

- Hierarchical K- and Ca-promoted ferrosilicates were prepared by impregnation
- FeO_x particles removal and acidity reduction were the most relevant modifications
- K-promoted ferrosilicates reached PO selectivities near 65% using O₂ as sole oxidant

K- and Ca-promoted ferrosilicates for the gas-phase epoxidation of propylene with O₂

*Jaime García-Aguilar, Diego Cazorla-Amorós, Ángel Berenguer-Murcia**

Materials Science Institute and Inorganic Chemistry Department, Alicante University, Ap. 99, E-03080 Alicante, Spain.

Keywords: sol-gel, propylene epoxidation, alkali promotion, ferrosilicate, dioxygen.

ABSTRACT: In the propylene epoxidation reaction with Fe-SiO₂ catalysts the presence of iron oxide particles has a detrimental effect due to the total combustion of propylene on these iron species. Thus, the complete elimination of the iron oxide particles is presented as a preliminary strategy in order to increase the selectivity towards propylene oxide in iron-based catalysts. In this sense, a simple post-treatment of the catalysts with alkali or alkaline-earth elements (such as K or Ca, respectively) has proven effective in the total elimination of these iron oxide particles. Furthermore, the addition of K and Ca has modified the physico-chemical properties of the catalysts, decreasing their superficial acidity and (for higher K or Ca loadings) masking/blocking the active sites responsible for the catalytic reaction. With all this, it is shown that K has a higher efficiency removing the iron oxide particles compared with Ca (for the same molar ratios) and that a higher amount of K (compared to Fe) is required for the complete elimination of the iron oxide particles. A considerable propylene oxide selectivity enhancement

(up to 65%) has been obtained for the K-promoted $\text{Fe}_{0.005}\text{SiO}_2$ and $\text{Fe}_{0.01}\text{SiO}_2$ catalysts using O_2 as sole oxidant.

1. Introduction

The production of propylene oxide (PO) by gas-phase catalysis is one of the most important challenges for the chemical companies due to its commercial interest. PO is a precursor of polyether polyols for urethanes, propylene glycols, and glycol ethers. At present, the production of this compound is mainly performed in liquid phase carried out by the chlorohydrin (in which Cl_2 is used as oxidant) process with approximately 40% of PO production [1–3].

Performing the epoxidation of propylene by heterogeneous catalysis in gas phase is nowadays one of the most interesting research topics in order to obtain an industrial catalyst towards a more environmentally friendly and applicable PO synthesis [4]. Despite the high price of gold and the need to use H_2/O_2 gas mixtures to feed the reactor, the $\text{Au}/\text{Ti-SiO}_2$ based catalysts are still under intense study due to high selectivities towards PO (at relatively low temperatures). This has given rise to recent studies in which the researchers have paid special interest to the reaction mechanism using this type of catalysts [5–9]. Other studies were focused on the synthesis of PO using only O_2 and propylene in the gas stream composition aimed at avoiding the use of H_2 . However, it is mandatory to increase the reaction temperature (compared with the abovementioned $\text{Au}/\text{Ti-SiO}_2$ catalysts which requires H_2/O_2 mixtures) to activate the gas molecules and obtain the desired compound. In this sense, Khatib et al. [3] have recently reported a review summarizing the catalysts used for PO formation using gaseous O_2 . Pure Ru, Ag and Cu (or mixed with other metals)-based catalysts must be mentioned as thoroughly studied due to their similar or higher propylene conversion than $\text{Au}/\text{Ti-SiO}_2$ catalysts but with slightly lower PO selectivity [10–18].

Recently, our research group reported the synthesis of PO using dioxygen and ferrosilicate catalysts prepared in a sol-gel one-step synthesis of well-dispersed iron oxide species into the silica structure [19]. In these materials, the propylene epoxidation reaction took place on the iron sites dispersed into the silica framework while the total combustion (towards CO₂) was preferentially occurring on the small iron oxide particles/clusters decreasing the PO selectivity [20]. Due to the synthesis procedure, even when the iron loading is 0.005 (Fe/Si molar ratio), the formation of extra-framework small iron oxide particles cannot be avoided. Addition of some alkali and alkaline earth elements after the synthesis of the catalysts reduces the presence of iron oxide particles as reported in the literature [21]. This strategy was also used in the above-mentioned catalysts (Ag, Cu or Ru) to increase PO selectivity, reaching the best improvements with the K and Ca-based catalysts [11,22–24]. Even for Fe-SiO₂ catalysts (where N₂O is used as oxidant), this addition has beneficial effects in the selectivity towards PO in spite of a reduction in propylene conversion [25–29].

