

Preparation and Catalytic Application of Transition Metal (Fe, V, or Cu) Oxides Homogeneously Dispersed in the Wall of Mesoporous Nb₂O₅

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Fe, V, or Cu oxide was mixed in mesoporous Nb₂O₅, at a few atom percent, and their extremely high dispersion was confirmed by elemental analysis in about 5-nm spots using TEM-EDS. These mesoporous Nb₂O₅ showed characteristic selectivity for cyclohexene oxidation depending on the kind of the doped metal oxide.

Mesoporous silica and metal oxides are regarded as advantageous matrix for supporting metal and metal oxides due to their high surface area.¹ Extremely high dispersion is also expected when the active homogeneous catalysts are anchored by reactions with surface hydroxy (OH) groups.¹ Although we have synthesized various mesoporous transition metal oxides, those of late transition metals, which are characteristic catalysts, could not be prepared. Accordingly, we attempted to highly disperse second transition metal oxide at a few atom percent in the inorganic network of mesoporous Nb₂O₅ materials, which have been recently prepared.² Sintering of the incorporated transition metal oxides are expected to be avoided at temperatures below crystallization temperature of Nb₂O₅ (773 K), where mesoporous structure is collapsed. Moreover, distinct catalytic behavior depending on the incorporated metal oxides, which would not be observed in the corresponding bulk materials, are expected because each transition metal atom is surrounded by Nb₂O₅. In this study Fe, V, and Cu oxides were homogeneously dispersed in mesoporous Nb₂O₅, and their catalytic activities were evaluated by cyclohexene oxidation.

A block co-polymer template (P85, PEO₂₆PPO₃₉, PEO₂₆, 1 g) was dissolved in 1-propanol (10 g) at ambient temperature followed by dispersion of a transition metal oxide (either Fe₂O₃, CuO, or V₂O₅, 0.07–0.35 mmol) by sonification for 5–15 min. Then, 7 mmol NbCl₅ was added with stirring for 5 min, and NaCl aqueous solution (0.05 M, 1 mL) was subsequently involved. The mixture was further stirred until the dispersed metal oxide powders were completely dissolved accompanied by evolution of HCl and the decrease in pH after NbCl₅ addition. The sol

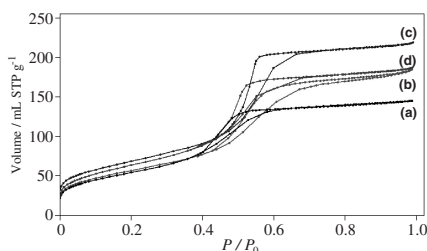


Figure 1. N₂ adsorption isotherms of Fe-doped mesoporous Nb₂O₅, (a) 0 mol%, (b) 1 mol%, (c) 3 mol%, and (d) 5 mol% Fe-doped mesoporous Nb₂O₅.

Table 1. Physical properties of doped mesoporous Nb₂O₅ materials

Doped Element	Content /mol %	S ^a /m ² g ⁻¹	Pore Size ^b /nm	Pore Volume /mLg ⁻¹	d(100) /nm
Pure Nb ₂ O ₅	—	202	4.1 ± 0.5	0.29	6.4
Fe	1.0	208	5.7 ± 0.8	0.37	6.3
Fe	3.0	254	5.0 ± 0.7	0.43	6.6
Fe	5.0	253	4.9 ± 0.6	0.37	6.3
V	3.0	200	4.0 ± 0.3	0.29	6.4
Cu	3.0	233	5.0 ± 0.8	0.38	7.1

^a BET surface area. ^b Errors were determined to involve 80% mesopores.

was aged at 313 K for 4–14 days until it was converted to dry films, and the surfactant was removed by calcination of the resulting transparent samples at 723 K for 5 h.³ Mesoporous Nb₂O₅ mixed with a transition metal oxide (Fe₂O₃, V₂O₅, or CuO) is hereafter referred to as “M-doped mesoporous Nb₂O₅ (M = Fe, V, or Cu)” for brevity.

N₂ adsorption isotherms of Fe-doped mesoporous Nb₂O₅ samples are compared in Figure 1. The amount of Fe₂O₃ was roughly adjusted to 1, 3, or 5 mol% of Nb₂O₅.⁴ All the Fe-doped Nb₂O₅ samples indicated the type IV isotherm pattern typical to mesoporous materials, and the estimated BET surface areas and pore volumes are summarized in Table 1 together with d(100) values in their XRD patterns.

