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Layered Nb_2O_5–WO_x Sheet Catalyst Composed of Nanofibers That Are Active in Friedel–Crafts Reactions

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We found that the post treatment of Nb_2O_5–WO_x fibers with an aqueous solution of oxalic acid resulted in the formation of nanosheet oxides with a layer-by-layer structure in which bundles of fibers were assembled. The oxalic acid-treated catalyst showed much better recyclability in Friedel–Crafts alkylation and acylation compared to untreated material.

The fabrication of solid acid oxide that shows active and durable catalytic performance is important in the field of heterogeneous catalysts. Such metal oxides are useful catalysts in the field, including in organic synthesis and the petroleum industry. Among various acidic oxides, tungsten-based oxides, represented by WO_3/ZrO_2, and heteropolyacid are promising because they possess strong acidity. These catalysts have been attracting attention not only as an acidic catalyst but also as a photocatalyst and as functional materials such as in electrochromic devices, including gas sensors.[1–3] We have also reported that Nb_2O_5–WO_3 prepared by coprecipitation was active in Friedel–Crafts alkylation.[4] Further, we have recently attempted to synthesize Nb_2O_5–WO_x using hydrothermal methods.[5] The hydrothermally synthesized Nb_2O_5–WO_x had a long nanocrystalline tetragonal tungsten bronze structure as observed by electron microscopy. The N_2-calcined Nb_2O_5–WO_x exhibited a much higher catalytic activity in Friedel–Crafts alkylation and acylation compared to Nb_2O_5–WO_3 prepared by coprecipitation. Taking account of the data of W L_3-edge XANES and electron microscopy, it was postulated that the formation of partially reduced tungsten atoms (probably W^{4+}) in the crystalline Nb_2O_5–WO_x during calcination in an N_2 flow was responsible for the evolution of catalysis in the Friedel–Crafts reactions. The activity of Nb_2O_5–WO_x was 10 times higher than that of β-zeolite, which is one of the best catalysts reported so far. However, the hydrothermally synthesized Nb_2O_5–WO_x showed difficulty in separation from the solution without centrifugation or filtration due to its needle-like morphology. Moreover, the hydrothermally synthesized Nb_2O_5–WO_x was fragile. The fibrous structure was readily destroyed by crushing with a mortar to form crystalline WO_3, which is almost inactive in Friedel–Crafts alkylation.

In this work, we attempted to treat the hydrothermally synthesized Nb_2O_5–WO_x with an aqueous solution of oxalic acid. The aim of this was to synthesize a characteristic solid acid catalyst that exhibits superior catalytic performance. It has been reported that the hydrothermal synthesis of WO_3 in the presence of oxalic acid resulted in the formation of regularly formed WO_3 particles with a spindle shape.[6] This suggests that the oxalic acid had a profound effect on the genesis of WO_3 crystals. Here, the hydrothermally synthesized Nb_2O_5–WO_x was treated with an aqueous solution of oxalic acid, and the catalyst was applied to Friedel–Crafts alkylation of anisole with benzyl alcohol and to acylation performed using octanoic acid as an acylating agent. Its catalytic performance and morphology was compared with that of a catalyst prepared by those of untreated NbW.

Nb_2O_5–WO_x was synthesized using a hydrothermal method. A solution of ammonium paratungstate, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (2.03 g) dissolved in 60 mL of water was mixed in a flask with ammonium niobium oxalate, $NH_4[NbO(C_2O_4)_2(H_2O)]\cdot xH_2O$ (CBMM Co., 0.263 g) dissolved in 10 mL of water and then bubbled with N_2. The mixed solution was placed in a Teflon-sealed autoclave. The hydrothermal synthesis was carried out at 443 K for 48 h while the bottle was continuously rotated at a speed of 15 rpm. After the synthesis, the formation of a white solid precipitate was observed at the bottom of the autoclave. The precipitate was treated with an aqueous solution of oxalic acid (0.2–$4.6\,mol\,L^{-1}$) at 353 K for 10 h. The treated white sample was calcined in an N_2 flow ($30\,mL\,min^{-1}$) at 723 K for 2 h prior to using it for characterization and catalytic reactions. This catalyst is denoted as o-NbW. o-NbW comprised shining grains with a dark blue color.[7] For comparison, the as-synthesized material was calcined in an N_2 flow at 773 K without treatment with oxalic acid. This sample will be denoted

