Synthesis of TiO₂/Nanozeolite Composites for Highly Efficient Photocatalytic Oxidation of Propene in the Gas Phase

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ABSTRACT: In this work, we reported the preparation of composites based on titania (TiO₂) and Zeolite Socony Mobil-5 (ZSM-5) nanozeolite, following two approaches (i.e., incorporating the presynthesized zeolite in the synthesis medium of TiO₂ and incorporating presynthesized TiO₂ in the synthesis medium of ZSM-5). The materials synthesized were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), ultraviolet–visible spectroscopy (UV–vis), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) spectrometry analysis, and their photocatalytic activities were assessed in the oxidation of propene in the gas phase. It was observed that the synthesis methodology affects the final properties of the composite, which ultimately affected their photocatalytic performance in the studied application. It was found that the Nano-ZSM5/TiO₂ composite was the most active among the investigated samples, which was attributed to the intimate contact between the two components of the composite, the preserved properties of the photocatalytic active phase in the final material, and the positive contribution of the nanozeolite by increasing the local concentration of propene.

1. INTRODUCTION

Volatile organic compounds (VOCs) abatement is still one of the important challenges of our society since these contaminants are very harmful for the environment and human health.1−5 These compounds can be present in indoor ambient and are responsible for a disease known as “sick house syndrome”.6,7 An interesting approach for VOC abatement is the use of photocatalytic reactions, which can totally remove these types of contaminants at low temperature, atmospheric pressure, and low concentrations.8−10 Propene can be used as a model molecule to study the low-molecular-weight VOC abatement using a photocatalytic methodology.11−14 Titanium oxide (TiO₂) has been the most widely investigated photocatalyst in the last decades, which is due to its interesting properties such as low cost, chemical stability, and resistance to photocorrosion. For this reason, TiO₂ has been extensively used in different photocatalytic applications both in gas and liquid phases (i.e., pollutant removal, water splitting, and CO₂ reduction, among others15−16). Nevertheless, TiO₂ presents some limitations related to its low absorption in the visible light range, a electron–hole pair (e−−h+) recombination rate, and a low surface area, which limits its photocatalytic activity.17,18

Achieving TiO₂ with well-developed porosity has been a common approach considered to improve its photocatalytic activity.19,20 Another interesting approach that has been tackled is the fabrication of TiO₂/adsorbent composites or supporting TiO₂ on adsorbents of diverse natures (i.e., carbon materials,21,22 silica,23−25 zeolites,26,27 MOFs,28−30 etc.). The resulting materials display enhanced performance, which results from their improved adsorption properties. Such properties allow the adsorption of molecules on the composite, which is followed by diffusion to the photocatalytic active sites where the photocatalytic reaction occurs.31−33 Among the adsorbents investigated, the use of zeolites has received significant attention in the last years. This derives from their interesting properties such as the possibility to vary the chemical composition, high surface area, modulation of pores size, photochemical stability, thermal and chemical inertness, and transparency to ultraviolet−visible (UV−vis) radiation above 240 nm.34−36

In this sense, several studies addressing the use of TiO₂/zeolites for various photocatalytic applications can be found. For instance, Liu et al. were pioneers in the synthesis of TiO₂/zeolites hybrids. They studied the TiO₂/zeolites composite synthesis by TiO₂ incorporation inside zeolite Y cavities through ion exchange.35 The same authors prepared TiO₂ encapsulated within zeolite Y, mordenite, or zeolite L, and the resulting materials were used for the photoreduction of methyl viologen to a methyl viologen radical cation. It was found that the encapsulated TiO₂ had a particle size in the nanometer
scale, which was responsible for the modified properties of TiO$_2$. Sampa et al. observed complete mineralization of pyridine with a zeolite-supported photocatalyst consisting of 75 wt % TiO$_2$ and 25 wt % mordenite, which had better catalytic activity than pure TiO$_2$. They also observed diffusional problems of pyridine within the zeolite-supported photocatalyst when the thickness of the photocatalyst exceeded the penetration illumination depth. Takeuchi et al. reported an interesting effect of the hydrophobicity of zeolites in TiO$_2$/Zeolite Socony Mobil-5 (ZSM-5) systems. It was observed that the composites with low content of Al$_2$O$_3$ in the zeolite (high hydrophobic zeolite) showed good photocatalytic activity, indicating that zeolites with hydrophobic properties promoted the photocatalytic activity of the TiO$_2$/HZSM-5 systems toward acetalddehyde degradation. The same group observed that toluene or benzene molecules strongly interacted with the Na$^+$ or H$^+$ sites of the ultrastable Y (USY) zeolites and thus indicated that zeolites with hydrophobic properties promoted the photocatalytic activity of the TiO$_2$/HZSM-5 systems toward acetalddehyde degradation.

