Generation of Ternary Pr−Mo−O Oxides by Solid State Reactions between Oxide Powders under Ultrasonic Stirring

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy are used to prove that the ultrasound used for the preparation of molybdenum- and praseodymium-based heterogeneous multiphase catalysts can induce solid-state reactions at room temperature between the binary oxides Pr_6O_{11} and MoO_3. Turbulent flows and shock waves produced by the ultrasonic cavitation are thought to cause particles to collide into one another and to generate local temperatures which are sufficiently high for inducing interparticle melting. Unequivocal evidence is provided by ToF-SIMS that the ultrasonic dispersion leads to the surface formation of the praseodymium molybdate phase $Pr_2Mo_3O_{12}$.

Introduction

Highly dispersed multicomponent and multiphase oxide-based materials generate great interest as heterogeneous catalysts for the gas phase partial oxidation of saturated and unsaturated hydrocarbons. During the preparation of such catalysts, ultrasound is commonly used[1−3] in order to achieve a high interdispersion of the starting powdered materials. The present work demonstrates that submitting multiphase oxide catalysts to such an ultrasonic treatment at room temperature is, by far, not unimportant, because surface solid-state reactions may be induced. This observation is obviously critical to understand the catalytic behavior of these catalysts, because the surface properties could be dramatically altered. The chemical effects of ultrasound have been extensively reviewed during the past few years[4−7] and are thought to result primarily from cavitation: this process refers to the formation, growth, and implosive collapse of bubbles created in the dispersion medium. Moreover, in solid−liquid systems, when a bubble collapses near an extended surface, high-speed liquid jets are produced that impinge on the surface and can lead to particle fracture or erosion.[8,9] In addition, the shock waves generated during the collapse can cause small particles to collide into one another at a speed of nearly half the sound velocity. In the case of metal powders, this has been shown to cause interparticle melting.[8,10−11] The local temperature obtained at the impact point of two sonicated metal particles has been estimated to be in the range 2800−3700 K.[8,11] For other sets of mixed-metal powders, the formation of intermetallic coatings has been observed, even in the case of metals which are well-known to be incompatible with respect to the formation of binary alloys or homogeneous solid solutions.[12,13] Nevertheless, although the ultrasound effects on pure oxides have been described by several authors,[8,14−16] there is so far, to our knowledge,

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no detailed study dealing with the chemical effects of ultrasonic waves in mixed-oxide powder systems.

Because the static SIMS (secondary ion mass spectrometry) technique[17] was recently shown to be an extremely powerful investigation tool for the surface characterization of complex molybdate-type catalysts,[18−20] this technique was implemented to investigate the influence of an ultrasonic dispersion of mixtures of molybdenum(VI) oxide (MoO_3) and praseodymium(III,IV) oxide (Pr_6O_{11}) in heptane.

Experimental Section

Starting Materials. Praseodymium(III,IV) oxide, Pr_6O_{11} (Janssen Chimica, 99.9%, mean particle size 2 μm), was used as received. MoO_3 (particle size 0.3−3 μm) was obtained by calcination of a citrate-type precursor at 673 K for 20 h.[1] The three pure praseodymium molybdates ($Pr_2Mo_3O_{12}$, Pr_2MoO_6, Pr_6MoO_{12}) were synthesized from solutions containing appropriate amounts of ammonium heptamolybdate (Merck, 99%) and praseodymium(III) nitrate hexahydrate (Aldrich, 99.9%) mixed with a solution of citric acid (Merck, 99.6%). The gel obtained after partial removal of water was subsequently heated under reduced pressure at 363 K for 20 h and, after grinding, at 973 K in air for a further 20 h period.[21]

