Alkane isomerization on MoO₃/ZrO₂ catalysts

J.C. Yori *, C.L. Pieck and J.M. Parera
Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), CONICET, FQ-UNL, Santiago del Estero 2654, 3000 Santa Fe, Argentina
E-mail: jyori@iqfqu.unl.edu.ar

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Molybdenum was used as an alternative to sulfate as promoter of zirconia for alkane isomerization reactions. It has similar effects to sulfate, tungstate and phosphate ions, modifying the physicochemical properties of unpromoted zirconia. Mo-promoted zirconia catalysts do not show any activity for n-C₄ isomerization. For n-C₇ isomerization, the catalytic activity depends on Mo content, crystalline structure of the support and the molybdenum oxospecies present on the surface of the catalysts.

Keywords: alkane isomerization, molybdenum±zirconia, oxoanion promotion

1. Introduction

A variety of physicochemical properties, such as acidic and basic behavior, reducing and oxidizing characteristics [1], thermal resistance capacity, etc. make zirconia an excellent material for many industrial applications. The addition of oxoanions (SO₄²⁻, WO₄²⁻, PO₄³⁻) gives more stability, inhibiting zirconia sintering and the tetragonal to monoclinic phase transformation. It also produces a material which can catalyze reactions demanding high acid strengths, such as alkane isomerization [2–4].

The first zirconia promoter used was SO₄²⁻ and the use of alternative promoters is an interesting field of research. Molybdenum may be one of them. In this area, literature is poor, reporting only a few attempts to incorporate molybdenum to zirconia and its applicability in some specific reactions such as alkene oxidation and oxidative dehydrogenation of alcohols [5]. Miyata et al. [6] studied the decomposition of propan-2-ol over zirconia with various Mo loadings, finding that the Mo content strongly modified the activity and selectivity. Arata [7], by using a recirculation reactor, reported that the MoO₃/ZrO₂ catalysts were effective in n-hexane isomerization and benzoylation of toluene with benzoic anhydride. In both reactions the effect of varying the Mo content was very important. A series of zirconia-supported molybdenum oxide catalysts with different Mo loadings prepared under conditions reported to generate “superacidity” have been evaluated for their performance as catalysts for methane oxidation [8].

The aim of this paper is to investigate the promotion of zirconia with molybdenum, testing the resulting catalysts in the alkane isomerization reaction (n-butane and n-heptane) in order to correlate the surface and bulk properties with the behavior during the reaction.

* To whom correspondence should be addressed.

2. Experimental

2.1. Catalysts preparation

Zr(OH)₄ was prepared by precipitation of an aqueous solution of ZrOCl₂·8H₂O (Strem, 99.998%) with an ammonia solution (Merck, 35%) up to pH = 10. Samples of the Zr(OH)₄ gel were calcined at 700 and 800 °C for 3 h in air and were transformed into crystalline ZrO₂. Solids with different molybdenum content (2.1, 4.3, 8.6 and 11.5% Mo) were prepared by immersion of Zr(OH)₄ without calcination in aqueous solutions of ammonium heptamolybdate of different concentrations. The impregnation time was 24 h, without agitation, and with a ratio of liquid/solid of 15 ml/g. Afterwards, the solids were carefully washed and dried at 120 °C overnight. They were then calcined in an air stream for 3 h at 600, 700 or 800 °C, and the resulting materials were indicated as 2.1MoZr, 4.3MoZr, 8.6MoZr and 11.5MoZr, according to the Mo concentration. The Mo loading is expressed in wt%.

A commercial monoclinic crystalline zirconia (Strem) was immersed in an aqueous solution of ammonium heptamolybdate at a concentration sufficient to obtain a 4.3% Mo in the final catalysts. The following treatment was similar to that described above. The sample calcined at 700 °C was called 4.3MoZrStr.

SO₄²⁻/ZrO₂ was prepared by sulfating Zr(OH)₄ with a 1 M H₂SO₄ solution according to [9] and was designated SZ.

2.2. Catalyst characterization

2.2.1. Mo content

The Mo content was determined by subtracting the contents of the mother impregnating solution and the filtrate (after impregnation). A gravimetric method was used. The MoO₃ was precipitated, calcined in muffle at 800 °C for 3 h and weighed.
2.2.2. Potentiometric titration

Surface charge versus pH measurements were obtained with the usual “fast” potentiometric titration procedure on suspensions of the oxides in KNO₃ [10].

2.2.3. XRD measurements

The XRD measurements were performed on a Shimadzu DX-1 diffractometer with Cu Kα radiation filtered with Ni. The spectra were recorded in the 20–65° 2θ range and scanning at a rate of 1.2°/min.