This work is focused on the reduction and/or removal of the small iron oxide particles /clusters observed in iron-based catalysts (Fe_{0.0X}SiO₂) in order to improve their catalytic performance. In order to increase the selectivity towards PO, the Fe_{0.0X}SiO₂ solids were impregnated after their synthesis with the nitrate salts of K and Ca to introduce the needed amount of the element. The removal of the small iron oxide particles was determined by different spectroscopy techniques such as UV-Vis, UV-Raman or FTIR. The promoted Fe_{0.0X}SiO₂ catalysts were tested in the propylene epoxidation reaction using O₂ as oxidant (avoiding the use of dangerous and harmful agents such as N₂O) with very promising results in terms of PO selectivity.

2. Experimental

2.1 Catalyst Preparation

2.1.1 Preparation of the $Fe_{0.0x}SiO_2$ Catalysts

Hierarchical Fe-doped silica catalysts were prepared following the synthesis described in [19]. In a typical synthesis, 0.400 g of surfactant (Pluronic® F127, Sigma-Aldrich), 0.452 g of urea (Sigma-Aldrich) and 5.052 g of an acetic acid solution (0.01 M) were mixed under vigorous stirring for 80 min, the final pH of the resulting solution being around 4. Then, the necessary amount of iron precursor (iron (III) nitrate nonahydrate, $(Fe(NO_3)_3 \cdot 9H_2O)$, 99.99%, Sigma-Aldrich) was added in the solution and the mixture was stirred for 1 h. Subsequently, the solution was cooled in an ice-water bath under stirring and the silica precursor was added dropwise (2.030 g Tetramethyl orthosilicate, TMOS, Sigma-Aldrich). This solution was kept under stirring for 40 min at 0°C.

Finally, the sol was introduced in a Teflon autoclave and heated at 40°C for 20 h to produce the aging of the sol (the pH after this step remained around 4). After this, the sample was submitted to a hydrothermal treatment at 120°C for 6 h, to decompose the urea (the final pH of the supernatant liquid being around 9-10). As a final step, the monolith was calcined at 550°C for 6 h under static atmosphere to eliminate the surfactant and the rest of unwanted precursors.

Three samples with different Fe/Si molar ratios were prepared $Fe_{0.005}SiO_2$, $Fe_{0.01}SiO_2$ and $Fe_{0.02}SiO_2$. The samples in this work were named according to the nominal molar Fe/Si ratio in each case, for example, $Fe_{0.01}SiO_2$ corresponds to the sample with 1 mol % Fe in the oxide (with respect to Si moles).

2.1.2 Preparation of the K and Ca-promoted $Fe_{0.0x}SiO_2$ Catalysts

Once the iron-based silica samples were calcined and milled, the samples were impregnated in excess volume using aqueous solutions containing the necessary amount of alkali (KNO_3) and alkaline earth ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) precursors. The stirring was maintained for 2 days, and then, the solvent was evaporated under stirring, heating the suspension at 80°C keeping the magnetic stirring until complete evaporation. Finally, the powder was calcined again in an oven at 550°C for 6 h. The samples are labelled as $\text{K}_{0.01}$, for the sample with a K/Si molar ratio of 0.01, before the $\text{Fe}_{0.0x}\text{SiO}_2$. For comparison purposes, Fe-free K and Ca-treated solids (with a molar ratio of 0.01) were prepared using pure silica and impregnating the alkali and alkaline earth salts as described above. In addition, a $\text{Fe}_{0.005}\text{SiO}_2$ sample was treated with a 1M HCl solution overnight, filtered the solid, washed until neutral pH and then dried at 100°C overnight. After the acidic treatment, a portion of the catalyst was treated with KNO_3 (using the necessary amount for a K molar ratio of 0.01) and calcined as described above.