Mixtures. Five different types of $Pr_6O_{11}-MoO_3$ mixtures were prepared: mixtures A are mechanical mixtures obtained by dry grinding of the Pr_6O_{11} and MoO_3 powders in an agate mortar; mixtures B are mechanical mixtures obtained by grinding the Pr_6O_{11} and MoO_3 powders in an agate mortar in the presence of distilled *n*-heptane; mixtures C are obtained by dispersing the adequate amount of the Pr_6O_{11} and MoO_3 oxides (total amount 4 g) under ultrasonic stirring in 100 mL of distilled *n*-heptane during 15 min, without intermediate homogenization (some other mixtures have been obtained under identical conditions but with longer sonication times, varying from 30 s to 52 h); mixtures D have been prepared by sonication of the powders in heptane during 7 h, with homogenization every hour. In preparation procedures where heptane was used, the hydrocarbon was slowly eliminated (ca. 1 h) up to dryness, under reduced pressure, at ambient temperature. All the above-mentioned ultrasonic treatments were carried out in a BRANSON MTH-3210E ultrasonic bath (130 W, 47 kHz). A last sample (mixture E) has been submitted to sonication during 15 min under more severe conditions by using a disintegrator probe (SANYO MSS150 CX3; 100 W; 23 kHz) introduced inside the reaction flask.

Secondary Ion Mass Spectrometry. Positive and negative time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed with a ToF-SIMS spectrometer from Charles Evans & Associates.[22−24] In the ToF-SIMS experiments, the sample was bombarded with pulsed primary $^{69}Ga^+$ ions (15 keV). The secondary ions were accelerated to ±3 keV by applying a bias on the sample. To increase the detection efficiency of high-mass ions, a postacceleration of 10 keV was applied at the detector entry. The analyzed area used in this work was a square of 100 μm × 100 μm. With a data acquisition time of 5 min, the total dose was about 10^{12} ions/cm^2, which ensured static conditions.[25]

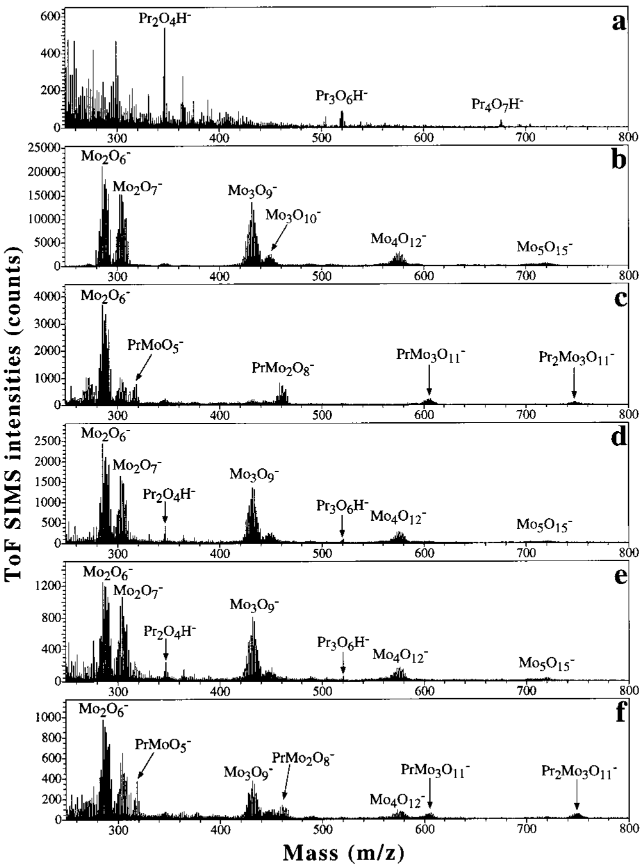

Figure 1. Part of the negative ToF-SIMS spectra from 250 to 800 *m/z* obtained for (a) Pr_6O_{11}, (b) MoO_3, (c) $Pr_2Mo_3O_{12}$, (d) A-type $Pr_6O_{11}-MoO_3$ dry mechanical mixture (Pr/Mo = 6), (e) B-type $Pr_6O_{11}-MoO_3$ mechanical mixture with *n*-heptane (Pr/Mo = 6), and (f) C-type $Pr_6O_{11}-MoO_3$ mixture with 52 h sonication (Pr/Mo = 6).