2.2.4. Temperature-programmed reduction

TPR analyses were made in an Ohkura TP2002 equipped with a thermal conductivity detector. Samples were pretreated in air at 500°C during 2 h. After pretreatments, they were heated from room temperature to 950°C at 10°C/min in a gas stream of 4.8% hydrogen in argon.

2.2.5. Catalytic test

n-butane and n-heptane isomerization reactions were performed using a fixed-bed flow quartz reactor operated in a gas stream of 4.8% hydrogen in argon. The reactor outlet passed through a sampling valve connected to a chromatograph on-line containing a FID detector and a 6 m long, 1/8” diameter column packed with 25% dimethylsulfolane on Chromosorb P for n-C₄ isomerization and a 100 m long capillary column packed with squalene, for n-C₇ isomerization.

3. Results and discussion

Surface area and crystalline structure data of the catalysts are shown in Table 1. It can be seen that Mo-promoted samples have a higher thermal stability as compared with unpromoted ZrO₂ (higher surface area retention both at 700 and 800°C). An increase in calcination temperature does not significantly affect the surface area as long as the ZrO₂ crystalline structure is not changed from tetragonal to monoclinic. This is the case of 4.3MoZr, which has a pure tetragonal structure both at 700 and 800°C.

Unpromoted ZrO₂ exhibits a pure monoclinic structure at calcination temperatures as low as 700°C. The incorporation of 4.3% Mo is enough to stabilize the tetragonal structure. Higher Mo loadings lead to modifications in the crystalline structure after calcination at 800°C (both monoclinic and tetragonal phases were detected). For these samples (8.6MoZr and 11.5MoZr), the diffractograms reveal the existence of MoO₃ tetragonal crystals (corresponding peak in the 25–29° 2θ degree range) after calcination at 800°C, as can be seen in figure 1. Such crystalline MoO₃ was also detected in 11.5MoZr calcined at 700°C. In the catalysts with lower Mo content (2.1MoZr and 4.3MoZr) only amorphous MoO₃ is present as a consequence of the high dispersion of Mo species on the ZrO₂ surface.

Surface polarization curves are shown in figure 2 for 8.6MoZr (calcined at 700 and 800°C) and unpromoted ZrO₂ (calcined at 800°C). It can be observed that Mo addition shifts ZPC (zero point charge) values towards lower pH values (ZPC(calc,800°C) = 5.5; ZPC(calc,86MoZr = 3.8 and ZPC(calc,86MoZr = 3.7), thus indicating a higher acidity in surface OH groups. An increase in calcination temperature does not significantly modify the polarization curve of 8.6MoZr (it must be recalled here that this catalyst has a different crystalline structure when calcined at 700 or 800°C).

These results lead to the conclusion that MoO₃⁺ is a textural/structural promoter of ZrO₂ with similar characteristics to SO₂⁺, WO₄⁻ and PO₄⁻² [2–4].

Figure 3 presents the TPR profiles of some representative samples. While ZrO₂ has very little hydrogen consumption up to 950°C [3], MoO₃ shows two reduction peaks (550 and 700°C) in the studied temperature range. The supported molybdenum on tetragonal zirconia system undergoes reduction at lower temperatures than bulk MoO₃. This behaviour was previously reported by Brown et al. [8], studying MoO₃/ZrO₂ with different Mo and tetragonal phase content. They found two peaks at a low Mo content (400 and 750°C). For a higher Mo content, an additional peak at 830°C appears in the TPR profile. 8.6MoZr displays a peak (400°C) and two shoulders (550 and 830°C). The supported molybdenum on monoclinic zirconia (4.3MoZrStr) presents a peak (700°C) and two shoulders (550 and 830°C). Smith et al. [11] reported similar results for MoO₃ supported on silica. So, we can conclude that there is not a unique molybdenum oxospecies present on the support surface. In this way, the peak at 400°C could be ascribed to the reduction of polynuclear species, while the peaks at 500–550°C and 700°C could be assigned to microcrystalline MoO₃ not evident to XRD. The oxospecies present on 8.6MoZr would be polymolybdate and microcrystalline MoO₃, while 4.3MoZrStr presents bands in the same region as those observed in bulk MoO₃.

Within the range of operational conditions used in the catalytic tests, the prepared samples were inactive for n-C₄ isomerization. Under such conditions, the promotion of ZrO₂ with SO₂⁺, WO₄⁻ and PO₄⁻² leads to active catalysts. This difference may indicate that MoO₃/ZrO₂ has sites with...