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Oxidative dehydrogenation of butane over substoichiometric magnesium vanadate catalysts prepared by citrate route

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Substoichiometric magnesium vanadate catalysts, (Mg–V*i* with $i = 1$, 2, and 3) with different V/Mg atomic ratios and stoichiometric ($Mg_3V_2O_8$, $Mg_2V_2O_7$ and MgV_2O_6), were prepared by citric acid technique. Characterization showed that substoichiometric samples correspond to well-dispersed VO_4 units in the MgO matrix. Moreover, taking into account the Raman data, the coexistence of ortho, pyro and meta vanadate phases cannot be discarded. The $Mg_3V_2O_8$ sample was more active for the oxidative dehydrogenation of *n*-butane, but less selective to C_4 alkenes than the $Mg_2V_2O_7$ sample. Stoichiometric samples produce mainly 1-butene, whereas for substoichiometric samples butadiene was the major reaction product for reaction temperatures higher than 748 K. The easily reducible VO_4 species, and eventually the coexistence of different vanadates phases, appear to be responsible for the catalytic behaviour displayed by the substoichiometric catalysts prepared by citrate technique.

1. Introduction

Butadiene is a very important industrial chemical used as monomer for the production of synthetic rubber. After the decrease between 2000 and 2001 the world demand for butadiene increased consistently between 2001 and 2006. Over the next five years demand is expected to grow at a rate just under 3%/year [1]. Butadiene is mainly produced by steam cracking of crude oil [2]. The unsteady crude oil price in parallel with the rising world demand of butadiene makes the oxidative dehydrogenation (ODH) of butane (low price alkane) an interesting route for butadiene production. Additionally ODH presents some advantages over the steam cracking process: conversion is not thermodynamically limited, reaction temperature is lower and the catalyst is continuously regenerated due to the O_2 presence in the reaction avoiding deactivation by coking.

Several catalytic systems have been studied for the ODH of alkanes [3]. The alkenes formed by ODH are more reactive than the corresponding alkanes and most catalytic systems produce mainly deep oxidation products (CO_2 and CO). The vanadium–magnesium based (V–Mg–O), which were first referred by Chaar, Patel and Kung [4,5] are between the best catalytic systems for the oxidative dehydrogenation of light alkanes. These authors attributed the high selectivity of these catalytic systems to two factors: the surface basicity facilitates the alkene desorption and the absence of V=O species decreases the oxidation activity of the surface.

Despite the large number of published papers, the identification of the active phase remains controversial. Several authors suggested that the isolated VO_X units, usually VO_4 tetrahedra, are the active and selective species for the oxidative dehydrogenation of light alkanes [6]. According to the authors these VO_X units only have a limited number of oxygen atoms thus limiting the oxygen insertion reactions. These units exist in both crystalline and amorphous $Mg_3V_2O_8$ (orthovanadate) [4,5]. The VO_X clusters having V–O–V–O chains are claimed to be responsible for the oxygen insertion reactions. Such clusters are present in the $Mg_2V_2O_7$ (pyrovanadate) phase [7]. In fact the nature of the vanadium units formed depends on the vanadium loading [8]. Pak et al. [9] referred that for surface density of VO_X species above $3.5VO_X/nm^2$ well-dispersed magnesium orthovanadate domains are formed. The fact that the catalytic behaviour depends on the V/Mg atomic ratio and the optimum ratio is observed for substoichiometric values [4] supports the attribution of the active phase to the isolated VO_X units.

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Besides it is noticeable that the catalytic performances are strongly influenced by the preparation method [10,11]. The non-uniform distribution of vanadium on the support seems to be the major factor [8] that can influence negatively the catalytic behaviour. Several techniques can be used to prepare vanadium supported catalysts [12]. The majority of authors prepare V–Mg–O catalysts by contacting the MgO commercial support with an aqueous solution containing the vanadium, or other conventional impregnation techniques. Ammonium metavanadate is usually used as vanadium source. These techniques are limited by the low solubility of the vanadium metavanadate. Some authors prepared catalysts by sol–gel like techniques, namely by citrate technique [13,14]. Lately R. Vidal-Michel and K. L. Hohn [15] reported a complex aerogel technique to prepare V–Mg–O catalysts with small size crystallites. The authors underline the relevance of the $Mg_3V_2O_8$ domains size on the catalytic performances for the ODH of butane.

Few researchers used solid state reaction techniques to prepare this type of catalysts. Chao and Ruckenstein [16,17] prepared V–Mg–O mesoporous catalysts. Their technique leads to catalysts with high surface areas. They prepared vanadium rich catalysts and reported a high dispersion of Mg in the V_2O_3 matrix. These catalysts had good catalytic performances for the ODH of propane.

Grafting techniques were also referred in the literature for preparation of V–Mg–O catalysts [18,19].

Lately Holgado et al. [20] prepared mixed magnesium vanadium oxides using layered double hydroxides (LDH) as precursors. They reported that $Mg_3V_2O_8$ was the main formed phase and underlined the high surface area of the samples obtained.

A simple technique was reported by Balderas-Tapia et al. [21] to prepare V–Mg–O biphasic mesoporous catalysts. According to the authors this technique inhibits the formation of undesirable V_2O_5 phase.

For improving the homogeneity of the V–Mg–O catalysts and their catalytic behaviour, in the present work catalysts were prepared by sol–gel like technique in the presence of citric acid. The effect of the vanadium content was evaluated for the ODH of *n*-butane.

