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Adsorption and reactions of butyl species over Mo_2C catalyst

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Abstract

The adsorption and reactions of butyl iodide on Mo_2C/ZSM-5 and Mo_2C/SiO_2 have been investigated by means of FTIR spectroscopy and mass spectrometry. Adsorption bands were observed following the adsorption of butyl iodide at 200–230 K that corresponds well to the vibrations of molecularly adsorbed C_4H_9I. At higher adsorption temperatures, bands due to the adsorbed butene and butylidyne also appeared. From the comparison of the adsorption and desorption characteristics determined on pure and Mo_2C-containing ZSM-5, it was concluded that the majority of butyl iodide is attached to ZSM-5. The presence of Mo_2C on ZSM-5 and SiO_2, however, enhanced the rate of the decomposition, promoted the coupling of butyl species and catalyzed the formation of xylene and benzene. It was assumed that Mo_2C interacting with the acidic sites of the support is the active center for the latter processes.

Keywords: Adsorption; Benzene; Butane

1. Introduction

In an effort to convert methane into more valuable compounds, extensive research has been performed in the last decades to develop an effective catalyst for its processes [1–3]. The finding that Mo_2C on ZSM-5 is capable of converting methane into benzene with 80% selectivity at 10–15% conversion is meant a significant achievement in this area [4–11]. Mo_2C/ZSM-5 also catalyzed the aromatization of ethane and propane [12–14]. Recently it was found that while *n*-butane undergoes dehydrogenation and cracking on pure ZSM-5 with the formation of a small amount of benzene, the deposition of Mo_2C markedly enhanced the yield and the selectivity of aromatics [15–18]. This observation suggested that Mo_2C opened a new route for the activation of butane, namely the generation of butyl species from the adsorbed butane molecule, which is effectively transformed into compounds leading to aromatics.

In order to establish the role of Mo_2C in the activation and reactions of alkanes, hydrocarbon fragments (CH_3, CH_2, C_2H_5, C_3H_5, etc.) were prepared on Mo_2C/Mo(1 0 0) by the adsorption and dissociation of the corresponding iodo compounds [19–23]. As appeared from previous studies on metal single crystal surfaces, alkyl iodides dissociate on metals at 100–300 K resulting in alkyl species, which, depending on the nature of the metals, undergo various reactions [24–27]. While this approach provided valuable informations on the bonding and reaction pathways of C_xH_y fragments on Mo_2C/Mo(1 0 0) surface under UHV conditions, a caution is needed to use the results in establishing the mechanism of the catalytic reactions occurring under different experimental conditions, namely on highly dispersed catalysts and at the atmospheric pressure. Another difference is that in the real catalyst, Mo_2C is deposited on ZSM-5, which also promotes some steps leading to aromatic compounds. To overcome this drawback, the adsorptions and reactions of butyl species formed in the dissociation of butyl iodide is examined on real catalysts, Mo_2C/ZSM-5, Mo_2C/SiO_2 and ZSM-5, under almost the same conditions as applied in the catalytic studies.

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2. Experimental

Two ZSM-5 samples were used with SiO_2/Al_2O_3 ratio of 80 and 280. The starting material was NH_4-ZSM-5 (Zeolite International), which was calcined to produce H-ZSM-5 in air at 863 K for 5 h. Silica was the product of Aerosil. Butyl iodide (Fluka) was cleaned by several freeze-pump-thaw cycles. MoO_3-containing catalysts were prepared by impregnating H-ZSM-5 or SiO_2 with a basic solution of ammonium heptamolybdate to yield different wt% of MoO_3. The suspension was dried at 373 K and calcined at 863 K for 5 h. Supported Mo_2C catalysts were produced by the carburization of calcined MoO_3/ZSM-5 or MoO_3/SiO_2 by ethane following the description of Green et al. [28]: the MoO_3-containing sample was heated under 10% (v/v) C_2H_6/H_2, from room temperature to 900 K at a heating rate of 0.8 K/min. After preparation, the catalysts were cooled down to room temperature under argon. The carbides were passivated in flowing 1% O_2/Ar at 300 K. Before most of the catalytic experiments, the samples were treated with H_2 at 873 K for 60 min to remove the excess carbon. Unsupported Mo_2C was also prepared by carburization of MoO_3 with ethane.

