

Alkane isomerization on MoO₃/ZrO₂ catalysts

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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 benzylation 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.

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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 K α radiation filtered with Ni. The spectra were recorded in the 20–65° 2 θ 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 under isothermal conditions at atmospheric pressure. Reaction conditions were: 0.5 g of catalysts, $T = 300$ °C, WHSV = 1.0 h⁻¹ and H₂ or N₂/*n*-C₄ or *n*-C₇ = 6. 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. For the promoted samples where changes in ZrO₂ crystalline structure were found, surface area values decrease.

Table 1
Specific surface area and crystallinity of samples calcined at 700 and 800 °C.

Catalyst	S_g (BET) (m ² /g)		ZrO ₂ crystalline structure ^a	
	$T_c = 700$ °C	$T_c = 800$ °C	$T_c = 700$ °C	$T_c = 800$ °C
ZrO ₂	25	8	M	M
2.1MoZr	55	51	M(–), T(+)	T
4.3MoZr	64	65	T	T
8.6MoZr	64	54	T	M(+), T(–) (x)
11.5MoZr	62	53	T (x)	M(+), T(–) (x)

^a T: tetragonal, M: monoclinic, (x): MoO₃T (MoO₃ with tetragonal crystalline structure), (+) and (–): majority and minority.

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° 2 θ 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 ($ZPC_{ZrO_2}^{800\text{ }^\circ\text{C}} = 5.5$; $ZPC_{8.6\text{MoZr}}^{800\text{ }^\circ\text{C}} = 3.8$ and $ZPC_{8.6\text{MoZr}}^{700\text{ }^\circ\text{C}} = 3.7$), 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 MoO₄^{2–} is a textural/structural promoter of ZrO₂ with similar characteristics to SO₄^{2–}, WO₄^{2–} and PO₄^{3–} [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 polymolybdate 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 SO₄^{2–}, WO₄^{2–} and PO₄^{3–} leads to active catalysts. This difference may indicate that MoO₃/ZrO₂ has sites with