2.2 Characterization

The catalysts were analyzed by Transmission Electron Microscopy (TEM, JEOL JEM-2010) with a coupled EDX detector. The microscope operates at 200 kV with a space resolution of 0.24 nm. For the TEM analysis, the sample was suspended in ethanol and sonicated for a few minutes. The suspension (one drop) was deposited onto a 300 mesh Lacey copper grid and left to dry at room temperature. This technique allows the observation of the iron particles in the catalysts and the detection of the metal (by EDX) if it is not possible to see the particles. The iron, potassium and calcium loadings were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin–Elmer Optima 4300 system. A few milligrams of the catalyst were dissolved in 0.1 ml of HF (5 vol. %) at room temperature, in order to ensure the total dissolution of the catalyst, and then diluted to the linear element detection range (0.05–10

ppm). The untreated and K and Ca-treated iron based catalysts were also characterized by N₂ adsorption-desorption isotherm at -196°C and by CO₂ adsorption at 0°C (Quantachrome, Autosorb 6B) to analyze the porous texture of this kind of materials.

Some spectroscopic techniques were used to analyze the physicochemical properties of the catalysts after K and Ca modification. UV-Vis analysis (V-670, JASCO) equipped with a double monochromator system, a photomultiplier tube detector and an integrating sphere (ISN-723 UV-Visible-NIR, JASCO) was used in transmittance mode to determine the speciation of the iron. The incorporation of the iron was analyzed by UV-Raman (NRS-5100, Jasco). The catalysts were irradiated for 30 min with a UV laser (HeCd, 325 nm, 1mW). The equipment is fitted with a Thorlabs 20x UV objective. Fourier Transform Infrared Spectroscopy (FTIR-4100, JASCO) was also used. The catalysts were diluted (using 1:50 weight ratio) in KBr and dried at 120°C for 12 h before the analysis. Pyridine adsorption was performed in order to characterize the modification of the surface acidity using a reported procedure [30]. The catalysts, diluted in KBr using the same weight ratio, were calcined at 500°C. Then they were exposed to pyridine vapours for 3 days in a vacuum desiccator. After pyridine adsorption, the physically adsorbed pyridine was removed at 100°C for one day. The FTIR spectra presented are the result of the subtraction of the spectra of the pyridine-treated to the spectra of the untreated catalysts.

2.3 Propylene Epoxidation Tests

The catalysts were tested under steady-state conditions at ambient pressure for at least 4 hours. The standard temperature of the analysis was 350°C, but to obtain reliable catalytic results, in some catalysts it was necessary to increase the temperature up to 400 or 450°C. A WHSV of 10000 ml·g⁻¹·h⁻¹ and a gas composition of 10% C₃H₆, 10% O₂, 80% He was used in the catalytic

tests. The gas composition was analyzed with a GC chromatograph (Agilent 7820A) equipped with two columns, PoraBond Q (Agilent) and CTR-I (Alltech), for the separation of the organic (propylene, propane, propylene oxide, acetaldehyde, acetone) and the inorganic (mainly, O₂ and CO₂) compounds respectively. Propylene conversion, PO yield and PO selectivity were calculated using the following equations and with the respective calibration of each compound in order to describe the catalytic behaviour of the samples.

$$\text{Propylene Conversion (\%)} = \frac{C_{C_3H_6-in} - C_{C_3H_6-out}}{C_{C_3H_6-in}} \times 100$$

$$\text{PO Yield (\%)} = \frac{C_{PO-out}}{C_{C_3H_6-in}} \times 100$$

$$\text{PO Selectivity (\%)} = \frac{C_{PO-out}}{C_{C_3H_6-in} - C_{C_3H_6-out}} \times 100$$

3. Results and discussion

3.1 Characterization of the Catalysts

For all the catalysts prepared in this work, the metal loadings were analyzed by ICP-OES. As in the previous work [19], it was observed that in the one-step preparation of the catalysts, not all the iron can be incorporated into the silica framework. The real Fe/Si molar ratios for the prepared catalysts were 0.0043 (Fe_{0.005}SiO₂), 0.0095 (Fe_{0.01}SiO₂), and 0.0186 (Fe_{0.02}SiO₂). From our observations, approximately 7% of the iron was removed in the supernatant liquid at the end of the sol-gel process. On the contrary and due to the methodology employed for their addition, the real loadings for K and Ca calculated by ICP-OES were in all cases quite close to the desired nominal loadings.

