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High-efficiency WO_3/carbon nanotubes for olefin skeletal isomerization

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Abstract

WO_3/carbon nanotube (CNT) catalysts with different WO_3 loadings were prepared by wet impregnation with ammonium paratungstate as precursor, characterized by X-ray diffraction, temperature-programmed reduction, transmission electron microscopy and X-ray photoemission spectroscopy. These materials were tested for C_6 olefin skeletal isomerization in different activation (pre-reduction) conditions and compared to a reference tungstated zirconia, WO_3/ZrO_2, catalyst. They led to very high skeletal isomerization selectivities at 200 °C at high conversion level without any observable deactivation.

Keywords: Carbon nanotubes; Skeletal isomerization; Tungsten oxide reducibility; Nanowire; Film

1. Introduction

Solid acid catalysts play an important role in chemical and petroleum industries in hydrocarbon conversion reactions required in octane enhancement processes, such as cracking, isomerization and alkylation [1–3], which can form highly branched isoparaffins. Such reactions require strong or moderate acid catalysts. The detrimental environmental impact of halide-type solid acids led to develop halide-free catalysts, and tungsten oxides supported on oxide carriers have, thus, extensively been investigated as alternative catalysts for hydrocarbon isomerization processes due to the acidic character of supported tungsten oxide [4–10]. Among different oxide support materials, Al_2O_3 and ZrO_2 have been widely used as support for tungsten oxide but very few investigations on the use of carbon as support for hydrocarbon reforming reactions have been reported [11–13], despite the important role of carbon as a support [14]. It is now admitted that both active-phase-support interaction and tungsten content have a high influence on the activity of WO_3-reduced supported catalysts towards skeletal isomerization due to the extension of tungsten species reducibility [15,16].

Among the carbon materials, carbon nanotubes (CNTs) have attracted attention in the last decade in the field of catalysis because of potential applications as catalyst support and peculiar behaviors in terms of conversion or selectivity, which were attributed to specific active-phase-support interaction, limitation of mass transfer phenomena problems and/or to the existence of confinement effects inside CNTs [17].

Up to now, the use of CNTs as support in the field of heterogeneous catalysis remains mainly devoted to liquid-phase reactions using supported metals. The aim of this article is to report on the gas-phase use of WO_3/CNTs as catalyst for the 4-methyl-1-pentene (4M1Pen) isomerization. The catalysts will be characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed reduction (TPR) and X-ray photoemission spectroscopy (XPS).

2. Experimental section

2.1. Catalyst preparation

Open multi-walled CNTs with inner and outer average diameters of 40 and 80 nm, respectively, and lengths up to about 200 μm were supplied by Appl. Sci. Inc. (OH, USA).

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They had a non-microporous specific surface area of 25 m^2/g obtained by BET measurement using N_2 at LN_2 temperature. Deposition of tungsten was performed by wet impregnation of the bare CNTs with an aqueous solution (20 mL) of ammonium metatungstate pentahydrate, $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, at pH close to 5. The CNTs were added to the precursor salt aqueous solution kept under vigorous stirring at 80 °C for 20 min before the slow evaporation of the solvent at room temperature. The resulting material was further dried overnight at 120 °C. The WO_3 content was taken at 4, 17 and 30 wt.% relative to the total weight of catalyst. The dried materials were finally calcinated at 350 °C for 2 h. Comparison was made with a WO_3 (25 wt.%)/ZrO_2 reference catalyst prepared following the same procedure and using commercially available monoclinic ZrO_2 supplied by Johnson Matthey [16]. Catalytic performances were reported in terms of specific rate of hydrocarbon transformation expressed in mol/s/(g of WO_3), isomerization selectivity and stability as a function of time.

2.2. Characterization techniques

Structural characterizations were done by powder XRD measurements on a Siemens Diffractometer Model D-5000, using Cu Kα radiation. The nature of the phase in the sample was checked using the database of the Joint Committee on Powder Diffraction Standards (JCPDS).

TPR measurements were performed by submitting the catalysts located in a quartz reactor between two quartz wool plugs to a H_2 (13 vol.%)/Ar flow (total flow rate of 50 mL/min) with a heating rate of 15 °C/min from room temperature to 930 °C, at which the catalyst was kept afterwards during 30 min. The H_2 consumption was followed by thermal conductivity catharometric detection.

Microstructural characterization was carried out by TEM on a Topcon 002B working at 200 kV accelerated voltage.

XPS spectra were recorded with pass energy of 20 eV on a ThermoVG Scientific apparatus equipped with an Al Kα source and a hemispherical analyser. The W_{4f} lines were analyzed with a curve fitting procedure according to the Doniach and Sunjic theory [18], using the Shirley background subtraction.

2.3. Catalytic device

The experiments were carried out under H_2 at atmospheric pressure with 100 mg of catalyst powder in a stainless steel micropilot equipped with a quartz reactor (10 and 300 mm of internal diameter and reactor length, respectively). The catalyst bed was thus about 5 mm height, centered in the 70 mm long isothermal zone of the reactor. The catalyst was first pre-reduced (i.e. activated) for 2 h under a 30 mL/min hydrogen flow at temperatures ranging from 200 to 550 °C (heating rate of 15 °C/min), and the reaction was further performed at 200 °C with a H_2 flow rate of 30 mL/min. Hydrocarbon pulses were manually introduced into the H_2 flow using a saturator kept at a constant temperature (−38 °C, obtained using an anisol/liquid nitrogen cooling mixture) leading to a partial pressure of 6.5 Torr of hydrocarbon in flowing H_2. The reactant and reaction products were analyzed on-line by gas chromatography (GC 8000, CEInstruments) equipped with a flame ionization detector. All the unsaturated products were hydrogenated on a separated Pt Adams-based hydrogenator before on-line analysis for easy detection and quantification.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD pattern of the WO_3/CNT catalysts with WO_3 content ranging from 4 to 30 wt.% and of the fresh CNT support given as reference. On the CNT support, the most intense diffraction peak characteristic of the CNTs at $2\theta = 25.8°$ corresponds to the interlayer scattering of the

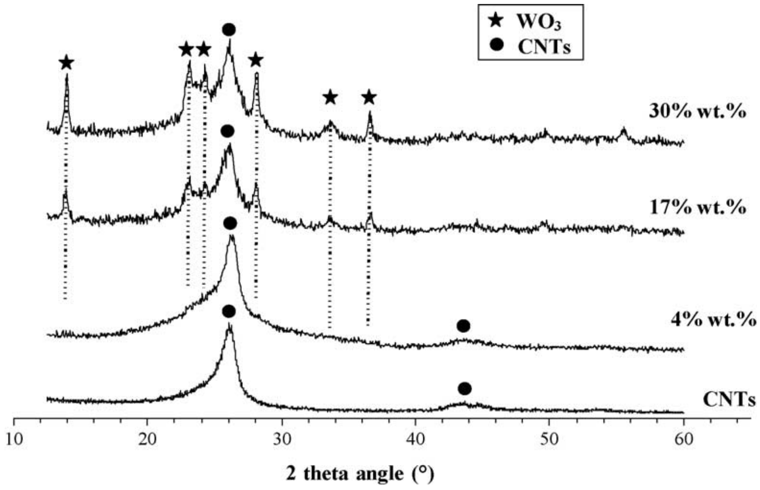

Fig. 1. X-ray diffraction pattern of the WO_3/CNT catalysts. Influence of the tungsten initial content.