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Sonosynthesis of VOx/MCM-41 nanocatalyst enhanced by various metal oxides (Mg, AL, Zr) for CO_2-oxidative dehydrogenation of ethane to ethylene

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ABSTRACT

To develop an efficient V-based catalyst for oxidative dehydrogenation of ethane by CO_2, MCM-41was modified with various metal oxides (Mg, Al, Zr) and then, impregnated with aqueous solution of NH_4VO_3 and then tested in dehydrogenation of ethane with CO_2 at different temperatures. The obtained catalysts have been characterized by powder X-ray diffraction, BET, FESEM, FTIR, EDX, TPD-NH_3 and UV-Vis. DRS analysis. The results show that introduction of various metal oxides alter structural properties of fabricated V/MCM-41catalyst, such as crystallography, vanadium oxo-species dispersion, particle size distribution and acid-base properties which can improve catalytic performance of synthesized nanocatalyst. Among the studied catalysts, the MCM-41 family catalyst containing MgO and ZrO_2 showed the best performance and effectively dehydrogenated ethane to ethylene in the presence of CO_2 at 700 °C giving 43% ethylene yield. This catalyst remained stable even after 10 h on stream.

1. Introduction

Silicon-based mesoporous materials have been used as support for many reactions due to their prominent properties [1–3]. On the other hand, in these materials, the appropriate control of surface chemistry and geometry leads to formation of catalysts with high surface area which facilitate the active phase dispersion and mass transfer of reactants and products [4,5]. Among the mesoporous materials, MCM-41 is widely studied [6–9]. MCM-41 has a hexagonal array and according to the structure directing agent used, the pore size tuned from 2 to 10 nm. The neutral nature of MCM-41 framework limits some of its utilization in the catalytic reactions especially in the reactions where acidic or basic sites are required. In recent years, the researchers have focused on the incorporation of trivalent cations on the silica structure [10]. The introduction of these cations into the silica framework develops Bronsted acid sites which are useful in many catalytic reactions such as C-H bond cleavage of alkane [11,12]. In fact, the presence of trivalent cation in the silica framework creates more electrons which are in equivalency with more positive charge.

CO_2-oxidative dehydrogenation of ethane to ethylene is one of the most favorable candidates in olefins production [13–16]. In the literature data, the obtained ethylene yield is mostly below 20% and doesn't meet the industry requirements to the ethylene productivity which is above 1 $g(C_2)/g_{cat}.h$ at temperature as low as possible [17,18]. Among the studied materials, the vanadium supported catalysts are very active and selective in ethane ODH [7,19–22]. Depending on the character of the support, the interaction of vanadium with support leads to formation of different structures. The most important vanadium species on the catalyst supports are monomeric $[VO_4]$, vanadate dimeric or oligomeric chain- or sheet-like structures, polyvanadate anions, and 3-D nano- and micro-structures of V_2O_5 at higher V-loadings [23]. Therefore, it can be concluded that, vanadium oxide species, supported on various metal oxides are completely different from bulk V_2O_5. Actually, for identification of crystalline V_2O_5, X-ray diffraction was used [24–26]; on the other hand, the recognition of non-crystalline vanadium species is usually carried out by UV–Vis spectroscopy (DRS) [27,28], Raman or IR spectroscopy [29,30] and temperature programmed reduction (TPR) [31]. In all catalytic reactions, the nature of the support determines the dispersion of active phase metal oxide. In the case of vanadium oxide species, interaction of vanadium with the support creates different configurations. Basic supports tend to form stable mixed oxide phases, while in the case of acidic supports; vanadia is highly dispersed on the surface. Thus, utilization of a support with acidic nature enhances catalytic activity toward ethylene production since it prevents the formation of polymeric vanadium oxide. In the current study, this goal could be achieved by introduction of metal

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oxide in the neutral MCM-41 framework [32]. The simultaneous presence of V^{+4} and V^{+5} ions in these catalysts is believed to promote the selective oxidation to the olefin or to the desired oxygenated compound via a redox process. The factors determining the ethane conversion and ethylene selectivity were reported to be the extent of vanadium loading [26,33], the vanadium surface coverage [34], the acidic or basic properties of support [35,36] and the reaction temperature.

As oxidant, O_2 and CO_2 were used in ethane ODH on vanadium oxide supported materials but due to environmental concerns and regulations, the application of carbon dioxide (CO_2, a greenhouse gas) in the production of high-value-added chemicals or fine chemicals is of immeasurable importance. CO_2 is abundant, non-toxic, inexpensive and non-flammable [37–39]. These features put it up as a renewable C_1 feedstock source [40–42]. On the other hand, stable nature of CO_2 makes its activation harder and affects the ethane conversion [43–45]. The aim of this work is attempting to determine the activity of vanadium containing MCM-41 materials in ODH of ethane. The main factors investigated are (a) the effect of various metals introduced to the MCM-41 framework on the activity and stability of catalysts in ODH of ethane, (b) the contribution of various configurations of vanadium oxo-species in the ethane ODH and (c) the effect of reaction temperature on the activity and selectivity of ODH of ethane. In order to achieve these objectives, first, MCM-41 substrate was synthesised by hydrothermal method; then metal oxides were precipitated on the surface of MCM-41, and finally, the vanadium oxo-species were dispersed over the support by ultrasound irradiation power. The synthesised catalysts were characterized by XRD, FESEM, PSD, EDX, BET, FTIR, TPD-NH3 and DRS analysis. The catalytic performance was evaluated for the oxidative dehydrogenation of ethane to ethylene in the presence of CO_2 under atmospheric pressure.

