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Hydrothermal synthesis and catalysis of Nb₂O₅–WO_x nanofiber crystal

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 $Nb_2O_5-WO_x$ synthesized by a hydrothermal method having a long nano-crystalline structure with *ca*. 10 nm diameter exhibited a high catalytic activity in the Friedel–Crafts alkylations and acylations when it was calcined in N_2 .

1. Introduction

Metal oxides that have an acidic character are promising catalysts in organic synthesis and gas-phase reactions. Many kinds of monolayer-type oxides such as WO₃/ZrO₂ and SO₄²⁻/ZrO₂ having an acidic character have been studied extensively.1 Another class of acidic oxides is mixed metal oxides including SiO₂-Al₂O₃, SiO₂-TiO₂, and SiO₂-ZrO₂.² Nb₂O₅ mixed with WO₃ or MoO₃ may be categorized to the latter classes in which oxides with 6+ and 5+ valence states are mixed together. Hino et al. reported that Nb₂O₅-WO₃ prepared by the coprecipitation method exhibited a high activity in alkane cracking and dehydration of ethanol.³ Recently, Tagusagawa and Domen et al. reported the mesopores Nb-W oxide catalyst active in the Friedel-Crafts alkylation and hydrolysis of sucrose.⁴ We have also found that Nb₂O₅-WO₃ prepared by the coprecipitation method was active in the Friedel–Crafts alkylation.⁵ On the other hand, Nb₂O₅-WO₃ attracted attention not only as an acidic catalyst but also as photocatalyst and functional materials such as electrochromic devices.⁶ By means of a conventional method, niobium tungstate with the tetragonal tungsten bronze structure has been synthesized by calcining the mixture of Nb₂O₅, NbO₂, and WO₃ at high temperatures.⁷ Similarly, Nb₂O₅-WO₃ mixed oxide has been prepared by the coprecipitation method in which a mixed solution of niobium oxalate and ammonium tungstate was evaporated and thereafter calcined in air.8 In this study, we made an attempt to synthesize Nb_2O_5 -WO_x by a hydrothermal method with the aim of synthesizing a characteristic crystal that exhibits high catalytic activity. Hydrothermal synthesis has been applied to synthesize crystalline oxides with a high surface area and unique morphology.8 For instance, recently, Song et al. succeeded in synthesizing WO₃ nanowires with this method.⁹ Unlike the usual synthesis method of Nb₂O₅-WO₃ that requires a high temperature, hydrothermal synthesis is possible at a low

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temperature. Thus, hydrothermally synthesized $Nb_2O_5-WO_x$ (abbreviated as h-NbW) is expected to have a high surface area and enhanced intrinsic catalytic activity. Here, h-NbW was applied to the Friedel-Crafts alkylation of anisole with benzyl alcohol and to acylations performed using carboxylic acids as acylating agents. Its catalytic performance was compared with that of a catalyst prepared by the conventional coprecipitation method (abbreviated as c-NbW). In particular, acylations performed using carboxylic acids seem important to yield ketones from the viewpoint of green chemistry because water is the only side product, unlike conventional acylations carried out using carboxylic anhydrates and carboxylic chlorides that accompany the formation of carboxylic acid and HCl.¹⁰ In the present study, in addition to the synthesis of Nb₂O₅–WO_x, the influence of the calcination method and Ar bubbling on the catalytic performance of Nb₂O₅–WO_x was studied in detail.

2. Experimental

 $Nb_2O_5-WO_x$ was synthesized by a hydrothermal method; typically, a solution of ammonium paratungstate, (NH₄)₁₀-W₁₂O₄₁·5H₂O (supplied by Wako Chemicals, 2.03 g), dissolved in 60 ml of water was mixed in a flask with ammonium niobium oxalate, $NH_4[NbO(C_2O_4)_2(H_2O)] \cdot xH_2O$ (supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM) co., 0.263 g) dissolved in 10 ml of water and then bubbled with N2. The mixed solution was placed in a Teflon-sealed autoclave. The hydrothermal synthesis was carried out at 443 K while the bottle was continuously rotated at a speed of 15 rpm. The typical synthesis time was 48 h. After the synthesis, the formation of a white solid precipitate was observed at the bottom of the autoclave. The precipitate was calcined in an N₂ flow (50 ml min⁻¹) or in air by using a furnace at 773 K for 2 h prior to using it for catalytic reactions. Dark blue and light yellow solids were obtained after the calcination in N₂ and air, respectively. For comparison, Nb_2O_5 -WO_x was prepared by the coprecipitation method. Hydrated niobium oxide, Nb₂O₅ $\cdot n$ H₂O (n = 3.8, measured by thermogravimetric analysis) kindly supplied by CBMM Co. was dissolved into an oxalic acid solution heated at 353 K. Similarly, (NH₄)₁₀W₁₂O₄₁ was thoroughly dissolved in deionized water at

