ELSEVIER

Catalysis Today 63 (2000) 175–181

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Mechano-catalytic overall water splitting on some mixed oxides

Go Hitoki [a], Tsuyosi Takata [a], Shigeru Ikeda [a], Michikazu Hara [a],
Junko N. Kondo [a], Masato Kakihana [a,b], Kazunari Domen [a,c,*]

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b] *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[c] *CREST, JST (Japan Science and Technology), Japan*

Abstract

Simple transition metal oxides such as NiO, Co_3O_4, Fe_3O_4 and Cu_2O were found to catalytically decompose water into H_2 and O_2 by mechanical energy. The reaction is regarded as “mechano-catalytic” overall water splitting” and is a quite novel catalytic reaction. In this paper, some general aspects on the mechano-catalytic overall water splitting are reviewed on simple oxides. In addition, recent results on the mechano-catalytic activity of a groups of mixed oxides, wolramite-type oxides with a formula of ABO_4 (A = Fe, Co, Ni and Cu, etc., B = W, Mo), are shown. AWO_4 (A = Fe, Co, Ni and Cu) decomposed water into H_2 and O_2 under the supply of mechanical energy, indicating that mechano-catalytic overall water splitting proceeded on wolframite-type compounds containing 3d-transition metals. $AMoO_4$ (A = Fe, Co, Ni) also decomposed water into H_2 and O_2 under supply of mechanical energy. The reaction properties on wolframite-type oxides are discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mechano-catalyst; Water splitting; Mixed oxides

---

1. Introduction

Production of H_2 from water is an attractive candidate to establish a clean energy system of the future without relying on the fossil fuel. Under UV light irradiation, overall water splitting on various heterogeneous photocatalysts has been well-established. From the view point of solar energy utilization, the development of the photocatalysts which have response under visible light irradiation is current research target. During such kind of efforts, we recently have found somewhat different type of overall water splitting reaction, i.e. mechano-catalytic overall water splitting. An overall water decomposition was accomplished when some simple oxide powders such as NiO, Co_3O_4, Cu_2O, and Fe_3O_4 were suspended in distilled water and rubbed against the bottom wall of the reaction vessel by magnetic stirring [1–5]. The reaction proceeded steadily without any supply of electric or photon energy as long as the suspension was stirred by a rotating stirring rod. This implies that the mechanical energy given by the rotating stirring rod is essential for the reaction to take place. The reaction is thus regarded as “mechano-catalytic” overall water splitting, which is a novel catalytic reaction where mechanical energy is continuously converted into chemical energy [1–5].

In this study, the mechano-catalytic overall water splitting on some mixed oxides, i.e. wolframite-type oxides, ABO_4 (A = Fe(II), Co(II), Ni(II) and Cu(II), etc., B = W and Mo) were investigated. The structure of ABO_4 materials is monoclinic with two formula unit cells (AO_6 and BO_6). BO_6 is characterized by

---

* Corresponding author. Tel.: +81-45-924-5238; fax: +81-45-924-5282.
E-mail address: kdomen@res.titech.ac.jp (K. Domen).

PII: S0920-5861(00)00457-0

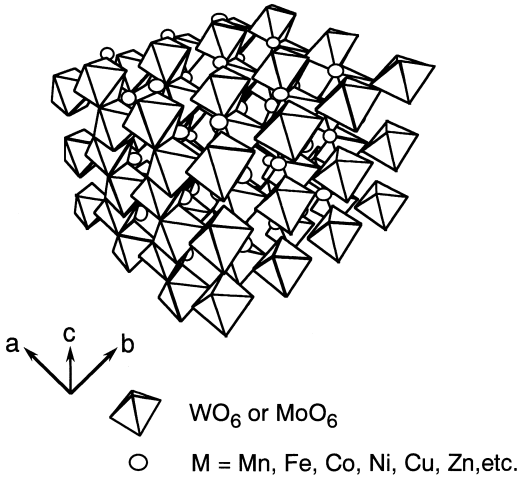

Fig. 1. Schematical structure of ABO_4 (A = Fe, Co, Ni and Cu, etc., B = W, Mo) compounds.

zigzag chains of oxygen octahedral coordinating the metal ions (A^{2+}) and aligned along the *c*-axis. There is a wide variety in wolframite-type oxide since the octahedral framework composed of WO_6 or MoO_6 can incorporate many different kinds of both non-transition and transition metals (Fig. 1). A systematic survey of the mechano-catalytic activity on the series of ABO_4 compounds would provide some information on the mechano-catalytic water decomposition in addition to our previous studies on simple oxides.