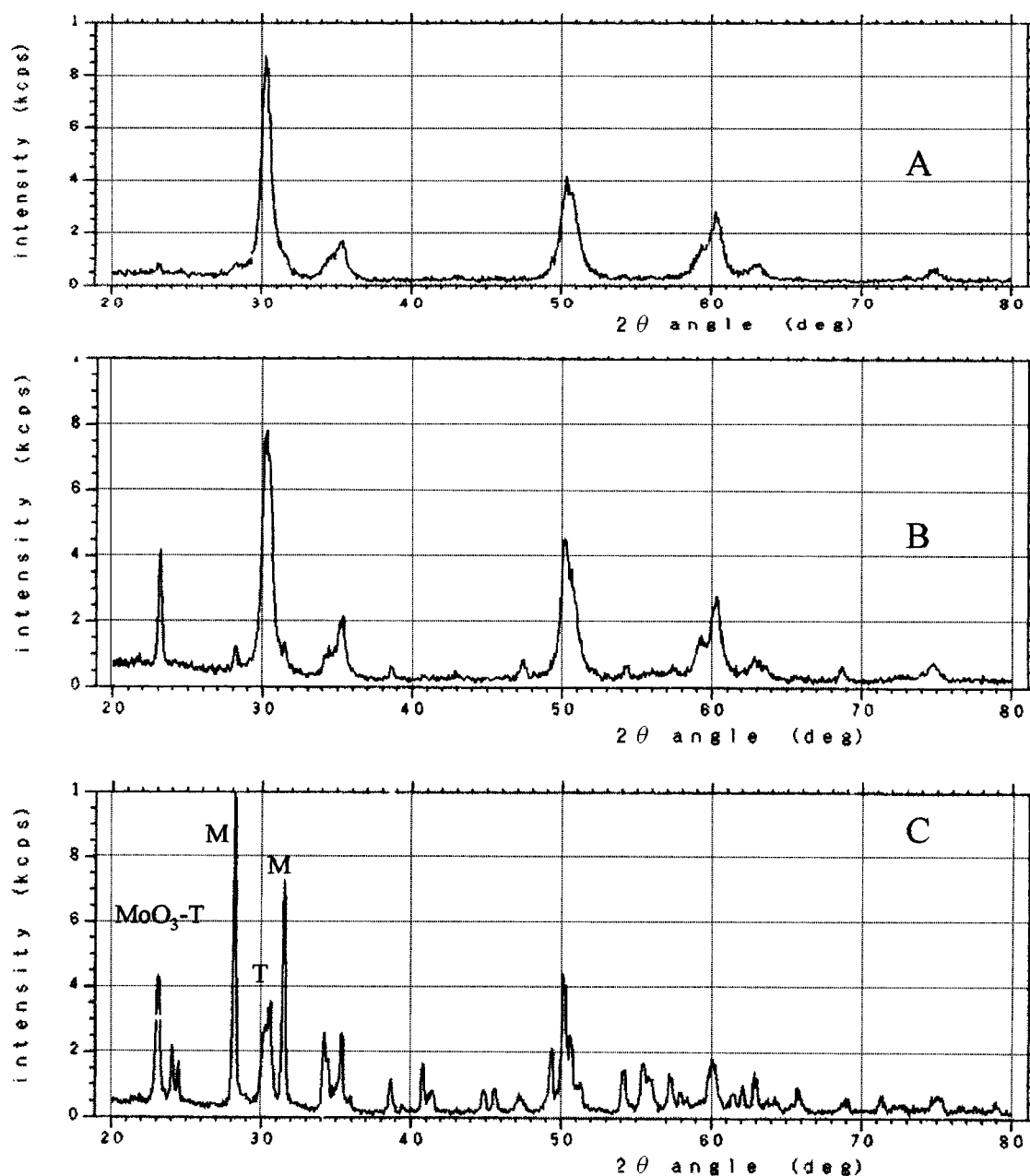


Figure 1. XRD diagrams: (A) 8.6MoZr calcined at 700 °C, (B) 11.5MoZr calcined at 700 °C and (C) 8.6MoZr calcined at 800 °C.

a lower acid strength. ZPC values in decreasing order are: MoO₃/ZrO₂ (3.7), PO₄³⁻/ZrO₂ (3.6), WO₄²⁻/ZrO₂ (3.2) and SO₄²⁻/ZrO₂ (2.0). Sulfated zirconia is the catalyst with the strongest acidity and the highest catalytic activity, in agreement to what is expected. But ZPC values of MoO₃/ZrO₂ and PO₄³⁻/ZrO₂ are similar; for this reason we can conclude that in this case another acidity characterization technique is necessary in order to explain why MoO₃/ZrO₂ does not show any activity in the *n*-C₄ isomerization reaction.

Results for *n*-C₇ isomerization are presented in figure 4. Total conversion and *i*-C₇ selectivity are plotted as a function of Mo content. Experimental values were taken after 5 min time on stream (TOS), using N₂ as a carrier gas. The samples were previously calcined at 700 °C.

An initial increase can be observed both in conversion and selectivity up to a maximum located at 8.6% Mo ($X = 30.9\%$, $S_{i-C_7} = 96\%$). For higher Mo contents both conversion and selectivity decrease ($X = 10.7\%$, $S_{i-C_7} = 55\%$). The decrease in *i*-C₇ selectivity is due to an increase in the formation of cracking products (C₁–C₄). It must be pointed out that the addition of Mo up to 4.3% leads to catalytically active materials compared to the formerly inactive ZrO₂, but conversion and selectivity levels are low. As opposed to that found for 11.5MoZr, the low *i*-C₇ selectivity is, in this case, due to an increase in the C₅–C₆ fraction of reaction products. These results indicate that the chemical nature or the structure of active Mo species is different depending on Mo level. An increase

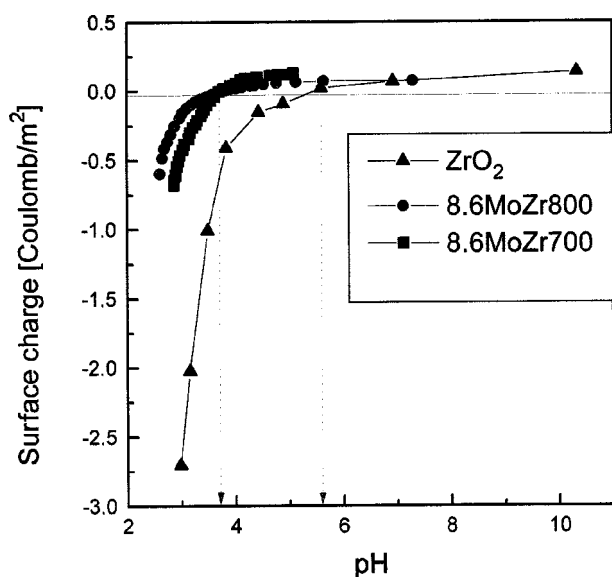


Figure 2. Potentiometric titration curves of ZrO₂ calcined at 800 °C and 8.6MoZr calcined at 700 and 800 °C.

