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Influence of the Degree of Crystallinity and of the Composition on the Activity of MoO_3–Bi_2O_3 Catalysts

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The influence of the degree of organization of the catalyst has been examined for the oxidation of butene into butadiene on bismuth molybdate. The results obtained show that the specific activity increases when the degree of crystallization decreases. The variation of this physical property of catalysts was easily obtained by bringing about the complete fusion of catalytic masses and by cooling at varying rates. Furthermore, the amorphous phases prepared in this way were processed at varying temperatures so as to cause their progressive crystallization. The structural stability of the solids obtained and the stability of the catalytic performances during the entire duration of the experiments proved to be quite good, thus enabling the above correlation to be determined. The variation of the Bi:Mo ratio also showed that, no matter what the degree of crystallization may be, catalytic activity appears at a value of about Bi:Mo = 1.

INTRODUCTION

Various research products (*1*, *2*, *3*) appear to have succeeded in determining the major outlines of the kinetic scheme and the mechanism of the oxidation of butenes on bismuth molybdate. In the field of crystallography, numerous compounds have been described in the Bi_2O_3–MoO_3 system:

(a) Bi_2O_3–4 MoO_3, pointed out by Muller (*4*).

(b) Bi_2O_3–3 MoO_3 and (c) Bi_2O_3–2 MoO_3, whose structures have been determined by Erman *et al.* and which, respectively, have monoclinic and tetragonal lattices (*5*, *6*).

(d) Bi_2O_3–MoO_3, which exists in two polymorphic forms, one (d_I) obtained at low temperatures and corresponding to orthorhombic koechlinite described by Zemann (*7*), and the other (d_{II}), obtained at high temperatures, pointed out by Bleijenberg *et al.* (*8*), Erman *et al.* (*5*), and determined by Blasse (*9*) from its isomorphism with tetragonal $(LaO)_2MoO_4$.

(e) 2 Bi_2O_3–MoO_3, mentioned by Gattow (*10*) but whose existence is contested.

(f) 3 Bi_2O_3–MoO_3 and (g) 10 Bi_2O_3–MoO_3, to which Sillen *et al.* (*11*) give, respectively, cubic and tetragonal lattices.

An investigation of the phase diagram of the Bi_2O_3–MoO_3 system (*8*, *12*, *13*) revealed only compounds (b), (d), (f), although their nature (compounds with congruent or noncongruent fusion) is contested. Whereas the characterization of these various compounds seems rather well established, controversies exist concerning the assigning of catalytic properties to one (or several) of them (*14*, *15*, *19*). Furthermore, a comparison of the published results shows that, for the same overall composition, the catalytic activity depends heavily on the method of preparation and that the variation of this activity with the Bi:Mo ratio is generally very complex (*14–17*).

In the present work, we attempted to determine if the state of organization in the solid was a major parameter for the level of catalytic activity—a parameter thus far neglected—and which may be responsible, in part, for the complexity observed.

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In order to isolate this variable, we compared the specific activity of various solids obtained, after fusion, by a more or less rapid cooling followed by an additional heat treatment. By so doing, different degrees of crystallinity could be obtained for the same overall value of the Bi:Mo ratio.

Experimental

1. *Producing Catalysts*

Two types of preparation were used.

a. Conventional method. The conventional type uses techniques which are described in the literature. Three series of catalysts were prepared in this manner:

Series CC. Catalysts produced by the coprecipitation of salts by ammonia (*1*), then by calcination of precipitate at 550°C.

Series HC. Catalysts produced by calcination of the dry mixture of hydroxides at 550°C.

Series SC. Catalysts produced by calcination of the dry mixture of salts at 550°C (*8*).

b. Special method. The special method used consists of pushing the heat treatment to the point of complete fusion of the catalyst, which enabled us to bring about a well-defined initial state independent of the nature of the precursor used, and to produce solids with a varying degree of crystallization by modifying the rate of cooling. This method was used to prepare the following series:

Series C. Catalysts produced by slow cooling (60°C/hr); made up of well crystallized solids.

Series G. Catalysts produced by very rapid cooling (liquid poured directly into water at 25°C); made up of very poorly crystallized solids having the appearance of glass. Although this quenching process is difficult to define, we succeeded in varying the transfer time of the liquid between 2 sec (Series G and RG) and $\frac{1}{2}$ sec (Series RG'). We call the transfer time the time it took to pour the liquid into the cold medium.