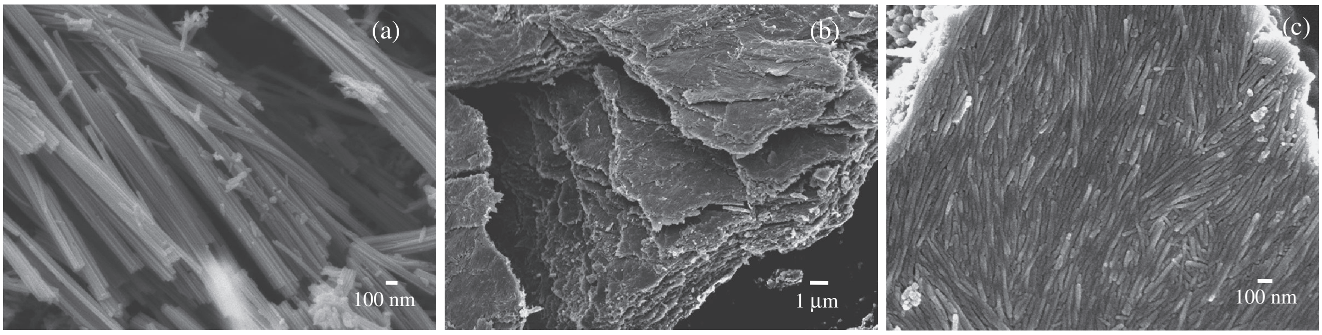

Figure 1. FE-SEM images of (a) NbW and (b), (c) o-NbW.

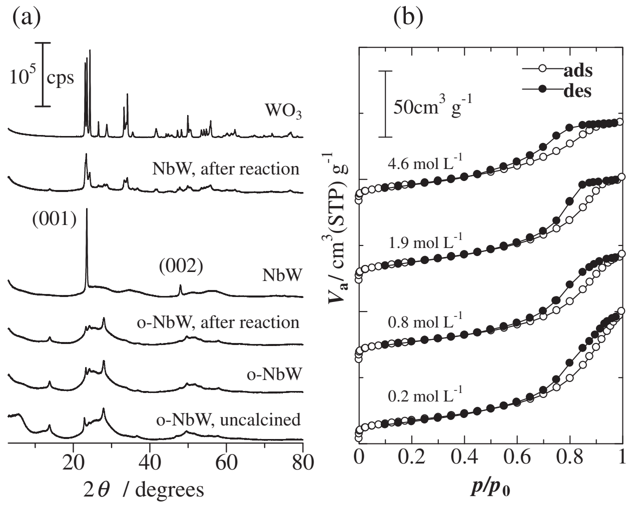

Figure 2. (a) XRD patterns of NbW and o-NbW measured before and after benzylation of the anisole; (b) N_2 adsorption isotherms of o-NbW. The numbers indicated the concentration of oxalic acid solutions for preparation of o-NbW.

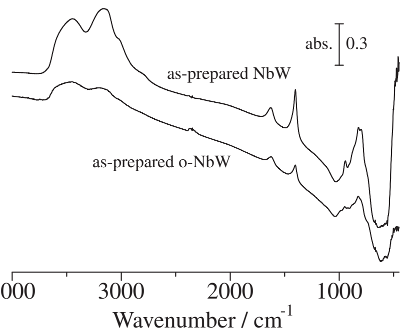

Figure 3. IR spectra of as-prepared NbW and o-NbW (uncalcined).

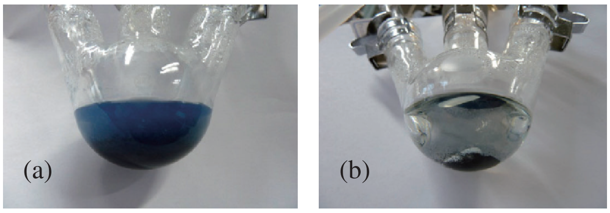

Figure 4. Pictures taken after the Friedel–Crafts acylation of anisole with octanoic acid after 0.5 h from stopping reaction. (a) NbW and (b) o-NbW.