Charge effects were compensated by means of a pulsed electron flood gun ($E_k = 24$ eV). The best mass resolution obtained with this ToF-SIMS spectrometer is $M/\Delta M \approx 11\,000$ at $m/z = 28$ on a Si wafer. For the present samples and analytical conditions, the mass resolution was about 3000 at $m/z = 29$. The powders were pressed on an indium foil used as support.

Scanning Electron Microscopy. Electron microscopy was implemented with a FEG digital scanning microscope 982 Gemini from Leo. Measurements were performed at magnification up to 400 000 and with an acceleration voltage of 1 kV.

Results and Discussion

Secondary Ion Mass Spectrometry Results. As far as the Mo-containing fragments are concerned, it is necessary to take into account the various Mo isotopes. However, although Figures 1−4 display or refer to the natural Mo isotope distribution, to alleviate the presentation of these data in the text, all the *m/z* values concerning Mo-containing fragments refer only to the isotope ^{98}Mo, which is the most abundant (23.7%). Figure 1 shows the negative ToF-SIMS spectra of (a) pure Pr_6O_{11}, (b) pure MoO_3, (c) pure $Pr_2Mo_3O_{12}$, (d) an A-type $Pr_6O_{11}-MoO_3$ mixture (Pr/Mo = 6), (e) an analogous B-type mixture, and (f) an analogous C-type mixture (52 h sonication). Only the masses ranging from 250 to 800 *m/z* are displayed. The assignment of some prominent peaks is also indicated. The comparison of these spectra suggests some comments. The spectrum of pure $Pr_2Mo_3O_{12}$ phase (Figure 1c) shows several

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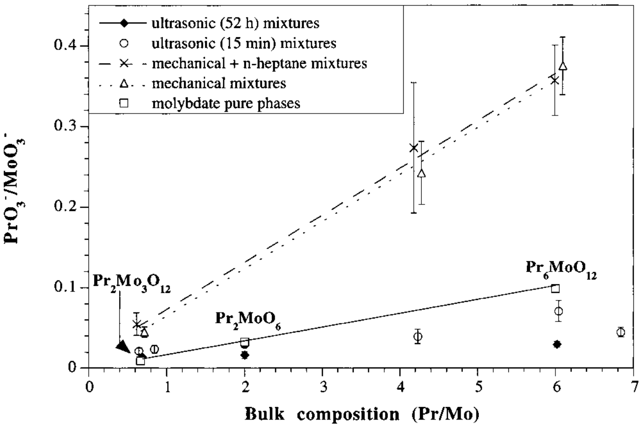

Figure 2. PrO_3^-/MoO_3^- intensity ratio as a function of the bulk Pr/Mo molar ratio.

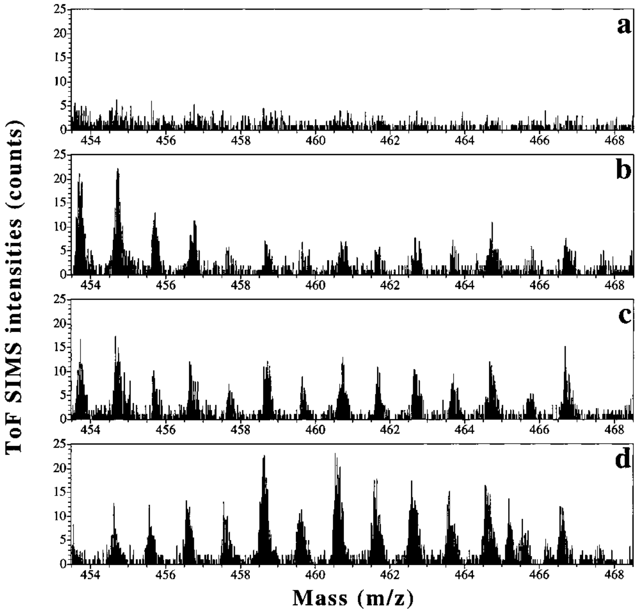

Figure 3. Evolution of the intensity of the $PrMo_2O_8^-$ fragment as a function of the sonication time of $Pr_6O_{11}-MoO_3$ C-type mixtures (Pr/Mo = 6): (a) without ultrasound, (b) 30 s ultrasound, (c) 5 min ultrasound, and (d) 52 h ultrasound.

