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[V,Al]-MCM-22 catalyst in the oxidative dehydrogenation of propane

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Abstract

MCM-22 zeolite containing vanadium atoms either at structural or at ion-exchange positions was synthesized and tested in propane oxidative dehydrogenation (ODH) reaction in a fixed bed reactor, at temperatures between 340 and 560 °C. Acidity of these materials, as well as of similar materials that did not contain vanadium, was characterized by ammonia temperature programmed desorption (TPD-NH_3). Vanadoaluminosilicates contain a higher number of acid sites, which present higher acidity in relation to the aluminosilicates. They also presented better performances in propane ODH, as they lead to higher values of conversion without loss of selectivity. Ion-exchange with alkaline ions leads to a decrease in cracking reactions, which are caused by strong Brønsted acid sites.

Keywords: [V,Al]-MCM-22; Vanadoaluminosilicates; Oxidative dehydrogenation of propane

1. Introduction

Oxidative dehydrogenation (ODH) of propane is a promising alternative to the traditional dehydrogenation for the production of propene, as it uses exothermic reactions that operate at lower temperatures. The greatest obstacle for its application is the reaction of overoxidation of propene to CO_x that occurs in high conversions of alkanes and that significantly limits the reaction yield [1].

Catalysts that have shown higher ODH rates and propene selectivities are usually based on supported V or Mo oxides [2–7]. Those traditional catalysts have, in general, low superficial areas and thus, a low number of exposed catalytic sites. Zeolitic catalysts, as having high superficial areas (and thus, a higher density of catalytic sites) may, in principle, favour an increase in selectivity for propene at higher conversions, as the reactions occur inside the restricted space of the zeolitic channels and/or cavities.

Zeolite-based catalysts have been tested in ODH of light alkanes [8–11], but the structure and acid sites roles have not yet been fully understood. ZSM-5 zeolite and ALPO-5 materials having MFI and AFI structures, respectively, were tested in propane ODH. In both cases the catalytic activity as well as the selectivity to propene can be enhanced by isomorphous incorporation of V ions in the zeolite framework [8–11].

The aim of this paper is to study the behaviour of V-modified MCM-22 zeolite towards propane ODH. Two different methods of insertion of vanadium in the MWW structure were used, hydrothermal one-pot synthesis ([V,Al]-MCM-22), and ion-exchange of VO_2^+ cations (VO-[Al]-MCM-22). Spectroscopic characterization of the samples is already reported elsewhere [12].

2. Experimental

2.1. Synthesis

Synthesis gels of [Al]-MCM-22 were prepared according to Marques et al. [13] in the following composition:

$$1.0\,SiO_2 : 0.02\,Al_2O_3 : 0.20\,NaOH : 0.60\,HMI : 30\,H_2O$$

where HMI stands for hexamethyleneimine, the structure directing agent. Hydrothermal treatments were carried out under static conditions at 150 °C for 240 h.

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Synthesis gels of V-MCM-22 were prepared in the following composition:

$$1.0\,SiO_2 : 0.02\,Al_2O_3 : 0.03\,VOSO_4 : 0.30\,NaOH : 0.60\,HMI : 30\,H_2O$$

The synthesis procedure was also adapted from Marques et al. [13] introducing $VOSO_4$ as the vanadium source. For preparation of the gel, $VOSO_4$ has been added together with the aluminum source, $Al(NO_3)_3$, and the method for preparing [Al]-MCM-22 has been followed as described [13]. Hydrothermal treatments were carried out under static conditions at 150 °C for 192 h.

The structure directing agent of [Al]-MCM-22 and [V,Al]-MCM-22 was removed by heating under argon from room temperature to 500 °C at a heating rate of 1 °C min^{-1} and leaving at this temperature for 12 h under argon flow. Subsequently, the sample was heated up to 580 °C under argon and the sample was left at this temperature for 6 h under dry oxygen flow.