TEM coupled with EDX characterization of the representative catalysts is presented in the Supplementary Information. From the TEM micrographs it is possible to see that no large iron oxide clusters/agglomerations are formed in most samples. Only for some samples in which the alkali loading is lower than that of Fe ($\text{K}_{0.005}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.005}\text{Fe}_{0.02}\text{SiO}_2$) some small particles can be observed. Despite the fact that it is not possible to see the possible K, Ca or Fe oxide species on the silica surface, the EDX analysis confirmed, in all cases, the presence of these elements. From the textural characterization of the samples (see Fig. S1 and Table S1 in the Supplementary Information) it is not possible to observe any significant modification in the N_2 isotherm shape or the textural properties (i.e., specific surface area, micropore volume or pore size distribution) after the treatment of the Fe-SiO₂ samples with K or Ca.

The spectroscopic techniques, such as UV-Vis, UV-Raman, and FTIR, are very useful to analyze the iron speciation in this kind of materials. Studying the UV-Vis absorption of the solid catalysts it is possible to determine the presence of iron incorporated into the silica framework and the existence of small particles of iron oxide deposited on the surface of the silica. In this sense, previous works reported the absorption of the incorporated iron in tetrahedral or pseudo-tetrahedral position into the silica framework in two bands located at around 220 and 260 nm (45000 and 38000 cm^{-1} , respectively). While the iron oxide particles present UV-Vis absorption near the 370 and 500 nm range (27000 and 20000 cm^{-1} , respectively). This effect allows the interpretation of the band gap energy (E_g) as a measure of the iron dispersion in this kind of materials [29,31]. It is very important to remark that some works attribute the absorption at around 280 nm to the octahedral coordinated Fe(III) species in this kind of materials [32–34]. The UV-Vis results (and each corresponding E_g values) of the K and Ca-promoted Fe-SiO₂ catalysts are presented in Fig. 1.