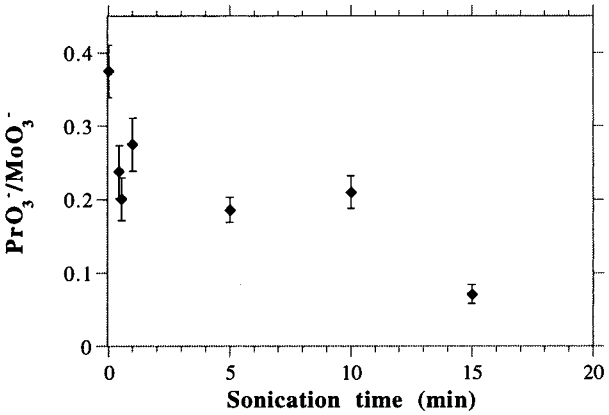

Figure 4. Evolution of the PrO_3^-/MoO_3^- intensity ratio in C-type $Pr_6O_{11}-MoO_3$ mixtures (Pr/Mo = 6) as a function of the sonication time.

ternary fragments characteristic of this phase (i.e. $PrMoO_5^-$, $PrMo_2O_8^-$, $PrMo_3O_{11}^-$, and $Pr_2Mo_3O_{11}^-$ at 319, 465, 611, and 752 *m*/*z*, respectively). Figure 1d,e displays the spectra of the mechanical mixtures. Peaks associated with the two starting oxides are observed ($Mo_xO_y^-$, PrO_x^-). The great similarity of these two spectra confirms that the treatment with *n*-heptane does not alter the sample's nature. However, new peaks appear in the spectrum of the mixture submitted to ultrasound (Figure 1f). They are related to the formation of a molybdate phase on the surface, similar to $Pr_2Mo_3O_{12}$. This demonstrates that ultrasound is able to induce a surface reaction between the two oxides, creating a molybdate phase. Identical conclusions can be drawn for the sample prepared with the disintegrator probe (spectrum not shown).

A second approach, described extensively elsewhere,[18] was aimed at evaluating the influence of the preparation method; it was based on the comparison between the PrO_3^-/MoO_3^- intensity ratio and the corresponding Pr/Mo molar ratio in the bulk, as illustrated in Figure 2. As expected, a linear relationship is observed for both mechanical mixtures (A and B), confirming that *n*-heptane has no effect during the preparation. A linear relationship is also observed for the three pure molybdate phases ($Pr_2Mo_3O_{12}$, Pr_2MoO_6, Pr_6MoO_{12}). Using ultrasound for the preparation (mixtures C with sonication of 15 min or 52 h) induces a marked decrease of the PrO_3^-/MoO_3^- intensity ratio, which reaches a value close to that observed in pure $Pr_2Mo_3O_{12}$.

A kinetic study of the influence of the ultrasonic treatment performed on the $Pr_6O_{11}-MoO_3$ C-type mixtures by SIMS shows that even a very short exposure can lead to the formation of the $Pr_2Mo_3O_{12}$ phase. As a matter of fact, only a 30 s sonication time induces the occurrence of ternary fragments. This phenomenon is clearly illustrated in Figure 3, where the *m*/*z* range corresponding to the isotope distribution of the $PrMo_2O_8^-$ fragment (*m*/*z* = 465), generated in sonicated $Pr_6O_{11}-MoO_3$ C-type mixtures (Pr/Mo = 6), is shown as a function of the sonication time. It has to be emphasized that Figure 3d reflects excellently the natural isotope abundance of molybdenum. Moreover, there is a marked decrease of the PrO_3^-/MoO_3^- intensity ratio (see Figure 4, for a mixture with Pr/Mo molar ratio = 6) as a function of the sonication duration. After 52 h sonication (not shown in the graph), the PrO_3^-/MoO_3^- intensity ratio is equal to 0.03.