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353 K. Both the solutions were mixed and stirred vigorously at 353 K and then evaporated to dryness. Thus-obtained materials were calcined at 773 K for 3 h in an N_2 flow. The molar ratio between Nb and W of c-NbW was 1 : 2.3.

Field emission scanning electron microscope (FE-SEM) images were taken by means of a JEOL JSM-6701F microscope with an acceleration voltage of 5 kV. Transmission electron microscope (TEM) images were taken by means of a HITACHI H-9000UHR microscope with an acceleration voltage of 300 kV. In order to confirm the special distribution of Nb and W, we also carried out the EDX analyses by means of a HITACHI HF-2000 microscope (acceleration voltage of 200 kV) equipped with a Kevex SIGMA spectrometer and a FEI Tecnai G2 F20 microscope (acceleration voltage of 200 kV) equipped with an EDAX r-TEM spectrometer. The specimen for TEM observation was prepared by the crushing method, and the TEM observations were carried out at room temperature. The crystalline structure was analyzed by XRD in ambient conditions using a Rigaku Ultima IV X-ray diffractometer with Cu K_a radiation. Data of N₂ adsorption isotherms were collected with BELSORP-max. Samples were dehydrated at 573 K under vacuum prior to the measurements.

Synchrotron radiation experiments were performed at the BL01B1 station with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2009A1055). A Si(111) single crystal was used to obtain a monochromatic X-ray beam. The measurement was carried out in a quick mode. For the collection of W L₃-edge data, the ion chambers filled with N₂ and N₂(50%)/Ar(50%) were used for I_0 and I, respectively. For the collection of Nb-K edge data, the ion chambers filled with Ar and Ar(75%)/Kr(25%) were used for I_0 and I, respectively. The energy was calibrated using W and Nb foils for the collection of W-L₃ and Nb-K edge XAFS data, respectively. The data were analyzed using the REX2000 ver. 2.5.9 program (Rigaku Co.). Fourier transformation of $k^3\chi(k)$ data were performed in a k range of 20–175 nm⁻¹ for the analysis of the W L₃-edge EXAFS spectra.

The acid property of synthesized Nb₂O₅–WO_x was measured by means of TPD of ammonia with an equipment of Japan Bel TPD-1-AT(NH3). The sample was evacuated at 673 K prior to the measurement. 13.3 kPa of ammonia were equilibrated with the pretreated sample at 373 K. The TPD data were collected with the temperature ramping rate of 10 K min⁻¹. A mass spectrometer was used to measure the desorbed NH₃. In the measurement, m/z = 16 was monitored to analyze the desorbed NH₃. This mass number was used instead of m/z = 17 in order to prevent the interference caused by water.

Benzylation of anisole (Friedel–Crafts alkylation) was carried out over the Nb₂O₅–WO_x catalysts (catalyst weight: 0.02 g). The reaction was performed using 10 g of anisole and 0.675 g (6.25 mmol) of benzyl alcohol in an oil bath at 353 K in an atmosphere of N₂ or with Ar bubbling (Ar: 99.9999%, 30 ml min⁻¹). Acylation of anisole with various straight-chain carboxylic acids (Friedel–Crafts acylations) was carried out in a manner analogous to the benzylation of anisole using 10 g of anisole and 2 mmol of carboxylic acids in an oil bath at 413 K (catalyst weight: 0.1 g). For recycling, the catalyst was separated by filtration followed by washing with anisole. It was then repeatedly used for further reaction without pretreatment. The products were



Fig. 1 Dependence of (a) the amount of solid and (b) W/Nb ratio plotted as a function of time for hydrothermal synthesis.

analyzed with a gas chromatograph (GC-2010, Shimadzu) equipped with a capillary column (InertCap 5) and an FID detector. In the analysis, tridecane was used as an internal standard.

