

Vanadyl hydrogenphosphate sesquihydrate as a precursor for preparation of $(VO)_2P_2O_7$ and cobalt-incorporated catalysts

Tomohiro Ishimura, Shigeru Sugiyama, Hiromu Hayashi*

Department of Chemical Science and Technology, Faculty of Engineering, University of Tokushima, Minamijosanjima, Tokushima 770-8506 Japan

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Abstract

Vanadyl hydrogenphosphate sesquihydrate ($VOHPO_4 \cdot 1.5H_2O$) was prepared by reduction of $VOPO_4 \cdot 2H_2O$ suspended in refluxed 1-butanol and activated at $480^\circ C$ over 10 h on-stream to give $(VO)_2P_2O_7$, which revealed high specific activity per unit surface area in the vapor-phase oxidation of *n*-butane. Cobalt-modified $(VO)_2P_2O_7$ catalysts were prepared in the present work by intercalating sesquihydrate precursor with cobaltous acetate employing 1-butanol as solvent. The catalysts prepared from cobalt-intercalated precursor showed high specific activity, but both selectivities to maleic anhydride and surface area decreased with increasing cobalt-contents. Presumably, intercalated cobalt species retarded topotactic dehydration of layered precursor to afford crystalline active species $(VO)_2P_2O_7$, leading to an increase in unfavorable combustion activity due to pentavalent β - $VOPO_4$ species. The activity of catalysts prepared for reference by kneading vanadyl hydrogenphosphate hydrates with an additive $Co_2P_2O_7$ was interpreted as the variation in surface area, and cobalt has none of positive effects in these catalysts. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Crystalline vanadyl pyrophosphate $(VO)_2P_2O_7$, which is an active species [1,2] for selective oxidation of *n*-butane to maleic anhydride, are prepared by the topotactic dehydration of vanadyl hydrogenphosphate hydrates $VOHPO_4 \cdot nH_2O$ ($n = 0.5$ and 1.5) at 400 – $500^\circ C$. The

hemihydrate precursor ($n = 0.5$) [3] with tetravalent vanadium, of which structure was determined by the X-ray single crystal analysis [4–6], are usually obtained by reduction of vanadium pentoxide in concentrated HCl, and/or alcohols followed by the reaction with 85% H_3PO_4 . Reduction of pentavalent vanadium species in rather strongly reductive alcohols such as 2-butyl [5], *i*-butyl and benzyl alcohol [7] also gives hemihydrate.

The sesquihydrate precursor ($n = 1.5$) was obtained by reducing $VOPO_4 \cdot 2H_2O$ in the less reductive 1-ols such as 1-butyl alcohol [8]. The layer structure of sesquihydrate with wide spac-

* Corresponding author. Tel.: +81-88-6567430; fax: +81-88-655-7025.

E-mail address: hayashi@chem.tokushima-u.ac.jp (H. Hayashi).

ing capable of intercalating additives appears of benefit for preparing improved catalysts. Activities of vanadyl pyrophosphate and cobalt-incorporated catalysts prepared by the sesquihydrate precursor are described in the present paper.

2. Experimental

Vanadium phosphate dihydrate $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (10.0 g, 50.5 mmol) was added to 150 ml of 1-butanol and refluxed at 80°C for 24 h. After being cooled to room temperature, the resultant precipitates were filtered, washed with acetone, and dried overnight in a desiccator to afford 9.3 g (yield 97%) of white-blue powder of $\text{VOHPO}_4 \cdot 1.5\text{H}_2\text{O}$. Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer RINT 2000 of Rigaku, Tokyo, using $\text{CuK}\alpha$ radiation at 40 kV and 100 mA. Chemical composition of catalysts and the precursors was analyzed by an inductively coupled plasma apparatus ICPS-5000 of Shimadzu, Kyoto. Thermogravimetric and differential thermal analysis (TG-DTA) was measured by a thermal analyzer, Model TAS-100 of Rigaku, Tokyo. Surface area was determined by nitrogen adsorption method with a volumetric apparatus P-700 of Shibata, Tokyo.

