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Acrolein production from methanol and ethanol mixtures over La- and Ce-doped FeMo catalysts

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ABSTRACT

The acrolein production from methanol and ethanol mixtures over iron-molybdate-based catalysts was studied. The reaction to acrolein can be described by two successive steps: the first consists on the oxidation of both alcohols into their corresponding aldehydes and the second step is the subsequent aldol condensation of the as-formed aldehydes. The iron-molybdate catalysts were modified by doping with La and Ce (1%mol) in order to improve the aldol condensation step of the process. Series of catalysts were thus synthesized with different Mo/Fe ratios (i.e., 1.5, 2.0 and 2.5) and calcined at three different temperatures (i.e, 350 °C, 400 °C and 450 °C). The best catalytic performance was observed for FeMoCe2.0 (400 °C) for which the acrolein yield reached 42% (T = 320 °C, MetOH/EtOH = 1, GHSV = 3900 h^{-1}). Furthermore, all the samples were characterised by TGA-DSC, HT-XRD, XPS, BET, LEIS, XRF, CO_2-TPD, Pyridine (FTIR) and NH_3 (calorimetry) adsorption. The increase in acrolein yield observed upon La and Ce doping was attributed to acid/base properties modification.

1. Introduction

Acrolein (propenaldehyde) is the simplest unsaturated aldehyde, which finds numerous applications in the chemical industry. Its most important use is the production of acrylic acid applied in the manufacturing of coating resins, polyacrylic acid (rheology modifiers), superabsorbents, detergents and others. The second main acrolein application is the production of methionine, which is an essential amino acid used for cattle feed and battery farming. Until now, the main method of acrolein production is propylene oxidation. However, the increasing demand as well as environmental requirements generated active research of alternative processes [1,2,3,4,5,6,7,8]. Unfortunately, due to the feedstock unstable prices and scaling-up issues, these methods cannot actually be used at the large scale. Recently, a new method of acrolein production was shown, [9,10,11,12] based on methanol and ethanol as raw materials. The mentioned feedstock can be obtained from biomass at competitive prices. This reaction can be schematically described as two concomitant steps, namely alcohol oxidation (Eq. (1)) and the as-formed aldehyde aldol condensation to acrolein (Eq. (2)):

$$CH_3OH + C_2H_5OH + O_2 \rightarrow HCHO + CH_3CHO + 2\,H_2O \qquad (1)$$

$$HCHO + CH_3CHO \rightarrow CH_2CHCHO + H_2O \qquad (2)$$

Note that the transformation of the alcohols into aldehydes (Eq. (1)) can also result from a dehydrogenation reaction, but for valorization of acrolein, very low propanaldehyde contents are necessary. This reaction has been achieved in the gas phase with the use of iron molybdate mixed oxides in one reactor, a catalytic system extensively described elsewhere [13,14] and industrially used to perform the methanol oxidation to formaldehyde [15]. This heterogeneous catalyst is composed of two major phases [2,16,17,18]: MoO_3 (#PDF 01-089-5108) and $Fe_2(MoO_4)_3$ (#PDF 00-031-0642), of which the relative proportion is closely related to the Mo/Fe ratio used during the preparation of the solid. This catalyst exhibits both an acidic and a redox behavior, the latter which is necessary for the considered reaction; while the former was evidenced in methanol rich oxidation condition by the formation of dimethoxymethane [19,20]. It has to be noted that the aldol condensation reaction can proceed as well over acid or basic sites. The presence of the acid sites over the FeMo formulation was previously attributed mainly to the creation of anionic vacancies acting as Lewis acid sites produced by dehydroxylation of the catalyst surface (upon reduction in the reactants atmosphere), while the redox properties are

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provided by the Fe active sites.

The bifunctional behavior of such a catalytic system, due to the synergetic effect between an adequate number of Mo sites and Fe sites, is crucial for the efficient conversion of methanol and ethanol mixtures to acrolein.

The aim of the present study was to improve the FeMo formulation to increase the acrolein yield by doping with La and Ce in order to tune the acid/base properties of the catalysts. The materials were prepared, characterized and their catalytic activity was measured in a fixed bed reactor in the gas phase.

2. Experimental

2.1. Materials

Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (AHM, Fluka, 99%), iron (III) chloride hexahydrate $FeCl_3\cdot 6H_2O$ (Sigma-Aldrich, 97%), lanthanum (III) nitrate hexahydrate $La(NO_3)_3\cdot 6H_2O$ (Aldrich, 99.99%), cerium (III) nitrate hexahydrate $Ce(NO_3)_3\cdot 6H_2O$ (Aldrich, 99.99%), stearic acid $C_{17}H_{35}COOH$ (Sigma-Aldrich, 98.5%), sodium chloride NaCl (Fluka, 99%), silver nitrate $AgNO_3$ (Aldrich, 99.99%), ethanol C_2H_5OH (Sigma-Aldrich, 99.8%), methanol CH_3OH (Sigma-Aldrich, 99.8%), helium (Air Liquide, alphagaz 99.9%) and oxygen (Air Liquide, 99.9%) were used as such without a further purification step.

