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Binder effect on the catalytic activity of MoO_3 bulk catalyst reduced by H_2 for *n*-heptane hydroisomerization

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HIGHLIGHTS

- MoO_3 bulk catalysts showed high activity for *n*-C_7 hydroisomerization than MoO_3 powder.
- MoO_3 bulk catalyst with SiO_2 shows low cracking and high selectivity to pentanes.
- No carbon deposits are observed in *n*-C_7 hydroisomerization using MoO_3 bulk catalysts.

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ABSTRACT

Two bulk catalysts containing about 70 wt.% of molybdenum trioxide and alumina or silica as binder were prepared by a gel method. They were characterized by X-ray diffraction, Raman spectroscopy, TGA in air and textural properties. The MoO_3 bulk catalysts were activated *in situ* by reduction with hydrogen and tested in the hydroisomerization of *n*-heptane using a fixed bed continuous flow microreactor coupled to gas chromatograph. The highest catalytic activity for hydroisomerization was obtained with the alumina-based bulk catalyst, although the silica-based bulk catalyst showed lower amounts of cracking products and a higher selectivity to dimethylpentanes. The bulk catalysts resulted more active than MoO_3 powder. The results indicate that the acid–base properties of the binder have a desirable effect on the acidity of the molybdenum trioxide powder as hydroisomerization catalyst.

1. Introduction

The alkanes present in the naphtha fraction of crude oils are predominantly linear or monobranched, and they must be converted into highly branched isomers or aromatic compounds through the isomerization and reforming processes in order to improve the octane number of gasolines. Existing technologies for isomerization of butane, pentane and hexane has not been applied to heptane and heavier alkanes because the formation of cracking products becomes too high as conversion increases. Molybdenum oxides are important compounds in catalysis. In the case of hydroisomerization, the catalytically active phase appears to be neither MoO_3 nor MoO_2 but rather a partially reduced molybdenum sub-oxide [1–3]. This molybdenum sub-oxide, mixed with other reduction products, can be prepared directly from MoO_3 by reduction at low temperature (623 K) under flow of a mixture of H_2/*n*-heptane [1–3], being the reduction of MoO_3 a crucial step in the generation of an active catalyst for hydroisomerization reactions [4–6].

The structures of supported molybdenum oxide species are a function of the specific support, extent of surface hydration–dehydration [7–9], surface molybdenum oxide coverage, surface impurities, and calcination temperature. Under ambient conditions, the surface metal oxides are extensively hydrated by water molecules adsorbed on the support surfaces and, therefore, possess structures affected by surface water. At elevated temperatures, the catalyst surfaces are dehydrated, and the surface metal oxides undergo significant structural changes [10].

There are many reports about the preparation procedure of supported MoO_3 catalysts; the most common way to prepare a MoO_3-based catalyst is to impregnate a molybdenum precursor on the support and subsequent decomposition of this precursor to MoO_3 via thermal treatment. The wet impregnation of ammonium heptamolybdate on silica, alumina or silica–alumina

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supports is commonly used for the preparation of MoO_3-based catalysts [11–19]. The details of the preparation method impact markedly on essential properties of the final catalytic material: morphology of the MoO_3 deposit, nature and proportion of molybdenum oxide species, and interaction of molybdenum atoms with the support. In turn, these properties are seen as crucial parameters that dictate the performance of the catalyst. However, the intricate relationships between (i) the preparation parameters, (ii) the catalysts properties and, (iii) their activity, remain unclear. It is widely accepted for example that well-dispersed MoO_x species, as opposed to MoO_3 crystals, are the precursors for active sites. Harsh thermal treatment might also promote the dispersion of molybdenum on the support [20,21] or provoke molybdenum losses. In general, molybdenum oxide is the active component of the catalyst and its loading is evidently crucial. In principle, the amount of active centers could be partially linked to the amount of molybdenum introduced in the formulation [22].

Currently, our research group is working in the development of an efficient hydroisomerization process for the production of C_6–C_8 branched compounds [23–26]. Thus, this work is focused on the study of the catalytic activity of H_2-reduced MoO_3 in powder form and extruded with silica or alumina, bulk catalysts, in *n*-heptane isomerization in order to use as a support for industrial catalysts due to its outstanding surface and mechanical properties, and relatively low cost. In addition, the characterization of these catalysts by X-ray diffraction, Raman spectroscopy and textural properties, before and after reaction, was compared with that of powdered molybdenum trioxide evaluated at the same experimental conditions with the aim of understanding the reaction mechanisms involved in the hydroisomerization process.

