

Liquid-phase oxidative coupling of 2-naphthol by vanadium catalysts supported on MCM-41

Takahiro Ikeda^a, Naohisa Misawa^c, Yuichi Ichihashi^c, Satoru Nishiyama^b, Shigeru Tsuruya^{c,*}

^a Division of Chemical Science and Engineering, Graduate School of Science and Technology, Kobe University, Nada, Kobe 657-8501, Japan

^b Environment Management Center, Kobe University, Nada, Kobe 657-8501, Japan

^c Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Nada, Kobe 657-8501, Japan

Received 7 December 2004; received in revised form 7 January 2005; accepted 7 January 2005

Abstract

The liquid-phase oxidative coupling reaction of 2-naphthol was carried out in dichloromethane solvent over vanadium catalysts supported on inorganic oxides such as MCM-41 using molecular oxygen as the oxidant. The main product was 1,1'-bi-2-naphthol, the oxidative C–C coupling product of 2-naphthol. The yield of 1,1'-bi-2-naphthol increased with the increasing amount of supported V, but leveled off when the amount of V was more than about 1 wt.%. The sterically bulky 1,1'-bi-2-naphthol was suggested to be mainly produced in the mesopores of the MCM-41 support in comparison with the activity of the V catalyst supported on NaZSM-5 support which has only micropores. The active vanadium species for the oxidative coupling product was found to be the tetrahedral V⁵⁺ species based on the correlation between the yield of 1,1'-bi-2-naphthol and the intensity of the tetrahedral V⁵⁺ species estimated by the DR spectra of the V/MCM-41 catalysts.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Vanadium; MCM-41; NaZSM-5; Naphthol; Oxidative coupling; 1,1'-Bi-2-naphthol

1. Introduction

1,1'-Bi-2-naphthol and its derivatives have been widely applied [1–7] in chirality induction and used in enantioselective synthesis. The synthesis of 1,1'-bi-2-naphthol (binaphthol) has been attempted via the oxidative coupling reaction of 2-naphthol using some transition metal ions and their complex catalysts including Cu²⁺ [8,9], Fe³⁺ [10], and V⁴⁺ [11]. The heterogeneity of the homogeneous metal catalyst has an advantage in the liquid-phase oxidation because of the easy separation of the catalyst from the oxidation product and no contamination of the product due to the homogeneous catalyst. The heterogenized Cu catalysts supported on Al₂O₃ have been reported using gaseous oxygen as an oxidant [12]. More recently, binaphthol based on the oxidative coupling of 2-naphthol was reported using Fe and Cu catalysts supported

on MCM-41 with a high selectivity for the proposed coupling product [13].

In this study, the liquid-phase oxidative coupling reaction of 2-naphthol was attempted using a vanadium catalyst impregnated on MCM-41 (V/MCM-41). The vanadium catalysts supported on NaZSM-5 and SiO₂ were also utilized as catalysts to study the influence of the pore size and the structure on the production of sterically bulky products via the oxidative coupling. The active vanadium species on the MCM-41 support for the oxidative coupling of 2-naphthol were discussed based on the diffuse-reflectance (DR) spectra of the V/MCM-41 catalysts.

2. Experimental

2.1. Catalyst preparation

MCM-41 was synthesized by the sol–gel method at room temperature in the atmospheric pressure according to a previ-

* Corresponding author. Tel.: +81 78 8036171; fax: +81 78 8036171.
E-mail address: tsuruyas@kobe-u.ac.jp (S. Tsuruya).

ous report [14]. The NaZSM-5 (Si/Al = 49) zeolite was synthesized by a conventional hydrothermal method according to a patent [15] except for no NaCl addition. NaX (Tosoh, Si/Al = 1.25) was commercially available. The vanadium catalysts (V/MCM-41, V/NaZSM-5, and V/NaX) supported on MCM-41, NaZAM-5, and NaX were prepared by a conventional impregnation method using vanadium oxyacetylacetonate in ethanol at 353–373 K. All the catalysts were dried at 393 K overnight and calcined at 773 K for 5 h in flowing air.