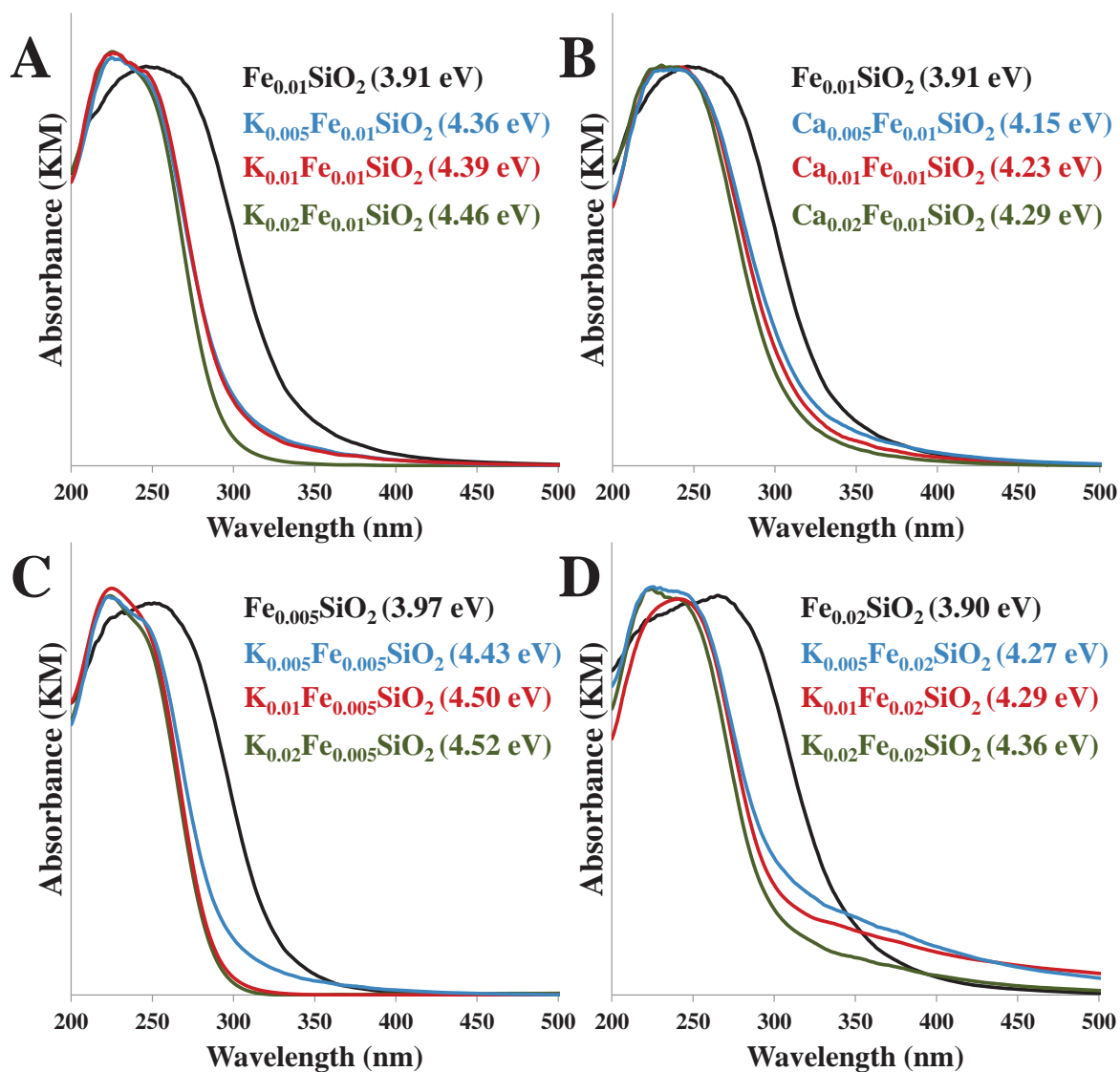


Fig. 1. Solid UV-Vis reflectance spectra (presented in Kubelka-Munk units) and their respective E_g value for the raw and post-K or Ca impregnation of the $\text{Fe}_{0.0x}\text{SiO}_2$ catalyst.

A) $\text{K}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, **B)** $\text{Ca}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, **C)** $\text{K}_{0.0x}\text{Fe}_{0.005}\text{SiO}_2$ and **D)** $\text{K}_{0.0x}\text{Fe}_{0.02}\text{SiO}_2$.

In order to select the appropriate promoter (K or Ca) which can yield a better removal of the iron particles and dispersion of the iron species, the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst was impregnated with the

3 different K or Ca/Si ratios (0.005, 0.01 and 0.02) and analyzed by UV-Vis reflectance (results presented in Fig. 1A and 1B). For the K-based catalysts, a substantial decrease in absorbance is observed for wavelengths above 300 nm. This can be associated to the removal of the iron oxide particles deposited on the silica surface. The total elimination of the iron oxide particles is reached for all samples in which the K content exceeded that of Fe. On the other hand, a reduction in the absorbance of the UV-Vis spectra near 280 nm after the addition of the alkali or alkaline earth based salts is also observed. This fact can be related to the removal of the small iron oxide clusters and/or extraction of the octahedrally coordinated iron species by the K treatment. These effects are observed also in the progressive increase of the E_g values obtained from the UV-Vis spectra, from the initial 3.91 eV for the raw $Fe_{0.01}SiO_2$ to the final 4.46 eV for the $K_{0.02}Fe_{0.01}SiO_2$ catalyst. In the case of Ca-based catalysts, the same trend is observed but it is not possible to remove all the particles of iron oxide produced during the synthesis of the material. All the samples, even the $Ca_{0.02}Fe_{0.01}SiO_2$, present a small but significant absorption at wavelengths higher than 300 nm and the increase of the E_g values is lower in the Ca samples than their K-based counterparts. The differences (in UV-Vis characterization) between the K and Ca-doped samples, when the small iron oxide particles and octahedral iron species removal is studied, allows us to confirm that for this kind of samples impregnation with K has a higher efficiency in reducing the number of iron oxide particles, as other authors have observed previously [27–29]. For this reason, the impregnation of the $Fe_{0.005}SiO_2$ and $Fe_{0.02}SiO_2$ samples was only studied with K.

The UV-Vis results of the K-impregnated catalysts in the $Fe_{0.005}SiO_2$ and $Fe_{0.02}SiO_2$ materials are presented in Fig. 1C and 1D, respectively. As it was previously studied, for all the raw catalysts, the amount of small iron oxide particles/clusters in extra-framework positions increases