The following two series of catalysts were obtained by heat treatment of glass:

Series RG. Heat treatment, at 550°C, of glass obtained with a transfer time of 2 sec, for several values of the Bi:Mo ratio.

Series RG'. Heat treatment at temperatures between 450° to 700°, from a glass with Bi:Mo = 1, obtained with a transfer time of $\frac{1}{2}$ sec.

2. *Characterization of the Catalysts*

The amounts of Mo and Bi in the catalyst were determined by X-ray fluorescence. Specific areas were measured by the BET method with krypton and eventually calculated from mercury porosimetry curves. These two methods gave concordant measurements. The structural investigation was made on the basis of the X-ray powder patterns. In order to determine the nature of the compounds involved, we referred to the powder patterns as precisely indexed in Erman and Blasse's results. The degree of crystallinity of the solids was determined in the standard way, both by the ratio

$$\frac{\text{area of lines corresponding to the amorphous phase}}{\text{total area of lines}}$$

of the diffraction patterns and by measuring the midheight width of the lines.

3. *Structural Stability of the Catalysts*

Generally speaking, the catalysts can be seen to vary during the reaction, as has already been mentioned (*18*); in our case, the effect of the temperature alone may cause carystallization of the poorly crystallized phases used. For these reasons:

(a) We studied the variation of our catalytic solids with the temperature and defined the conditions for their thermal stability, in an air atmosphere before any reaction had occurred. The structural modification of amorphous phases (Series G) was followed by a differential thermal analysis. With the G_8 catalyst, for example, for which the Bi:Mo ratio is 1, recrystallization (exothermic peak) occurs around 380°C (Fig. 1) and fusion at 670°–690°C (endothermic peaks). In all the amorphous catalysts studied, recrystallization appears between 300° and 400°C.

The use of an amorphous phase can be

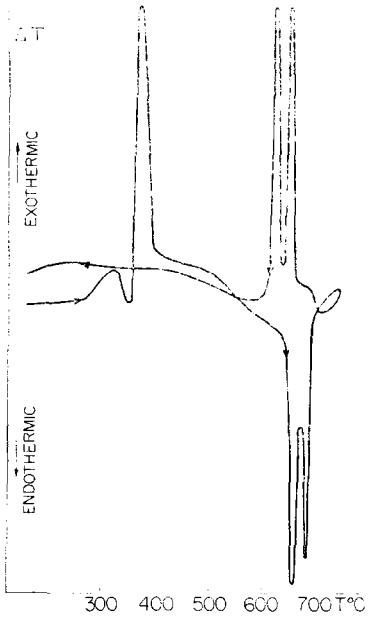

FIG. 1. Differential thermal analysis of amorphous catalyst (heating rate, 12°C/min).

expected only at a temperature below its recrystallization temperature. In order to use a reaction temperature of 450°C, which enables good yields to be obtained, a heat treatment of the amorphous phases was conducted during 4 hr at a temperature $\geqslant$ 500°C. Experiments showed that, for a given temperature, the structure had completely evolved after 1 hr, with stability control having been achieved during 10 hr. The RG and RG′ series were prepared in this way.

(b) We verified the stability of catalytic performances during experimentation.

(c) Strictly speaking, it would be necessary to determine the structure and texture of the catalysts under the reaction conditions. This requirement being very difficult to satisfy, we characterized the catalysts after the reaction at the end of a quick quench in the reaction atmosphere. These results are the ones which have been used for studying the influence of the degree of crystallinity on the specific activity.

4. *Measuring Catalytic Activity*

After fusion, the solids, produced in the form of chips, did not have sufficiently large specific surface areas to promote catalytic reaction. Grinding followed by sieving at a sufficient granulometry (0.04 to 0.1 mm) served to increase the geometric surface area so as to produce specific areas of approximately 0.05 m^2/g on which catalytic activity could easily be measured. The value of this surface area, which is larger than that provided by spheres with a diameter of 0.07 mm is indicative of the existence of noticeable roughness.

Experimentation was done in a tubular quartz reactor using the dynamic method without recycling. The catalyst was diluted in an alternating-layer form by quartz wool in a manner which proved to be perfectly reproducible. All analyses were made by gas-liquid chromatography.

The reference operating conditions used were for the reaction mixture, 17% 1-butene, 17% oxygen, 66% nitrogen (in vol); for the temperature, 450°C; for the contact time, $\theta = m/F = 1$ or 2 sec g cm^{-3}, with m being the catalyst mass ($\sim$10 g) and F the NTP flow in cm^3 sec^{-1}.