2.2. Liquid-phase oxidative coupling reaction of 2-naphthol

2-Naphthol (Nacalai Tesque, guaranteed reagent) and dichloromethane (Nacalai Tesque, guaranteed reagent) were commercially available and used without further purification. The reaction was carried out using a batch glass reactor with a magnetic stirrer immersed in a constant-temperature water-bath. Usually, 1.0 mmol of 2-naphthol and 0.2 g of catalyst were stirred in 10 ml of dichloromethane solvent at 303 K for 24 h under atmospheric oxygen. The analyses of the oxidation products were performed using an HPLC (Hitachi, L-6200 Intelligent Pump, L-2200 UV–VIS Detector) with a GH-C18 column. A mixture of acetonitrile and an aqueous solution of 5 vol.% trifluoroacetic acid (volume ratio, 1:1), as the mobile phase, was pumped at 1 ml/min. The amount of leached V was estimated by measuring the V amount dissolved in the reaction filtrate using an atomic absorption spectrometer (Shimadzu type AA-6200) after separating the solid catalyst from the reaction solution by centrifugation.

2.3. Measurement of FT-IR spectra of oxidation products

The FT-IR spectra of the oxidation products were measured using an FT-IR spectrophotometer (Nihon Bunkou Model VALOR-III). The sample disk was prepared at a pressure of 40 kg/cm² for 5 min without a binder.

2.4. XRD measurement of supported V catalysts

The X-ray powder diffraction (XRD) patterns of the catalysts were recorded at room temperature using a Rigaku RINT 2001 XRD diffractometer with a Cu K α source.

2.5. BET measurement of supported V catalysts

The surface areas of the catalysts, which were in first degassed at 473 K for 2 h, were measured by the BET method based on the nitrogen adsorption at 77 K using a micro-adsorption vacuum apparatus.

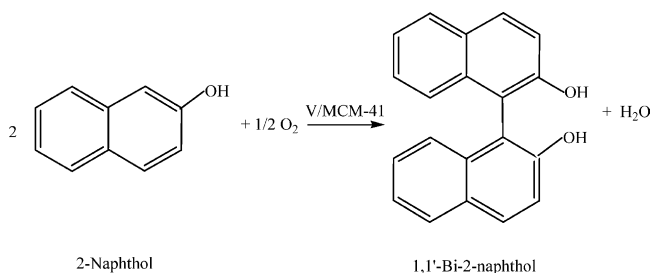
2.6. Measurement of DR spectra of supported V catalysts

The UV–vis diffuse-reflectance (DR) spectra of the supported V catalysts were measured by an electronic absorption

spectroscopy (Hitachi U-3210D) equipped with an integral sphere (Hitachi 150-0902). The measurement was carried out using an in situ cell with a side portion for sample pretreatment, which can be degassed by connection to a vacuum line. The reflectance of the obtained spectra was transformed into a Kubelka–Munk (K–L) function using an applied program (U-3210/U-3410).

3. Results and discussion

The main product of the liquid-phase oxidation of 2-naphthol over the supported vanadium catalysts was 1,1'-bi-naphthol. Another oxidation product, assumed to have a quinone structure (vide infra), was also produced under certain reaction conditions. The amount of V dissolved in the reaction solution from the V catalyst supported on MCM-41 during the oxidative coupling reaction was less than 1%. The V species supported on MCM-41, rather than the V species dissolved in the solvent, were thus confirmed to be catalytic active sites for the oxidative coupling of 2-naphthol.