2. Experimental

ABO_4 was prepared from either MnO, Co_3O_4, NiO or CuO as a starting material A, and WO_3 or MoO_3 as B. The stoichiometric mixture of these metal oxide powders were calcined at 1173 K for 24 h [6–17]. The particle sizes and surface areas of prepared ABO_4 compounds were estimated to be about 0.5–10.0 μm by SEM and 0.1–3.0 $m^2\,g^{-1}$ by BET measurements, respectively. Although very weak diffractions' due to unreacted WO_3 and MoO_3 appeared in the XRD patterns for the ABO_3, it was confirmed that most part of the sample was composed of ABO_4 structure.

The reaction was carried out in a flat-bottomed reaction vessel made of Pyrex glass which was attached to a closed gas circulation system (about 800 cm^3) equipped with an evacuation line and a gas chromatograph. 0.1 g of catalyst was suspended in 200 cm^3 of distilled water by a revolving PTFE-sealed triangular pillar-shaped stirring rod on the flat bottom of reaction vessel. The stirring rod was revolved by a magnetic stirrer (F205, Tokyo Garasu Kikai) at the revolution rate of 1500 rpm. Before the reaction, the gas phase was completely evacuated for removing dissolved O_2 and N_2 in distilled water. In order to perform the reaction in dark, the reaction vessel was completely shielded from any light by aluminum foils and a black cloth. The evolved gas was accumulated and was analyzed by gas chromatograph.

3. Results and discussion

3.1. Summary of the mechano-catalytic water decomposition on simple oxides

Fig. 2 shows typical time courses of H_2 and O_2 evolution on one of the simple oxides, NiO. The reaction system was evacuated at 10–15 h intervals. Stoichiometric evolution of H_2 and O_2 was observed, while the rate of H_2 and O_2 evolution decreased with the accumulation of the evolved gas probably due to the effect of the gas phase pressure. Remarkable point to be mentioned is that the total amounts of evolved H_2 and O_2 reached to 1700 and 850 μmol after five runs, respectively, while the amount of the used NiO was 1300 μmol (0.1 g). Thus, the amounts of evolved H_2 and O_2 exceeded that of the used NiO implying that the reaction proceeded catalytically. Similar time courses were also observed when either Co_3O_4, Cu_2O, or Fe_3O_4 were used. Inductively coupled plasma (ICP) and pH measurements showed that there was neither appreciable dissolution of the oxides nor the change of pH in suspension during the reaction. The origin of evolved O_2 was verified by using a $H_2{}^{16}O/H_2{}^{18}O$ mixture, and clearly confirmed that the evolved O_2 originated from water [5].

The shape of the stirring rod was examined. In one experiment, 0.1 g of NiO powder was suspended in distilled water by rotating the stirring rod (a) which was kept from contact with the bottom wall of the reaction vessel and there was no evolution of H_2 and O_2. In another experiment, ca. 0.01 g of NiO was stuck onto the bottom face of the stirring rod (b) with a flat bottom and the rod was rotated on the bottom of

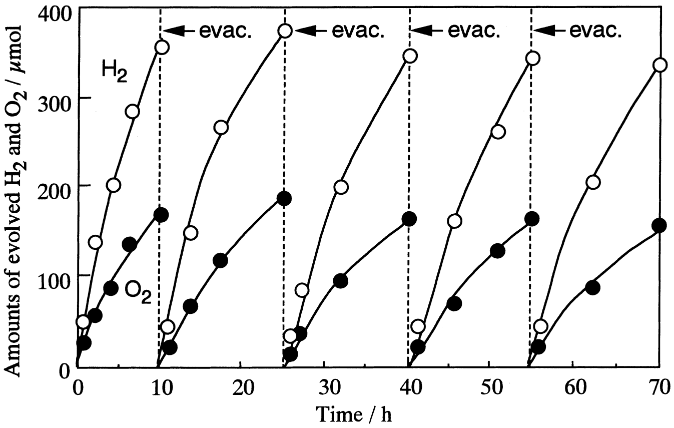

Fig. 2. Time course of H_2 (open circles) and O_2 (filled circles) evolution from NiO suspended in distilled water system. The gas phase was evacuated at 10 h after startup (Run 1) and at 15 h intervals in subsequent runs. Catalyst (NiO): 0.1 g, H_2O: 200 cm^3, stirring rate: 1500 rpm.

the reaction vessel in distilled water without any suspended powders of NiO. Similarly to the suspension system shown in Fig. 2, a stoichiometric evolution of H_2 and O_2 was observed this time (Fig. 3). These results proved that the reaction was driven by the mechanical energy consumed at the interface between the rotating stirring rod and the bottom of the reaction vessel.