2. Experimental

2.1. Preparation of the catalysts

Samples of V–Mg–O catalysts with different V/Mg atomic ratios (0.1:0.2:0.35) were prepared by citric acid technique [22]. These catalysts will be referred in the text as Mg–V1, Mg–V2 and Mg–V3 respectively. Additionally MgO and three stoichiometric magnesium vanadates ($Mg_3(VO_4)_2$, $Mg_2V_2O_7$, and MgV_2O_6) were prepared by the same technique. Hot (≈80 °C) aqueous solutions (150 cm^3) of magnesium nitrate ($Mg(NO_3)_2\cdot 6H_2O$, *p.a.*, Aldrich) and ammonium metavanadate (NH_4VO_3, *p.a.*, Aldrich), with the required amounts of Mg and V, were prepared separately. Each solution contained 1:1 mole of citric acid (*p.a.*, Merck) to mole of magnesium or vanadium. The vanadium solution initially yellow/orange (V^{+5}) turned to dark blue (V^{+4}) by heating in the presence of citric acid. Indeed citric acid acts as a weak reducing [23,24]. The vanadium/citric acid solution was added dropwise, under vigorous stirring, to the magnesium/citric acid solution. No precipitation occurs. The resulting solution, pale yellow, was heated until a high viscous gel was formed by water evaporation. During this step, the colour of the solution changes from pale yellow to dark blue, through several green shades. The green colour is ascribable to the presence of V^{+5} and V^{4+} at once [23,24]. No characterization of V–citrate, Mg–citrate or V–citrate–Mg complexes probably formed was performed. Conversely, due to the biological relevance of V–citrate complexes, several papers on the subject have being already published. The vanadium citrate complexes were described as dimmers of two penta-coordinated vanadium centres doubly bridged by alkoxide oxygen atoms [25].

The gel (dark blue) was dried overnight at 413 K. Low densities yellow shade foams, depending on the vanadium content, were formed after this step. The foams were easily crushed in a pyrex mortar.

Calcination was performed in two steps: pre-calcination in crucible at 623 K to remove carbon compounds, followed by calcination in tubular quartz reactor under air flow. Catalysts were kept 4 h at the highest temperature 870 K. During the pre-calcination the samples become incandescent due to burning of the carbon compounds. The second calcination step was accomplished in order to remove the remaining, on the catalysts surface, carbon compounds responsible for the grey colour of the samples leaving the first calcination step. During the first calcination step the established temperature was greatly exceeded since samples become incandescent. Thus, it is believed, that the second calcination step has almost null effect on the catalyst characteristics.

Low density powders resulted after calcination steps.

2.2. Characterization of the catalysts

The surface areas of the calcined catalysts samples were measured by BET method with a Coulter SA 3100 apparatus. Bulk elemental analyses were performed by Induced Coupled Plasma (ICP) with a Perkin Elmer Plasma 400.

The characterization by SEM microscopy and EDS was performed with a HITACHI S2400 scanning electron microscope with a RONTEC energy dispersive X-ray high vacuum detector (W filament, $E = 25$ kV).

The XRD patterns of the fresh samples were recorded at room temperature using a Rigaku Geigerflex diffractometer with Cu K_α radiation (Ni filter) at 40 kV and 30 mA. Data were acquired from 15° to 75° at 2°/min. For the micro Raman spectra a Spex 1877 triplemate spectrometer with the 514.5 nm line as exciting radiation was used. For substoichiometric samples, Raman spectra were fitted to symmetric Gaussian shape lines [26] in order to identify the overlapped bands.

The diffuse reflectance UV–VIS spectra, of fresh catalysts, were collected using a Cary 5000 Varian equipment with a DRA 2500 diffuse reflectance accessory (integration sphere).

The study of surface basicity of prepared catalysts was performed by CO_2 TPD. The sample (200 mg) was previously submitted to pre-treatment by heating (10 K/min) under He (60 cm^3/min). After reaching 773 K, the sample was cooled to 303 K and exposed to CO_2 pulses (5 cm^3). The sample was then flushed at 303 K with He for 1 h to remove CO_2 excess. Finally the adsorbed CO_2 was thermally desorbed (10 K/min) under He flow from 303 to 773 K. The amount of CO_2 desorbed was measured by TCD detector.

Temperature Programmed Reduction (TPR) of fresh catalysts (50 mg of powder) was performed under flow of 5% H_2 in Ar (2 NL/h) using a SETARAM TG-DTA-DSC apparatus (LABSYS). The DTG curves were recorded from room temperature to 1100 K with a heating rate of 2 K/min. A slow heating rate was used in order to obtain total reduction of the samples.

The Raman and the UV–VIS spectra and the CO_2-TPD and TPR profiles were deconvoluted using symmetric Gaussian shape lines [26].

2.3. Catalytic tests

For the catalytic tests was used a fixed-bed continuous flow tubular quartz reactor. The catalyst charge was 0.5 g (0.3–0.5 mm) mixed with inert quartz sand (volume ratio of 1:2 catalyst to quartz). The reactor was heated in a furnace with air circulation. Such air circulation improves the heat transfer thus contributing to a “flat” temperature profile in the catalyst bed. For minimizing the homogeneous phase reactions, the reactor was packed with inert