3.1. Influence of vanadium source of supported V catalyst on the oxidation of 2-naphthol

The influence of the vanadium source on the yield of the 1,1'-2-bi-naphthol (2-binaphthol) was investigated using the V catalysts supported on both SiO₂ and MCM-41 prepared from five kinds of vanadium salts and their complexes (Table 1). The MCM-41 support was more favorable for the production of 2-binaphthol than the SiO₂ support, irrespective of the vanadium sources used in this study. Vanadium oxyacetylacetonate (VO(C₅H₇O₂)₂), among the utilized vanadium sources, produced a high yield of

Table 1
Influence of vanadium source on the yield of 1,1'-2-bi-naphthol^a

Vanadium source	Yield of 1,1'-2-bi-naphthol (%)	
	SiO ₂ support	MCM-41 support
VO(C ₅ H ₇ O ₂) ₂	16.2	23.4
V(C ₅ H ₇ O ₂) ₃	15.9	19.2
VCl ₃	12.3	17.5
VO ₂	10.0	16.2
NH ₄ VO ₃	8.0	12.8

^a Catalyst (V = 1 wt.%), 0.2 g; calcination temperature, 773 K; 2-naphthol, 1 mmol; reaction time, 24 h; reaction temperature, 303 K; solvent, 10 ml of dichloromethane; 0.1 MPa O₂.

Table 2
Influence of solvent on the yield of 1,1'-2-bi-naphthol^a

Solvent	Yield of 1,1'-2-bi-naphthol (%)
Dichloromethane	23.4
1,2-Dichloroethane	20.7
Chlorobenzene	18.2
Chloroform	8.4
Benzene	6.0
Ethanol	≅0

^a Catalyst V/MCM-41 (V = 1 wt.%, V source = VO(C₅H₇O₂)₂), 0.2 g; calcination temperature, 773 K; 2-naphthol, 1 mmol; reaction time, 24 h; reaction temperature, 303 K; solvent, 10 ml of dichloromethane; 0.1 MPa O₂.

2-binaphthol, though the difference in the yields was not very prominent.

3.2. Influence of solvent on the oxidation of 2-naphthol

The influence of the solvent on the yield of 2-binaphthol was investigated using V(1)/MCM-41 (impregnated V = 1 wt.%) catalyst prepared from VO(C₅H₇O₂)₂ (Table 2). The hydrocarbon solvent containing chlorine atoms in the molecule gave a comparatively high yield of 2-binaphthol. Ethanol had no activity for the oxidative coupling reaction of 2-naphthol. 1,2-Dichloromethane was hereafter used as the solvent in this study.

3.3. Influence of support oxide on the oxidation of 2-naphthol

The influence of the support oxide of the supported V catalysts on the yield of 2-binaphthol was investigated using MCM-41, NaX, NaZSM-5 and SiO₂ as the support to clarify the effect of the pore size of the support on the oxidative coupling which produces a sterically bulky coupling product (Table 3). The highest yield of 2-binaphthol was obtained using the MCM-41 support which has one-dimensional mesopores (31 Å [14]). The V catalysts supported both the NaX and the NaZSM-5 zeolite, which have three-dimensional micropores rather than mesopores, produced comparatively low yields of 2-binaphthol. The results in Table 3 suggest that the oxidative coupling of 2-naphthol mainly occurs in the pores of the oxide supports, and the oxidative coupling product, 2-binaphthol, which has the dimensions of 11.53 × 9.14 × 10.05 Å [13] can be produced in the mesopores of the MCM-41 support and easily diffuse

Table 3
Influence of oxide support on the yield of 1,1'-2-bi-naphthol^a

Support	BET surface area (m ² /g)	Yield of 1,1'-2-bi-naphthol (%)
MCM-41	1010	22.8
SiO ₂	305	16.3
NaX	555	5.6
NaZSM-5	350	4.2

^a Catalyst (V = 1 wt.%, V source = VO(C₅H₇O₂)₂), 0.2 g; calcination temperature, 773 K; 2-naphthol, 1 mmol; reaction time, 24 h; reaction temperature, 303 K; solvent, 10 ml of dichloromethane; 0.1 MPa O₂.