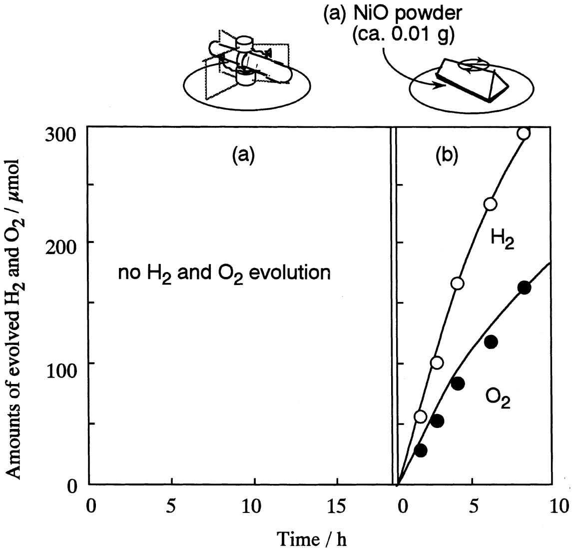

Fig. 3. Change by stirring manner of the rates of H_2 (open circles) and O_2 (filled circles) evolution. (a) Stirring NiO (0.1 g)-suspended distilled water with a floating type stirring rod, the stirring rod was rotated without contact with the bottom of the reaction vessel. (b) Both-sided adhesive tape was stuck on the flat bottom of the stirring rod and ca. 0.01 g of NiO powder was stuck onto the other side of the tape. Stirring the NiO (ca. 0.01 g)-glued flat-bottomed rod in suspension-free water. H_2O: 200 cm^3, stirring rate: 1500 rpm.

3.2. Mechano-catalytic water decomposition on ABO_4 compounds

The rates of H_2 and O_2 evolution by mechano-catalytic water decomposition on ABO_4 are listed in Table 1. The rates of evolution were measured for 1 day after beginning of the reaction. As shown in Table 1, stoichiometric H_2 and O_2 evolution was observed on tungstates containing Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. It is noted that Cu^{1+} containing oxides such as Cu_2O and $CuFeO_2$ were active but CuO was not in our previous work. Although a small amount of stoichiometric H_2 and O_2 evolution was observed on $SrWO_4$ at the early stage of the reaction the rates of H_2 and O_2 evolution decreased with time. Among molybdates, the reaction proceeded on those containing Fe^{2+}, Co^{2+} and Ni^{2+}, but Cu^{2+} was not active.

Fig. 4 shows typical time courses of H_2 and O_2 evolution by mechano-catalytic water decomposition on $CoWO_4$ which exhibited a high and stable activity among the prepared samples. The reaction proceeded without noticeable decrease in activity by 100 h, while the rates of H_2 and O_2 evolution gradually decreased with reaction time after reaction for ca. 100 h. The rates in Run 16 decreased to ca. 1/20 of the initial rates.

Table 1
Rate of H_2 and O_2 evolution on various ABO_4 (A = Mn, Fe, Co, etc., and B = W and Mo) compounds

AWO_4 or $AMoO_4$	Transition metal tungstates and molybdates	Rate of gas evolution ($\mu mol\ h^{-1}$)	
		H_2	O_2
AWO_4	$MnWO_4$	Trace	0
	$FeWO_4$	28	13
	$CoWO_4$	40	19
	$NiWO_4$	54	23
	$CuWO_4$	36	17
	$ZnWO_4$	0	0
	$MgWO_4$	0	0
	$CaWO_4$	0	0
	$SrWO_4$	0	0
	$BaWO_4$	2	1
$AMoO_4$	$MnMoO_4$	0	0
	$FeMoO_4$	16	4
	$CoMoO_4$	13	7
	$NiMoO_4$	39	36
	$CuMoO_4$	Trace	Trace
	$ZnMoO_4$	0	0
	$MgMoO_4$	Trace	0
	$CaMoO_4$	Trace	0
	$SrMoO_4$	Trace	Trace
	$BaMoO_4$	Trace	0

Total amounts of evolved H_2 and O_2 after the reaction for ca. 400 h were 6.7 and 3.5 mmol, respectively, which exceeded the amount of $CoWO_4$ used (0.1 g, 330 μmol). Such catalytic property was also confirmed for all the compounds listed in Table 1. In the reaction on these ABO_4, there was no H_2 and O_2 evolution without stirring, and by the restart of stirring the reaction proceeded in a similar manner before stopping

