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Oxidative dehydrogenation of ethane over vanadium supported on mesoporous materials of M41S family

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ABSTRACT

The contribution deals with mesoporous materials of M41S family post-synthetically dopped with vanadium oxo-species. The performance of V-HMS, V-MCM-41 and V-SBA-15 catalysts with varying vanadium loadings was studied in oxidative dehydrogenation (ODH) of ethane. The objectives of this study were to determine a possible activity of vanadium species supported on mesoporous materials of M41S family and to optimize reaction conditions. We contribute to the understanding of the relationship between the activity of vanadium species in ODH of ethane and its distribution. Vanadium-based catalysts were analyzed by UV–vis spectroscopy, voltammetry of microparticles (VMP), and nitrogen adsorption (determination of specific surface area). The most active catalysts contained 2–4.5 wt.% V finely dispersed over mesoporous support in the form of isolated monomeric and oligomeric vanadium species. V-HMS, V-MCM-41 and V-SBA-15 exhibited comparable activity in ODH of ethane.

1. Introduction

In recent years there is a pronounced tendency of chemical industry to adopt selective oxidation reactions as an alternative way to functionalize low molecular weight paraffins. Oxidative dehydrogenation (ODH) of low paraffins, such as ethane and propane, offers an attractive alternative to currently used steam cracking, catalytic dehydrogenation and fluid catalytic cracking. However, a low yield and selectivity to olefins still prevent the industrial applications of ODH. Most catalytic systems reported in the literature give ethene yield below 20% and the industry requires the ethene productivity above 1 $g(C_{2=})\,g_{cat}^{-1}\,h^{-1}$ at temperature as low as possible [1].

A large number of catalysts have been studied in ODH of ethane and propane. A review of the recent literature shows that vanadium-based catalytic system is one of the most active and selective single-metal catalysts in ODH [1–3]. They encompass: mixed oxide catalysts containing vanadium and vanadium supported on mesoporous inorganic solids or micro- and mesoporous materials. It has been accepted that structural, textural and acide/base properties play important roles in the activity of mesoporous material in ODH. V-MCM-41 [4], V-alumina [5] and V-mesoporous alumina [6] have been reported as active catalysts in ODH of ethane. Moreover, V-mesoporous silica of M41S family (V-HMS [7], V-MCM-48 [8] and V-SBA-15 [9]) exhibit high activity in ODH of propane, but there is a lack of complex information on its activity in ODH of ethane.

In this work we attempt to contribute to understanding the activity of vanadium containing HMS, MCM-41 and SBA-15 materials in ODH of ethane. The main attention is given to (a) the activity of vanadium-based catalysts in ODH of ethane, (b) the effect of reaction conditions (temperature, oxygen and ethane concentration, and contact time) on the activity/selectivity of V-HMS (a chosen catalytic system) in ODH of ethane and (c) the relation between the structure of vanadium species and their activity/selectivity in ODH of ethane. To analyze the effect of vanadium concentration on distribution of vanadium species and their activity, vanadium-based catalysts were characterized by UV–vis spectroscopy, voltammetry of microparticles (VMP), and nitrogen adsorption.

2. Experimental

2.1. Preparation of catalysts

Hexagonal mesoporous silica (HMS) was synthesized according to the procedure reported by Tanev and Pinnavaia [10]. HMS

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($835\ m^2\ g^{-1}$, average pore diameter 3.7 nm) was prepared by dissolving 13.6 g dodecylamine (DDA, Aldrich) in the mixture of 144.6 ml ethanol and 200 ml re-H_2O (re-distilled water). After stirring for 20 min, 56 ml of tetraethylorthosilicate (TEOS, Aldrich) in 81 ml ethanol was added drop-wise and stirred. The reaction was performed at RT for 18 h under static conditions. The solid product was filtered, washed with re-H_2O and finally calcined in air at 450 °C for 8 h. MCM-41 ($977\ m^2\ g^{-1}$, average pore diameter 2.7 nm) was prepared by dissolving 2.4 g *n*-cetyltrimethylammonium bromide (CTAB, Aldrich) in 120 g of de-ionized water. The mixture was stirred until it turned to a homogeneous and clear solution. Afterwards 10 ml of ammonium hydroxide (25%, Aldrich) was added, the mixture was stirred for 5 min and later on 10 ml of tetraethylorthosilicate (TEOS, Aldrich) was added. The synthesis was performed at 100 °C for 16 h under the static conditions. The solid product was filtered and washed with de-ionized water and ethanol. Calcination was performed at 500 °C for 8 h. SBA-15 ($959\ m^2\ g^{-1}$, average pore diameter 5.8 nm) was synthesized according to the procedure of Zhao et al. [11] by crystallization from acidic solutions of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) copolymer (Aldrich, $M_{avg} = 5800$) and tetramethylorthosilicate (TMOS, Aldrich). The procedure was modified to reduce the microporosity by increasing the duration of the hydrothermal treatment [12]. Vanadium-based catalysts (0.3–9 wt.% V) were prepared by impregnating HMS, MCM-41 or SBA-15 with solution of vanadyl(IV) acetylacetonate in ethanol. After impregnation, the catalysts were filtered and dried for 24 h at room temperature. Calcination was carried out for 8 h at 600 °C in air. Adsorption and subsequent thermolysis of $VO(acac)_2$ on a silica support can yield tetrahedral VO_x species.