Preliminary experiments showed that diffusion phenomena had no influence on the operating conditions.

Since the obtention selectivity of the butadiene is quite large, we shall characterize the catalytic performances by the yield Y for for butadiene without bringing in the other compounds (mainly CO_2)

$$Y = \frac{C_4H_6 \text{ formed}}{C_4H_8 \text{ introduced}}$$

The isomerizing activity of the catalyst is not considered in this work.

RESULTS

We began by checking the published kinetic findings and found first order for butene and zero for oxygen. Therefore, the activity of the catalyst can be defined by a first order rate constant (*1*)

per gram

$$k = \frac{1}{\theta} 2.3 \log \frac{1}{1 - Y} \text{ in } cm^3\ g^{-1}\ sec^{-1}$$

per surface area unit

$$k_S = \frac{k}{S} = \frac{1}{\theta S} 2.3 \log \frac{1}{1 - Y}$$

which is the specific rate constant in cm sec^{-1}.

1. *Performances of Conventional Catalysts*

The activity of these catalysts (Series CC, HC, SC) was measured at 450°C with a contact time of 2 sec. The results obtained with 2- to 4-mm granulometry samples are given in Table 1.

It was found that catalytic activity occurred for $35 < Bi:Bi + Mo < 70$, hence for $Bi:Mo \simeq 1$, but the variation of k_S is complex, especially for catalyst CC. In addition, it depends on the type of preparation.

An examination of the X-ray diffraction patterns furnished by all these catalysts led to the conclusion that a high degree of crystallization occurred in the samples. The identity of patterns for the same value of the Bi:Mo ratio—no matter what type of preparation is used—invalidates the hypothesis of the presence of a determined well-crystallized compound alone being responsible for the catalytic activity, since this activity depends on the preparation used.

2. *Influence of the Degree of Organization of the Catalyst*

a. Experiments at low temperatures. At 350°C, the recrystallization of a catalyst (Bi:Mo = 1) belonging to Series G only becomes apparent after prolonged treating (>6 hr). By operating at 340° and 350°C, a level of performance is attained that can be measured with sufficient accuracy and which remains stable during the entire experiment (3 to 4 hr). This makes it possible to compare the specific activities of catalysts G, RG, and C (Table 2).

A rapid comparison of performances and of X-ray diffraction patterns given in Fig. 2 shows that catalytic activity effectively depends on the degree of organization of the catalyst, but a more precise analysis of these diffraction patterns must be attempted.

This analysis, made first for the crystal in Fig. 2, enables (according to Erman's results) the lines for three compounds to be recognized: (c) Bi_2O_3–2 MoO_3, +; (b) Bi_2O_3–3 MoO_3, ○; and Bi_2O_3–MoO_3 high temper-

TABLE 1
INFLUENCE OF THE ATOMIC RATIO Bi:Mo ON THE CATALYTIC ACTIVITY OF CONVENTIONAL CATALYSTS[a]

Catalyst	$\frac{Bi}{Bi + Mo}$ atomic ratio	S (m^2/g)[b] After reaction	$Y \times 10^2$	$k \times 10^3$ ($cm^3\ g^{-1}\ sec^{-1}$)	$k_S = \frac{k}{S} \times 10^4$ ($cm\ sec^{-1}$)
CC, HC, and SC	100 to 70	—	Very low	Very low	Very low
CC_1	68	2.08	0.5	2	0.001
CC_2	60	0.63	69.3	590	0.936
CC_3	54	0.39	72.1	637	1.635
CC_4	51.5	0.85	73.2	657	0.774
CC_5	45.5	0.37	62.7	492	1.331
CC_6	36	0.76	16.6	90	0.119
CC, HC, and SC	30 to 0	1	Very low	Very low	Very low
HC_1	67	1.05	30.2	179	0.171
HC_2	50	0.64	65.7	534	0.835
HC_3	33.3	0.62	35.3	217	0.351
SC_1	67	0.6	24.8	142	0.237
SC_2	60	0.33	19.6	109	0.330
SC_3	50	0.62	12.1	64	0.104
SC_4	40	0.7	5.4	27	0.039
SC_5	33.3	0.32	1.4	7	0.022

[a] m = 16 g; temp., 450°C; θ, 2 sec g^{-1} cm^{-3}; 1-butene, 17%; O_2, 17%.
[b] The specific area of the catalyst varies during the reaction within a 5–10% range.