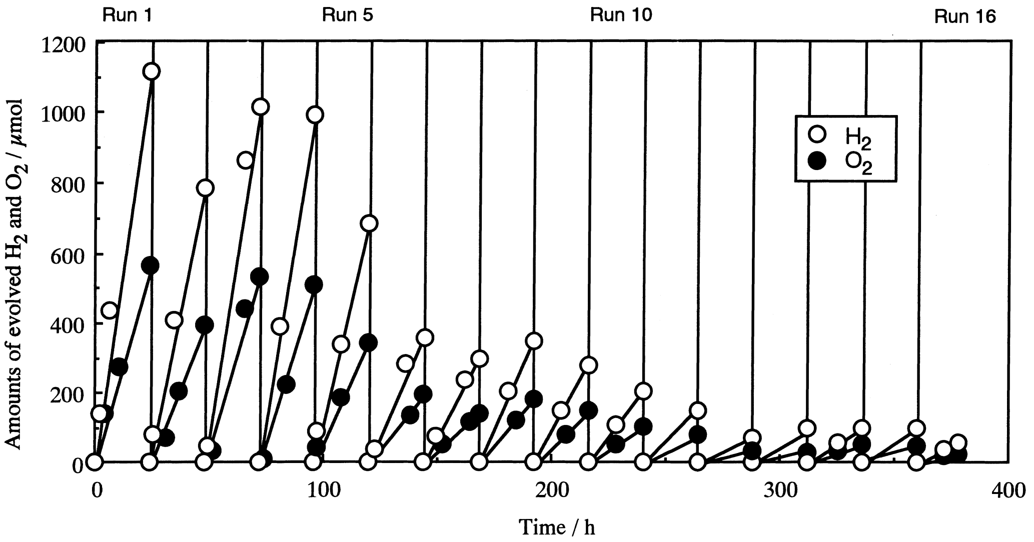

Fig. 4. Time course of H_2 (open circles) and O_2 (filled circles) evolution from $CoWO_4$ suspended in distilled water system. The gas phase was evacuated at the interval of 24 h. Catalyst ($CoWO_4$): 0.1 g, H_2O: 200 cm^3, stirring rate: 1500 rpm.

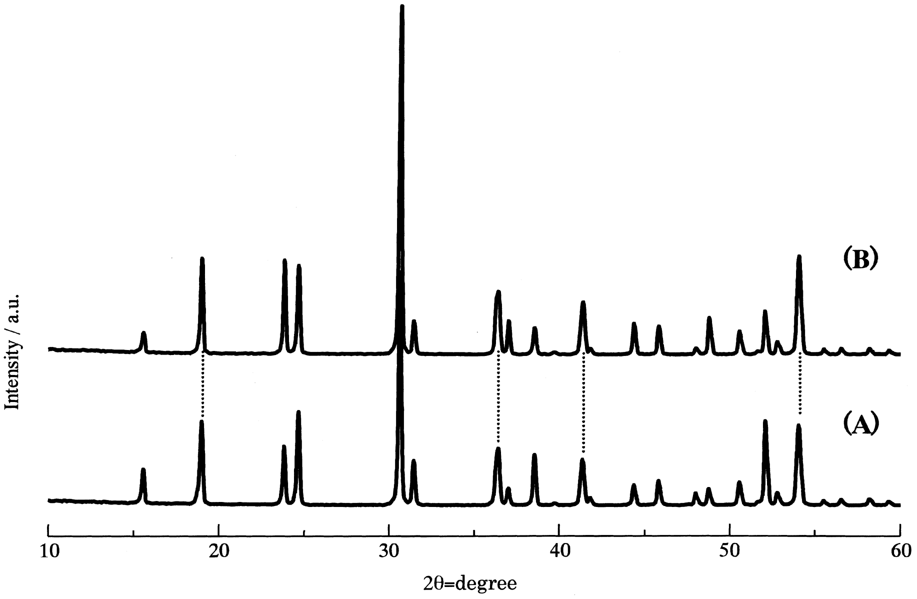

Fig. 5. XRD patterns of $CoWO_4$ before (A) and after (B) the reaction.

of stirring. Furthermore, as shown in Fig. 5, there was no noticeable change in XRD patterns of $CoWO_4$ before and after the reaction. These results indicate that these ABO_4 catalysts catalytically decomposes water into H_2 and O_2 by mechanical energy as well as Cu_2O, Fe_3O_4, Co_3O_4 and NiO [2]. We, therefore, conclude that mechano-catalytic overall water splitting proceeds on these ABO_4 compounds.