2.2. Characterization of catalysts

Specific surface area of HMS, MCM-41, and SBA-15 materials and vanadium-based catalysts was measured by N_2 adsorption. The structure and crystallinity of the mesoporous supports was probed by X-ray diffraction and scanning electron microscopy. UV–vis spectroscopy and voltammetry were used to distinguish different vanadium oxo-species in the catalysts.

2.2.1. UV–vis spectroscopy

UV–vis diffuse reflectance spectra of dehydrated granulated (0.25–0.50 mm) materials were recorded using GBS CINTRA 303 spectrometer equipped with a diffuse reflectance attachment with a $BaSO_4$-coated integrating sphere against a $BaSO_4$ reference. The reflectances were re-calculated to the absorption using the Schuster–Kubelka–Munk equation, $F(R_\infty) = (1-R_\infty)^2/2R_\infty$, where R_∞ is the diffuse reflectance from a semi-infinite layer. Spectra were deconvoluted to the Gaussian bands using the OriginPro 7.5 software (OriginLab Corp., USA). The dehydration of vanadium-based catalysts was carried out in the stream of oxygen in two steps: 120 °C for 30 min and 450 °C for 60 min. Than the reactor was cooled down to 150 °C and evacuated for 30 min. This procedure guaranteed complete dehydration of catalysts. After the dehydration, the samples were cooled down to ambient temperature and transferred into the optical cell of 5 mm thickness under vacuum and sealed.

2.2.2. Voltammetry

Voltammetry of microparticles was performed with a paraffin-impregnated graphite rod as a working electrode and saturated calomel reference electrode (SCE). The measurements were performed by cyclic voltammetry at $10\ mV\ s^{-1}$ scan rate from the open circuit potential to −1.3 V and a reverse scan to +0.7 V vs. SCE in an acetic acid–sodium acetate buffer (HOAc to NaOAc 1–9, total acetate 0.2 M). Solid-state electrochemistry of V^{5+} species have been studied rather extensively, using either carbon paste electro active electrodes [13,14] or VMP [15]. Both methods revealed very colorful patterns of the electrochemical reduction of V^{5+} oxides in aqueous electrolytes depending on their phase composition as well as physical or chemical forms in supported forms [15,16]. VMP is a method more suitable to a routine electrochemical analysis [17]. Its interpretation is mostly qualitative, hence it is a very effective method to estimate the number of species (physical or chemical forms) of electrochemically active elements and phases in the solid state.

2.2.3. Nitrogen adsorption

The N_2-adsorption isotherms were obtained at −196 °C using the through-flow chromatographic method. The relative pressure of nitrogen was varied in the range of 0.01–0.30. Prior to the measurements, all the samples were dehydrated at 200 °C for 2 h. The specific surface area (S_{BET}) was determined by the fitting of the experimental data to the BET isotherm. The mesopore-size distribution was measured using Quantachrome NOVA 4000e analyzer and it was evaluated by the Barett–Joyner–Halenda method from the adsorption branch of the isotherm using a cylindrical model.

2.3. ODH reaction

The ODH of ethane was carried out in a quartz through-flow micro-reactor at 500–700 °C and atmospheric pressure, typically with 200 mg (generally 50–400 mg) of the catalyst (0.25–0.50 mm) diluted with $1\ cm^3$ of silicon carbide inert. The reaction mixture consisted of 1–10 vol.% C_2H_6, 1–10 vol.% O_2 and a rest of He was kept at a total flow of 100 ml/min (typical reaction mixture consisted of 7.5 vol.% C_2H_6, 2.5 vol.% O_2 and a rest of He, W/F $0.12\ g_{cat}\ s\ ml^{-1}$). Catalysts were pre-treated in an oxygen stream at 450 °C for 1 h before each catalytic test. Gas chromatographic (Shimadzu) on-line analysis was carried out using Carboxen^{TM} 1010 PLOT (30 m × 0.53 mm) and RT-S-PLOT (30 m × 0.53 mm) enabling separation and analysis of CO, CO_2, O_2, hydrocarbons, alcohols and aromatics.

3. Results and discussion

3.1. Catalyst characterization

Specific surface areas of HMS, MCM-41 and SBA-15 materials were 835, 977 and $959\ m^2\ g^{-1}$, respectively. Fig. 1 shows the dependence of specific surface area of V-HMS catalysts on the vanadium concentration. A minimal decrease of S_{BET} was observed up to 2 wt.% of V. A further increase of vanadium content caused much more pronounced decrease of S_{BET}. S_{BET} of V-HMS catalysts with 7.5 and 8.8 wt.% V dropped to approximately $100\ m^2\ g^{-1}$, as formation of the bulky vanadium oxide species started (see below). The surface vanadium density (V/nm^2) represents a parameter that allows comparing V-HMS catalysts in a wide range of vanadium concentration and specific surface area [18]. A surface vanadium density increased with an increasing vanadium content (Fig. 1-line b). V-HMS catalysts up to 4.5 wt.% had a vanadium surface density below the theoretical monovanadate monolayer ($2.3\ V/nm^2$ [18]). On the other hand, V-HMS-impr with 7.8 and 8.8 wt.% of V had a vanadium surface density above the theoretical polyvanadate monolayer ($7.5\ V/nm^2$ [18]). S_{BET} of V-MCM-41 (Fig. 1-line c) and of V-SBA-15 (Fig. 1-line d) exhibited the same tendency as S_{BET} of V-HMS (Fig. 1-line a). The specific surface area of mesoporous supports as well as the decrease of S_{BET} for vanadium-based catalysts with vanadium loading up to 4.5 wt.% of V are