2.2. Doped iron molybdate catalysts synthesis

The iron molybdate catalysts were synthetized using a coprecipitation method described by Pernicone et al. [17,21,22]. In the case of the reference FeMo catalyst, aqueous solutions of AHM and iron (III) chloride hexahydrate were prepared based on a Mo/Fe ratio equal to 2 (as for the industrial FeMo catalysts used for methanol oxidation to formaldehyde) and heated under vigorous stirring to a temperature between 50 and 60 °C. The pH of the ammonium molybdate tetrahydrate solution was adjusted at 1 by adding concentrated HCl. Afterwards, the $FeCl_3\cdot H_2O$ solution was slowly added dropwise to the AHM solution and a yellow precipitate was obtained. The stirring was kept for 1 h and followed by several hours of decantation. Then, a chloride removal step was performed by washing the obtained precipitate with distilled water until the Cl^- content became lower than 2000 ppm. Later, the precipitate was filtrated and subsequently dried in an oven at 120 °C for 4 h. The obtained solid was crushed in a mortar and mixed with 1 wt.% of stearic acid before calcination under air flow (0.3 mL/min) at 450 °C. The way we will call the samples is the following: FeMoLa(Ce)*X*, where *X* is the Mo/Fe ratio and La or Ce as doping element.

In the case of doped FeMo catalysts, nitrate solutions of lanthanum and cerium [1 mol%] were prepared and added to the iron chloride solution at the very beginning of preparation. During the synthesis of these materials, the Mo/Fe ratios were varied (*i.e.*, from 1.5 to 2.5) as well as the calcination temperature (*i.e.*, 350, 400 and 450 °C).

2.3. Characterization

The freshly prepared dried samples (non-calcined) were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) using a TA Instruments SDT-Q600 apparatus with alumina as a reference. The measurement was performed under air flow (100 mL/min) while increasing the temperature to 600 °C at a rate of 5°/min up).

High-temperature X-ray diffraction (XRD) was performed using a Brüker D8 apparatus (Brüker AXS, Cu-$K_{\alpha 1}$ $\lambda = 1.5406$ Å) to follow the temperature of phases crystallization. The analysis was performed under air flow from 50 °C to 500 °C with a heating rate of 10°/min. The diffractograms were recorded each 25 °C for 2θ values in the 10° to 60° range, using a 0.02° step and a 0.5 s integration time. The results interpretation was made based on the database from the Joint Committee on Powder Diffraction Standards (JCPDS) using the EVA X-ray diffraction analyses software.

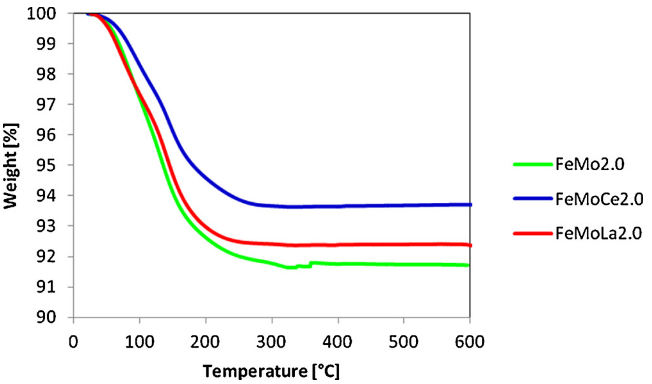

Fig. 1. TG for: FeMo2.0, FeMoLa2.0, FeMoCe2.0. The analysis was performed in the 20–600 °C temperature range with heating rate of 10 °C/min under air flow.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis spectrometer apparatus with an alumina Kα radiation (1486.6 eV) under vacuum. All the results were treated using the CasaXPS software, and the surface compositions were determined from the various observed peaks (*e.g.*, Mo 3d, Fe 2p…) recorded at a 40 eV pass energy. The reference was taken for the C 1 s level binding energy for C-(C, H) bonds fixed at 285 eV.

Low energy ion scattering (LEIS) experiments were performed in a Qtac100 instrument (ION-TOF GmbH) at a pressure of 10^{-8} mbar. This instrument is fitted with a double toroidal energy analyzer (DTA), which collects the scattered ions at a scattering angle of 145° from all azimuth angles. The samples were analyzed using a 3 keV He^+ primary ion beam directed perpendicularly to the target surface. The area of analysis is 1 mm x 1 mm and the experiments were performed with a total dose per spectrum of $1{,}9 \times 10^{14}$ ions/cm^2. Quantification and simulation of the peaks were carried out using the SurfaceLab software. As LEIS is highly sensitive to the outermost surface, before analysis, the pressed samples were cleaned from carbon contamination by using an atomic oxygen plasma (1–2 × 10^{-5} mbar, 10 min).

The specific surface area was measured using the single-point BET method (Brunauer, Emmett, Teller) based on nitrogen adsorption and desorption using Micrometrics Flowsorb II Surface Area Analyzer. The analysis was performed on 200 mg of calcined catalyst placed in a glass chamber and outgassed at 150 °C during 20 min in order to remove the surface impurities. Afterwards, the glass chamber was dived in liquid nitrogen in order to perform the adsorption/desorption procedure followed by a TCD signal.

X-ray fluorescence (XRF) was performed for calcined samples using a S2Ranger Bruker apparatus placed in a tube through Mylar Sheet 6 microns under helium flow.The presence of basic sites on the catalysts' surface was examined with CO_2-temperature programmed desorption (CO_2-TPD). The measurement was performed on calcined samples with Micrometrics Autochem 2920 apparatus coupled with a MS Pfeiffer. First, the catalysts were pretreated under a He flow (50 mL/min) at 200 °C (temperature reached at a rate of 10 °C/min) during 1 h. Then, CO_2 adsorption was performed at room temperature during 30 min using a carbon dioxide flow (5% CO_2, 95% He). Finally, desorption was performed until 700 °C (this temperature being reached at a rate of 10 °C/min) during 30 min in helium (30 mL/min).

The presence of acid sites on the catalysts was measured by pyridine adsorption followed by FT-IR spectroscopy. The adsorption line was coupled with a Nicolet Protege 460 infrared spectrometer equipped with a MCT detector allowing the quantification of the acidic sites. Before analysis, weighted catalysts were ground in an agate mortar and pressed to get self-supporting wafers. Then, they were placed in the