Prior to the comparative reaction studies, the tetravalent sesquihydrate precursor was activated by dehydrating under butane-oxidation conditions at least 10 h on-stream at 480°C to afford vanadyl pyrophosphate $(\text{VO})_2\text{P}_2\text{O}_7$ with high surface area. The vapor-phase catalytic oxidation of *n*-butane was carried out by a conventional fixed-bed flow apparatus at $300\text{--}480^\circ\text{C}$ with a space velocity (SV) of 2040 ml/g-cat/h for a feed gas composition of 2% *n*-butane and 20% oxygen with helium balance.

3. Results and discussion

3.1. Reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in alcohols to $\text{VOHPO}_4 \cdot n\text{H}_2\text{O}$

Vanadyl hydrogenphosphate hydrates $\text{VOHPO}_4 \cdot n\text{H}_2\text{O}$ are usually prepared by reduction of pentavalent vanadium species. Fig. 1(a) shows a pair of TG-DTA curves of a hemihydrate ($n = 0.5$) prepared by reduction of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ in 2-butanol, signifying a single stage dehydration of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ to $(\text{VO})_2\text{P}_2\text{O}_7$ at 450°C . Powder XRD patterns of the hemihydrate and pyrophosphate prepared therefrom are shown in Fig. 1(b1) and (b2), respectively, and agreed well with literature [2,5,9].

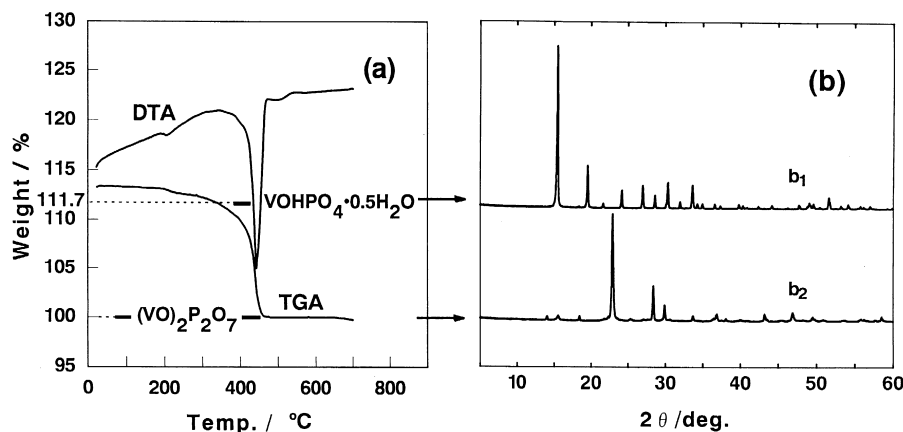


Fig. 1. TG-DTA (a) and powder XRD patterns (b) for $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. XRD patterns: (b1), authentic $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$; (b2) $(\text{VO})_2\text{P}_2\text{O}_7$ obtained at 700°C under nitrogen.

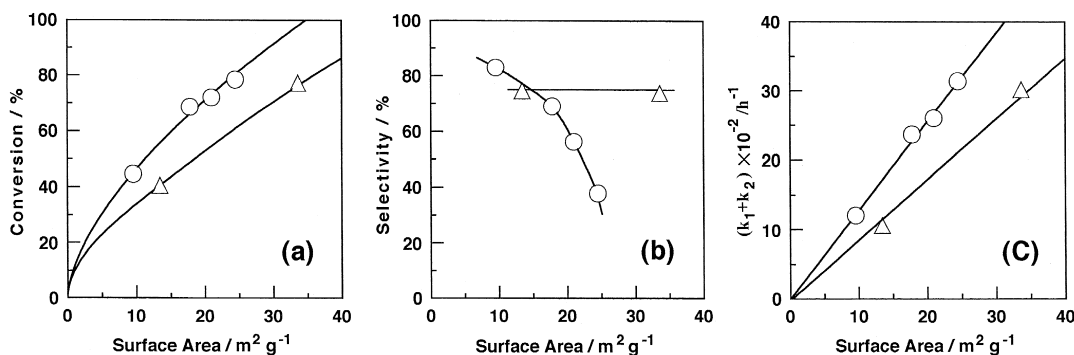


Fig. 3. Effect of surface area on conversion of *n*-butane (a), selectivity to maleic anhydride (b) and Hutchings' plot [11] (c) in the vapor-phase oxidation of *n*-butane over $(VO)_2P_2O_7$ catalysts. Slope in (c) indicates specific activity. Catalyst precursors: triangles, $VOHPO_4 \cdot 0.5H_2O$; circles, $VOHPO_4 \cdot 1.5H_2O$. Reaction conditions: temperature, 420°C; feed composition, $C_4H_{10}:O_2:He = 1:10:40$, flow rate, 51 ml/min; space velocity, 2040 ml/g-cat/h.