3. Results and discussion

3.1. Hydrothermal synthesis of Nb_2O_5 -WO_x

 Nb_2O_5 -WO_x was hydrothermally synthesized using a mixed solution of $(NH_4)_{10}W_{12}O_{41}$ and $NH_4[NbO(C_2O_4)_2(H_2O)]$. In Fig. 1a, the amount of the obtained solid precipitate is plotted as a function of the synthesis time. A steep increase in the amount of the precipitate was observed in less than 12 h. The yield of the obtained h-NbW was calculated from the loaded amount of $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ and $NH_4[NbO(C_2O_4)_2(H_2O)] \cdot xH_2O$ was found to be 72% and 92% after 48 h and 336 h from the beginning of the synthesis, respectively. In contrast, no precipitate was found to form over $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ without the addition of Nb source or $NH_4[NbO(C_2O_4)_2(H_2O)] \cdot xH_2O$ without the addition of W source, implying that the combination of W and Nb was necessary to form a solid precipitate. In Fig. 1b, the molar ratio between W and Nb of the synthesized oxide is plotted as a function of the synthesis time. The composition of Nb₂O₅- WO_x was measured by the inductively coupled plasma (ICP) method after melting Nb₂O₅-WO_x with KOH at 773 K and then dissolving the obtained residue in water. Fig. 1b indicates that the W/Nb ratio tended to decrease with an increase in the synthesis time, meaning an increase in the amount of Nb incorporated into Nb₂O₅-WO_x.

3.2. Structural and acidic characterizations

Fig. 2 shows the FE-SEM images of h- and c-NbW with the magnitude of $\times 100\ 000$. The image of c-NbW calcined in N₂ was almost shapeless (Fig. 2a). In contrast to this, the formation of fiber-like shape, which aggregate and make bundles, was clearly seen in the image of h-NbW calcined in N₂ (Fig. 2b). The maximum length of the fibers was at least several micrometres. The diameter of the fibers was *ca*. 10 nm. The fiber-like shape was almost collapsed after grinding in a mortar or calcination in air at 773 K to give aggregates of round-shaped particles (Fig. 2c and d). These FE-SEM images indicated that the formation of nanofiber was realized only when h-NbW was calcined in N₂. TEM images of h-NbW calcined in an N₂ flow are shown in Fig. 3. In agreement with the FE-SEM images (Fig. 2b),



Fig. 2 FE-SEM images of (a) c-NbW calcined in N_2 , (b) h-NbW calcined in N_2 , (c) h-NbW calcined in N_2 followed by grinding with a mortar, and (d) h-NbW calcined in air at 773 K.



Fig. 3 The TEM image and the electron diffraction pattern (inset) of h-NbW calcined in an N_2 flow.



Fig. 4 FFT images of the region a-c in the TEM image of Fig. 3.

crystallites with fiber-like shape are clearly visible in the images. The electron diffraction patterns taken from the nanofibers indicated that the fiber was single-crystalline which has tetragonal structure similar to tetragonal tungsten bronze (TTB), $Na_{1,2}Nb_{1,2}W_{0.8}O_6$, with a preferential growth in the [001] direction.¹¹ However, the broadness of the diffraction spots as shown in the inset of Fig. 3 suggested the low crystallinity of the



Fig. 5 TEM images of h-NbW: (a and b) as prepared and (c and d) calcined in an N_2 flow at 773 K. EDX semi-quantitative analyses were made in regions indicated by red squares.

Table 1 Atomic (molar) ratio of Nb : W in different regions of Nb₂O₅–WO_x fibers in Fig. 5

Image no.	Region	W/Nb atomic ratio
a	1	8.75
a	2	10.95
b	1	8.96
b	2	8.44
b	3	7.79
b	4	8.57
с	1	9.56
с	2	9.50
d	1	9.78
d	2	8.31



Fig. 6 Bright field and EDX spectrum images of h-NbW calcined in N_2 . (a) Bright field, EDX mapping of (b) Nb-K_{α} and (c) W-L_{α}.

synthesized fiber. The appearance of streaks also suggested that single fiber contains several planar defects. Fig. 4 shows FFT images of the TEM lattice images of the region a-c in Fig. 3. No significant difference in the patterns was found in these images, indicating the homogeneous structure in a Nb-W nanofiber. In order to measure the distribution of Nb and W atoms, EDX semi-quantitative analysis in different regions of Fig. 5 with area from 5 to 500 nm φ was made using Nb-K_{α} and W-L_{α} lines. The measured composition of the sample was listed in Table 1. No substantial deviation from the ratio Nb: W = 1:9.1 was found before and after the calcination in N_2 . That is to say, the average molar ratio of as prepared and the calcined samples were calculated to be 8.9 and 9.3, respectively, which almost agreed with the bulk composition (W/Nb = 9.1) of the Nb-W measured by ICP (Fig. 1b, 48 h). Further, EDX spectra images (mapping) of Nb-K_{α} and W-L_{α} of h-NbW calcined in N₂ were displayed in Fig. 6. We confirmed that Nb and W were homogeneously distributed in the nanofiber, suggesting the formation of solid solutions.