2. RESULTS AND DISCUSSION
2.1. Characterization of the Composites. This section includes the results and discussion concerning the characterization of the prepared Nano-ZS5/ TiO$_2$, TiO$_2$/Nano-ZS5, and Com-ZS5/TiO$_2$ composites and the pure TiO$_2$, Nano-ZS5, and Com-ZS5 for comparison purposes (see Section 4.2).

X-ray fluorescence (XRF) analysis shows the presence of TiO$_2$ and zeolite in all composites prepared in this study. The Nano-ZS5/TiO$_2$ composite (preshyntehsized nanozeolite incorporated in the TiO$_2$ synthesis medium) is composed of 56 wt % TiO$_2$ and 44 wt % Nano-ZS5, while the TiO$_2$/Nano-ZS5 composite (preshynthesized TiO$_2$, incorporated in nanozeolite synthesis medium) has a much lower proportion of TiO$_2$ (19 wt % of TiO$_2$ and 81 wt % of Nano-ZS5), which indicates that the TiO$_2$ incorporated in the medium used for the synthesis of the zeolite may be dissolved or degraded by some of the reagents, such as NaOH under the synthesis conditions. The Com-ZS5/TiO$_2$ composite (commercial zeolite incorporated in the TiO$_2$ synthesis medium) is composed of 60 wt % of TiO$_2$ and 40 wt % of Com-ZS5. The amount of TiO$_2$ and zeolite obtained in the Com-ZS5/TiO$_2$ composite is similar to that obtained for the Nano-ZS5/TiO$_2$ sample because in both composites, the same synthesis methodology was followed (See Section 4.2).

The X-ray diffraction (XRD) patterns of the composites and the pure phases, TiO$_2$ with hierarchical porosity and ZSM-5 zeolite, are depicted in Figure 1. As it has been previously reported, TiO$_2$ with hierarchical porosity only shows the characteristic peaks ascribed to the anatase phase. All of the composites displayed the peaks attributed to the presence of TiO$_2$ and nanozolate. The obtained diffractograms indicate that the TiO$_2$/Nano-ZS5 composite has a larger proportion of nanozolate, while a larger proportion of TiO$_2$ is present in

Figure 1. XRD patterns of TiO$_2$/nanozeolite composites. The diffractograms of TiO$_2$, ZSM-5 nanozolate, and commercial ZSM-5 zeolite are shown for comparison. Key: A = anatase phase (TiO$_2$) and Z = ZSM-5 nanozolate.
the Nano-ZSM5/TiO2 composite, which is in good agreement with XRF results. The Com-ZSM5/TiO2 composite shows the same crystalline phases (anatase and ZSM-5 phases) as those observed in the Nano-ZSM5/TiO2 composite (Figure 1).