As observed in the shift of the P/P₀ value corresponding to capillary condensation, pore size of the samples increased from ca. 4.0 to 5.0 nm by Fe-involvement. BET surface area and pore volume also increased by mixing a small amount of Fe₂O₃ in the mesoporous Nb₂O₅. Because d(100) values were almost the same as that of pure Nb₂O₅, the wall of mesoporous samples is considered to become thinner than the pure Nb₂O₅. Because 3% Fe-doped mesoporous Nb₂O₅ sample possessed the largest pore volume and BET surface area, its pore arrangement was directly observed by TEM. In Figure 2, TEM images of Fe(3%)-doped mesoporous Nb₂O₅ are shown, which are viewed from perpendicular and vertical to the direction of straight pore channels. Considering the wormhole-like pore structure of pure mesoporous Nb₂O₅ (not shown), doping of a small amount of

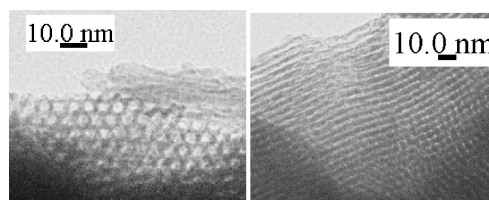


Figure 2. TEM images of Fe(3%)-doped mesoporous Nb₂O₅.

different element improved the ordering of the mesoporous structure. The pore structure of the other Fe-doped mesoporous Nb₂O₅ samples (1 and 5 mol %), were less ordered than those observed in Figure 2.






V- and Cu-doped mesoporous Nb₂O₅ were also prepared at 3 mol % addition, and their properties are shown in Table 1. In both cases, high BET surface area and pore volume were maintained. Pore size was not affected by V-addition, while Cu-doped mesoporous Nb₂O₅ had a pore size distribution centered at about 5.2 nm similarly to the case of Fe-doping. Pore arrangements of the V- and Cu-doped mesoporous Nb₂O₅ samples were worm-hole structure similarly to the non-doped mesoporous Nb₂O₅ (see TEM image of Cu-doped sample in graphical abstract).

Next, the dispersion of the Fe and V species in 3 mol % doped Fe and V were evaluated in 5.0-nm diameter ranges by the elemental analysis (EDS) using TEM apparatus.⁵ 2.2 and 3.4% were given as averaged doping amount of Fe and V, while ICP analysis indicated 2.7 and 3.8% for the same samples. Although ICP measurements showed slightly larger value, the high dispersions of Fe and V in both samples were confirmed by EDS. Therefore, homogeneous mixing of a different transition metal oxide in Nb₂O₅ was successful by dissolving the metal oxide in acidic solution of NbCl₅, even after calcinations at 723 K.

Catalytic properties of the M-doped (M = Fe, V, and Cu) mesoporous Nb₂O₅ samples were evaluated by oxidation of cyclohexene using *tert*-butylhydroperoxide (TBHP).⁶ As listed in Table 2, various oxidized products were obtained besides cyclohexene oxide; 2-cyclohexen-1-one, 2-cyclohexen-1-ol, 1,2-cyclohexanediol, and 1,2-cyclohexanedione. 1,2-cyclohexanediol was obtained as a main product in the case of mesoporous Nb₂O₅ due to the hydrolysis of the cyclohexene oxide produced by oxidation of cyclohexene. Both oxidation ability and acidity of Nb₂O₅ resulted in the high selectivity to 1,2-cyclohexanediol because no such oxidation products were produced over Nafion, a representative acid catalyst, under the same condition nor over a non-acidic CuO (Table 1). The selectivity of 2-cyclohexen-1-ol decreased and 1,2-cyclohexanedione was produced over Fe-doped mesoporous Nb₂O₅. In the case of V-doped mesoporous Nb₂O₅, the increases in conversion and selectivity to cyclohexene oxide were observed. Considering the slight increase in selectivity to 1,2-cyclohexanediol over V-doped mesoporous Nb₂O₅, the oxidation to cyclohexene oxide is encouraged by V-doping, followed by consequent increase in formation of 1,2-cyclohexanediol through the acid catalyzed hydrolysis by Nb₂O₅.