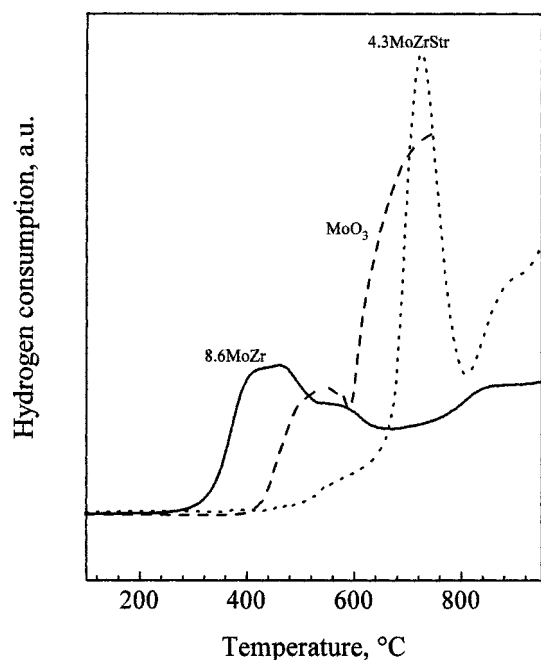


Figure 3. Temperature-programmed reduction.

in calcination temperature (800 °C) causes a decrease both in conversion and selectivity. At this calcination temperature level, 2.1MoZr, 4.3MoZr and 11.5MoZr did not show any significant catalytic activity. Conversion and selectivity values for 8.6MoZr were 12.9 and 21%, respectively, the lower selectivity being due to a higher C₁–C₄ production. It must be recalled that, in this case, diffractograms reveal the existence of crystalline MoO₃ as a separate phase, as observed for 11.5MoZr calcined at 700 °C. According to these results, it seems that the isomerization capacity of such materials (when N₂ is used as *n*-C₇ diluent) is closely related to the surface concentration of amorphous Mo species. An

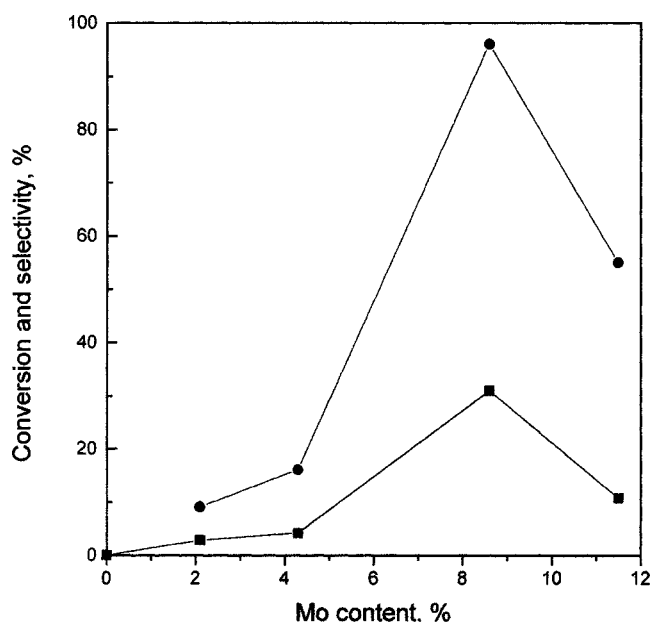


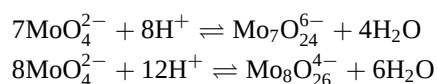
Figure 4. Conversion of *n*-C₇ and selectivity to *i*-C₇ of MoO₃/ZrO₂ catalysts calcined at 700 °C as a function of Mo content. Carrier gas N₂, 5 min TOS.

increase in cracking activity is observed, in contrast, when such species disappear to form crystalline MoO₃. The Mo content of catalysts drastically modifies both activity and selectivity for *n*-C₇ isomerization; these results are similar to those of Miyata et al. [6] for isopropanol dehydration.