The results of the N2 adsorption–desorption measurements at −196 °C are depicted in Figure 2 and the textural properties

Table 1. Textural Properties of the Composites

| support               | surface area (m²/g) | \(V_{\text{DR}}\) (cm³/g) | \(V_{\text{mesopores}}\) (cm³/g) | \(V_{\text{t}}\) (cm³/g) |
|-----------------------|---------------------|-----------------------------|----------------------------------|--------------------------|
| TiO2                  | 83                  | 0.03                        | 0.19                             | 0.22                     |
| Nano-ZSM5             | 431                 | 0.19                        | 0.16                             | 0.35                     |
| Com-ZSM5              | 425                 | 0.17                        | 0.04                             | 0.21                     |
| Nano-ZSM5/TiO2        | 254                 | 0.10                        | 0.36                             | 0.46                     |
| TiO2/Nano-ZSM5        | 234                 | 0.10                        | 0.12                             | 0.22                     |
| Com-ZSM5/TiO2         | 248                 | 0.10                        | 0.30                             | 0.40                     |
| PM                    | 263                 | 0.08                        | 0.17                             | 0.25                     |

Data for TiO2, Nano-ZSM5, Com-ZSM5, and PM are shown for comparison purposes.

as collected in Table 1. The N2 physisorption isotherm of TiO2 showed a combination of type I and IV isotherms, which is typical of mesoporous materials with a certain degree of microporosity, as previously reported by our research group.49 Both commercial ZSM-5 zeolite and ZSM-5 nanozeolite show a type I isotherm48 but the last one shows a slightly larger contribution of micropores than the commercial counterpart. ZSM-5 nanozeolite displays some slope from relative pressures higher than 0.2 and a small hysteresis loop at high relative pressures, which is due to the presence of a small number of mesopores and to the adsorption of N2 in the interparticle space. TiO2/Nano-ZSM5 and Nano-ZSM5/TiO2 composites show a combination of isotherms from TiO2 and ZSM-5. TiO2/Nano-ZSM5 shows a less marked hysteresis than Nano-ZSM5/TiO2 due to the lower content of TiO2 in the TiO2/Nano-ZSM5 composite. Concerning the Com-ZSM5/TiO2 composite, this composite presents a combination of isotherms between TiO2 and ZSM-5 obtaining type I and IV isotherms, as it was observed in the Nano-ZSM5/TiO2 composite.

Composite materials containing ZSM-5 nanozeolite have adequately developed porosity, confirming the suitability of the experimental procedure carried out in the synthesis of the studied materials (Table 1). As previously mentioned, the TiO2/Nano-ZSM5 and PM samples present a lower volume of mesopores compared to the Nano-ZSM5/TiO2 sample (Table 1), which can be attributed to the lower content of TiO2 in the first and to the milling process used in the synthesis of the second material (PM). Concerning the Com-ZSM5/TiO2 composite, it shows a slightly lower volume of mesopores than Nano-ZSM5/TiO2.

Ti 2p and O 1s X-ray photoelectron spectroscopy (XPS) spectra for the composites are shown in Figure 3. Figure 3A depicts the Ti 2p spectra of TiO2 and for Nano-ZSM5/TiO2 and TiO2/Nano-ZSM5 composites. Concerning bare TiO2, Ti present in the sample TiO2 with hierarchical porosity is as Ti(IV) (Ti 2p\(1/2\) (464−465 eV) and Ti 2p\(3/2\) (458.5−459 eV) transitions are in agreement with Ti(IV)51). The Ti 2p XPS spectrum of the Nano-ZSM5/TiO2 composite (Figure 3A) shows peaks corresponding to Ti 2p\(1/2\) (464−465 eV) and Ti 2p\(3/2\) (458.5−459 eV) transitions, indicating that Ti is in a Ti(IV) form.52,53 However, Ti is almost not detected in sample TiO2/Nano-ZSM5, which is not only due to the low TiO2 content in this sample (19 wt % compared to 60 wt % in the other composite) but also due to the possibility that the TiO2 phase can be encapsulated by Nano-ZSM5, considering the experimental method used (i.e., ZSM-5 precipitation on TiO2 particles added to the reaction medium). In the Ti 2p XPS spectrum, a blue shift was observed in Nano-ZSM5/TiO2 with respect to the peak of TiO2. This might be due to sample charging under X-ray radiation, as it has been described in the literature.53