Fe^{2+}, Co^{2+} and Ni^{2+} which are contained in active ABO_4 mechano-catalysts are also involved in mechano-catalytically active Fe_3O_4, Co_3O_4 and NiO, respectively. This suggests that Fe^{2+}, Co^{2+} and Ni^{2+} are related to the mechano-catalytic overall water splitting. In our previous study, we surveyed various binary metal oxides as mechano-catalysts for overall water splitting and confirmed that there was no H_2 and O_2 evolution on CuO and WO_3, while $CuWO_4$ mechano-catalytically decomposed water as shown in Table 1 in this study. In addition , $CuMoO_4$ was almost inactive for the reaction.

It should be noted that the large decrease of wolframite in activity with reaction time. Except $CuWO_4$, there were no noticeable change in XRD patterns, XP spectra, particle sizes and surface areas of the catalysts before and after the reaction (400 h) even when the rates of H_2 and O_2 evolution fell to ca. 1/20 of those at the early stage of the reaction. Because mechano-catalytic overall water splitting proceeds by rubbing the catalysts, the grinding of catalyst particles may participate in the reaction as well as mechano-chemical reaction.

Fig. 6 shows the XRD patterns of $CuWO_4$ before and after the reaction for 100 h. Three new diffraction peaks ($2\theta = 36$, 48 and 53°) appeared in the XRD pattern after the reaction and were attributed to the diffraction of Cu_2WO_4 composed of Cu^{1+}. The peak intensities remained unchanged after 100 h. On the other hand, there was no noticeable difference between the XRD patterns of $CuMoO_4$ before and after stirring for 100 h, and the formation of Cu^{1+}-containing species was not observed on $CuMoO_4$. Considering that the reaction does not proceed on CuO but Cu_2O, stoichiometric H_2 and O_2 evolution on $CuWO_4$ is attributable to Cu_2WO_4 formed by reduction of $CuWO_4$. Although, we cannot explain why Cu^{1+}-containing wolframite is not formed on $CuMoO_4$ but on $CuWO_4$, the characteristic structure of $CuWO_4$ may be related to the reduction of $CuWO_4$. $CuWO_4$ is regarded as a “distorted” wolframite which should be represented as $CuWO_{4-x}$ rather than wolframite since $CuWO_4$ has oxygen defects. The distorted structure of $CuWO_4$

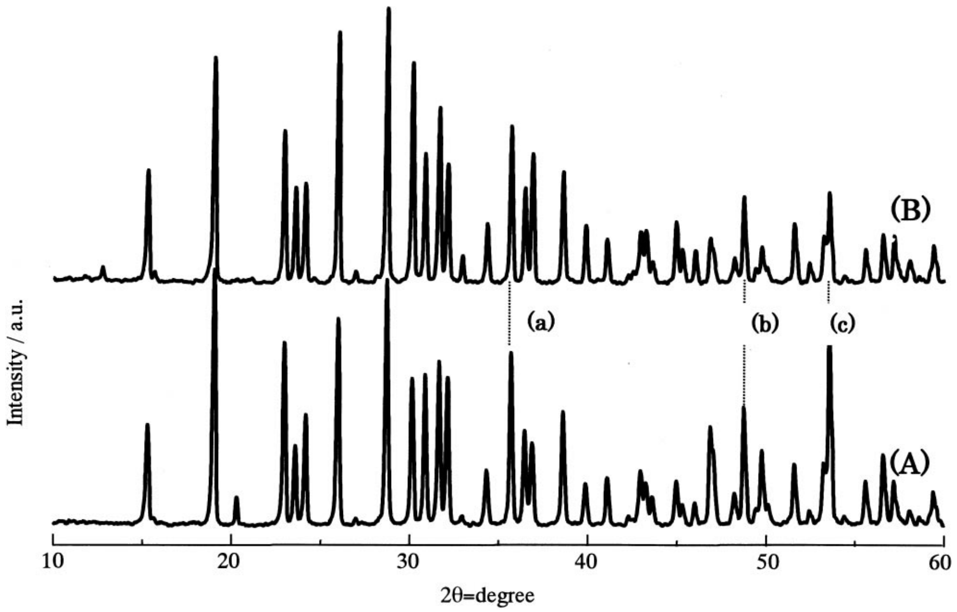

Fig. 6. XRD patterns of $CuWO_4$ before (A) and after (B) the reaction. The diffraction peaks indicated by (a), (b) and (c) are attributed to Cu_2WO_4.

might lead to the formation of Cu_2WO_4 and to the mechano-catalytic overall water splitting.