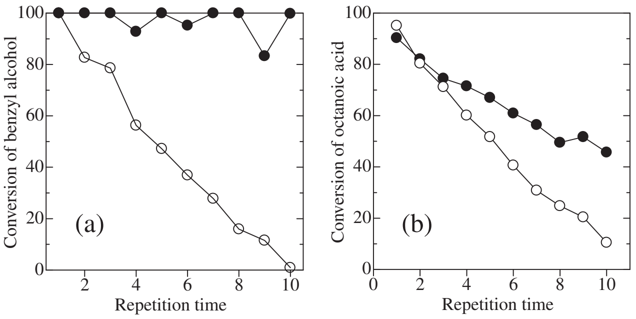

Figure 5. Conversion plotted as a function of repetition time in the Friedel–Crafts reaction. (a) Alkylation of anisole using benzyl alcohol and (b) acylation of anisole using octanoic acid. ○ NbW; ● o-NbW (oxalic acid: 1.9 mol L^{-1}).

as NbW. Benzylation of anisole (Friedel–Crafts alkylation) was carried out over the catalysts (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 with Ar bubbling (30 mL min^{-1}). Acylation of anisole with octanoic acid (Friedel–Crafts acylation) was carried out in a manner analogous to the benzylation of anisole, using 10 g of anisole and 0.288 g (2 mmol) of octanoic acid in an oil bath at 413 K (catalyst weight: 0.1 g).

Figure 1 shows field emission scanning electron microscopy (FE-SEM; JEOL JSM-6701F) images of NbW and o-NbW. In the NbW image (Figure 1a), the formation of the fiber-like shape, which aggregated and formed bundles, was clearly seen. The maximum length of the fibers was at least several micrometers. These bundles of fibers in NbW were randomly oriented. In the o-NbW image (Figure 1b), in a marked difference from NbW, a characteristic sheetlike structure can be seen. The sheets showed a layer-by-layer stacking configuration. This feature did not change after the calcination in N_2, meaning the formation of the stacked sheets was realized when as-synthesized NbW was treated with oxalic acid rather than calcination in N_2. Figure 1c shows the FE-SEM image of the surface of the sheetlike structure measured with higher magnitude (×40000). It can be seen in the image that the fibrous structure assembled to form a sheet. The thickness of the sheet was estimated to be 25 nm, which accorded with the diameter of one nanofiber (25 nm). The length of each fiber composing the sheet was approximately 0.27 µm, which was shorter than that of as-synthesized NbW. This indicated that the fibers were cleaved during treatment with oxalic acid. In agreement with the short length of the nanofibers, X-ray diffraction (XRD) peaks assignable to planes (001) and (002) became smaller after treatment with oxalic acid (Figure 2a, o-NbW).

Figure 2b shows the N_2 adsorption isotherms of o-NbW, which was prepared by using a different concentration of oxalic acid. The specific surface area of the o-NbW was 59–64 $m^2 g^{-1}$, which agrees with that of NbW (62 $m^2 g^{-1}$). o-NbW showed the N_2 adsorption isotherms categorized to type IV, indicating the presence of mesopores. The pore structure probably came from the interspaces of nanofibers or the boundaries of sheets. The averaged pore diameter size was 3.1–4.6 nm. The mesopore diameter became smaller as the concentration of oxalic acid increased from 0.2 to 4.6 mol L^{-1}. The mesopore volume was 0.10–0.15 $cm^3 g^{-1}$. The W/Nb ratio of o-NbW was 22, as measured by ICP; this was close to that of as-synthesized NbW (W/Nb = 21). The genesis of the stacked nanosheet structure was not revealed at this stage; however, the treatment of as-synthesized NbW with oxalic acid resulted in the decrease in the number of OH groups on the surface of the nanofibers as measured by IR spectra given in Figure 3, which appeared at 2900–3700 cm^{-1} (OH stretching mode). This suggested that the dehydration and connection of the fibers took place to create a sheet structure under acidic conditions. The acid properties of

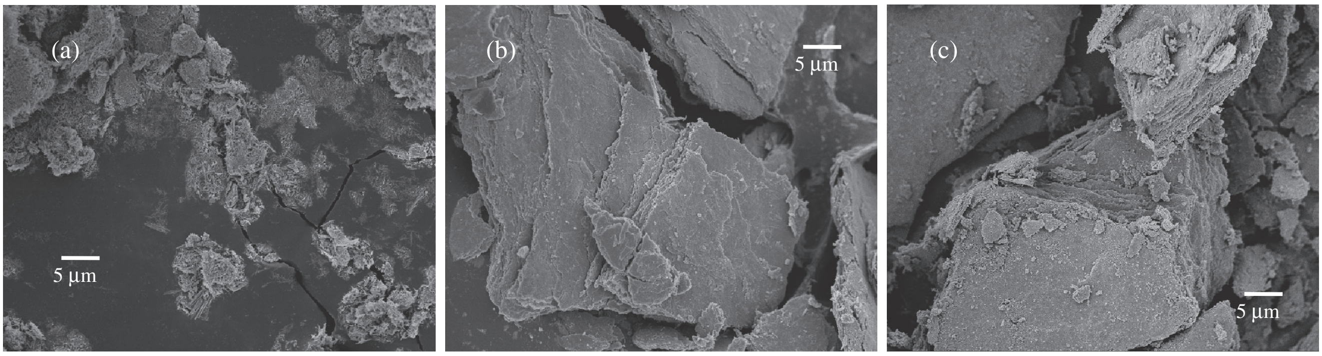

Figure 6. FE-SEM images of (a) NbW, (b) o-NbW taken after the Friedel–Crafts alkylation (after first run), and (c) o-NbW taken after the Friedel–Crafts acylation (after 10th run).