For a better understanding of the interaction between TiO2 and ZSM-5 nanozeolite in the composites, O 1s XPS spectra are analyzed (Figure 3B). The Nano-ZSM5/TiO2 composite shows the characteristic peaks of a Ti–O bond (529.6 eV) and a Si–O bond (533.4 eV), indicating the presence of TiO2 and...
zeolite in the composite material, respectively.\textsuperscript{54,55} Moreover, the Nano-ZSM5/TiO\(_2\) composite shows a peak at 531.7 eV, which could be related to the presence of a Si—O—Ti bond due to good interaction between TiO\(_2\) and the zeolitic phase. The TiO\(_2\)/Nano-ZSM\(_5\) composite only shows a characteristic peak at 533.4 eV (Si—O bond), which is ascribed to the zeolitic material, while signals related to TiO\(_2\) are not detected. TiO\(_2\) shows the characteristic peak of the Ti—O bond (529.6 eV) and a small peak at 531.4 eV, which is the characteristic of the organic matter present in the sample, although these materials have been calcined, and this value (531.4 eV) being very similar to the characteristic peak of the Si—O—Ti bond (531.7 eV).\textsuperscript{55} From XRF and XRD, it can be concluded that TiO\(_2\) is partially dissolved during the synthesis process and that the remaining TiO\(_2\) present in the composite is covered by ZSM-5.

Figure 4 shows the UV—vis absorption spectra of the composites synthesized in this study and bare TiO\(_2\). TiO\(_2\)/Nano-ZSM\(_5\) and Nano-ZSM\(_5\)/TiO\(_2\) composites (TiO\(_2\)/Nano-ZSM\(_5\), Nano-ZSM\(_5\)/TiO\(_2\), and Com-ZSM5/TiO\(_2\)) have a similar absorption edge and band gap compared to the bare TiO\(_2\) with hierarchical porosity, previously described by our research group.\textsuperscript{49} This fact indicates the presence of the anatase phase in the materials (3.12 eV).\textsuperscript{13} However, the composite TiO\(_2\)/Nano-ZSM\(_5\) shows lower absorption than the Nano-ZSM\(_5\)/TiO\(_2\) sample in the 200—350 nm range (UV light), possibly due to the encapsulation and/or partial dissolution of the TiO\(_2\) phase.

Figure 5 includes the transmission electron microscopy (TEM) micrographs of the composites and pure components (i.e., TiO\(_2\), ZSM-5 nanozeolite, and commercial ZSM-5 zeolite). Concerning the morphology of the zeolitic phase, TEM images show that the ZSM-5 nanozeolite (Figure 5B) has smaller crystallite size than commercial zeolite (Figure 5C). The histogram of the nanozeolite (counting 100 crystallites of ZSM-5) shows that it has a narrow crystallite size distribution and average crystallite size of 120 ± 16 nm. However, the commercial zeolite (counting 50 crystallites of ZSM-5) has a much wider crystallite size distribution and an average crystallite size of 290 ± 120 nm, with small crystallites of 60 nm up to larger ones of 500 nm in size.

As for the composites, all of them show the presence of both components but important differences were observed. The Nano-ZSM5/TiO\(_2\) composite (Figure 5D) shows that there is a good dispersion of the TiO\(_2\) phase on the ZSM-5 crystals, indicating good interaction between TiO\(_2\) and nanozeolite in the Nano-ZSM\(_5\)/TiO\(_2\) composite, while the composite prepared by physically mixing the two solids shows a poorer dispersion of TiO\(_2\) on the surface of the zeolite (Figure 5G).

Such good dispersion of TiO\(_2\) on the nanozeolite crystals can be related to the higher volume of mesopores (Table 1), which increases the number of nucleation sites for Ti species during the growth of TiO\(_2\), thus leading to an improved interaction between TiO\(_2\) and nanozeolite components with respect to the Com-ZSM5/TiO\(_2\) composite (Figure 5F). Moreover, this interaction can be due to the employed sol—gel methodology, which can favor the interaction between the components since TiO\(_2\) can grow on the Si—OH anchoring points of the zeolite, leading to a better interaction in the composite than in the sample prepared by a physical mixture. The micrographs of the TiO\(_2\)/Nano-ZSM\(_5\) composite (Figure 5E) show a morphology, which is very similar to that of the pure zeolite (Figure 5B), suggesting that ZSM-5 nanozeolite is covering the TiO\(_2\) phase.

Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectrometry mapping images of the Nano-ZSM\(_5\)/TiO\(_2\), TiO\(_2\)/Nano-ZSM\(_5\), and PM composites are depicted in Figures 6 and 7, respectively. The Nano-ZSM\(_5\)/TiO\(_2\) composite (presynthesized nanozeolite incorporated in the TiO\(_2\) synthesis medium) shows that the TiO\(_2\) phase almost completely covers the nanozeolite (Figures 6A and 7A), which is in agreement with the previously discussed XPS results. In the case of the TiO\(_2\)/Nano-ZSM\(_5\) composite
(presynthesized TiO₂ incorporated in nanozeolite synthesis medium), ZSM-5 nanozeolite partially covers the surface of the TiO₂ phase (Figures 6B and 7B). However, the composite prepared from a physical mixture of both components (PM) displayed a heterogeneous distribution of both phases (Figures 6C and 7C).

Breakthrough curve measurements of propene (Table 2) show that zeolites have an adsorption capacity, which is two orders of magnitude higher than that of TiO₂. In addition, the propene adsorption capacity of the nanozeolite is slightly higher than that of the commercial counterpart.

### 2.2. Photocatalytic Activity

In this section, the results of propene conversion and the CO₂ production rate of the materials studied in the present work are included, focusing on the effect of the synthesis methodology used for composite preparation and the synergetic effect between TiO₂ and ZSM-5 zeolite. Besides, the effect of the zeolite crystal size (290 ± 120 and 120 ± 16 nm, for commercial ZSM-5 and ZSM-5 nanozeolite, respectively) in the photocatalytic activity displayed by the composites is also included in this section.

The photocatalytic results of the composites and bare TiO₂ are shown in Figure 8. The Nano-ZSM5/TiO₂ photocatalyst shows the best propene conversion among the investigated samples, even being superior to pure TiO₂ (active phase), which indicates that the incorporation of the nanozeolite has a positive effect on the final activity. However, TiO₂/Nano-ZSM5 material presents a low propene conversion because this composite has a low amount of TiO₂ (see XRF analysis described in Section 2.1). Moreover, TiO₂ (active phase) might have been deteriorated in the zeolite synthesis medium or blocked by the growing nanozeolite, causing the low propene conversion displayed by this composite. The superior performance of the Nano-ZSM5/TiO₂ composite is further evidenced by normalizing the CO₂ production rate per mol of the TiO₂ active phase. This observation confirms the importance of the synthesis methodology used for the composite preparation. In this sense, the TiO₂/Nano-ZSM5 composite displays a low CO₂ production rate since TiO₂, which is the photocatalytic active phase, is deteriorated during the composite preparation or unaccessible due to the zeolite phase covering TiO₂.

With the aim of studying the synergetic effect between TiO₂ and zeolite in the composites, a physical mixture of both materials (PM) was tested. The PM composite shows a similar propene conversion to TiO₂ despite the PM having 56 wt % of TiO₂ (active phase), indicating that the presence of zeolite in the composite improves the final performance, even in this sample in which there is no intimate contact between both phases. Comparing PM with the Nano-ZSM5/TiO₂ composite in terms of propene conversion, the Nano-ZSM5/TiO₂ composite shows higher conversion, indicating a synergetic effect between TiO₂ and ZSM-5 nanozeolite due to good interaction between both components in the composite with respect to the composite prepared by a physical mixture since the employed sol–gel methodology may favor the interaction between the components since TiO₂ can grow on the Si–OH anchoring points of the zeolite, leading to a better interaction in the composite than in the sample prepared by a physical mixture. When analyzing the CO₂ production rate per mol of TiO₂, Nano-ZSM5/TiO₂ and PM composites show higher values than those achieved with pure TiO₂, corroborating the positive effect of the incorporation of the nanozeolite in the composite. Such enhancement observed upon using TiO₂/Nanozeolite composites might be related to the zeolite.
adsorption properties, see Table 2, which leads to the increase in the concentration of propene molecules near the photocatalytic active sites, thus improving the final performance of the materials.