with the Fe loading of the samples [19]. A progressive reduction in the absorption for the $K_{0.0x}Fe_{0.005}SiO_2$ series at 280 nm and above 300 nm (corresponding to the aforementioned species) is observed as the K content is increased in the catalysts. In the $K_{0.02}Fe_{0.01}SiO_2$ catalyst, when the K content is higher than the Fe molar content in the silica based catalysts (as with samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$), an almost total quenching of the absorption at wavelengths above 300 nm is observed, demonstrating the total removal of the iron oxide particles formed in the raw catalysts synthesis. The removal of the iron oxide particles produces the increase of the band gap energy up to 4.50 and 4.52 eV in the case of samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$, respectively. Finally, in the catalysts prepared with the highest iron content ($Fe_{0.02}SiO_2$) the addition of K has a different result, as it is possible to check in Fig. 1D. Even with the increase of the E_g up to 4.36 eV for the sample $K_{0.02}Fe_{0.02}SiO_2$ mainly due to the reduction in the absorption band located at 280 nm, there is a slight increase of the UV-Vis absorption in the 300-400 nm range. It is possible that the amount of iron oxide particles is too high for the K to remove all of them. All these UV-Vis results are corroborated by the colour of the catalysts and by the TEM micrographs presented in the SI. As K or Ca loading increases in the catalysts, the initial colour of the Fe-SiO₂ (slightly brown for $Fe_{0.01}SiO_2$ and $Fe_{0.02}SiO_2$) gradually disappears until total decolouration of the catalysts for all the $Fe_{0.005}SiO_2$ samples and the $K_{0.02}Fe_{0.01}SiO_2$.

Another complementary technique that can be used to analyze the structural modifications produced by the K and Ca addition is UV-Raman spectroscopy. The results of the prepared catalysts together with the blank silica and the K- and Ca-impregnated silica are shown in Fig. 2. Different regions of the spectra can be clearly distinguished depending on the species involved. The symmetric Si-O-Si stretching appears at 485 cm^{-1} for pure silica [35]. Close to this band, a

broad shoulder appears from 500 to 650 cm^{-1} , which we previously identified in bulk Fe_2O_3 and appears as a broad shoulder in samples $\text{Fe}_{0.01}\text{SiO}_2$ and $\text{Fe}_{0.02}\text{SiO}_2$ [19]. As it was previously reported, in the 800 cm^{-1} region for the pure SiO_2 sample it is possible to observe a low-intensity band that can be attributed to the vibration mode of siloxane linkage [25] or to the presence of defects [27]. In the 950-1150 cm^{-1} range three characteristic bands are observed in the SiO_2 and Fe-SiO_2 samples corresponding to different vibrations; 990 (Si-O-Si near iron species or other defect sites such as silanol groups) [25,27,35], 1080 (1016 cm^{-1} in [35], 1025 cm^{-1} in [36], 1074 cm^{-1} in [27] and 1090 cm^{-1} in [25]) and 1135 cm^{-1} (1115 cm^{-1} in [35], 1138 cm^{-1} in [27] and 1150 cm^{-1} in [36], not presented in ref. [25] maybe due to the use of a 244 nm laser irradiation), corresponding to vibrations of O_3SiO^- units with a very strong interaction with heteroatoms such as Fe-O-Si when the Fe is well-dispersed in isolated tetrahedral or pseudotetrahedral iron into the silica framework [19,25–27,36].