X-Ray diffraction (XRD) patterns of h-, c-NbW and reference samples are presented in Fig. 7. The pattern of h-NbW calcined in air at 773 K (d) was close to that of monoclinic crystalline WO₃ (e), indicating crystalline WO₃ and amorphous Nb₂O₅ were segregated. In contrast to this, the pattern of h-NbW calcined in N₂ was almost featureless, but intense diffraction peaks appeared at $2\theta = 23.3$ and 47.7°, which were tentatively assignable to the (001) and (002) planes from the comparison with the XRD pattern of TTB structure, respectively.¹¹ Intensity of these diffraction lines became smaller after grinding in a mortar (b), probably due to the disruption of the nanofiber as observed in FE-SEM images (Fig. 2c). Although the intensity of the peaks



Fig. 7 Powder XRD patterns of Nb₂O₅–WO_x and reference samples. (a) h-NbW calcined in N₂, (b) h-NbW calcined in N₂, followed by grinding with a mortar, (c) c-NbW calcined in N₂, (d) h-NbW calcined in air, (e) WO₃, and (f) Nb₂O₅.



Fig. 8 N_2 adsorption isotherms of (a) c-NbW calcined in N_2 , (b) h-NbW calcined in N_2 , (c) h-NbW calcined in N_2 , followed by grinding with a mortar, and (d) h-NbW calcined in air. Closed symbols: adsorption branches; open symbols: desorption branches.

was broad and smaller, a similar pattern was observed in the XRD of c-NbW (c).¹²

Fig. 8 shows N₂ adsorption isotherms of h- and c-NbW. The N₂ adsorption isotherms categorized to the type II were obtained in these samples. The Brunauer–Emmett–Teller (BET) surface area of h-NbW calcined at 773 K in an N₂ flow was 63 m² g⁻¹, which was much higher than that calcined in air (16 m² g⁻¹), h-NbW ground with a mortar (39 m² g⁻¹) and c-NbW (15 m² g⁻¹). The low specific surface area of h-NbW calcined in air may be due to the formation of crystalline WO₃ as confirmed by the XRD pattern shown in Fig. 7d. Thus, it is noted that the hydrothermal synthesis coupled with calcination in an N₂ flow was effective in increasing the surface area of Nb₂O₅–WO_x due to the persistence of fiber-like structure.

Fig. 9 shows the W L₃-edge EXAFS spectra of h-NbW $k^3\chi(k)$ and their Fourier transforms. The EXAFS spectrum of h-NbW calcined in air was similar to that of crystalline-WO₃, in agreement with the XRD data. In the W L₃-edge EXAFS Fourier transform of h-NbW calcined in N₂, the peak assignable to the



Fig. 9 W L₃-edge EXAFS of h-NbW calcined in N₂, air and reference samples: (a) $k^3\chi(k)$ and (b) Fourier transforms.



Fig. 10 (a) W L_3 - and (b) Nb K-edge XANES of h-NbW calcined in N_2 and in air and those of reference samples.

W-O-W bond could be seen at 0.37 nm (Fig. 9b). This feature was partially similar to that of WO₂, suggesting the formation of W⁴⁺ species. This peak corresponded to the characteristic rapid oscillations that can be observed at 80–170 nm⁻¹ in the $k^3\chi(k)$ spectra (Fig. 9a). Fig. 10a gives the W L3-edge XANES of h-NbW calcined at 773 K in N2 and in air, together with those of the reference samples. The steep white line appeared at 10 209 eV. This is attributed to the electronic transition from $2p_{3/2}$ to the vacant 5d orbital. Therefore, the white line reflects the electronic state of the vacant d orbitals of the W atom.¹³ The intensity of the white line of h-NbW calcined in air was comparable to that of WO₃, meaning that the valence of the uncalcined sample was 6+. Unlike this, the intensity of h-NbW calcined in N2 was comparable to that of WO2, suggesting that W was reduced to tungsten oxide with a lower valence state (4+) as a result of calcination in N2 at 773 K. In agreement with the XANES data, the color of h-NbW changed from white (uncalcined sample) to dark blue as a result of calcination in N2, while the color of h-NbW calcined in air was light yellow. Fig. 10b presents the Nb K-edge XANES of h-NbW calcined in N2 and air, together with that of bulk Nb₂O₅. The spectra of h-NbW were similar to that of Nb₂O₅, suggesting that the valence of niobium oxide was 5+. Fig. 11 shows the temperatureprogrammed desorption (TPD) of ammonia from the prepared



