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Oxidative dehydrogenation of *i*-butane over nanostructured silica-supported NiMoO₄ catalysts with low content of active phase

Rodica Zăvoianu^a, Cristina Rebelo Dias^b, Ana Paula Vieira Soares^{b,*}, Manuel Farinha Portela^b

 ^a University of Bucharest, Faculty of Chemistry, Department Chemical Technology and Catalysis, Bd. Regina Elisabeta, No 4-12 S.3, 030018 Bucharest, Romania
^b ICEMS-UQUIMAF-GRECAT, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, s/n DEQ, Torre Sul, 1049-001 Lisboa, Portugal

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Abstract

NiMoO₄ silica-supported samples (6.5% w/w) were prepared by coprecipitation technique. In order to study the influence of the surface area of the support material, silicas with different surface areas have been used: Durosil (60 m²/g) and Sipernat 22 (190 m²/g) from Degussa and silica prepared in the laboratory (590 m²/g). Nanosized grains of β -NiMoO₄ phase were obtained for all the prepared samples. The crystallinity of the active phase (mixed oxide) depends on the nature of the support material. The laboratory-made silica allowed reaching the highest degree of nanocrystallinity (observed by TEM) for the active phase. Results from TPR and ITR show that the sample reducibility depends on the size and crystallinity of the dispersed active phase. All the prepared samples were more reducible than the unsupported NiMoO₄ sample due to the presence of β -phase instead α -NiMoO₄ phase. In the tested conditions the sample prepared using the silica with the highest surface area displays the highest *i*-butane conversion, the highest *i*-butane selectivity and the lowest selectivity towards deep oxidation products. \bigcirc 2005 Elsevier B.V. All rights reserved.

Keywords: Supported catalysts β-NiMoO₄ i-butane; i-Butene; Oxidative dehydrogenation; Nanostructure; TPR; CO₂-TPD; NH₃-TPD; SEM-EDS; TEM-EDX

1. Introduction

Stoichiometric or nonstoichiometric (usually Mo-rich) nickel molybdates have been frequently used in the oxidative dehydrogenation of light alkanes, such as propane, *n*-butane or *i*-butane. The oxidative dehydrogenation of light alkanes may be an important alternative for the production of olefins such as propene and *i*-butene, which are used for the synthesis of acrolein, acrylic acid, acrylonitrile and fuel additives (MTBE) [1-4].

Generally, the stoichiometric NiMoO₄ is prepared by coprecipitation using aqueous solutions of nickel nitrate and

ammonium heptamolybdate [1,5,6], or molybdic acid [7–11]. The characteristics of the product thus obtained depend on the preparation conditions, namely on the concentration of the reacting ions in the solution, the temperature, the pH and the duration of the precipitate ageing process. The achievement of the pure stoichiometric compound is conditioned by the careful control of the preparation parameters [1,5,6]. The preparation of nickel molybdate by processes such as sol–gel like techniques and mechanical mixture has been described in literature, as well [8].

Some authors reported that the catalytic activity of the nickel molybdate is influenced by its crystallographic structure. At atmospheric pressure, the NiMoO₄ may exist in two different structures, the so-called low-temperature phase (α), and the high-temperature phase (β), respectively [1,5–8,12–16]. The α -phase is characterised by the presence of Mo species in distorted octahedral environment, while in β -phase the Mo is in distorted tetrahedral sites. The $\alpha \rightarrow \beta$ transition starts at 873 K

^{*} Corresponding author. Tel.: +351 218417873; fax: +351 218499242. *E-mail addresses:* zavoianu.rodica@unibuc.ro (R. Zăvoianu),

crdias@mail.ist.utl.pt (C.R. Dias), apsoares@mail.ist.utl.pt (A.P.V. Soares), mfportela@ist.utl.pt (M.F. Portela).

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and 948 K total conversion to β be achieved [1,5,7]. The reverse $(\beta \rightarrow \alpha)$ transition occurs at lower temperatures [7]. These transition temperatures depend on several factors, such as the Ni/Mo ratio and previous thermal treatments of the sample [6,7]. Using thermogravimetry, the α - to β -phase transition, for a sample with a Ni/Mo ratio of 1.2, was detected at ca. 923 K and, by cooling down the sample the reverse transformation was observed at ca. 323 K [6]. In a different study, the $\alpha \rightarrow \beta$ transition was observed at 563 K [8].

Several papers mention that the β -phase has better catalytic properties in the oxidative dehydrogenation processes [1,17,18]. Therefore, it became important to study the parameters that enhance its formation and stabilisation. Earlier investigations performed by Plyasova et al. [5] pointed out that the β -phase could be stabilised, at room temperature, after precipitation and calcination of mixed oxides with a Ni/Mo ratio above 1, presumably by formation of a solid solution with the Ni oxide. However, in this case, competitive side-reaction were observed [13,14].