Scanning Electron Microscopy Results. Scanning electron micrographs of $Pr_6O_{11}-MoO_3$ mixtures (Pr/Mo = 6) illustrate the occurring phenomena (Figure 5). Figure 5a corresponds to an A-type mixture, Figure 5b to the $Pr_2Mo_3O_{12}$ phase, Figure 5c to a C-type mixture (1 h sonication), Figure 5d to a C-type mixture (52 h sonication without homogenization), Figure 5e to a D-type mixture (7 h sonication with intermediate homogenization), and Figure 5f to an E-type mixture (sonicated 15 min with the disintegrator probe). The identification of the two starting oxides in the $Pr_6O_{11}-MoO_3$ dry mechanical mixtures (Figure 5a) is rather easy because MoO_3 appears as nice crystallites, while the shape of the Pr_6O_{11} particles is much more irregular. The comparison of the micrographs obtained for mechanical mixtures (Figure 5a) and ultrasonicated samples (1 h in heptane) (Figure 5c) shows that the ultrasonic treatment provides more intimate mixtures and that it induces particles smoothing and melting between the two oxides at the impact point. When long sonication

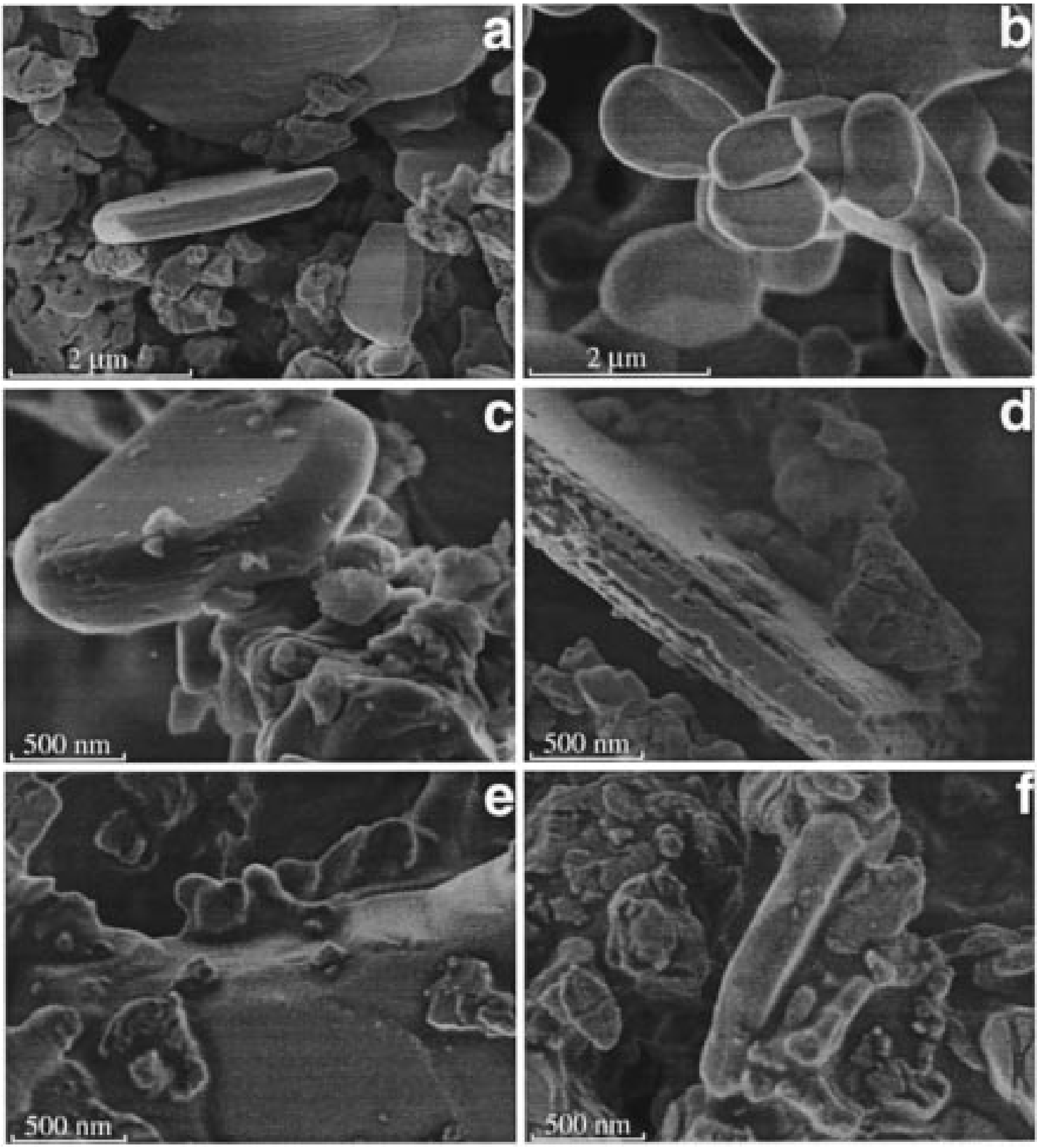

Figure 5. Scanning electron micrographs of (a) A-type $Pr_6O_{11}-MoO_3$ mixture (Pr/Mo = 6), (b) $Pr_2Mo_3O_{12}$ phase, (c) C-type $Pr_6O_{11}-MoO_3$ mixture (Pr/Mo = 6; 1 h sonication), (d) C-type $Pr_6O_{11}-MoO_3$ mixture (Pr/Mo = 6; 52 h sonication without homogenization), (e) D-type $Pr_6O_{11}-MoO_3$ mixture (Pr/Mo = 6; 7 h sonication with intermediate homogenization), and (f) E-type $Pr_6O_{11}-MoO_3$ mixture sonicated 15 min with the disintegrator probe (Pr/Mo = 6).

times are used (Figure 5d), a dramatic erosion of the particles appears which can be explained by cavitational phenomena. Furthermore, intermediate homogenizations (Figure 5e) cause a drastic enhancement of the melting effect, which becomes comparable to the one observed in the mixtures prepared with the disintegrator probe (Figure 5f).