Fig. 11 Temperature-programmed desorption of ammonia from (a) h-NbW calcined in air, (b) h-NbW calcined in N_2 , (c) h-NbW calcined in N_2 , followed by grinding with a mortar and (d) c-NbW calcined in N_2 .

itry (Catalyst	Calcination condition	Bubbling ^f	Benzyl alcohol conv. (%)	Benzyl anisole yield (%)	Dibenzyl ether yield (%)	Material Balance (%)	TON^g
	WdN-r	Air		0	0	0	100	0
	J-NbW	Air	Ar	0	0	0	100	0
. 4	NbW	\mathbf{N}_2		34	26	3	98	550
. =1	NbW	N ₂		51	41	3	97	830
. =1	NbW	N ₂	Ar	66	89	4	98	1600
. =1	NbW	\mathbf{N}_2	Ar	68	60	4	100	4400
4	NbW	N,	$Ar + 0.3\% O_2$	18	15	7	100	290
5	-NbW	N,	Ar	1	1	0	100	20
. 4	NbW	\mathbf{N}_2	Ar	2	2	0	100	25
4	H-β zeolite ^{e}	\mathbf{N}_2	Ar	13	5	2	96	36

осн₃

OCH₃

Table 2 Friedel–Crafts alkylation over Nb₂O₅–WO_x catalysts⁴

samples. A broad desorption peak of ammonia is observed in these spectra. The acid amount was calculated from the desorbed ammonia. The acid amounts of h-NbW samples that were calcined in N₂ and air were determined to be 0.25 and 0.09 mol kg⁻¹, respectively, indicating that the calcination of the sample in N₂ was effective in enhancing the acid amount of h-NbW. The amount decreased to 0.19 mol kg⁻¹ after grinding with a mortar. The acid amount of c-NbW calcined in N₂ was 0.21 mol kg⁻¹. The amount of c-acid NbW was much lower than that of h-NbW.

3.3. Friedel–Crafts alkylations

Table 2 lists the data of the Friedel-Crafts alkylation of anisole with benzyl alcohol carried out over the h- and c-NbW catalysts. First, the influence of the gas atmosphere on the calcination of h-NbW was investigated. h-NbW calcined in air was completely inactive in the reaction (entry 1), probably due to the formation of crystalline WO₃, as evidenced by XRD and EXAFS. However, the conversion of benzyl alcohol increased from 0% to 34% through the calcination of h-NbW in N₂ (entry 3), indicating that the calcination in N2 in place of air was effective in enhancing the catalysis of h-NbW. Second, the influence of Ar bubbling (30 ml min⁻¹) over the h-NbW catalyst calcined in N₂ was examined. From the comparison of the data of entries 3 and 5, a remarkable enhancement in the catalytic activity was confirmed. That is, the conversion of benzyl alcohol increased from 34% to 99% through the application of Ar bubbling into the solution. The ratio of the p and o-alkylated products was 58 : 42, as analyzed by the GC. Formation of the multiply alkylated products was not observed. The amount of dibenzyl ether (byproduct) formed was less than 4% in every reaction. The reaction was performed after the addition of a dried molecular sieve in order to check the possibility accelerating catalysis through the removal of H₂O accompanied by Ar bubbling as a result of a shift in the reaction equilibrium (entry 4). Although the conversion of benzyl alcohol increased from 34% to 51% by the addition of the molecular sieve, the extent of improvement was much lower than that obtained by Ar bubbling (entry 5), indicating that the effect of H₂O removal by Ar bubbling was limited. Although the remarkable effect of Ar bubbling on the catalytic activity is not fully understood at this stage, one hypothesis is that Ar was effective in keeping the air-free conditions; thus, the low valence state of W oxide and the fiberlike shape were maintained during reactions as evidenced by TEM and FE-SEM. In agreement with this, the addition of 0.3% O₂ in Ar resulted in severe deactivation of the catalyst (conv. = 18%, entry 7). Third, the effect of preparation method was examined. As compared with N2-calcined samples, h-NbW exhibited much higher conversion and TON (entry 5, conv. = 99%, TON= 1600) in comparison with c-NbW (entry 8, conv. = 1%, TON = 20) and H- β zeolite (entry 10, conv. = 13%, TON = 36). The h-NbW ground with a mortar was almost inactive in the reaction (entry 9, conv. = 2%, TON = 25) despite the presence of substantial acid amount as measured by NH₃-TPD (0.19 mol kg^{-1}). The fact suggested that the nanofiber structure was important in the evolution of catalytic activity. In order to examine the possibility for the dissolution of W in anisole, the concentration of W in anisole was measured by the ICP method after the reaction performed using h-NbW. The dissolved amount of W was less than 0.2% of the total W present in the catalyst. Furthermore, no reaction proceeded after the addition of substrates into the filtrate. These facts suggested that the reaction proceeded on the solid h-NbW catalyst. As a whole, the following three prerequisites are necessary to evolve high activity in a Nb₂O₅–WO_x catalyst: (1) hydrothermal synthesis, (2) calcination in N_2 and (3) Ar bubbling during reactions.