2. Experimental section

2.1. General comments and material

Unless otherwise specified, all solvents and reagents were used without further purification. Molybdenum trioxide (99.5 wt.%, Fermont), Molybdenum dioxide (99 wt.%) boehmite (72.0 wt.%, Sasol), formic acid (85.0 wt.%, AyT), aqueous colloidal silica (40 wt.%, Intercat), ethylene glycol (99 wt.%, Aldrich), *n*-heptane (99.4 wt.%, Merck), hydrogen (99.999 + % UHP, Praxair), nitrogen (99.9 + %, Praxair).

2.2. Catalyst preparation

Two bulk catalysts containing about 70 wt.% of molybdenum trioxide and alumina or silica as binder were prepared by a gel method. Thus, the required amounts of molybdenum trioxide and ethylene glycol were added to the corresponding amount of aqueous colloidal silica and mixed at 296 K, the excess water was evaporated by heating with vigorous stirring. When the mixture became too stiff to stir, the paste was extruded into rods of 2 mm in diameter. The wet pellets were dried at 286 K overnight and at 383 K in air for 6 h, and then calcined at 823 K in air for 2 h. In the case of alumina-based bulk catalyst, the boehmite was peptized with a 1 M aqueous solution of formic acid (0.4 milliequivalents of acid per gram of boehmite). The alumina- and silica-based molybdenum catalysts were denoted as Mo–Al and Mo–Si, respectively.

2.3. Catalytic experiments

The catalytic experiments were carried out in a fixed bed continuous flow microreactor (stainless steel, 9 mm i.d.) coupled to gas chromatograph with a flame ionization detector (Agilent 6890 equipped with a 100-m PetrocTM DH column and Chem Station/ Hydrocarbon ExpertTM PIANO software) for on-line analysis. The *n*-heptane and hydrogen were fed to the reactor by an Eldex metering pump and a Brooks 5850E mass flow controller, respectively.

The reaction conditions of this study were established from our experimental results obtained previously [23–26] and those reported elsewhere [1–6]. In a typical experiment, one gram of molybdenum trioxide with a particle size of about 20 m was introduced into the reactor under nitrogen atmosphere at 296 K and heated to 623 K at rate of 4 K/min, and then reduced by a stream of hydrogen (0.1 L/min) under a pressure of 2 kg/cm^2 at 623 K for 24 h. After hydrogen reduction, a stream of *n*-heptane (0.083 ml/min) was passed through the catalyst bed at 17.5 kg/cm^2 and 623 K for 12 h; this stage is considered as an activation period. The hydroisomerization of *n*-heptane was performed at 18.5 kg/cm^2 and 643 K. Reaction products were analyzed on-line by GC at 2, 4, 6 and 8 h of time on stream at 643 K. Finally, the reactor was cooled down to 296 K under nitrogen flow and then the catalyst was recovered and characterized. The alumina- and silica-supported molybdenum catalysts were evaluated in the same conditions but using 1.43 gram of sample with a particle size of about 20 μm in order to maintain the relation of molybdenum trioxide.

The catalytic activity of the catalysts was expressed as the transformation rate of *n*-heptane and the selectivity towards dimethylpentanes principally. Thus, the *n*-heptane conversion, dimethylpentanes selectivity and cracking selectivity were calculated using the following equations:

$$\text{Conversion} = \frac{(nC_7^0 - nC_7^f)}{nC_7^0}\,\frac{wt}{wt} \times 100$$

$$\text{Selectivity to isomers} = \frac{C_7\text{isomers}}{nC_7^0}\,\frac{wt}{wt} \times 100$$

$$\text{Selectivity to cracking} = \frac{\text{Total cracking}}{nC_7^0 - nC_7^f}\,\frac{wt}{wt} \times 100$$

where nC_7^0 and nC_7^f are the concentration of nC_7 compound at beginning and end of the catalytic tests, respectively.

2.4. Characterization

The components of the materials were examined by X-ray diffraction (XRD) using a Siemens diffractometer (Model D5000) with Cu K radiation and a Ni filter. The operating conditions were 35 kV and 25 mA in the angular range 4–50° in 2θ. Phase identification based on XRD patterns was aided by the ICDD-PDF-2 database.

The Raman spectra were recorded in air at 296 K with a triple monochromator using a Raman spectrometer SPEX model 1403 using an Ar$^+$ ion laser that delivered 20 mW of incident radiation. The excitation line of the laser was 514.5 nm. The Raman signal was detected with a photomultiplier and a standard photon counting system.

The TGA was carried out with an analyzer Netzsch STA 409 PC/PG using air (50 mL/min) and 20 mg of sample, the heating rate was 5 K/min.

Surface area, total pore volume and pore size distribution were determined by BET method using a Micromeritics ASAP-2401 system.

The acidity of the catalysts was determined via pyridine and ammonia adsorption followed by diffuse reflectance FTIR spectroscopy using a Nicolet Protege 460 spectrometer. The spectra were collected in the range of 4000–1000 cm^{-1} averaging 50 scans at

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