TABLE 2

INFLUENCE OF THE CRYSTALLINE DEGREE ON THE SPECIFIC ACTIVITY[a]

T (°C)	Nature of the catalyst	S (m^2/g) After reaction	$Y \times 10^2$	$k \times 10^3$ ($cm^3\ g^{-1}\ sec^{-1}$)	$ks = \frac{k}{S} \times 10^4$ ($cm\ sec^{-1}$)
340°	Glass G	0.05	1.27	12.88	0.257
	Recrystallized glass RG	0.05	0.27	2.76	0.055
	Crystal C	0.03	0.09	0.92	0.031
350°	Glass G	0.05	2.81	28.29	0.565
	Recrystallized glass RG	0.05	0.68	6.90	0.138
	Crystal C	0.03	0.24	2.53	0.084

[a] Bi:Mo = 1; m = 15 g; θ = 1 sec g cm^{-3}; 1-butene, 17%; O_2, 17%.

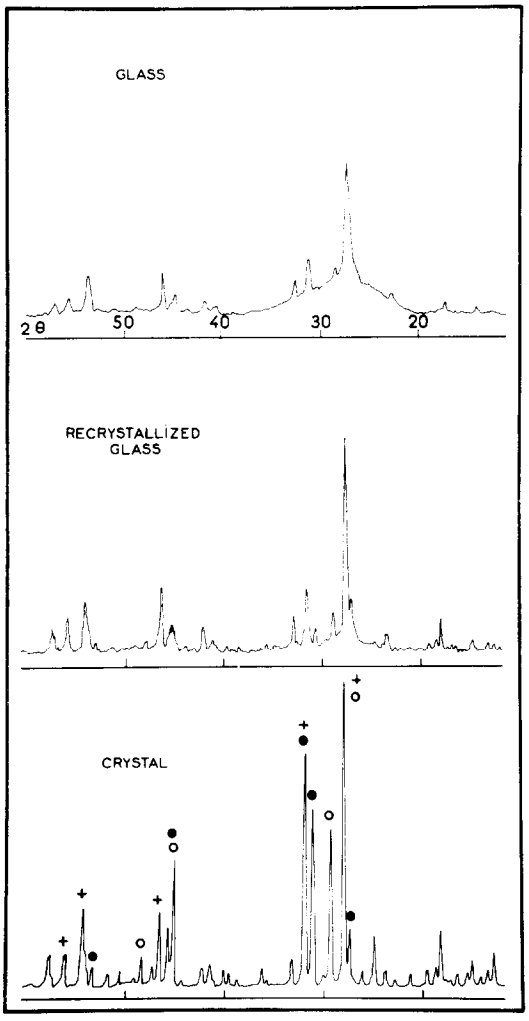

FIG. 2. X-Ray diffraction patterns for catalysts mentioned in Table 2 (Cu $K\alpha$ ray). ●, Bi_2O_3–MoO_3 (high-temperature form); +, Bi_2O_3–$2MoO_3$; ○, Bi_2O_3–$3MoO_3$.

ature (d_{II}), ●. The first compound is the most abundant and the intensities of its four major lines (3.19, 2.80, 1.951, 1.683 Å) are in the same order as in the reference pattern. The two other compounds are present with a weak concentration that is difficult to pinpoint; as a matter of fact, the major lines of the reference compounds do not always appear in the right position (2.84 Å for Bi_2O_3–3 MoO_3, for example), or with the correct relative intensity (2.87–3.25 Å for Bi_2O_3–MoO_3). These difficulties stem on one hand from the closeness of several lines (3.18–3.19 Å for Bi_2O_3–3 MoO_3 and Bi_2O_3–2 MoO_3; 2.002–2.00 Å for Bi_2O_3–3 MoO_3 and Bi_2O_3–MoO_3; 2.80–2.79 Å for Bi_2O_3–2 MoO_3 and Bi_2O_3–MoO_3), and on the other hand from the contested existence of solid solutions.

The same lines exist in the diffraction patterns for glass and recrystallized glass in Fig. 2, and the same problems occur with greater intensity as these solids are less crystallized. However, the compound Bi_2O_3–2 MoO_3 is always dominant.