3.4. Friedel–Crafts acylations

h-NbW calcined in N_2 was applied to the Friedel–Crafts acylation of anisole by using various carboxylic acids. The catalyst was calcined at 773 K in an N_2 flow prior to the reactions. Table 3 lists the data of the acylations performed with Ar bubbling. h-NbW exhibited high activity in the reaction performed using various carboxylic acids, with an exception of benzoic acid (entry 9). *p*-Acylated ketones were obtained as primary products, where the molar ratio of *p*- and *o*-acylated products was 98 : 2. The yield of

 Table 3 Friedel–Crafts acylations of anisole with various straight-chain carboxylic acids^a

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$$PCH_3 + P_2O$$
 $PCH_3 + H_2O$

Entry	R	Catalyst	Carboxylic acid conv. (%)	Ketone yield (%)	Methyl ester yield (%)	Phenyl ester yield (%)	Material balance (%)	TON ^e
1	C_3H_7	h-NbW	93	82	1	0	91	98
2^{b}	C_3H_7	h-NbW	90	76	1	0	87	95
3	C_5H_{11}	h-NbW	97	93	0	0	103	102
4	$C_{5}H_{11}$	c-NbW	0	0	0	0	100	0
5	$C_{5}H_{11}$	H- β zeolite ^d	46	35	0	0	90	7
6	C_7H_{15}	h-NbW	91	82	1	1	93	96
7	$C_{9}H_{11}$	h-NbW	98	89	0	3	94	103
8	$C_{11}H_{23}$	h-NbW	77	62	1	2	85	81
9	$C_6H_5^{\frac{2}{c}}$	h-NbW	33	22	0	0	90	35

^{*a*} Reaction conditions: anisole (92.5 mmol), carboxylic acid (2.0 mmol), catalyst (0.1 g), 413 K, 3 h, Ar bubbling (30 ml min⁻¹). ^{*b*} 2nd run. ^{*c*} Benzoic acid. ^{*d*} H-β-20 (Si/Al₂ = 25), supplied by PQ company. ^{*e*} Turnover numbers calculated based on the conversion of carboxylic acids and acid amounts determined by NH₃-TPD. esters was less than 3% in every reaction. In marked contrast to h-NbW, in agreement with the data of alkylations given in Table 2, c-NbW was almost inactive in the reaction (entry 4). In addition, the yield of ketones was almost three-times higher than that obtained with H- β zeolite (supplied by PQ Co., Si/Al₂ = 25, entry 5). This fact indicated the superior nature of h-NbW calcined in N₂. The recycle use of the h-NbW catalyst was possible, as can be seen in the reaction data using butanoic acid (entry 2).

