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ScienceDirect
Applied Catalysis A: General 323 (2007) 104–109
APPLIED CATALYSIS A: GENERAL
www.elsevier.com/locate/apcata

Effect of Co addition for carburizing process of Ti-oxide/SiO_2 into TiC/SiO_2

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Received 27 December 2006; received in revised form 29 January 2007; accepted 5 February 2007
Available online 16 February 2007

Abstract

Lowering the carburization temperature of Ti-oxide into TiC down to 1173 K could be achieved by the addition of Co. Co-promoted TiC/SiO_2 catalysts were prepared by the temperature programmed reaction (TPR) method. Co–Ti/SiO_2 precursors were prepared by use of the successive impregnation method (sc) and the co-impregnation method (co). Samples were characterized by X-ray absorption fine structure (XAFS) measurements and X-ray diffraction (XRD) results. The carburization degree of TiC was affected by the method of Co addition. The carburization degree of sc Co–TiC/SiO_2 was better than that of co Co–TiC/SiO_2. The activity of thiophene hydrodesulfurization reaction at 693 K on sc Co–TiC/SiO_2 was higher than that on co Co–TiC/SiO_2. The HDS activity was related to the carburization degree of TiC.

Keywords: TiC catalyst; XAFS; Co additive; Carburization

1. Introduction

Small atoms, such as carbon or nitrogen, dissolved interstitially in the lattices of early transition metals produce a class of compounds with unique physical and chemical properties [1,2]. These interstitial compounds are referred to as early transition metal carbides (ETMC) and nitrides (ETMN). ETMC and ETMN were found to have similar activities to those of the group 8–10 metals (Pt, Pd, Rh, etc.) [3–6].

Most of works on the catalytic applications of ETMC have been focused on Mo_2C and WC [7–10]. In contrast, very few works have been reported on the groups 4 and 5 metal carbides such as TiC and NbC [11–14]. The focus on Mo_2C and WC has occurred in part because they could be prepared with high surface areas at moderate synthesis temperatures in the range between 900 K and 1100 K [7–10]. On the other hand, it has been reported that the carburization of bulk TiO_2 into TiC requires a high temperature; 1410 K [5]. Using high temperature caused a sintering of TiC, and decreased the surface area of TiC. The lowering of carburizing temperature is required for the catalytic application of TiC. We have demonstrated that the carburizing temperature could be lowered by supporting the metal species on amorphous silica [15,16].

Co addition could be expected to promote the carburization with activating methane by dehydrogenation because it has been used for Fischer–Tropsch catalysts [17]. In this work, in order to lower carburization temperature, we added Co to TiO_2, and then demonstrated carburization. In addition, Co–TiC/SiO_2 was prepared. For the preparation of Co–Ti/SiO_2, two different methods were applied. One is successive impregnation method (sc), and the other is co-impregnation method (co). Co–Ti/SiO_2 precursors were carburized by using temperature programmed reaction (TPR) method. Carburization degree of Ti was characterized by using Ti K-edge XAFS (X-ray absorption fine structure) measurements. In order to investigate the effect of Co addition, Co K-edge XAFS was also measured. Thiophene HDS (hydrodesulfurization) reactions were demonstrated to investigate the relationship between the carburization degree of TiC activity and the HDS.

2. Experimental

Co–Ti/SiO_2 precursors were prepared by sc method (sc Co–Ti/SiO_2) and co method (co Co–Ti/SiO_2). The preparation

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doi:10.1016/j.apcata.2007.02.012

process of sc Co–Ti/SiO_2 consisted of two stages. First, intermediate precursors of Ti/SiO_2 were obtained by impregnating SiO_2 (Aerosil, #200) with $TiCl_4$/HCl solutions at RT for 24 h. To decompose the titanium chloride, we calcined the intermediate precursor at 623 K in air for 2 h. Second, Co–Ti/SiO_2 was obtained by impregnating Ti/SiO_2 with aqueous cobalt chloride solution at RT for 24 h. To decompose the cobalt chloride, we calcined the precursor at 623 K in air for 2 h. Ti loading was regulated to 5 wt% with a Co/Ti molar ratio of 0.25. The co-impregnation catalyst was prepared as follows: an HCl aqueous solution of $TiCl_4$ and $CoCl_2$ was impregnated with SiO_2 at RT for 24 h. To decompose the titanium chloride and the cobalt chloride, we calcined the precursor at 623 K in air for 2 h (co Co–Ti/SiO_2).

The Co–Ti/SiO_2 precursor was carburized in a 20% CH_4/H_2 mixed gas stream to produce Co–TiC/SiO_2 in the TPR process. This process involves two steps: (1) raising the temperature at a linear rate of 10 K min^{-1} to 1273 K and (2) maintaining the sample at the final temperature for a certain period.

