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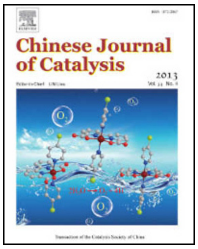

Article

Temperature-programmed desorption and surface reaction studies of CO on Co_2C

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ABSTRACT

Cobalt carbide (Co_2C) samples were prepared by carburizing Co with CO at 473 K for in excess of 400 h and were characterized by X-ray diffraction, transmission electron microscopy, CO temperature-programmed reduction, CO temperature-programmed desorption (CO-TPD), and CO temperature-programmed surface reaction. The prepared Co_2C samples were composed of bulk Co_2C with a surface CoO passivation layer. The passivation layer could be removed by reaction with CO at 477 K. CO desorbing at low temperature in CO-TPD experiments likely originated from chemisorbed CO. CO desorbing at high temperature was likely due to residual CO within the Co_2C crystal lattice. CO adsorbed on Co_2C reacted with H_2 to form alcohol.

1. Introduction

Transition metal carbides behave similarly to noble metals in heterogeneous catalysis and have received much attention since the first report by Levy and Boudart [1]. They exhibit outstanding performance in hydrogenation [2], ammonia synthesis [3], hydrodesulfurization [4], hydrodenitrogenation [5], water-gas shift reaction [6], hydrocarbon isomerization [7], and methane reforming [8]. However, few literatures were reported about the fundamental studies on the properties of transitional metal carbide catalysts. This is particularly so for cobalt carbide (Co_2C), whose formation is regarded as a deactivation sign of Fischer-Tropsch catalysts [9,10]. Ding et al. [11,12] recently reported that the generation of C_1–C_{18} linear alcohols over activated carbon-supported Co catalysts could occur via the formation of Co_2C. The presence of Li or La tuned the formation of Co_2C and thus influenced the selectivity of the alcohols [13–16].

CO temperature-programmed desorption (CO-TPD) and CO temperature-programmed surface reaction (CO-TPSR) are widely used surface sensitive techniques. They can provide information about CO adsorption and the reaction mechanism of different catalyst systems [17]. Volkov et al. [18] suggested that Co_2C could adsorb CO without rupture, in such a way that formed alcohols. To our knowledge, the adsorption properties of CO on Co_2C have not yet been reported. Optical spectroscopy is of limited use in investigating CO adsorption on Co_2C because Co_2C is opaque in the infrared region. The adsorption and reaction of CO on Co_2C can be investigated using CO-TPD and CO-TPSR, to better understand its catalytic behavior.

Herein, Co_2C was prepared according to the literature [19] and characterized by physical and chemical methods. CO ad-

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sorption and reaction on Co_2C were then investigated using CO-TPD and CO-TPSR.

2. Experimental

2.1. Co_2C preparation

Co_3O_4 (10.0 g) was reduced in flowing H_2 (60 ml/min) at 523 K for 4 h and then carburized in flowing CO (60 ml/min) at 493 K. Samples carburized for 468 and 605 h were denoted Co_2C-A and Co_2C-B, respectively, and were investigated for comparison. After reaction, samples were quenched to room temperature under Ar and then passivated in flowing 1 vol% O_2/Ar (60 ml/min) for 2 h before exposure to the atmosphere.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed on a PANalytical X′Pert PRO diffractometer, using Cu $K_{\alpha1}$ radiation at an operating voltage and current of 40 kV and 40 mA, respectively. The scan range was 2θ = 20°–60°, and scan speed was 6°/min.

High resolution transmission electron microscopy (HRTEM) measurements were carried out using a FEI Tecnai G2 F30 microscope at an accelerating voltage of 300 kV.

CO-temperature-programmed reduction (CO-TPR) was carried out using a Micromeritics Autochem 2910 apparatus. A 200 mg sample was treated in flowing CO (20 ml/min), and the reduction temperature was increased from room temperature to 573 K at a rate of 5 K/min. CO consumption and CO_2 generation were recorded with an Omnistar 300 quadrupole mass spectrometer.

