyDTA than NTA. The information obtained in the present work should be relevant not only to HDS or HYD but also to other hydrotreating reactions.

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References

[1] H. Topsøe, B.S. Clausen, Catal. Rev.-Sci. Eng. 26 (1984) 395, and references cited therein.
[2] B. Delmon, G.F. Froment, Catal. Rev.-Sci. Eng. 38 (1996) 69, and references cited therein.
[3] J.A.R. van Veen, E. Gerkema, A.M. van der Kraan, A. Knoester, J. Chem. Soc., Chem. Commun. (1987) 1684.
[4] M.S. Thompson, Eur. Pat. Appl., EP 0181035, (1986).
[5] S.M.A.M. Bouwens, J.A.R. van Veen, D.C. Koningsberger, V.H.J. de Beer, R. Prins, J. Phys. Chem. 95 (1991) 123.
[6] S.M.A.M. Bouwens, F.B.M. van Zon, M.P. van Dijk, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, D.C. Koningsberger, J. Catal. 146 (1994) 375.
[7] J.A.R. van Veen, H.A. Colijn, P.A.J.M. Hendriks, A.J. van Welsenes, Fuel Proc. Technol. 35 (1993) 137.
[8] T. Shimizu, S. Kasahara, T. Kiyohara, K. Kawahara, M. Yamada, Sekiyu Gakkaishi, J. Jpn. Pet. Inst. 38 (1995) 384.
[9] K. Hiroshima, T. Mochizuki, T. Honma, T. Shimizu, M. Yamada, Appl. Surf. Sci. 121/122 (1997) 433.
[10] M. Yamada, A. Saito, T. Wakatsuki, T. Obara, J.-W. Yan, A. Amano, Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) 30 (1987) 412.
[11] M. Yamada, Y.-L. Shi, T. Obara, K. Sakaguchi, Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) 33 (1990) 227.
[12] T. Obara, M. Yamada, A. Amano, Chem. Lett. (1986) 2003.
[13] S. Kasahara, S. Miyabe, T. Shimizu, H. Takase, M. Yamada, Sekiyu Gakkaishi (J. Jpn. Pet. Inst.) 38 (1995) 81.
[14] N. Koizumi, M. Iijima, S. Kasahara, M. Yamada, Chem. Lett. (1996) 815.
[15] N. Koizumi, K. Takahashi, M. Yamazaki, M. Yamada, Catalysis Today 45 (1998) 315–320.
[16] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. de Beer, B.C. Gates, H. Kwart, J. Catal. 61 (1980) 523.
[17] T. Kabe, A. Ishihara, Q. Zhang, Appl. Catal. A 97 (1993) L1.
[18] T. Shimizu, K. Hiroshima, T. Mochizuki, M. Yamada, submitted for press.
[19] M.A. Freeman, F.A. Schultz, C.N. Reilley, Inorg. Chem. 21 (1982) 567.