Taking account of the W L3-edge XANES data, TEM and SEM images, it is postulated that the formation of partially reduced tungsten atoms (probably W4+) in the crystalline Nb2O5- WO_x during the course of calcination in an N_2 flow was responsible for the evolution of catalysis in the Friedel-Crafts reactions. This assumption is in agreement with the result reported by several groups in that partially reduced tungsten oxides exhibit the Brønsted acid character.14 Probably, the oxalate anion or ammonium cation acted as a reductant for tungsten oxide during calcination of h-NbW in N2. Consistent with the assumption, it has been reported that the formation of tungsten bronze through the decomposition of ammonium paratungstate changed depending on the gas employed. Namely, the calcination of ammonium paratungstate in He and O2 resulted in the formation of partially reduced tungsten bronze and crystalline triclinic WO₃, respectively.¹⁵ Therefore, it is inferred that the role of N₂ is to keep the inert atmosphere while reducing nanofibers with oxalate anions or ammonium cations.

4. Conclusions

Hydrothermal synthesis of Nb₂O₅–WO_x was carried out over a mixed solution of Nb and W in an autoclave at 443 K. Synthesized Nb₂O₅–WO_x had a long nano-crystalline structure with *ca.* 10 nm diameter as observed by FE-SEM and TEM. It exhibited a high catalytic activity in the Friedel–Crafts alkylations and acylations when it was calcined in N₂. Ar bubbling was effective in enhancing the catalytic activity of N₂-calcined Nb₂O₅–WO_x. Comparison of the catalytic performance and structural characterizations revealed that the nanofiber structure with partially reduced tungsten oxide species was indispensable to afford high catalytic activity in the Friedel–Crafts reactions.

References

- M. Hino and K. Arata, *Chem. Commun.*, 1988, 1259; X. M. Song and A. Sayari, *Catal. Rev. Sci. Eng.*, 1996, **38**, 329.
- 2 K. Tanabe, in *Catalysis-Science and Technology*, ed. J. R. Anderson and M. Boudart, Springer-Verlag, Berlin, 1981; T. Shishido, T. Kitano, K. Teramura and T. Tanaka, *Catal. Lett.*, 2009, **129**, 383.
- 3 M. Hino, M. Kurashige and K. Arata, *Catal. Commun.*, 2004, 5, 107; M. Hino, M. Kurashige, H. Matsuhashi and K. Arata, *Appl. Catal.*, *A*, 2006, 310, 190.
- 4 C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi and K. Domen, *Angew. Chem.*, *Int. Ed.*, 2010, 49, 1128.
- 5 K. Yamashita, M. Hirano, K. Okumura and M. Niwa, *Catal. Today*, 2006, **118**, 385.
- 6 P. R. Bueno, C. Gabrielli and H. Perrot, *Electrochim. Acta*, 2008, 53, 5533; C. Martin, I. Martin, V. Rives, G. Solana, V. Loddo, L. Palmisano and A. Sclafani, *J. Mater. Sci.*, 1997, 32, 6039; M. L. Sanjuan, A. Kuhn, M. T. Azcondo and F. Garcia-Alvarado, *Eur. J. Inorg. Chem.*, 2008, 49.
- 7 F. Krumeich, M. Worle and A. Hussain, J. Solid State Chem., 2000, 149, 428.
- 8 W. Ueda, K. Oshihara, D. Vitry, T. Hisano and Y. Kayashima, *Catal. Surv. Jpn.*, 2002, **6**, 33.
- 9 X. C. Song, Y. F. Zheng, E. Yang and Y. Wang, *Mater. Lett.*, 2007, 61, 3904.
- 10 K. Okumura, J. Jpn. Pet. Inst., 2009, 52, 219.
- 11 M. L. Sanjuán, A. Kuhn, M. T. Azcondo and F. García-Alvarado, *Eur. J. Inorg. Chem.*, 2008, 49.
- 12 P. Botella, É. García-González, B. Solsona, E. Rodríguez-Castellón, J. M. González-Calbet and J. M. López Nieto, J. Catal., 2009, 265, 43.
- 13 S. Yamazoe, Y. Hitomi, T. Shishido and T. Tanaka, J. Phys. Chem. C, 2008, 112, 6869.
- 14 H. Belatel, H. Al-Kandari, F. Al-Kharafi, F. Garin and A. Katrib, *Appl. Catal.*, *A*, 2007, **318**, 227; A. Benadda, A. Katrib, J. W. Sobczak and A. Barama, *Appl. Catal.*, *A*, 2004, **260**, 175.
- 15 O. Kirilenko, F. Girgsdies, R. E. Jentoft and T. Ressler, *Eur. J. Inorg. Chem.*, 2005, 2124; I. M. Szilágyi, F. Hange, J. Madarasz and G. Polol, *Eur. J. Inorg. Chem.*, 2006, 3413.