It should be noted that the catalytic tests of propene oxidation for the composites and pure materials were performed until steady-state conditions were reached. This means that the zeolite pores act as reservoirs for propene, which is continuously adsorbed and oxidized. Thus, the effect of the adsorption is to increase the propene concentration in the vicinity of the reaction sites, as it has been previously indicated. If there was only adsorption, the removal of propene would only be observed until the saturation of the adsorbent is reached. Since adsorption is coupled with photocatalytic oxidation, the complete removal of propene is reached during the complete time of the reaction studied. Then, the contribution of a pure adsorption process to the continuous complete oxidation of propene during the time of the experiments at a steady state is negligible.

Regarding the effect of using a nanozeolite in the final photocatalytic performance, it was observed that the results achieved by the Com-ZSM5/TiO2 composite with commercial ZSM-5 show a moderate improvement as compared to the performance displayed by the pure TiO2 phase, while a much significant enhancement was achieved by the Nano-ZSM5/TiO2 composite. Such beneficial effect of using ZSM-5 nanozeolite can be attributed to the smaller and more homogeneous crystallite size of the Nano-ZSM5 shown in the composite, which favors a more exposed surface area and better contact between the TiO2 and nanozeolite.33,43

Considering the results obtained in this study in terms of characterization of the samples and their performance in the photocatalytic oxidation of propene at low concentrations, the most promising outlook seems to be the following: (1) this work presents different strategies for the preparation of TiO2 and zeolite (ZSM-5) composites, indicating that the synthesis methodology has a great effect on the final properties of the composite; (2) the TiO2 phase of the composite is the catalytic active phase of the composite, and for this reason, it is important that TiO2 is not degraded or blocked in any way during synthesis; (3) the synergetic effect between TiO2 and zeolite takes place due to an intimate contact between both components. The zeolitic phase acts as the adsorbent for the propene molecules and this favors the final photoactivity of the resulting composites; and (4) the selection of a zeolite with interesting properties, such as small and homogeneous crystallite size and a suitable porous structure, allows an improved photocatalytic activity of the composite.

For all of these reasons, the Nano-ZSM5/TiO2 composite, prepared using an adequate synthesis methodology that does not affect the photocatalytic active phase, displays a remarkably higher photocatalytic activity than bare TiO2. In this sense, the composite prepared using a nanozeolite with adequate porosity and homogenous small crystallite size (Nano-ZSM5/TiO2) showed the highest photocatalytic activity in the propene photooxidation in the gas phase at low concentration among investigated ones.

3. CONCLUSIONS

In this study, we studied the TiO2/nanozeolite composites focusing on two different synthesis methodologies, either incorporating the presynthesized zeolite in the synthesis medium of TiO2 or incorporating presynthesized TiO2 in the synthesis medium of ZSM-5. We also studied the effect of using nanozeolite or commercial zeolite in the synthesis of the composites for photocatalytic applications. The obtained results give evidence that the synthesis methodology is an important factor in the preparation of TiO2/Nanozeolite composites. It was observed that the composites prepared by incorporating the zeolite in the TiO2 medium synthesis displayed better results toward the photodegradation of propene than those composites in which presynthesized TiO2 was incorporated in the synthesis medium of ZSM-5 or the physical mixture of both components. The beneficial role of the zeolitic phase was related to its adsorption properties, which led to an increase in the concentration of propene molecules near the photocatalytic active sites, thus resulting in an enhanced performance compared with that of bare TiO2.

It was also observed that the zeolite crystal size has an effect on the final performance of the composites in the studied application. Nano-ZSM5/TiO2 showed a much superior performance than Com-ZSM5/TiO2 which was ascribed to the smaller crystal size that is responsible for the larger exposed external surface area and better contact with the photoactive TiO2 phase.

