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Supplementary Information

Preparation of single-site Ti-containing mesoporous silica with nanotube architecture and its enhanced catalytic activities

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Materials for synthesis of CNF, TS-1 and Ti-HMS. Nickel(II) nitrate hexahydrate, HNO_3 (60%), HF (55%), HCl (36%), tetraethyl orthosilicate (TEOS), ethanol and 2-propanol were purchased from Nacalai Tesque Inc. Titanium isopropoxide (TIP) and dodecylamine (DDA) were obtained from Wako Pure Chemical Ind., Ltd. Tetrapropylammonium hydroxide (TPAOH) and fumed silica were also obtained from Aldrich. All chemicals were used without further purification.

Synthesis of CNF. Ni/SiO_2 catalyst (40 wt% nickel as metal) was prepared by an impregnation method from an aqueous solution of nickel(II) nitrate hexahydrate using fumed silica as a support. After evaporation of water, obtained sample was dried at 373 K for 1 h and then heated at 573 K for 5 h. Calcination of this sample was carried out at 873 K for 5 h in air. In order to synthesis of CNF, decomposition of CH_4 gas over Ni/SiO_2 was carried out by using a conventional gas flow reactor just after pretreatment of sample under hydrogen flow at 773 K for 1 h. The decomposition of CH_4 for synthesis of CNF was performed at 773 K for 12 h (flow rate of CH_4: 60 ml/min). Obtained sample was treated by HF (55 %), dilute HNO_3 (20 %), and then washed repeatedly by water for removal of Ni/SiO_2 catalyst. After vacuum drying at 298 K for 24 h, thus obtained carbon nanofiber (CNF) was used as a hard template for synthesis of Ti-MST.

Synthesis of TS-1. Ti-containing zeolite (TS-1, Si/Ti = 200) was synthesized by direct hydrothermal synthesis method using TEOS (Si source), TIP (Ti source) and TPAOH (structure directing agent). In a typical synthesis, an aqueous solution of TPAOH (20 wt%) was added dropwise to a mixture of TEOS and TIP with vigorous stirring until homogeneous clear solution is obtained. The resulting mixture was kept at 60 °C for 3 h, and a portion of distilled water was occasionally added to compensate for evaporation. The chemical composition of the gel was adjusted to be as follows; TEOS : TPOT : TPAOH : H_2O = 1 : 0.005 : 0.46 : 35. Subsequently, the mixture was transferred to a Teflon vessel autoclave and heated at 448 K for 24 h. After cooling to room temperature, the product was separated by centrifugation, washed several times with ion exchanged water, dried at 373K for 12 h, and then calcined at 823K for 5 h in air.

Synthesis of Ti-HMS. Ti-containing mesoporous silica (Ti-HMS, Si/Ti = 200) was prepared by using TEOS (Si source), TIP (Ti source) and DDA (structure directing agent). Firstly, mixture of TEOS, TIP and 2-propanol was added to the mixed solution of DDA, water, ethanol and HCl under vigorous stirring. The composition was as follows; TEOS : TIP : DDA : ethanol : 2-propanol : H_2O : HCl = 1 : 0.005 : 0.27 : 6.54 : 1 : 36.4 : 0.07. The mixture was aged at 298 K with vigorous stirring. After stirring for 24 h, the product was washed with ion exchanged water, dried at 373 K for 12 h, and then calcined at 823 K for 5 h in air.

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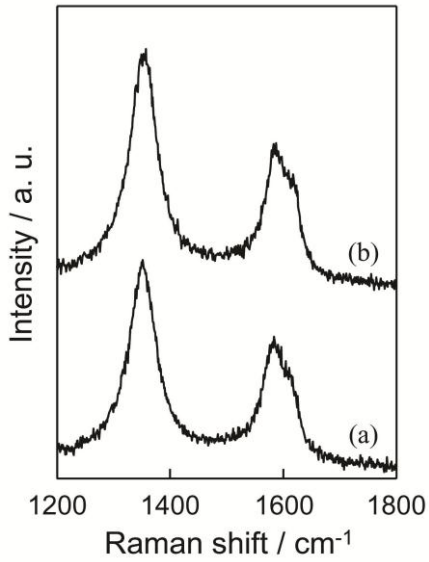

Fig. S1 Raman spectra of (a) CNF-Ni/SiO_2 and (b) CNF (after acid treatments of (a)).

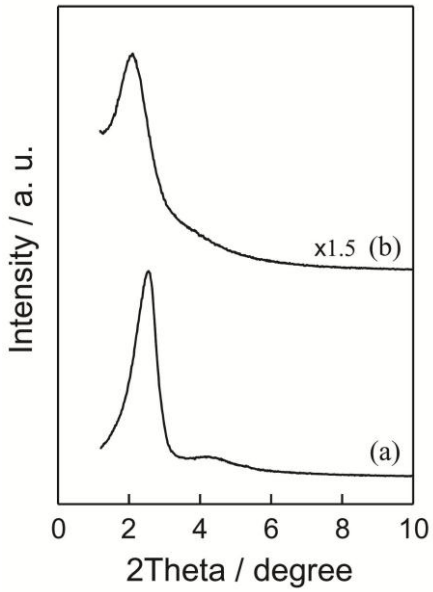

Fig. S2 XRD patterns of (a) Ti-MS and (b) Ti-MST.

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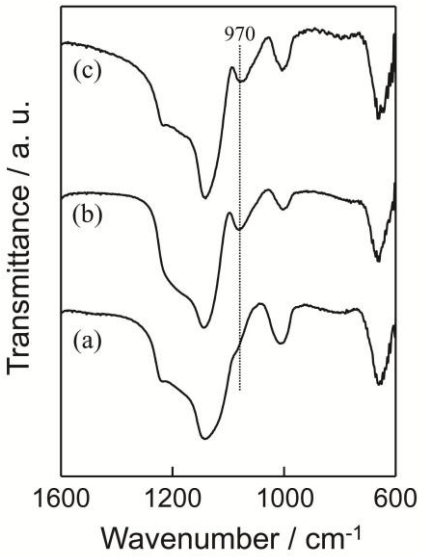

Fig. S3 FT-IR spectra of (a) mesoporous silica, (b) Ti-MST, and Ti-MS.