hemihydrate (Fig. 3(c), triangles). A catalyst obtained by the stepwise dehydration of the sesquihydrate precursor through intermediate as given in Fig. 2(b2) showed a low surface area of 9.6 m^2/g , but the activity lies on a same line of sesquihydrate (Fig. 3(c), circles). The slope of Hutchings' plot indicates the specific activity and thus Fig. 3(c) shows higher specific activity of catalyst prepared from the sesquihydrate precursor. Conversion of *n*-butane increased in parallel with increasing surface area for both catalysts as in Fig. 3(a), but it appears worthwhile to note that the selectivity to maleic anhydride on $(VO)_2P_2O_7$ catalysts prepared from sesquihydrate decreased with increasing surface area (circles) while unchanged over a wide range of surface area in the case of hemihydrate precursor (triangles) as compared in Fig. 3(b).

3.3. Structure of vanadyl hydrogenphosphate hydrates

Vanadyl monohydrogenphosphate hemihydrate $VOHPO_4 \cdot 0.5H_2O$ crystallized from aqueous media is orthorhombic with $a = 7.420(1)$, $b = 9.609(2)$, $c = 5.6931(7)$ Å, $Z = 4$ and space group $Pm\bar{m}n$ [4–6]. Powder XRD pattern of sesquihydrate $VOHPO_4 \cdot 1.5H_2O$ was tentatively indexed in the previous communication [8] based on the powder XRD data taken in the range of $2\theta = 10$ – 50° , and a layer structure

similar to the hemihydrate was proposed for orthorhombic unit cell with lattice constants $a = 7.43$, $b = 9.62$ and $c = 7.97$ Å. Enlarged layer interstices of 7.97 Å in sesquihydrate compared with that of 5.70 Å in hemihydrate appears quite reasonable to hold another molecule of water in agreement with TG-DTA in Fig. 2(a).

However, an extended diffraction measurement toward lower angles ($2\theta = 3$ – 60°) in this work revealed a strong new reflection at around 5.5° ($d = 16$ Å) as shown in Fig. 2(b1), suggesting the structure based on the above mentioned indexing [8] leaves further improvements. We could not yet fully figure out at present, but the structure of $VOHPO_4 \cdot 1.5H_2O$ appears quite reminiscent of α - $Zr(HPO_4)_2 \cdot H_2O$, of which structure was extensively investigated [13,14] to be a layer structure with a lattice constant of $c = 15.414$ Å and the layer separation of 7.6 Å. The wide layer spacing of sesquihydrate capable of intercalation would be of benefit for providing a general procedure in the preparation of modified $(VO)_2P_2O_7$ catalyst incorporated additives.

3.4. Cobalt-incorporated $(VO)_2P_2O_7$ catalysts

A number of promoters, e.g., Co, Ni, Fe, Mo and Nb, have been shown to be effective for improving vanadium phosphorus oxide catalysts

[11,15]. However, it appears not yet clear where is the effect coming from. It is rather common that the preparation procedure strongly affects the activity of modified catalysts with additives. Attempts were made in the present work to compare cobalt-incorporated $(VO)_2P_2O_7$ catalysts prepared by kneading and intercalation methods. Coprecipitation and impregnation [16], and doping [17] were employed for preparing cobalt-modified catalysts, but intercalation has not yet been reported.

3.4.1. Intercalation of cobalt acetate into the layer spacing of $VOHPO_4 \cdot nH_2O$

Intercalation of additives in the interstices of catalyst precursor with a layer structure such as $VOHPO_4 \cdot nH_2O$ is of interest, if possible, to assure the atomic dispersion of additives to afford well-defined catalysts. However, hemihydrate ($n = 0.5$) precursor was intact with an aqueous solution of $Co(OAc)_2$ refluxed at $80^\circ C$ for 80 h. Attempted intercalation of cobalt into the wide layer spacing of sesquihydrate ($n = 1.5$) in aqueous phase also resulted in failure to decompose the structure of vanadyl hydrogen-phosphate hydrate, which dissolved in aqueous cobaltous acetate within 10–20 h under reflux at $80^\circ C$ to give dark blue solution followed by the precipitation of deep green powder during pro-