When remembering that ToF-SIMS demonstrated unequivocally that the $Pr_2Mo_3O_{12}$ phase was generated at the surface of ultrasonicated $Pr_6O_{11}-MoO_3$ mixtures, we should notice that the comparison of the electron micrographs of the sonicated mixtures (parts c, d, e, and f of Figure 5) with the one of $Pr_2Mo_3O_{12}$ (Figure 5b) cannot allow us to draw a similar conclusion.

It should also be noted that the small macroscopic temperature variations in the ultrasonic bath used for the preparation of the C- and D-type mixtures evidently play no role in the observed melting phenomenon, because these changes are restricted to increases of 2 K (15 min sonication) or 30 K (52 h sonication), depending on the treatment time. Solid-state reactions leading to the generation of lanthanide molybdates are known besides to require much higher temperatures. In particular, reactions between MoO_3 and Pr_6O_{11}, La_2O_3, or CeO_2 are reported in the literature to start only at ca. 773,[1,26] 843,[27] and 923 K,[28] respectively.

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Consequently, the generation of praseodymium molybdate in our $Pr_6O_{11}-MoO_3$ mixtures was unexpected and can be understood only by considering the unusual physical conditions developed during the ultrasonication dispersion. Namely, extremely high local temperatures are reached, determined to be in the 2300−5300 K range according to the investigation method used.[11,29−30] Moreover, high pressures ($>10^8$ Pa),[2] rapid particle velocities (ca. 150 m/s),[13] and fast quenching rate (10^{10} K/s)[2] are also inherent to cavitational phenomena.

Conclusion

ToF-SIMS is shown to be a very powerful technique which allows us to reveal the formation of the praseodymium molybdate phase $Pr_2Mo_3O_{12}$ at the surface of $Pr_6O_{11}-MoO_3$ catalysts when they are prepared by ultrasonic dispersion. Moreover, scanning electron microscopy demonstrates that this treatment induce dramatic modification of the catalyst surface morphology. It is consequently essential to realize that the implementation of ultrasonic procedures for interdispersion of catalysts is, by far, not benign and could in some cases alter very significantly the surface properties of the obtained catalysts.

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