The catalysts have been characterized by XPS measurements. The binding energies for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) were 227.8–228.2 and 230.7–231.1 eV, respectively, and for C(1s) 283.8 eV. These values are consistent with those attributed to Mo_2C [8,11,29]. Infrared transmission spectra were recorded with a FTIR spectrometer (Bio-Rad, 155) with a wavenumber accuracy of $\pm 4\,cm^{-1}$. Typically 16 scans were recorded. All the spectra presented are different. Subtractions of the spectra were taken without use of a scaling factor ($f = 1.0000$). The reaction of butyl iodide was followed in a closed circulation system; the amount of catalyst was 0.2 g. The products were analyzed by a quadruple mass spectrometer.

3. Results

3.1. Infrared studies

First, the adsorption of butyl iodide was investigated by means of FTIR spectroscopy. Fig. 1A shows the IR spectra of Mo_2C/SiO_2 sample following the adsorption of C_4H_9I (1.0 Torr) at 200–230 K, and after subsequent evacuation, major bands appeared at 2966, 2937, 2879, 2841, 1466, 1430, 1383, 1370 and 1356 cm^{-1}. Heating the adsorbed layer to higher temperature, the bands gradually attenuated, but it did not lead to any spectral changes. The bands completely disappeared above 300 K.

In the next experiments, the Mo_2C/SiO_2 sample was heated in the presence of C_4H_9I (1.0 Torr) at different temperatures, and after 20 min the cell was evacuated for 10 min at the temperature of the adsorption. Spectra obtained are displayed in Fig. 1B. New bands, not observed previously, appeared at 2921, 2912, 2902, 2873, 1459 and 1419 cm^{-1} at 300–373 K. Raising the adsorption temperature led to an intensification of these bands up to 473 K, and then to their attenuation. Similar measurements were carried out with the SiO_2 support alone. We detected the characteristic absorption bands of adsorbed C_4H_9I, which disappeared after evacuation at 373 K.

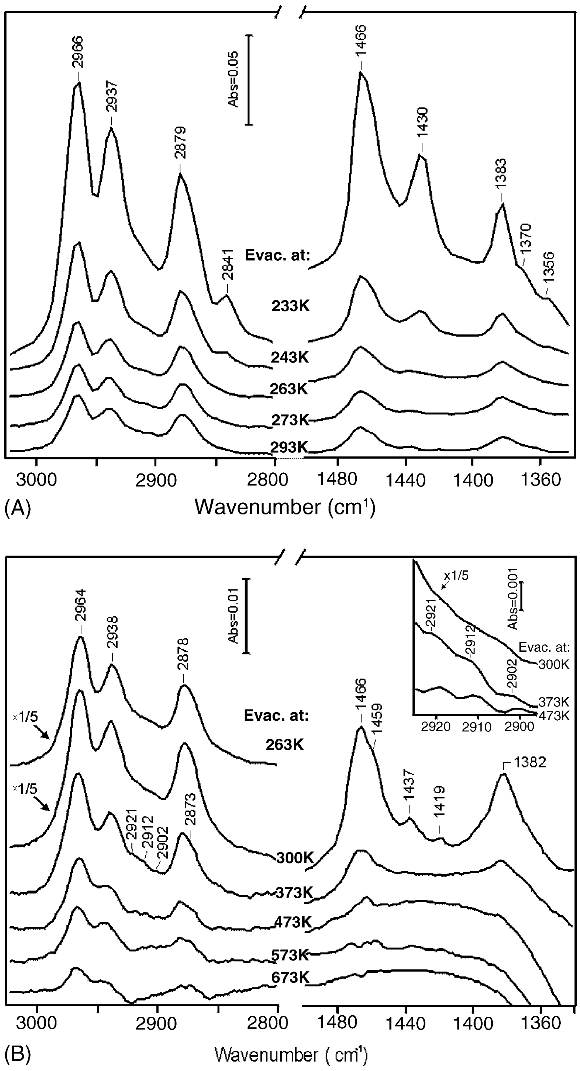

Fig. 1. (A) FTIR spectra of 1.4% Mo_2C/SiO_2 following the adsorption of butyl iodide (1.0 Torr) at 200 K and subsequent evacuation at different temperatures. (B) FTIR spectra of 1.4% Mo_2C/SiO_2 following the adsorption of butyl iodide (1 Torr) at different temperatures. The samples were degassed at the temperature of the adsorption before registering the spectra.

Adsorption of 1.0 Torr of C_4H_9I on Mo_2C/ZSM-5(80) at 200–230 K gave similar spectral features as observed for Mo_2C/SiO_2 samples with only small alterations (Fig. 2A). Spectra obtained after heating the Mo_2C/ZSM-5(80) with C_4H_9I (1 Torr) at 263 K caused a slight shift in the position of the bands registered at lower temperature and produced only new weak bands at 2909, 2905 and 2864 cm^{-1}. Adsorption at higher temperature led to attenuation of all spectral features (Fig. 2B).