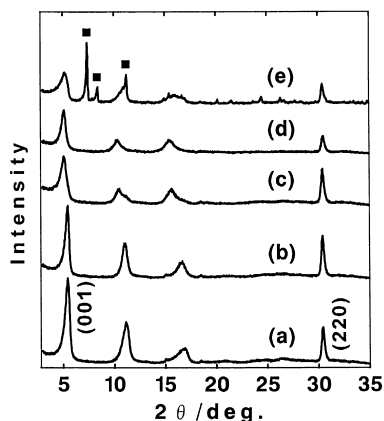


Fig. 4. Powder XRD patterns of cobalt-intercalated $VOHPO_4 \cdot 1.5H_2O$. Co/V (atomic ratio): (a), 0.00; (b), 0.05; (c), 0.10; (d), 0.28; (e), 0.90. ■: $Co_3(OAc)_5(OH)$.

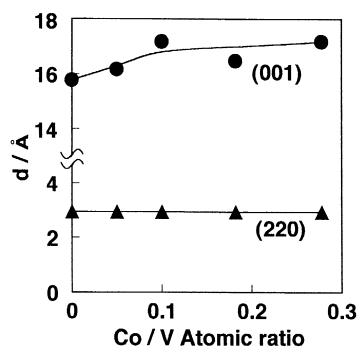


Fig. 5. Lattice constants of cobalt-intercalated $VOHPO_4 \cdot 1.5H_2O$.

longed refluxing for 40–80 h. The precipitates attempted to activate at $480^\circ C$, as usual, showed low activity and the major component detected by XRD was V_2O_5 .

For topotactic dehydration [4–6] of the precursor hydrates to afford active species $(VO)_2P_2O_7$, the layer structure should be retained in the intercalation of additives. To avoid decomposition as observed in aqueous phase, another attempt has been made in the present work to intercalate cobalt species in 1-butanol, which was employed as reducing solvent in preparing sesquihydrate. To a solution of 100 ml of 1-butanol containing 1.006 g (4.0 mmol) of $Co(OAc)_2 \cdot 4H_2O$ was added 7.597 g (40.0

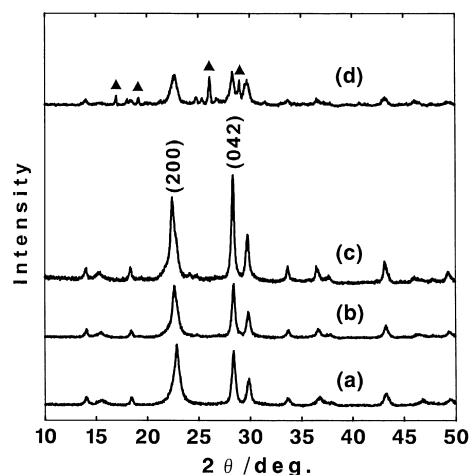


Fig. 6. Powder XRD patterns of $(VO)_2P_2O_7$ catalysts prepared from cobalt-intercalated $VOHPO_4 \cdot 1.5H_2O$. Co/V (atomic ratio): (a), 0.00; (b), 0.05; (c), 0.10; (d), 0.18. ▲: $\beta\text{-VOPO}_4$.

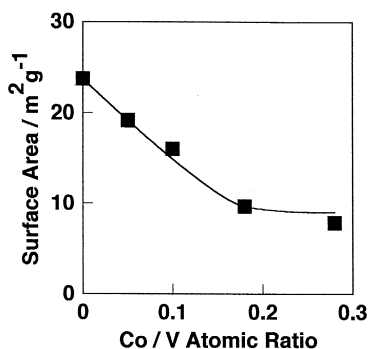


Fig. 7. A decrease in surface area of $(\text{VO})_2\text{P}_2\text{O}_7$ catalysts prepared from cobalt-intercalated $\text{VOHPO}_4 \cdot 1.5\text{H}_2\text{O}$ with increasing cobalt-contents.