4. MATERIALS AND METHODS

4.1. Materials. Tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich), aluminum isopropoxide (98%, Sigma-Aldrich), tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma-Aldrich), sodium hydroxide (≥98%, Sigma-Aldrich), titanium-(IV) tetrabutoxide (TTB, 97%, Sigma-Aldrich), urea (99%, Merck), Pluronic F-127 (F-127, Sigma-Aldrich), glacial acetic acid (HAc, 99%, Sigma-Aldrich), formamide (FA, 99.5%, Fisher Scientific), commercial zeolite (NH4-ZSM-5, Zeolyst International), and deionized water were used in the present work. All reactants were used as received, without further purification.

4.2. Sample Preparation. In this work, we have performed the preparation of TiO2/Nanozeolite composites using two different synthesis approaches: In the first approach, a presynthesized ZSM-5 nanozeolite, which was prepared by following the protocol described by Nejad-Darzi, 48 was incorporated in the synthesis medium of TiO2 with hierarchical porosity, previously described by our research group. 49 The resulting composite was denoted as Nano-ZSM5/TiO2. In the second approach, the presynthesized TiO2 with hierarchical porosity was incorporated in the synthesis medium of ZSM-5 nanozeolite. 48 The resulting composite was denoted as TiO2/Nano-ZSM5. To obtain an insight into the effect of the zeolite crystal size, the first approach was also performed using commercial ZSM-5 zeolite in an acidic form. The resulting material was named as Com-ZSM5/TiO2. The synthetic protocols are described below.

The first approach (preparation of Nano-ZSM5/TiO2) was performed as follows. First, two solutions were prepared for the synthesis of TiO2 with hierarchical porosity: 49 5 g of the titanium precursor (titanium tetrabutoxide, TTB) was weighed and dissolved in 7.9 g of EtOH, and the mixture was stirred vigorously for 10 min (“solution A”). Then, in this order, 1.6 g of deionized water, 7.9 g of EtOH, 0.3 g of F-127, 0.4 g of FA, 0.4 g of urea, and 1.6 g of HAc were weighed and added in a separate vessel. The mixture was stirred for 10 min (“solution B”). Then, the previously synthesized and calcined (at 500 °C for 6 h) nanozeolite was incorporated in solution B and the resulting mixture was dispersed with an ultrasound probe.
The synthesized composite was calcined at 500 °C for 6 h. The resulting material was named as PM. We also prepared a physical mixture of both components (nanozeolite and TiO₂), mixing both components with an agate mortar, with the aim of studying the synergetic effect in the prepared TiO₂/nanozeolite composites. The resulting material was named as PM.

The individual components (i.e., TiO₂ with hierarchical porosity, ZSM-5 nanozeolite, and commercial ZSM-5 zeolite) were used as reference samples. The synthesis of TiO₂ with hierarchical porosity has been performed following the first approach without the incorporation of the correspondent zeolite. The ZSM-5 nanozeolite was synthesized using the second approach without the incorporation of the TiO₂. The commercial zeolite (NH₄-ZSM-5, Zeolyst International) was converted into its acidic form by calcining the ammonium zeolite at 500 °C for 5 h.