From these results, we can conclude that both binary metal oxide and wolframite-type oxides containing Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{1+} attained the mechano-catalytic overall water splitting. This suggests that these transition metal cations play an important role in the reaction. Table 1 also shows that tungstates containing Fe^{2+}, Co^{2+} and Ni^{2+} have higher catalytic activities for the water splitting than corresponding molybdates.

Although the gradual decreases of the rates of H_2 and O_2 evolution with reaction time were observed on Fe_3O_4, Co_3O_4 and NiO, it was confirmed that the reaction was independent from the grinding of the catalyst particle. Secondary electron microscope (SEM) and BET measurements exhibited that the particles of these wolframite-type oxides were not ground during the reaction. On the other hand, the magnetic stirring rod was gradually covered with some tarry material, probably the worn PTFE, during the reaction. When the stirring rod was once washed by hexane, the reactivity was recovered. Therefore, the catalysts themselves were not regarded as being deactivated, which is consistent with the long lifetime of simple oxides as we previously reported [5].

4. Conclusion

Inevitable conclusion from the experimental results as a whole is that the simultaneous H_2 and O_2 evolution on these oxides was the “mechano-catalytic” overall water splitting in which mechanical energy supplied by the “rubbing” of these oxide powders was somehow converted to chemical energy with a help of these oxide powders as a catalytic material.

This study revealed that binary metal oxide and wolframite-type oxides containing Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{1+} worked as mechano-catalyst for overall water splitting. Further studies are now being proceeded to improve the catalytic activity and reveal the whole reaction mechanism.

Acknowledgements

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Area of “Catalytic

Chemistry of Unique Reaction Fields-Extreme Environment Catalysts” from the Ministry of Education, Science, Sports, Culture, Japan, by Research for the Future Program, the Japan Society for the Promotion of Science, by Research of Innovative Technology for the Earth (RITE), and by Core Research for Evolutional Science and Technology (CREST).

References

[1] M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J.N. Kondo, K. Domen, Chem. Commun. (1998) 357.
[2] S. Ikeda, T. Takata, T. Kondo, G. Hitoki, M. Hara, J.N. Kondo, K. Domen, Chem. Commun. (1998) 2185.
[3] M. Hara, M. Komoda, H. Hasei, M. Yashima, S. Ikeda, T. Takata, J.N. Kondo, K. Domen, J. Phys. Chem. B 104 (2000) 781.
[4] M. Hara, H. Hasei, M. Yashima, S. Ikeda, T. Takata, J.N. Kondo, K. Domen, Appl. Catal. A 190 (1999) 35.
[5] S. Ikeda, T. Takata, M. Komoda, A. Tanaka, H. Hosono, H. Kawazoe, M. Hara, J.N. Kondo, K. Domen, Phys. Chem., Chem. Phys. 1 (1999) 4485.
[6] T.R. Zhao, M. Hasegawa, H. Takei, J. Cryst. Growth 154 (1995) 332.
[7] I. Lindqvist, Acta Chem. Scand. 4 (1950) 1064.
[8] L. Kihlborg, E. Gebert, Acta Cryst. B 26 (1970) 1020.
[9] L.G. Van Uitert, J.J. Rubin, W.A. Bonner, J. Am. Ceram. Soc. 46 (1963) 512.
[10] L.G. Van Uitert, R.R. Soden, J. Appl. Phys. 31 (1960) 328.
[11] R.O. Keeling Jr., Acta Cryst. 10 (1957) 209.
[12] S.C. Abrahams, J.L. Bernstein, P.B. Jamieson, J. Chem. Phys. 48 (1968) 2619.
[13] B.M. Wanklyn, J. Mater. Sci. 7 (1972) 813.
[14] V.M. Gredescul, S.A. Gredescul, V.V. Eremenko, V.M. Naumenko, Phys. Chem. Solids 33 (1972) 859.
[15] R. Bharati, R.A. Singh, B.M. Wanklyn, J. Mater. Sci. 15 (1980) 1293.
[16] R. Bharati, R.A. Singh, B.M. Wanklyn, J. Mater. Sci. 16 (1981) 775.
[17] H. Levia, K. Dwight, A. Wold, J. Solid State Chem. 44 (1982) 113.