mmol) of $\text{VOHPO}_4 \cdot 1.5\text{H}_2\text{O}$ and the magnetically stirred suspension was heated at 80°C under reflux. The wine-red color quickly disappeared within 10 min, indicating the effective uptake of cobalt species into the precursor hydrate without decomposition of the skeletal lattice. After 1 h of refluxing, the precipitates were filtered, washed with acetone, and dried overnight in a desiccator to afford 8.279 g of grayish white-blue powder. The filtrate was colorless and atomic ratio of Co/V in the solid mass analyzed by ICP was found to be 0.104, showing that every cobalt species in the ingredient was entrapped into the precursor hydrate. Powder XRD patterns given in Fig. 4 show less

crystalline sesquihydrates with increasing intercalated cobalt. In case of higher concentrations of cobaltous acetate in 1-butanol, the resultant cobalt-intercalated sesquihydrate was contaminated as in Fig. 4(e) with $\text{Co}_3(\text{OAc})_5(\text{OH})$ [18], which is very soluble in water and could be removed with great ease by washing quickly with a small amount of water. Slightly enlarged lattice constants of (001) reflections (*c*-axis) due to intercalation of cobalt species without change in those of (220) reflections (*ab*-plane) are shown in Fig. 5, signifying an easy access of cobalt species to the wide layer spacing along *c*-axis without decomposing the structure. Thus, the upper-limit for sesquihydrate precursor capable of intercalating cobalt species was at around $\text{Co}/\text{V} = 0.28$.

3.4.2. Activity of cobalt-incorporated V–P–O catalysts

The cobalt-intercalated precursors were activated as usual at 480°C under butane-oxidation conditions at least over 10 h on-stream to afford active $(\text{VO})_2\text{P}_2\text{O}_7$ phase as evidenced in Fig. 6 without appreciable change in the XRD patterns at low contents of cobalt (Fig. 6(b,c)). However, pentavalent $\beta\text{-VOPO}_4$ phase was detected along with $(\text{VO})_2\text{P}_2\text{O}_7$ as shown in Fig. 6(d) for

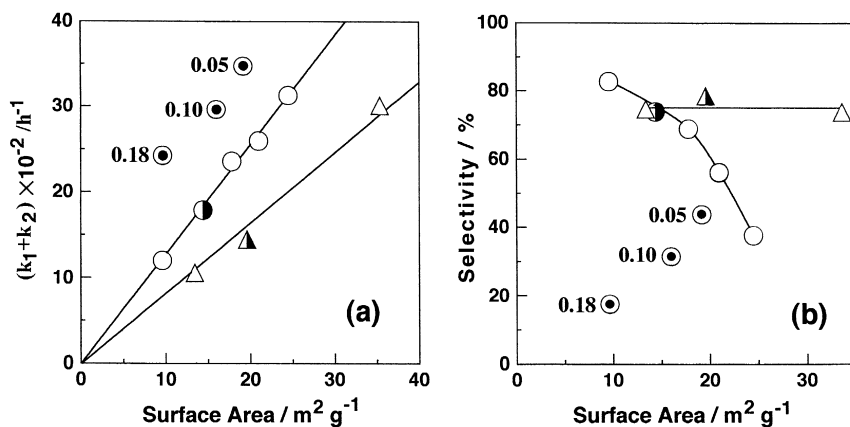


Fig. 8. Activity (a) (Hutchings' plot [11]) and selectivity patterns (b) of catalysts with and without incorporated cobalt in the vapor-phase oxidation of *n*-butane. Slope in (a) indicates specific activity. Catalyst precursors: triangles, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$; circles, $\text{VOHPO}_4 \cdot 1.5\text{H}_2\text{O}$. White symbols, without Co; Half-black symbols, kneaded with $\text{Co}_2\text{P}_2\text{O}_7$; Center-black circles, cobalt-intercalated $\text{VOHPO}_4 \cdot 1.5\text{H}_2\text{O}$ (with $\text{Co}/\text{V} = 0.05, 0.10$ and 0.18). Reaction conditions: same as in Fig. 3.

catalyst with a high cobalt-content. Surface area of catalysts decreased with increasing cobalt-contents as shown in Fig. 7.