4.3. Sample Characterization. The composition of the composites was determined by X-ray fluorescence spectroscopy (XRF) using a PHILIPS MAGIX PRO spectrometer. The crystal phase composition and crystallinity of TiO₂ were determined by X-ray diffraction (XRD) analysis using a Miniflex II Rigaku with Cu Kα radiation and a scanning rate of 2°/min, in the 2θ range of 5°–80°. Nitrogen adsorption–desorption isotherms were performed at −196 °C in an Autosorb-6B apparatus from Quantachrome Corporation. Prior to the analysis, samples were degassed at 250 °C for 4 h under vacuum. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) and total micropore volume (V_{DR}) were determined by applying the Brunauer–Emmett–Teller (BET) equation and the Dubinin–Raduskevich (DR) equation to the N₂ adsorption data obtained at −196 °C, respectively. Total pore volumes (V₁) were determined from the adsorbed nitrogen volume at a relative pressure of 0.95. The interaction between the TiO₂ and zeolite in the composites was analyzed by X-ray photoelectron spectroscopy (XPS) using a Kα spectrometer from Thermo-Scientific, equipped with an Al anode. The optical absorption properties were studied using a UV–vis/DR spectrometer (Jasco V-670). BaSO₄ was used as the reference standard and the reflectance signal was calibrated with a Spectralon standard (Labsphere SRS-99-010, 99% reflectance). The absorption edge wavelength was estimated from the intercept at zero absorbance of the high slope portion of each individual spectrum in the range 200–800 nm (absorbance method). Then, the band gap was calculated with the following equation (eq 1)

\[ E_g = \frac{1239.8}{\lambda} \]  

where \( E_g \) is the band gap energy (eV) and \( \lambda \) is the edge wavelength (nm).

4.4. Catalytic Tests. The photocatalytic performance in propene photoxidation at low concentration of the different photocatalysts studied in this work was assessed using an experimental setup, previously reported by our research group. This experimental setup is based on a vertical quartz reactor where the photocatalyst was placed on a quartz wool bed. The reactor has the following dimensions: 50 mm in height, 20 mm in diameter, and a quartz wool support of approximately 10 mm in height. A commercial UV lamp with the radiation peak at 365 nm (Philips, TL 8W/05 FAM, 1 W) was used to irradiate the photocatalyst in a parallel position at a distance of 1 cm. The UV lamp and quartz reactor with the photocatalyst were surrounded by a cylinder covered with an aluminum foil.

The photocatalytic tests were performed under flow conditions at room temperature and with a low concentration of propene (100 ppmv in air), using a calibrated gas cylinder supplied by Carburros Metálicos, S.A. First, the photocatalyst (0.11 g) was incorporated in the quartz reactor, and then the reactor was purged with a helium flow of 30 (STP) mL/min to clean the surface of the catalyst. The propene-containing stream of 30 (STP) mL/min was passed through the calibration setup until the propene concentration was stable (~3 h) to calibrate the concentration of propene. After that, propene was passed through the reactor with the photocatalyst, and the lamp was switched on at the same time and kept working until steady-state conditions were reached (~ 3 h).
The outlet gas was continuously analyzed by a mass spectrometer (Balzers, Thermostar GSD 301 01). Propene conversion was calculated using the following expression (eq 2)

\[
\text{propene conversion(\text{%})} = \frac{C_{\text{initial C}_3\text{H}_6} - C_{\text{steady state C}_3\text{H}_6}}{C_{\text{initial C}_3\text{H}_6}} \times 100
\]

where \(C_{\text{initial C}_3\text{H}_6}\) is the initial propene concentration (100 ppmv), and \(C_{\text{steady state C}_3\text{H}_6}\) is the propene concentration at steady-state conditions in the outlet gas when the UV light is switched on. The CO\(_2\) production rate per mol of the active photocatalyst is defined as the molar flow rate of \(\text{CO}_2\) generated (moles \(\text{CO}_2/s\)) and \(n\) is the moles of the photocatalyst (moles of TiO\(_2\)). Total oxidation of propene to \(\text{CO}_2\) takes place under reaction conditions \(^4\) so that there is no effect of accumulation of byproducts on the catalytic sites.

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J.F.-C., D.C.-A., and A.B.-M. conceived and designed the experiments; M.S.-R. and J.F.-C. performed the experiments; M.S.-R. and J.F.-C. analyzed the experiments; M.S.-R. and J.F.-C. performed the experiments; J.F.-C., D.C.-A., and A.B.-M. conceived and designed the experiments; M.S.-R. and J.F.-C. analyzed the experiments; M.S.-R. and J.F.-C. performed the experiments; J.F.-C., D.C.-A., and A.B.-M. supervised the research.

**Notes**

The authors declare no competing financial interest.

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