Results obtained when H₂ was used instead of N₂ as a carrier gas are shown in figure 5. As found when using N₂ as carrier, there is a maximum in conversion at 8.6% Mo (conversion values are similar). Conversion values for the rest of the promoted samples were extremely low. The selectivity pattern for 8.6MoZr catalysts was strongly affected by the presence of H₂ as carrier: C₈ isomers were mainly found in products as opposed to the high *i*-C₇ selectivity achieved with N₂ as the gas carrier.

Table 2 shows the conversion and selectivity of 8.6MoZr catalysts at different calcination temperatures using N₂ as a carrier gas. A maximum is observed in both activity and selectivity that corresponds to a calcination temperature of 700 °C. In a H₂ stream, the results indicated in table 2 are similar but the selectivity to products is strongly modified.

It is interesting that the maximum in activity occurs in catalysts with 8.6% Mo; with a higher Mo content, the activity decreases coincident with the formation of crystalline MoO₃. The coverage of ZrO₂ with MoO₃ depends on the impregnation of Zr(OH)₄ with molybdates. When solutions of molybdates are acidified, polymerization occurs with the formation of isopolyanions, according to the following equilibria [12]:



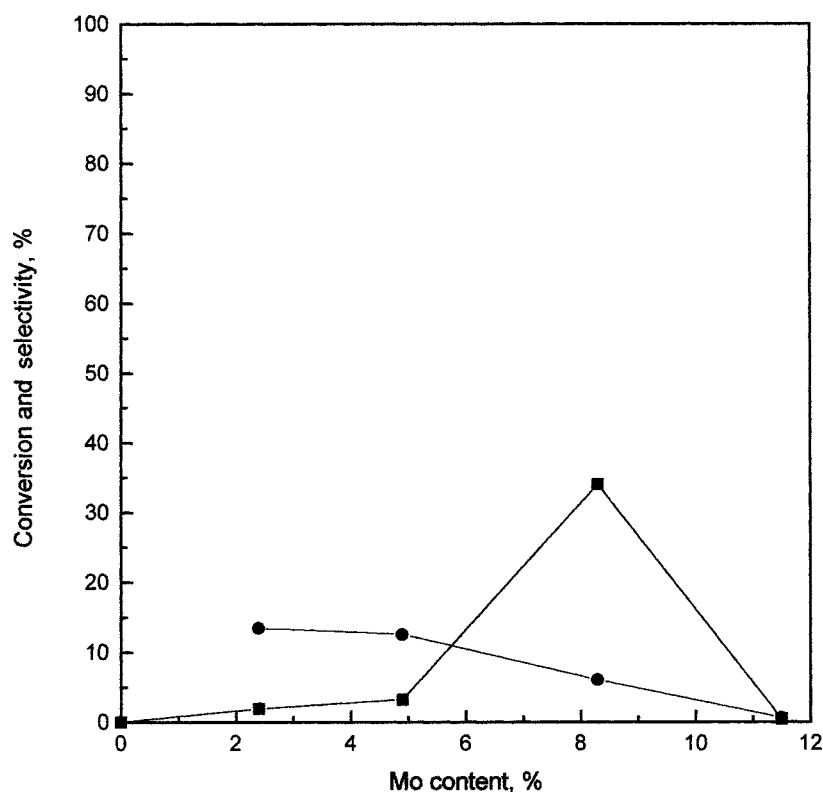


Figure 5. Conversion of *n*-C₇ and selectivity to *i*-C₇ of MoO₃/ZrO₂ catalysts calcined at 700 °C as a function of Mo content. Carrier gas H₂, 5 min TOS.

Table 2
Product distributions in the conversion of *n*-heptane on 8.6MoO₃/ZrO₂ catalysts calcined at 600, 700 and 800 °C.

	Catalyst		
	8.6MoZr600	8.6MoZr700	8.6MoZr800
Carrier gas: N ₂			
Conversion (%)	13.17	29.21	12.99
Selectivity (%)			
Isomerization ^a	2.37	95.65	25.86
Cracking ^b	14.88	3.87	65.73
Cyclization ^c	32.03	0.48	4.32
Others ^d	50.69	–	3.84
Carrier gas: H ₂			
Conversion (%)	6.71	34.28	3.37
Selectivity (%)			
Isomerization	4.77	1.69	12.75
Cracking	32.19	9.42	85.76
Cyclization	41.58	3.12	–
Others	21.46	85.77	1.48

^a Isomerization products: 2-MH, 3-MH, DMP, 3-EP, 2-2-3-TMB.

^b Cracking products: C₁–C₆.