Fig. 8 compares activity (a) and selectivity to maleic anhydride (b) in the vapor-phase catalytic oxidation of *n*-butane over cobalt-incorporated V–P–O catalysts prepared by the intercalation (center-black circles) and kneading method (half-black symbols) on Hutchings' plot. Results of catalysts without cobalt (white symbols) given in Fig. 3 are also plotted for reference. Sesquihydrate precursor gives active $(VO)_2P_2O_7$ catalysts as demonstrated in Fig. 3(a), and catalysts from cobalt-intercalated precursor were much more active as in Fig. 8(a), scattering beyond the sesquihydrate line, but selectivity to maleic anhydride decreased with increasing cobalt-content as shown in Fig. 8(b) (center-black circles).

Cobalt-incorporated catalysts were prepared by another method for reference, where the precursor hydrate $VOHPO_4 \cdot nH_2O$ and an additive $Co_2P_2O_7$ were kneaded with a small amount of toluene, and activated as usual at 480°C. The catalyst thus obtained showed powder XRD pattern of $Co_2P_2O_7$ along with activated $(VO)_2P_2O_7$. Both activity (a) and selectivity (b) of catalysts (half-black symbols) were found on the same lines of each precursor hydrates as shown in Fig. 8 ($n = 0.5$, triangles; $n = 1.5$, circles). Thus, the specific activities were retained, and cobalt has none of the positive effects in these catalysts prepared by simple kneading procedure.

4. Conclusions

Vanadyl hydrogenphosphate sesquihydrate $VOHPO_4 \cdot 1.5H_2O$ was prepared by reduction of $VOPO_4 \cdot 2H_2O$ in refluxed 1-butanol and activated at 480°C over 10 h on-stream to give $(VO)_2P_2O_7$, which revealed high specific activity in the vapor-phase oxidation of *n*-butane. Employing 1-butanol as solvent, the sesquihy-

drate could be intercalated with cobaltous acetate to afford modified $(VO)_2P_2O_7$ with high activity, but both selectivity to maleic anhydride and surface area decreased with increasing cobalt-contents. Presumably, intercalated additives retarded topotactic dehydration of layered precursor to afford the crystalline active species $(VO)_2P_2O_7$, leading to an increase in the unfavorable combustion activity due to pentavalent β - $VOPO_4$ species. Cobalt has none of the positive effects in catalysts prepared by simple kneading procedure.

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References

- [1] G. Centi, F. Trifiro, J.R. Ebner, V.M. Franchetti, *Chem. Rev.* 88 (1988) 55.
- [2] E. Bordes, *Catal. Today* 1 (1987) 499.
- [3] F. Cavani, F. Trifiro, in: G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs, P. Grange (Eds.), *Preparation of Catalysts VI*, Elsevier, Amsterdam, 1995, p. 1.
- [4] M.E. Leonowicz, J.W. Johnson, J.F. Brody, H.F. Shannon Jr., J.M. Newsam, *J. Solid State Chem.* 56 (1985) 370.
- [5] J.W. Johnson, D.C. Johnston, A.J. Jacobson, J.F. Brody, *J. Am. Chem. Soc.* 106 (1984) 8123.
- [6] C.C. Torardi, J.C. Calabrese, *Inorg. Chem.* 23 (1984) 1308.
- [7] G. Busca, F. Cavani, G. Centi, F. Trifiro, *J. Catal.* 99 (1986) 400.
- [8] I. Matsuura, T. Ishimura, N. Kimura, *Chem. Lett.* (1995) 769.
- [9] JCPDS 37-0269.
- [10] JCPDS 38-0291.
- [11] G.J. Hutchings, R. Higgins, *J. Catal.* 162 (1996) 153.
- [12] I. Matsuura, M. Yamazaki, in: G. Centi, F. Trifiro (Eds.), *New Developments in Selective Oxidation*, Elsevier, Amsterdam, 1990, p. 563.
- [13] K. Segawa, Y. Nakajima, *J. Catal.* 101 (1986) 81.
- [14] J.M. Troup, A. Clearfield, *Inorg. Chem.* 16 (1977) 3311.
- [15] G.J. Hutchings, *Appl. Catal.* 72 (1991) 1.
- [16] V.A. Zazhigalov, J. Haber, J. Stoch, A.I. Pytnitzkaya, G.A. Komashko, V.M. Belousov, *Appl. Catal.* 96 (1993) 135.
- [17] B.K. Hodnet, B. Delmon, *Appl. Catal.* 6 (1983) 245.
- [18] JCPDS 22-0582.