In conclusion, despite a possible variation in the percentage of the different components, the most conclusive variation is that of the degree of crystallinity, enabling this parameter to be correlated with the greatest probability to the value of the specific activity. This activity increases as the degree of crystallization decreases.

b. Experiments at high temperatures (450°C). Comparisons can only be made between Series RG, C, and CC (Fig. 3) (and also HC and SC) because at 450°C amorphous catalysts are recrystallized. This com-

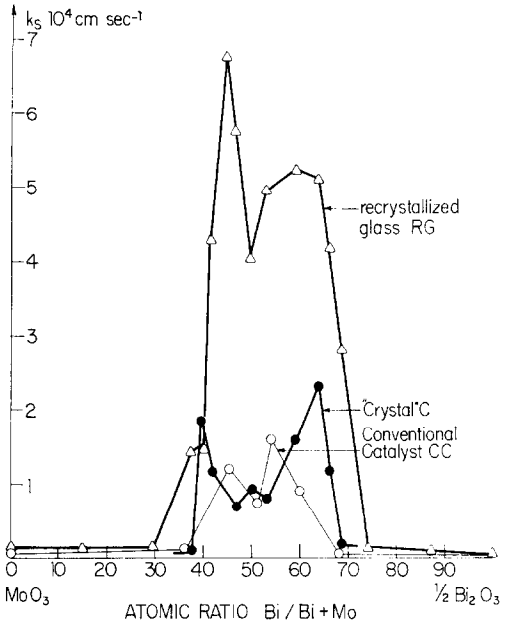

FIG. 3. Influences of the degree in crystallinity and of composition on the specific rate constant.

parison was made for different values of the Bi:Mo ratio. An examination of the X-ray diffraction patterns (an example being given in Fig. 2), covering the entire range of Bi:Bi + Mo ratios, also serves to link the upper activity of Series RG compared with Series C to a lesser degree of organization of the solid. In these two series the position and number of diffraction lines, with the same approximation as above, are the same for a given composition. Series CC is very well crystallized and proves to have a specific activity of the same order of magnitude as that of Series C, but the two cannot be compared because certain diffraction lines are not common to both Series C and CC.

It can be seen that, no matter what the degree of organization of the solid is, catalytic activity only exists when $35 < \text{Bi}:\text{Bi} + \text{Mo} < 75$, which is in favor of the intervention of species defined from the stoichiometric point of view if not from that of the crystalline structure.

c. Influence of heat-treatment temperature. In order to follow the influence of the degree of organization of the catalyst, we made this parameter vary regularly by heating amorphous samples to different temperatures (Series RG′) before measuring their catalytic activity at 450°C under standard conditions.

Figure 4 shows a correlation between the decrease in the butadiene yield and the decrease in the width of the diffraction line, or of the amorphous-phase percentage, which expresses an increase in the degree of organization when the treatment temperature of the sample decreases.

The X-ray diffraction patterns in Fig. 5 are given as an example for three heat-treatment temperatures—550°, 610°, and 650°C—so as to provide an accurate picture of the difficulty of isolating the variable crystallinity. It is easy to verify that attempts to make a precise analysis of the different compounds come up against the difficulties mentioned earlier, but also that the compound Bi_2O_3–2 MoO_3 is always the most abundant. The formal correlations between the butadiene yield and the mid-height width of the Bi_2O_3–2 MoO_3 lines or the percentage of the amorphous phase are

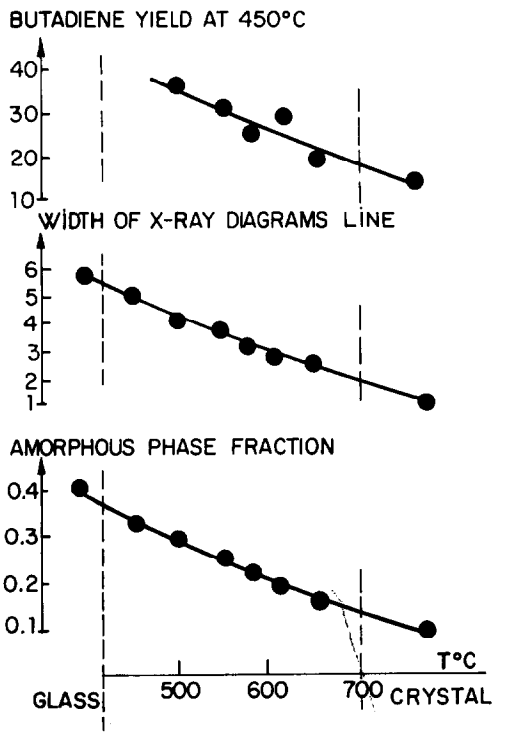

FIG. 4. Influences of the temperature of recrystallization of an amorphous catalyst.