^c Cyclization products: CP, MCP, benzene, CH, MCH, ECP, toluene.

^d Others: C₈ isomers.

The adsorption of anions can be considered as purely electrostatic: in all preparations the impregnating solution has a pH = 5, which is lower than the isoelectric point of Zr(OH)₄ (IEP = 6–7). The amount of the Mo surface species needed to form a monolayer, e.g., react with all the available OH groups, varies with the adsorbed species, and they are indicated in table 3. Although some uncer-

Table 3
Theoretical Mo surface charge needed for forming a monolayer.^a

Species	Stoichiometry atoms Mo : OH	Mo (%)
MoO ₄ ^{2–}	1 : 2	4.2
Mo ₇ O ₂₄ ^{6–}	1.1 : 1	9.6
Mo ₈ O ₂₆ ^{4–}	2 : 1	16.6

^a The average of the calculated hydroxyl group density was 8 OH/nm² [8].

tainty exists, it could be considered that in the pH region 4–5 the system is represented by an equilibrium between molybdate (MoO₄^{2–}) and heptamolybdate (Mo₇O₂₄^{6–}). When the pH of the solution is decreased, the heptamer decreases and the predominant species is the octamolybdate (Mo₈O₂₆^{4–}). We can then consider that the charge of Mo necessary to form a monolayer will be a function of the concentration ratio MoO₄^{2–}/Mo₇O₂₄^{6–} and will have an optimum value between 4.2 and 9.6%. Arata [13] proposed a value of 6.6 wt% Mo as the amount that strongly interacts with ZrO₂ to form a monolayer. In our case 4.3% Mo is enough to stabilize the tetragonal form of ZrO₂, which plays an important role on the catalytic activity of the materials, as shown with other oxoanions as promoter (SO₄^{2–}, WO₄^{2–} and PO₄^{3–}). Then for the maximum catalytic activity, the amount of Mo will be the necessary to stabilize the tetragonal form of ZrO₂ and to produce a monolayer of MoO_x.

Table 4

Product distribution on 8.6MoZr ($T_c = 700\text{ }^\circ\text{C}$) and SZ catalysts in the isomerization of *n*-heptane, using different carrier gas (N₂ or H₂).^a

	Catalyst			
	8.6MoZrN ₂	8.6MoZrH ₂	SZN ₂	SZH ₂
Conversion (%)	29.21	34.28	19.26	13.68
Selectivity (%)				
Isomerization	95.65	1.69	2.69	4.6
Cracking	3.87	9.42	96.83	93.20
Cyclization	0.48	3.12	0.46	1.90
Others	—	85.77	—	0.3

^a 8.6MoZrN₂ and SZN₂: N₂ used as a carrier gas. 8.6MoZrH₂ and SZH₂: H₂ used as a carrier gas.

In order to compare the effect of the type of carrier gas used on the selectivity of an isomerization catalyst without Mo, similar *n*-C₇ isomerization runs were performed using ZrO₂/SO₄²⁻ as a catalyst. Results are indicated in table 4. No major difference both in conversion and selectivity was found when N₂ or H₂ were used as carrier gas ($X = 13.4\%$, $S_{i-C_7} = 8\%$) and the low selectivity is due to cracking products.

4. Conclusions

It can be concluded that the system MoO₃/ZrO₂ exhibits an interesting behavior as an isomerization catalyst. Its characteristics under our operational conditions may be briefly described as follows:

- MoO₄²⁻ ion is a textural and structural promoter of ZrO₂ with similar properties as SO₄²⁻, WO₄²⁻ and PO₄³⁻.
- Mo-promoted ZrO₂ catalysts do not possess any activity for *n*-C₄ isomerization, probably due to the lack of acid sites with sufficient strength.

- Mo-promoted ZrO₂ catalysts with tetragonal crystalline structure have significant activity for the less demanding *n*-C₇ isomerization which is strongly dependent on the Mo content. The isomerization activity seems to be closely related to the presence of amorphous Mo species on the tetragonal ZrO₂ surface.
- The *n*-C₇ isomerization activity of the 8.6MoZr catalyst is higher than that obtained for SO₄²⁻/ZrO₂, probably due to a higher surface concentration of acid sites with moderates strength. Regarding selectivity, substantial differences were found between these two catalysts when N₂ or H₂ was used as *n*-C₇ diluent. On SO₄²⁻/ZrO₂ the gas carrier had no effect but it has a great influence on MoO₃/ZrO₂.

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