CO-TPD was carried out on the same instrument. A 200 mg sample was used for each test. The samples were first pre-reduced in-situ in flowing CO, and the temperature was raised from room temperature to 523 K at a rate of 5 K/min and maintained there for 1 h. Samples were purged with He at 523 K for 0.5 h, cooled to 323 K under flowing He, and purged with He for a further 40 min to remove adsorbed species. CO was pulsed over pre-treated Co_2C samples at 323 K until the TCD signal reached a constant value. Samples were flushed with He for 10 min, and the temperature linearly increased from 323 to 1173 K at 5 K/min under flowing He. The CO-TPD result of a 200 mg Co_2C-A sample under He was used as a blank experiment. Desorbed exit-gases were analyzed with an Omnistar 300 quadrupole mass spectrometer.

CO-TPSR was carried out on the same instrument. Sample (200 mg) was pre-reduced in flowing CO at 523 K for 1 h, purged with He at 523 K for 30 min, and cooled to 323 K. CO adsorption was carried out at 323 K by pulsing CO until the TCD signal reached a constant value. Samples were flushed with He for 10 min, and 10% H_2/Ar was allowed to flow through the sample bed. The temperature was increased to 1000 K at 5 K/min, and mass spectrometry was used for detection.

3. Results and discussion

3.1. XRD and TEM

Figure 1 shows XRD patterns of Co_2C-A and Co_2C-B. Both samples exhibit five identical diffraction peaks at 2θ = 37.0°, 41.3°, 42.5°, 45.7°, and 56.6°, ascribed to the characteristic peaks of Co_2C (PDF 01-072-1369). No peaks of Co or CoO are observed, indicating that the bulk sample phase was Co_2C.

Figure 2 shows representative HRTEM images of Co_2C-A. Figure 2(a) shows a lattice spacing of 2.16 Å, ascribed to the (111) plane of Co_2C (PDF 01-072-1369). The lattice spacing of 2.46 Å in Fig. 2(b) is ascribed to the (111) plane of CoO (PDF 00-009-0402). Combined with XRD results, it suggests that samples were composed of bulk Co_2C with a surface CoO passivation layer.

3.2. CO-TPR

The passivation layer is reported to impact on the adsorption and reaction behavior of transitional metal carbides, and is typically removed before reaction [20,21]. The reduction behavior of the passivation layer of Co_2C-A was investigated by CO-TPD, as shown in Fig. 3. The CO consumption peak is at 477 K, and a CO_2 peak was simultaneously generated. This suggests that the passivation layer may have been reduced by the presence of CO.

3.3. CO-TPD

Figure 4(a) shows CO-TPD profiles of Co_2C-A and Co_2C-B, in which there exist two peaks for each sample. Peaks of Co_2C-A

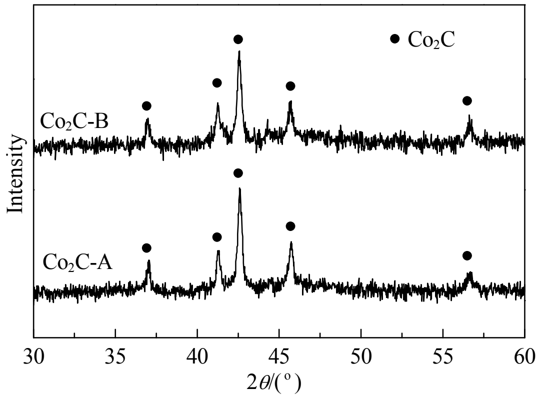

Fig. 1. XRD patterns of Co_2C samples.

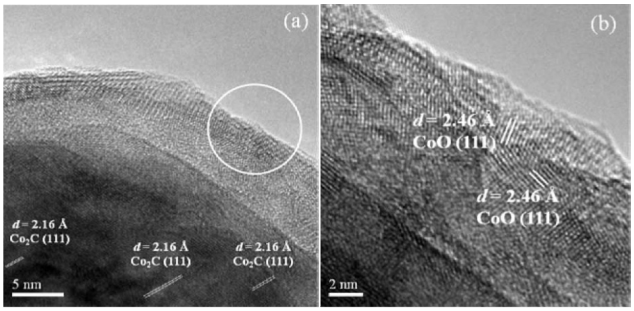

Fig. 2. HRTEM images of Co_2C-A. The circled region in (a) is shown at higher magnification in (b).