out. The super cage of the NaX zeolite will be able to offer a reaction field for the oxidative coupling and accommodate 2-binaphthol, but the sterically bulky product will very slowly diffuse out because of the dimensions of the window (around 7.4 Å) from which the product must leave, as previously suggested [13]. The micropores (around 5.3–5.6 Å) of the NaZSM-5 will be too small to carry out the oxidative coupling of 2-naphthol, so that 2-binaphthol produced using the V(1)/NaZSM-5 catalyst may be due to the active V species present on the outer surface of the NaZSM-5 zeolite. The V catalyst (V(1)/SiO₂ (V = 1 wt.%) supported on amorphous SiO₂ produced a lower yield of 2-binaphthol than that over the V/MCM-41 catalyst. The coordinating state of the V species supported on SiO₂ was found to be different from those on MCM-41 based on the comparison of the DR spectra of both catalysts as will be discussed later.

3.4. Influence of calcination temperature of the V/MCM-41 catalysts on the oxidation of 2-naphthol

The influence of the calcination temperature of the V(1)/MCM-41 catalysts on the yield of 2-binaphthol was investigated at the calcination temperatures of 673–973 K as shown in Table 4. The yield of 2-binaphthol increased with the calcination temperatures up to about 873 K, while a further increase caused only a small increase in the oxidative coupling yield. However, the conversion of 2-naphthol (defined as [2-naphthol fed – 2-naphthol recovered]/[2-naphthol fed] × 100) almost linearly increased with the increase in the calcination temperature. This result means that the oxidation product(s) other than 2-binaphthol is produced over the V(1)/MCM-41 catalyst calcined at higher temperatures. The reaction solution over the V(1)/MCM-41 catalyst calcined at more than 873 K gradually changed from a light yellow to a dark-red color with the reaction time, in contrast to the corresponding solution over the catalyst calcined at 673–773 K, which maintained the light-yellow color. The electronic absorption spectrum of the dark-red solution showed an absorption peak at around 410 nm, in which no peak was observed in both 2-naphthol and 2-binaphthol dissolved in dichloromethane. The IR spectra of the solid residue obtained by evaporating the dichloromethane solvent showed

Table 4
Influence of calcination temperature of the V/MCM-41 on the yield of 1,1'-2-bi-naphthol^a

Calcination temperature (K)	Yield of 1,1'-2-bi-naphthol (%)	Conversion of 2-naphthol (%)
673	17.0	18.0
773	25.2	28.9
873	30.8	51.3
973	31.8	62.2

^a Catalyst V/MCM-41 (V = 1 wt.%, V source = VO(C₅H₇O₂)₂), 0.2 g; 2-naphthol, 1 mmol; reaction time, 24 h; reaction temperature, 303 K; solvent, 10 ml of dichloromethane; 0.1 MPa O₂.

an IR peak at around 1700 cm^{-1} , a peak that is well known to be due to the C=O stretching band. From these observations, the oxidation product(s) possessing a quinone-like structure, though we could not exactly identify the oxidation product(s), is thought to be produced, in addition to 2-binaphthol, over the V/MCM-41 catalysts calcined at the higher temperatures.

The oxidation of 1,1'-bi-2-naphthol (2-binaphthol), in place of 2-naphthol, was attempted at 303 K for 24 h under atmospheric O_2 using the V(1)/MCM-41 catalyst calcined at 973 K, however, no conversion of 2-binaphthol was observed under the reaction condition. This result suggests that a quinone-like product(s) is produced, together with 2-binaphthol, in a parallel manner, rather than the consecutive manner via 2-binaphthol.