Cu-doped mesoporous Nb₂O₅ showed evident effects of doping; more than twice of conversion of pure Nb₂O₅ was obtained with a high selectivity to 2-cyclohexen-1-one. The result over Cu-doped mesoporous Nb₂O₅ should be compared with

Table 2. Oxidation of cyclohexene over doped mesoporous Nb₂O₅ materials⁶

Catalyst	Conversion /%	Selectivity /%						
							alcohols	ketones
Pure Nb ₂ O ₅	6.5	8.5	12.1	14.4	64.8	0.0	89.2	12.1
Fe (3%)-doped	6.5	6.8	11.7	4.8	68.8	7.8	73.6	19.5
V (3%)-doped	10.6	13.0	12.4	3.6	70.9	0.0	74.5	12.4
Cu (3%)-doped	14.0	1.8	80.1	2.2	5.9	9.7	8.1	89.8
CuO	2.1	11.0	71.5	17.0	0.0	0.0	17.0	71.5
Cu (3%)-loaded	6.3	4.2	72.8	15.5	7.4	0.0	22.9	72.8

those over pure CuO and CuO-loaded mesoporous Nb₂O₅.⁷

The high selectivity to cyclohexen-1-one was found to be originated from CuO. Considerable selectivity to cyclohexene oxide was observed on pure CuO, while decrease of it was accompanied by the formation of 1,2-cyclohexanediol over CuO-doped and CuO-loaded mesoporous Nb₂O₅ due to combination of CuO with the acidic Nb₂O₅. However, only 3 mol % involvement of Cu species in Nb₂O₅ effectively suppressed the acid catalyzed reaction over pure Nb₂O₅ owing to the high dispersion. Although the selectivity to cyclohexene oxide was not improved, the advantages of the presently prepared Cu-doped mesoporous Nb₂O₅ among the three types of CuO catalysts are; (1) it improved the original conversion more than twice, (2) nearly 90% selectivity was attained for production of ketones, and (3) the acid catalysis of Nb₂O₅ was suppressed by only 3 mol % doping. Therefore, present strategy, preparation of a homogeneously dispersed second transition metal element in mesoporous metal oxide, is considered to be advantageous to the conventional loading method in regard with the preparation of unique catalysts. Moreover, selections of the doped element and the original mesoporous metal oxide would lead to new types of characteristic catalysts.

References and Notes

- 1 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli, and O. M. Yaghi, *Chem. Mater.*, **11**, 2633 (1999), and the references therein.
- 2 B. Lee, J. N. Kondo, D. Lu, and K. Domen, *Chem. Lett.*, **2002**, 1058; B. Lee, J. N. Kondo, D. Lu, and K. Domen, *J. Am. Chem. Soc.*, **124**, 11256 (2002).
- 3 X-ray diffraction (XRD) was measured on Rigaku RINT200 diffractometer with Cu K α radiation, and N₂ adsorption isotherms were measured by COULTER OMNISORP 100CX and SA3100 systems. BET surface area was obtained at relative pressure (P/P_0) in 0.005–0.2 range, and pore size distribution was obtained from the analysis of the adsorption branch of the isotherms using the BJH (Barrett–Joyner–Halenda) method. Transmission electron microscope (TEM) images were obtained on a JEOL 2010F electron microscope operated at 200 keV. Inductively coupled plasma (ICP) atomic emission analysis was performed on a Shimadzu ICPS-8100 after dissolving the sample by HF solution to adjust to 5–10 mg·L⁻¹.
- 4 The ratio was determined by the number of metal in metal oxide.
- 5 Cu was not quantified owing to the use of Cu grid for TEM observations. 10 particles were selected for each sample, and the elemental analyses were performed on 60 and 64 spots for Fe- and V-doped mesoporous Nb₂O₅ samples.
- 6 0.20 g catalyst and 36 mmol cyclohexene were mixed in 5 mL acetonitrile, followed by addition of 6.6 mmol *tert*-butylhydroperoxide (TBHP) at 333 K. The products were analyzed by a gas–chromatograph (Shimadzu, GC-18A) with a capillary column (J&W capillary column, DB-FFAP). Acetonitrile was used as an internal standard.
- 7 CuO-loading (3%) was performed by dispersing mesoporous Nb₂O₅ in 0.01 M CuSO₄ aqueous solution, followed by calcination at 573 K in air. The amount of loaded CuO was measured as 3.4% by ICP analysis.