XAFS spectra at Ti K-edge and Co K-edge were measured at RT in transmission mode at BL-10B (Co K-edges), BL-7C, 9C and 12C (Ti K-edges) using the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization (PF, IMSS-KEK) (Proposals nos. 2002G116, 2005G214). Synchrotron radiation emitted from a 2.5 GeV storage ring was monochromatized by a Si(3 1 1) channel cut monochromator or a Si(1 1 1) double crystal monochromator at BL-10B or BL-7C, 9C, 12C, respectively. Each sample was pressed into a pellet, which was 10 mm in diameter. Curve-fitting analysis of EXAFS oscillations was conducted by the EXAFS analysis program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift functions) were extracted from EXAFS oscillations observed for standard materials (TiO_2, TiC, $CoTiO_3$, Co foil, Co_3O_4 and CoS), or they were created by FEFF.

The XRD (X-ray diffraction) analysis (Bruker axs, MXP3) was also carried out. HDS of thiophene was performed in continuous flow system interfaced to a gas chromatograph (SHIMADZU, GC-8A) with a TCD detector. The main products were 1-butene and 2-butene. The catalyst (0.4 g) was pretreated under H_2 flow (10 ml min^{-1}) for 0.5 h at 1073 K or 773 K, prior to use. HDS reaction was monitored under 2.8% thiophene/H_2 (5 ml min^{-1}) at 693 K.

3. Results and discussion

3.1. Carburization of bulk TiO_2

XRD patterns of TiO_2, TiC, carburized TiO_2 and carburized Co–TiO_2 are shown in Fig. 1. In the case of carburized TiO_2, the Ti_3O_5 phase was observed and no peak attributed to TiC was appeared. On the other hand, the patterns for carburized Co–TiO_2 showed TiC phase clearly. Such results mean that TiO_2 was not carburized at 1273 K without Co additive, but was carburized to produce TiC with Co additive. In the case of carburized Co–TiO_2, Co metal phase was observed as well as TiC phase. It was found that Co oxide was reduced to Co metal during the carburization. We supposed that the carburization of TiO_2 proceeded focusing around reduced Co.

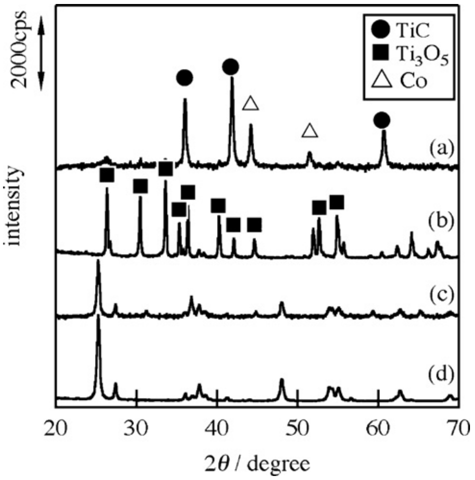

Fig. 1. XRD patterns of (a) carburized Co–TiO_2, (b) carburized TiO_2, (c) Co–TiO_2 and (d) bulk TiO_2.

In order to optimize the carburization condition, we prepared carburized Co–TiO_2 by controlling the carburization temperature and the retention time. Fig. 2 shows XRD patterns of carburized Co–TiO_2 as a function of carburization temperature (1273 K, 1223 K, 1173 K and 1073 K). The XRD pattern of Co–TiO_2 carburized at 1073 K shows only Ti_3O_5 phase. It can be said that TiC was not formed by a carburization temperature as low as 1073 K. In the case of Co–TiO_2 carburized at 1173 K, however, TiC phase was observed slightly besides the main Ti_3O_5 phase. It was found that TiC was formed by the carburization above 1173 K. In other words, the carburization temperature of Ti-oxide into TiC could be lowered down to 1173 K by addition of Co. In the case of Co–TiO_2 carburized at 1223 K, the TiC phase was larger compared to the case of Co–TiO_2 carburized at 1173 K. Raising the carburization temperature up to 1273 K, we could distinctly observed the TiC phase

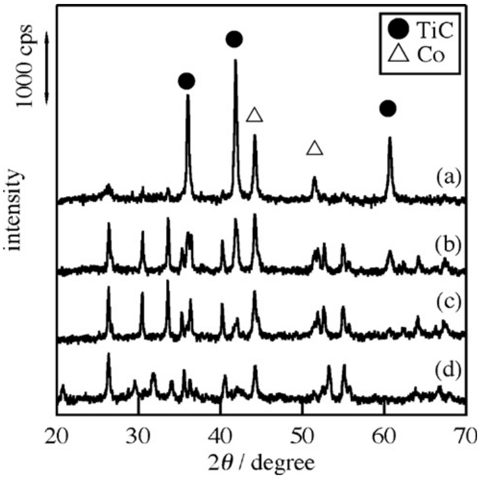

Fig. 2. XRD patterns of carburized Co–TiO_2 varied with the carburization temperature: (a) 1273 K, (b) 1223 K, (c) 1173 K and (d) 1073 K.