3.5. Influence of the amount of V supported on the V/MCM-41 catalyst on the oxidation of 2-naphthol

The influence of the amount of supported V on the yield of 2-binaphthol is illustrated in Fig. 1A using both the V/MCM-41 and the V/NaZSM-5 catalysts. The variation in the yield of 2-binaphthol for low amounts of the supported V increased compared to the behaviors of both catalysts (Fig. 1B). No 2-binaphthol was obtained over only the MCM-41 or the NaZSM-5 support without V species. It is obvious that the V species supported on MCM-41 have a higher activity for the oxidative coupling of 2-naphthol than those supported on NaZSM-5. The yield of 2-binaphthol over the V/MCM-41 catalyst almost linearly increased with the increase in the amount of supported V for V amounts of approximately 1 wt.%, but leveled off with further increases in the amount of the supported V. The structural destruction of the MCM-41 support by the high amount of supported V may be thought to be one of the causes for the leveling off of the 2-binaphthol yield for supported V amount of more than about 1 wt.%. The XRD measurements of the V(1, 3, 4)/MCM-41 (supported V = 1, 3, and 4 wt.%, respectively) catalysts were obtained, but the XRD patterns due to the MCM-41 supports of these catalysts were retained though the peak intensities tended

to decrease with the increase in the supported V amount (figure not shown). The possibility of an adsorbed product, i.e., 2-binaphthol, acting as a catalytic inhibitor was then investigated. The oxidative coupling reaction of 2-naphthol was thus attempted by pre-mixing 2-binaphthol in the starting reaction solution however, no decline in the yield of 2-binaphthol was observed. This suggests that the produced 2-binaphthol does not basically inhibit the oxidative coupling.

The yield of 2-binaphthol over the V/NaZSM-5 catalyst varied in an S-shaped fashion; the V/NaZSM-5 catalyst with only a small amount of supported V had no catalytic activity for the oxidative coupling of 2-naphthol, in contrast to the V/MCM-41 catalyst (Fig. 1B). 2-Binaphthol was produced using supported V amount of more than about 0.2 wt.% and the yield leveled off at the V amounts of more than 1 wt.%. These results suggest that the low V species amount is almost completely supported within the micropores ($5.3\text{--}5.6\text{ \AA}$) of the NaZSM-5 support, and the reactant, the 2-naphthol molecule, cannot access the active V species present in the micropores. Some of the V species will be supported on the outer surface of the NaZSM-5 zeolite with an increase in the supported V amounts. 2-Binaphthol produced over the V/NaZSM-5 catalysts with V amounts of more than 0.2 wt.% is thought to be due to the V species supported on the outer surface of the NaZSM-5 support.

3.6. UV-vis diffuse reflectance (DR) spectra of the V species supported on MCM-41

The DR spectra of the supported V catalysts utilized in this study were used to investigate the coordinated states of the supported V species. The MCM-41 support itself did not have a DR peak in the wavelength range of 200–400 nm (Fig. 2(a), ---). The V(1)/MCM-41 catalyst had a DR peak at around 260 nm (Fig. 2(e), —). The DR spectra of the V(1)/SiO₂ (Fig. 2(b), ----), V(1)/NaX (Fig. 2(c), —), and V(1)/NaZSM-5 (Fig. 2(d), ----) catalysts had a peak at around 320 nm, in addition to a shoulder at around 260 nm. The DR peaks of the V species at 260 nm, 320 nm, and 330–500 nm have been