Besides that, other papers report that the β -phase could also be stabilised by supporting the NiMoO₄ on different carriers such as Al₂O₃ [19,20], SiO₂ [21–27], activated carbon [28], or TiO₂ [29]. In this case, the catalytic performances are also influenced by the specific characteristics of the support and the dispersion of the active sites of the catalyst.

Since the surface area of the NiMoO₄ is rather low [1,8], it may be assumed that its catalytic performances would be improved by deposition on a support of higher surface area. Taking into account that silica is a cheap support that has a large surface area it becomes interesting to use it for supporting the NiMoO₄. Different methods of preparation have been used until now for supporting NiMoO₄ on silica.

Brito and Laine [21] prepared silica-supported nickel molybdate catalysts by the double impregnation method, the first step being the impregnation with a solution containing one of the components of the active phase, e.g. Ni or Mo, respectively, followed by drying, calcination and impregnation with the solution containing the second component, e.g. Mo or Ni, respectively [21]. According to a different method, supported molybdate catalysts, including nickel molybdate, were prepared by refluxing aqueous solutions of the appropriate metal nitrate salt with ammonium molybdate in the presence of silica sol [24]. In a recent work [25], a sol-gel method via silicon alkoxides was developed for the preparation of silicasupported NiMoO₄ catalysts. A previous work [26] reports the preparation of the stoichiometric NiMoO₄ phase by direct precipitation of the active phase over the SiO₂ carrier. This technique was also used for the preparation of TiO₂-supported NiMoO₄ catalysts [29].

For the most part of the supported catalysts used in the above-mentioned studies, the concentration of active phase was higher than 10% w/w and the active phase had not the stoichiometric composition.

Therefore, it seemed interesting to investigate how the stabilisation of the β -phase, the surface properties of the catalysts and their performances are influenced when

supporting a lower amount of active phase on silica carriers having different surface areas. The present paper reports results concerning *i*-butane oxidative dehydrogenation on silica-supported NiMoO₄ catalysts with low content of active phase, correlating their catalytic behaviour to their physical– chemical properties. For this purpose, three catalysts with low loading of NiMoO₄ (e.g. 6.5% w/w) were prepared using different silica supports with surface areas ranging from 60 to 509 m² g⁻¹ The catalysts have been characterised by XRD, SEM–EDX, TEM–EDX, TPR, TPD-NH₃, TPD-CO₂, and isothermal reduction under *i*-butane.

2. Experimental

2.1. Preparation of the catalysts

The pure stoichiometric NiMoO₄ was prepared by coprecipitation using Ni(NO₃)₂·6H₂O (Merck, p.a.) and (NH₄)Mo₇O₂·4H₂O (Merck, p.a.). The precipitation was always performed at 358 K using an aqueous solution of ammonium heptamolybdate (0.04 M) and a concentrated aqueous solution of nickel nitrate (1.2 M). NH₃ aqueous solution 25%, w/w (Merck, p.a.) was added to the Mo solution to ensure the transformation of the ammonium heptamolybdate into ammonium molybdate, (NH₄)₂MoO₄ which reacts in equimolar amounts with the nickel nitrate. The used amount of NH₃ solution adjusted the pH of the reaction mixture to 5.2.

For the preparation of supported catalysts, three different silica supports were used: (i) Durosil (Degussa), (ii) Sipernat 22 (Degussa), and (iii) LAB (SiO₂ prepared in the laboratory). LAB silica was prepared by precipitation at pH 8.5, using a 10%, w/w aqueous solution of Na₂SiO₃ (Fluka, p.a.) and HNO₃ (Merck, p.a., 65%). The resulting gel was washed until the neutral value of the pH of the washing water was reached. Then, the precursor of silica was dried at 383 K during 24 h, and calcined at 823 K during 8 h. The above-mentioned SiO₂ samples had surface areas of 60, 190 and 509 m²/g, respectively.

As reported before [27] the amount of active phase required to obtain one monolayer on the support material was estimated by the formula:

$$\frac{\text{weight of active phase}}{\text{weight of support}} = S\rho(M/N_{\rm A})^{1/3} \times 10^4,$$

where *S* represents the specific area of the support material (m²/g), ρ , the real density of the active phase (g/cm³), N_A , the Avogadro number and *M* is the molecular weight of the active phase. For Durosil (the support material with the lowest surface area) one monolayer corresponds to 13% [27]. Thus 6.5% (w/w) of the active phase was used in order to obtain samples with low content of the active phase. The choice of this value was conditioned by the fact that XRD detection level is around 5% (w/w).

The nickel molybdate was supported by precipitation over the support at 358 K, using a method similar to that previously described for the preparation of the pure NiMoO₄. The appropriate amounts of nickel nitrate, ammonium Download English Version:

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