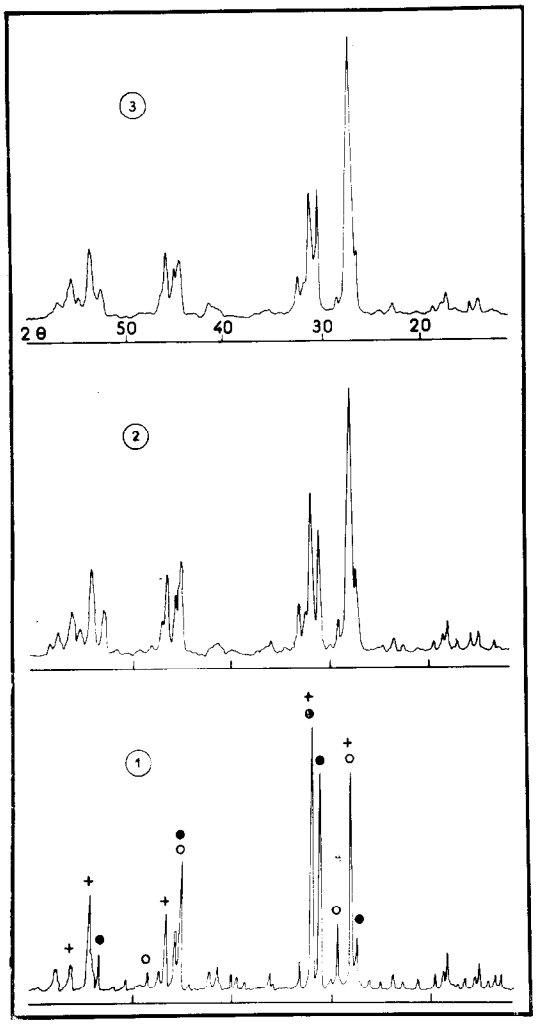

FIG. 5. X-Ray diffraction patterns for different temperatures of recrystallization of an amorphous catalyst (Cu $K\alpha$ ray): 1, 650°C; 2, 610°C; 3, 550°C; ●, +, ○, as in Fig. 2.

hence sufficiently conclusive to show how the degree of crystallinity influences the values of the specific activity.

Note well that the activity of the catalyst recrystallized at 550°C in this new Series RG′ is greater than that of catalyst RG in Fig. 2, which was recrystallized at the same temperature. A comparison of the two diffraction patterns shows that the difference is linked to a lesser state of organization in catalyst RG′. This may be due to the quench, which is deliberately quicker. Furthermore, this shows that, if the correlation between the activity and the degree of disorganization is thus confirmed, it is on the other hand difficult to master the preparation process so as to produce a perfectly defined degree of organization.

CONCLUSION

These experiments first of all enabled us to show that the catalytic activity of bismuth molybdates occurs for a Bi:Bi + Mo ratio between 35 and 70. This finding, which was already known for catalysts prepared by conventional methods, is valid both for well-crystallized catalysts and for poorly crystallized catalysts, thus leading us to make a correlation between the activity and the presence of definite species rather than of structurally well defined compounds.

In the domain thus delimited, specific catalytic activity depends on the degree of organization of the solid. A decrease in the degree of crystallization brings about an increase in the specific activity.

This fundamental finding shows that a study of the Bi:Bi + Mo ratio can only be done in a significant manner at an isocrystalline level. The different performances observed by various authors for the same value of this ratio are partly due to the influence of the crystallinity factor. In effect, the results refer to catalysts prepared from different precursors, by different methods, and heat-treated at various temperatures. Therefore, it is highly improbable that the solids produced will have the same degree of crystallinity. Likewise, the complex variation of the activity in the function of the Bi:Bi + Mo ratio that is observed can express the influence of this factor. Indeed, it can be seen that even by preserving an identical preparation process, it is very difficult to produce the same degree of crystallinity and that the activity variation caused by the crystallinity of a given catalyst composition is comparable to that caused by the variation of this composition with the same preparation process. Therefore, it is difficult to separate the influences of the ratio Bi: Bi + Mo and the crystallinity. Such a separation might be attempted by making a continuous series of preparations for each

composition and by using an accurate method of measuring the degree of crystallinity, which would enable the isocrystallinity curves to be plotted.

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