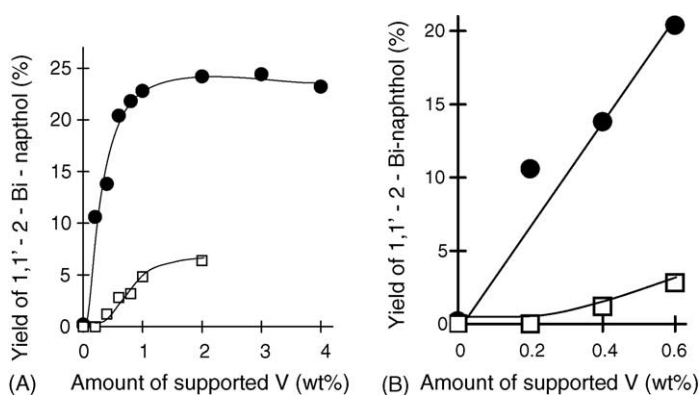


Fig. 1. Dependence of the yield of 2-binaphthol on the amount of supported V. (A) 2-Naphthol, 1 mmol; solvent 10 ml of dichloromethane; reaction temperature, 303 K; reaction time, 24 h; Catalyst, 0.2 g; ●, V/MCM-41; □, V/NaZSM-5. (B) Enlarged section of the region of low amounts of supported V.

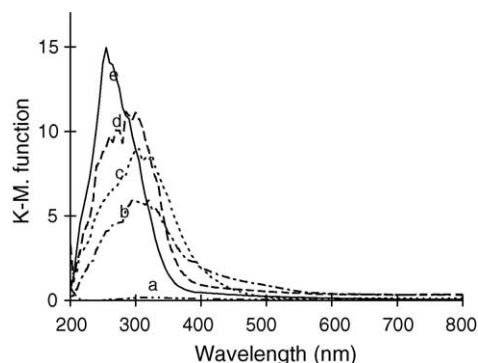


Fig. 2. DR spectra of V catalysts supported on inorganic oxides. (a) ----, MCM-41; (b) - · - ·, V(1)/SiO₂; (c) —, V(1)/NaX; (d) · · · ·, V(1)/NaZSM-5; (e) — — —, V(1)/MCM-41.

identified as tetrahedral V⁵⁺, polymeric V⁵⁺, and octahedral V⁵⁺ species, respectively [16,17]. The V species (1 wt.%) supported on the MCM-41 are thus thought to be mainly present as tetrahedral V⁵⁺ species. On the other hand, the V species on the V(1)/SiO₂, V(1)/NaX, and V(1)/NaZSM-5 catalysts will be supported as the mixed states of both the polymeric V⁵⁺ species and tetrahedral V⁵⁺ ones, among which the mixed states of the former ones seem to be higher than the latter ones.

3.7. Variation in DR spectra of the V/MCM-41 catalysts on the amount of supported V

The variation in DR spectra of the V/MCM-41 catalysts on the amount of supported V is illustrated in Fig. 3. The intensity of the DR peak at around 260 nm increased with the increase in the amount of the supported V up to about 1.0 wt.%. However, the V(3.0)/MCM-41 catalyst had a DR peak at around 320 nm in addition to one around 260 nm, and the broad DR band was also observed in the region around 400–500 nm. The coordination states of the V species supported on the MCM-41 thus varied for supported V amounts of more than around 1 wt.%. The V species on the V/MCM-41 catalysts with a low amount of supported V are mainly present as tetrahedral V⁵⁺ species, and both the tetrahedral

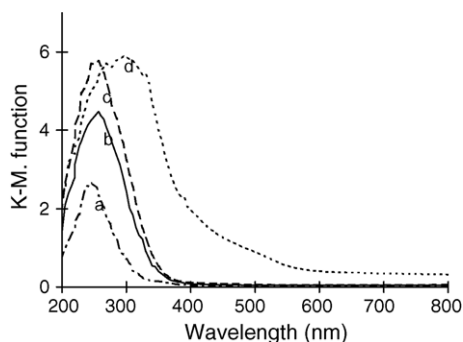


Fig. 3. Variation in DR spectra of V/MCM-41 catalysts vs. the amount of supported V. Supported V amount: (a) ----, 0.4 wt.%; (b) —, 0.6 wt.%; (c) - · - ·, 1.0 wt.%; (d) · · · ·, 3.0 wt.%.

and polymeric V⁵⁺ species coexist on the surface of the catalyst with a high amount of supported V. The octahedral V⁵⁺ species may also present on the catalyst with a high V amount because the broad DR band was observed in the region around 400–500 nm. The leveling off of the yield of 2-binaphthol for amount of supported V of more than about 1 wt.% (Fig. 1A) will be interpreted in connection with the results of the DR spectra if it is assumed that the tetrahedral V⁵⁺ species present on the catalyst are the active V species for the oxidative coupling of 2-naphthol to 2-binaphthol and both the polymeric and octahedral V⁵⁺ species have no catalytic activity.