o-NbW were characterized by the temperature-programmed desorption of ammonia. Broad desorption of ammonia was observed in the temperature range between 400 and 700 K.[7] The amount of desorbed ammonia from o-NbW was 0.21–0.28 $\mathrm{mol\,kg^{-1}}$. The amount of acid of o-NbW was slightly higher than that of NbW (0.19 $\mathrm{mol\,kg^{-1}}$).

NbW and o-NbW were utilized for the Friedel–Crafts alkylation of the anisole with benzyl alcohol. Figure 4a displays the picture of NbW taken 0.5 h after stopping the reaction. The reaction solution that had been allowed to stand was turbid because deposition of NbW was slow. Therefore, separation of the catalyst by decantation was difficult. Figure 5a (○) shows the change in the conversion of benzyl alcohol, plotted as a function of recycling times for reactions using NbW. The conversion gradually decreased with times for recycling; they eventually dropped to 2% after being used 10 times. The deterioration of the catalytic activity in NbW could probably be ascribed to the destruction of the fibrous structure to give WO_3 and Nb_2O_5. In fact, intensity of the diffraction of (001) and (002) planes of nanofibers decreased after reaction. Instead, new peaks assignable to the WO_3 appeared after the reaction, which can be seen from the comparison with that of crystalline WO_3 as shown in Figure 2a (NbW, after reaction). Further, aggregated fragments of the nanofibers were observed by FE-SEM (Figure 6a). The amount of acid of NbW decreased from 0.19 to 0.15 $\mathrm{mol\,kg^{-1}}$ owing to the mechanistic destruction of the nanofiber structure.

In contrast with NbW, in the case of o-NbW prepared with 1.9 $\mathrm{mol\,L^{-1}}$ oxalic acid, high activity was maintained, even after being used 10 times iteratively (Figure 5a, ●). Diffraction assignable to crystalline WO_3 did not appear in o-NbW, even after its use for reactions (Figure 2a; o-NbW, after reaction). In agreement with the XRD patterns, stacks of the nanosheet structure were retained, as observed in the FE-SEM image (Figure 6b). The ratio of the *p*- and *o*-alkylated products was 60:40, as analyzed by the GC; this was not dependent on the time of recycling.[7] The yield of benzyl anisole over o-NbW was almost independent of the concentration of oxalic acid except for NbW prepared with 4.6 $\mathrm{mol\,L^{-1}}$ of oxalic acid that showed lower catalytic activity.[7] Little change in the amount of acid was observed before 2.1 $\mathrm{mol\,kg^{-1}}$ and after 2.0 $\mathrm{mol\,kg^{-1}}$ in the reactions measured by NH_3 TPD. Unlike NbW, o-NbW precipitated on the bottom of the flask immediately after use for reaction due to the formation of grains with a stacked nanolayer structure (Figure 4b). Therefore, the separation and recycling of o-NbW was easy, it was possible to separate the catalyst simply by decantation or suction of supernatant solution.

Finally, Friedel–Crafts acylation between anisole and octanoic acid was carried out over NbW and o-NbW. Figure 5b shows the conversion of octanoic acid, plotted as a function of repetition times for reaction. Although both catalysts showed monotonous decrease in the activity, o-NbW (●) showed better recyclability compared to NbW (○). The FE-SEM image of o-NbW taken after the 10th run is displayed in Figure 6c. The surface of the o-NbW seemed to be rough and debris of the stacked sheet was observed, suggesting the mechanistic destruction of the stacked nanosheet structure occurred during repeated reactions. Probably, this is the reason for gradual decrease in activity during repeated reactions.

In conclusion, we found that a stacked sheet of nanofibers forms from the treatment of Nb_2O_5–WO_x with an aqueous solution of oxalic acid, while maintaining the specific surface area and acid properties of parent nanofibers. The catalyst obtained in this way exhibited much better reusability in Friedel–Crafts alkylation and acylation than untreated NbW.

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