Calcined [Al]-MCM-22 sample were ion-exchanged with Na^+, K^+ or NH_4^+ (0.1 mol L^{-1} sodium nitrate, potassium nitrate or ammonium acetate solutions at a ratio of 10 mL of solution/gram of zeolite, stirring at 60 °C for 24 h), while calcined [V,Al]-MCM-22 samples were ion-exchanged with Na^+ or NH_4^+ following the same procedure as for [Al]-MCM-22. The exchanged samples were heated up to 500 °C under Ar flow, and once the temperature was reached, the gas was changed to oxygen and the sample left in this condition for 6 h. These samples were named Na-[Al]-MCM-22, K-[Al]-MCM-22, H-[Al]-MCM-22, Na-[V,Al]-MCM-22 and H-[V,Al]-MCM-22, respectively.

VO-[Al]-MCM-22 samples were made by ion-exchange of [Al]-MCM-22 with 0.1 mol L^{-1} $VOSO_4$ solution (at a ratio of 10 mL of solution/gram of zeolite, stirred at 60 °C for 24 h; pH 1.6 with concentrated H_2SO_4).

2.2. Catalyst characterization

2.2.1. Elemental analysis

Elements concentration was determined by solubilizing the samples by oxidizing alcaline fusion with lithium metaborate. The resulting material was dissolved and the elements were determined by atomic absorption with a Varian A-5 spectrophotometer, using a nitrous oxide/acetilene flame.

2.2.2. X-ray diffraction (XRD)

Data were collected for the as-synthesized and calcined samples as hand-pressed wafers on a Shimadzu XRD 6000 diffractometer at room temperature with CuK_α radiation, generated at 40 kV and 30 mA from 1.4 to 50° 2θ at a rate of 2° min^{-1} and slits of 0.5°, 0.5° and 0.3 mm for exit, reception and divergence, respectively.

2.2.3. Pore-structure analysis

Textural properties of the samples were determined on a Micromeritics ASAP 2000 instrument using N_2 at 77 K as adsorbate.

2.2.4. Temperature programmed ammonia desorption (NH_3 TPD)

NH_3 TPD was done by using a Micromeritics TPD/TPR 2900 analyser, equipped with a TC detector and coupled with a Hiden HPR 20 mass spectrometer. Samples were satured with pure ammonia at 100 °C for 1 h and, after being purged with pure He for 2 h at room temperature, were heated until 700 °C at a 10 °C min^{-1} rate under He flow (25 cm^3 min^{-1}).

2.3. Catalytic activity measurements

Catalytic activity tests of propane oxidative dehydrogenation were carried out in a fixed bed quartz micro reactor operating under atmospheric pressure. The feed composition was 2.5% propane, 5% O_2, He balance (in volume). The contact time was fixed at 0.11 g h dm^{-3} and the reaction temperature ranged from 340 to 560 °C. Analysis of hydrocarbons was performed by an on-line Hewlett-Packard HP5890A (series II) gas chromatograph equipped with a Poraplot capillary column and a flame ionization detector (FID). Concentration of O_2, CO and CO_2 was measured by an on-line Hartmann & Braun URAS 10 E continuous analyser. Water produced by the reaction was retained by a $CaCl_2$ trap, in order to avoid condensation in the cold parts of the experimental apparatus.

3. Results and discussion

The elements concentration in the calcined and/or exchanged [Al]-MCM-22 and [V,Al]-MCM-22 samples, determined by element analysis, are reported in Table 1.

A comparison between XRD of [V,Al]-MCM-22, calcined [Al]-MCM-22 and VO-[Al]-MCM-22 can be observed in

Table 1
Composition of the samples, determined by elemental analysis and predominant type of vanadium species present in the samples

Sample	%V_2O_5 (m/m)	Type of V species	SiO_2/Al_2O_3	SiO_2/V_2O_5	Al/V	Na/Al	K/Al
H-[Al]-MCM-22	–	–	60	–	–	0.02	–
Na-[Al]-MCM-22	–	–	62	–	–	0.28	–
K-[Al]-MCM-22	–	–	69	–	–	0.04	0.89
[V,Al]-MCM-22	0.57	Aggregates	40	473	12	0.09	–
H-[V,Al]-MCM-22	0.25	Isolated	30	1036	35	0.02	–
Na-[V,Al]-MCM-22	0.27	Isolated	34	999	30	0.20	–
VO-[Al]-MCM-22	0.14	Isolated	42	1886	45	0.02	–