3.8. Variation in DR spectra of the V/MCM-41 catalysts on the calcination temperature

The influence of the DR spectra on the calcination temperature of the catalyst was investigated using the V(1)/MCM-41 catalyst (Fig. 4). The DR spectra of the V(1)/MCM-41 calcined at 673 K had a DR peak at 260 nm but trailed off in the direction of the long wavelengths. The DR peak at around 260 nm increased with the increasing calcination temperature, but the extent of the DR peak increase tended to decrease with the increase in the calcination temperature. The yield of 2-binaphthol increased with the increase in the calcination temperatures of the V/MCM-41 catalyst, though the quinone-type product(s) other than 2-binaphthol were produced over the catalyst treated at the higher calcination temperature (Table 4). A similar trend in the variation of both the DR peak intensity at 260 nm of the DR spectra and the yield of 2-binaphthol on the calcination temperature once again supports the fact that the tetrahedral V⁵⁺ species present on the MCM-41 support are the active V species for the production of 2-binaphthol.

3.9. Active V species supported on the MCM-41 for the oxidative coupling of 2-naphthol

To more quantitatively confirm that the tetrahedral V⁵⁺ species are responsible for the oxidative coupling of 2-

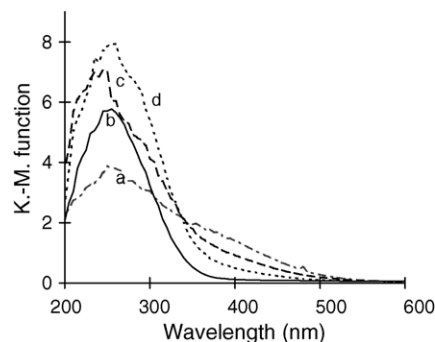


Fig. 4. Variation in DR spectra of V(1)/MCM-41 catalyst vs. the calcination temperature. Calcination temperature: (a) ----, 673 K; (b) —, 773 K; (c) - · - ·, 873 K; (d) · · · ·, 973 K.

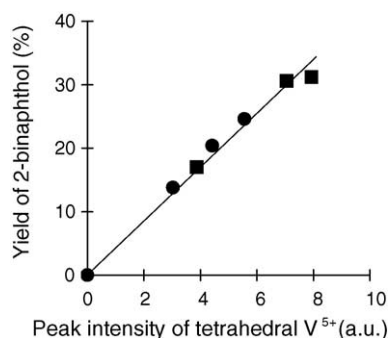


Fig. 5. Relationship between yield of 2-binaphthol and DR peak intensity of tetrahedral V⁵⁺. Catalyst, V/MCM-41; intensity of the DR peak at around 230 nm; ●, data obtained from the variation in the amount of supported V; ■, data obtained from the variation in the calcination temperature.

naphthol, the yield of 2-binaphthol was plotted versus the intensity of the DR peak at around 260 nm, of which the DR peak intensity was assumed to be a measure of the amount of the tetrahedral V⁵⁺ species present on the catalyst surface (Fig. 5). The plot of the yield of 2-binaphthol and the amount of the surface tetrahedral V⁵⁺ species using the V/MCM-41 catalysts prepared by the different conditions was a linear line passing through the original point within the conditions investigated in this study. Fig. 5 results clearly indicate that the tetrahedral V⁵⁺ species supported on the MCM-41 directly participate in the oxidative coupling reaction of 2-naphthol to 2-binaphthol, though we have no information on the active sites for the formation of the other quinone-like product(s) over the supported V catalysts prepared at the high calcination temperatures.