2. Materials and methods

2.1. Materials

Cetyltrimethyl-ammonium bromide ($C_{19}H_{42}BrN$, Merck, extra pure) was used as the template, H_2SO_4 was used to control the pH of the solutions and sodium metasilicate (Na_2O_3Si, Aldrich, 99.9%) was applied as silica source. Mg $(NO_3)_2.6H_2O$ (Merck), $ZrO(NO_3)_2.6H_2O$ (Merck) $Al_2O_3.9H_2O$ (Dae-Jung) were used as metal precursors introduced in the MCM-41 framework. NH_4VO_3 was used as active phase precursor and was purchased from Aldrich Company. NH_4OH was applied to control the pH of the solutions. These materials were used as received and were not purified further. C_2H_6 (99.9%), CO_2 (99.99%), air (99.999%) and N_2 (99.9995%) were all of high purity and were purchased from Technical Gas Services in Ajman, UAE.

2.2. Nanocatalysts preparation and procedures

MCM-41 mesoporous substrate was synthesized by hydrothermal method according to the reported method in the literature [46]. Fig. 1s in supplementary information shows schematically the methodology of the preparation method of MCM-41 support. Desired amounts of cetyltrimethyl-ammonium bromide and 40 ml water were mixed and dissolved; then sodium metasilicate was added to the solution and stirred, and thereafter sulphuric acid 4 N was added to the solution to reduce the pH to 10.5. The resulting homogenous solution was transferred into an autoclave and kept in an oven at 140 °C for 12 h. The solid product after cooling to room temperature was filtered, washed and dried at 110 °C for 6 h and then calcined at 550 °C for 6 h in a furnace to remove the template. As can be seen in Fig. 2s in supplementary information, the supports were prepared as follows: an appropriate amount of MCM-41 was added to the aqueous solution of applied metal precursors: ($Al(NO_3)_3·9H_2O$, Mg $(NO_3)_2·6H_2O$ and ZrO $(NO_3)_4·xH_2O$), followed by drop wise addition of 25% aqueous solution of ammonia with stirring until the final pH reached 8. The precipitated product was filtered, washed and dried at 110 °C and finally calcined at 600 °C. The prepared support was impregnated with NH_4VO_3 aqueous solution. After that, appropriate amounts of NH_4VO_3 and support were dissolved in water and afterward, the solution was exposed to high-intensity ultrasonic irradiation (90 W) for 60 min, using a titanium tip of 1 cm^2 (Fig. 3s in supplementary information). The resulting solution was dried at 110 °C for 6 h and then calcined at 700 °C for 3 h.

2.3. Nanocatalysts characterization

In order to identify crystalline phases of nanocatalysts, powder X-ray diffraction (XRD) analysis was performed. The XRD patterns were collected on a Siemens diffractometer D5000 with monochromatized Cu-K radiation at 40 kV and 30 mA and a scanning angle (2θ) range of 20°–90° and scanning rate of 0.02°/s. Microstructure, particle size distribution, morphology and surface particle size distribution of nanocatalysts were investigated by field emission scanning electron microscopy (VEGA\\\\TESCAN, BSE DETECTOR). The specific surface area (BET) of nanocatalysts was measured by N_2 adsorption and desorption isotherms obtained at 77 K using a Quantachrome ChemBET-3000. Infrared analysis of the nanocatalysts was carried out by a UNICAM 4600 FTIR spectroscopy addressing surface functional groups in the range of 400–4000 cm^{-1} wave numbers. Energy dispersive X-ray analysis (EDX) was done by VEGA\\\\TESCAN, BSE DETECTOR for elemental analysis. The acidity of nanocatalyst was measured by ammonia-temperature programmed desorption (NH_3-TPD) using NanoSORD analyzer with a TCD detector. In this regard, 0.05 g of nanocatalyst was preheated at 500 °C for 60 min under a nitrogen gas flow. Eventually, the nitrogen flow was passed through the nanocatalysts by increasing the temperature up to 800 °C. In order to determine the vanadium oxo-species configuration, UV-Vis diffuse reflectance spectra (DRS) were taken in the wavelength range 200–1000 nm with a spectrometer (Scinco S4100, Korea) equipped with a PC for data acquisition and analysis.

2.4. Nanocatalysts performance test

In order to investigate the oxidative dehydrogenation of ethane (ODH) over synthesized catalysts, a U-shape quartz tube packed bed reactor with 6 mm i.d and 200 mm length was applied. 500 mg of nanocatalyst was charged to the reactor and all experiments were done at atmospheric pressure. To provide isothermal condition, before the ODH reaction, the feed gas was preheated and the catalyst particles were rarified with quartz sand. The reactor configuration is shown schematically in Fig. 1. In order to remove water or inorganic compounds available on the catalyst's surface, a flow of dry air is required to pass through the catalyst bed. On the other hand, dry air flow increases oxygen capacity of the particles of catalyst. Experiments were performed at temperatures ranging from 600 to 700 °C. A mixture of carbon dioxide, ethane and nitrogen (feed) at a $CO_2/C_2H_6/N_2 = 4/1/5$ ratio was supplied through mass flow controllers (Beijing Sevenstar Electronics Co., Ltd.) to the nanocatalyst bed at the specified reaction condition. Compositions of feed and reactor effluent gas were monitored by a gas chromatograph (GC Chrom, Teif Gostar Faraz) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) and a methanizer and a Carboxen-1000 column (Agilent).

3. Results and discussions

3.1. Characterization

3.1.1. XRD analysis

The powder X-ray diffraction patterns of synthesized catalysts are shown in Fig. 2. It can be observed that all samples display an intense peak at 2θ = 2.1°, as apparent from the narrow (100) reflection which can be demonstrated on a hexagonal framework of MCM-41 (JCPDS 00-