4. Conclusions

The liquid-phase oxidative coupling reaction of 2-naphthol into 1,1'-bi-2-naphthol (2-binaphthol) was attempted over the supported vanadium (V) catalysts. The V catalyst (V/MCM-41) supported on MCM-41 that has a high surface area and mesopores had a comparatively high activity for the formation of 2-binaphthol. The yield of 2-binaphthol for the oxidative coupling of 2-naphthol was low over the V catalyst (V/NaZSM-5) supported on NaZSM-5 that has only micropores. The access of 2-naphthol to the active V species present in the micropores was suggested to be inhibited by the shape selectivity of the sterically bulky reactant. The yield

of 2-binaphthol increased with an increase in the amount of V supported on the V/MCM-41 catalyst up to the V amount of about 1 wt.%, then leveled off with a further increase in the V amount. The variation in the tetrahedral V⁵⁺ species on the V/MCM-41 catalyst, identified by the DR spectra, versus the amount of supported V showed a similar trend to the yield of 2-binaphthol. The yield of 2-binaphthol increased with the increasing calcination temperature of the V/MCM-41 catalyst, although the quinone-like oxidation product(s) increased over the catalyst prepared at the high calcination temperature. Both the yield of 2-binaphthol and the tetrahedral V⁵⁺ species present on the MCM-41 support had a linear relationship. The tetrahedral V⁵⁺ species was thus confirmed to be the active ones for the oxidative coupling of 2-naphthol into 2-binaphthol.

Acknowledgement

We thank Mr. Kenji Nomura of Kobe University for his technical assistance during this study.

References

- [1] R. Noyori, H. Takaya, *Acc. Chem. Res.* 23 (1990) 345.
- [2] B.M. Trost, *Pure Appl. Chem.* 64 (1992) 315.
- [3] T. Hayashi, A. Kudo, F. Ozawa, *Pure Appl. Chem.* 64 (1992) 421.
- [4] H.B. Kagan, O. Riant, *Chem. Rev.* 92 (1992) 1007.
- [5] K. Mikami, M. Shimizu, *Chem. Rev.* 92 (1992) 1021.
- [6] J. Bao, W.D. Wulff, A.L. Rheingold, *J. Am. Chem. Soc.* 115 (1993) 3814.
- [7] G. Kaupp, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 728.
- [8] B. Feringa, H. Wynberg, *Bioorg. Chem.* 7 (1978) 397.
- [9] P. Mastrorilli, F. Muscio, G.P. Suranna, C.F. Nobile, M. Latronico, *J. Mol. Catal.* 165 (2001) 81.
- [10] D. Kuiling, W. Yang, Z. Lijun, *Tetrahedron* 52 (1996) 1005.
- [11] D.-R. Hwang, C.-P. Chen, B.J. Uang, *Chem. Commun.* (1999) 1207.
- [12] T. Sakamoto, H. Yonehara, C. Pac, *J. Org. Chem.* 59 (1994) 6859.
- [13] E. Armengol, A. Corma, H. Garcia, J. Primo, *Eur. J. Org. Chem.* (1999) 1915.
- [14] J. Okamura, S. Nishiyama, S. Tsuruya, M. Masai, *J. Mol. Catal. A: Chem.* 135 (1998) 133; H. Fujiyama, I. Kohara, K. Iwai, S. Nishiyama, S. Tsuruya, *J. Catal.* 188 (1999) 417.
- [15] R.J. Argauer, G.R. Argauer, G.R. Landolt, US Patent 3,702,886 (1972).
- [16] K.J. Chao, C.N. Wu, H. Chang, *J. Phys. Chem. B* 101 (1997) 6341.
- [17] M.L. Pena, A. Dejob, F. Rey, M.I. Vaquez, *Appl. Catal. A* 209 (2001) 155.