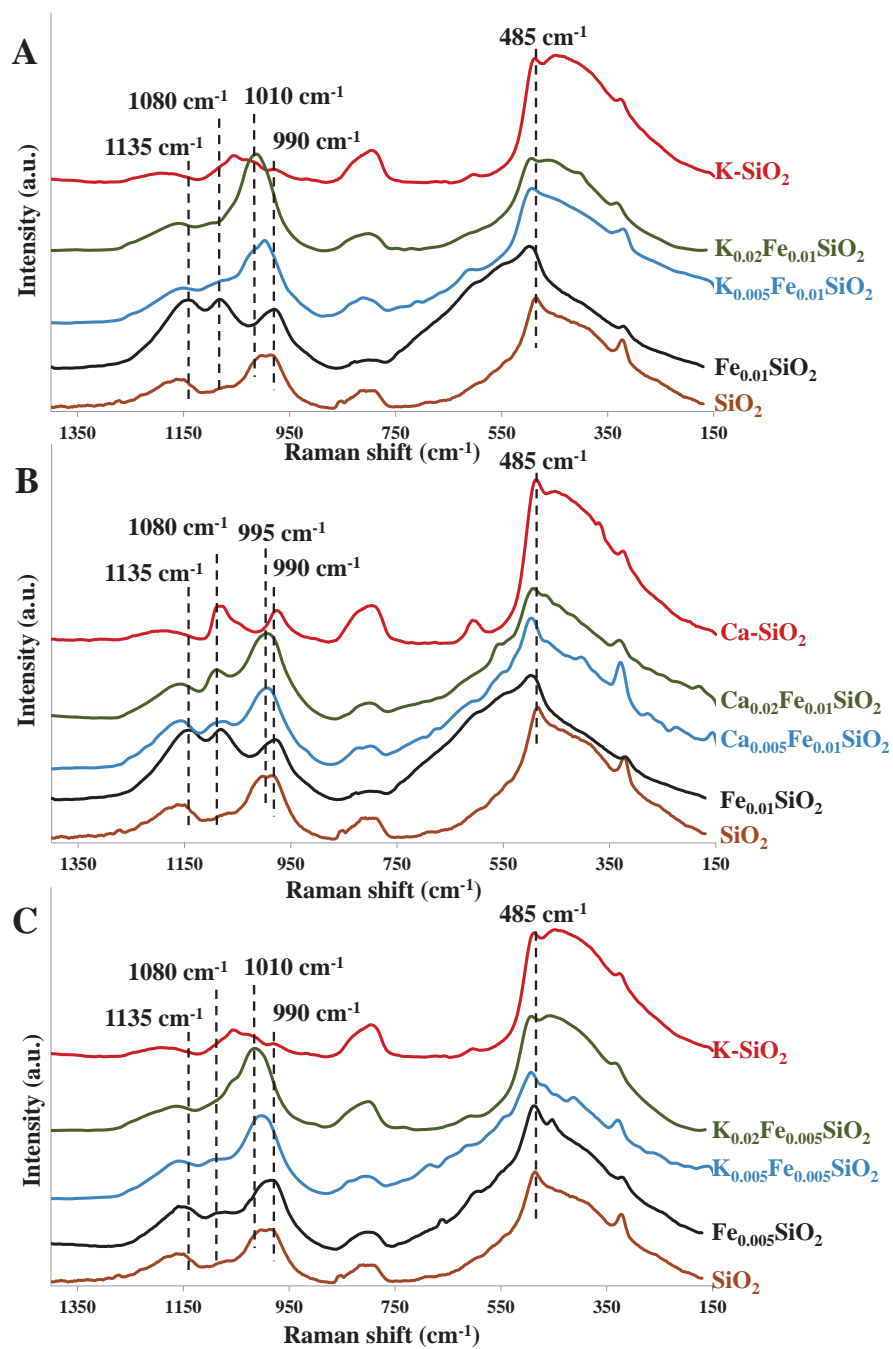


Fig. 2. Normalized UV-Raman analysis of representative catalysts prepared in this work.

A) $K_{0.0x}Fe_{0.01}SiO_2$, B) $Ca_{0.0x}Fe_{0.01}SiO_2$ and C) $K_{0.0x}Fe_{0.005}SiO_2$ series compared with the pure SiO₂ and its respective K or Ca-SiO₂ excited with a UV laser of 325 nm.

In all the studied series presented in Fig. 2, deposition of the K or Ca salt on the Fe-SiO₂ solids does not produce any important change in the band located at 485 cm⁻¹ corresponding to the symmetric Si-O-Si stretching. This band is slightly shifted to higher wavenumbers due to the incorporation of iron into the silica framework [19,35] and is not affected by the deposition of the K and Ca oxides on the silica (K-SiO₂ and Ca-SiO₂) indicating that post-impregnation does not produce modifications in the silica framework and the oxides are only deposited on the silica surface. Important changes in the UV-Raman spectra are observed after the modification of the iron-based catalysts. In the raw Fe_{0.01}SiO₂, a shoulder is observed from 500 to 650 cm⁻¹ (Fig. 2A and 2B) which is not observed for the SiO₂ and K or Ca-treated materials. As the K or Ca loading increases, this band reduces its intensity down to values similar to the pure silica solid. It is possible to assign this shoulder to the small iron oxide clusters/particles or iron in octahedral coordination in the original Fe-SiO₂ materials which are dispersed and removed after K or Ca impregnation [27–29].

In the 800 cm⁻¹ region, a weak signal is observed for the pure silica and the raw Fe-SiO₂ samples. However, when the K or Ca oxides are loaded on the silica surface the band becomes more intense and its shape is modified. The same band is obtained for the samples with the highest K loading (0.02), especially for the Fe_{0.005}SiO₂ sample. This fact might be due to the excess potassium used in the impregnation producing potassium oxide (as observed for the K-SiO₂ sample). This was also observed for the Ca-containing sample.

The assignation of each band within the 990-1135 cm⁻¹ region might be done with existing literature. The band at 1165 cm⁻¹ has been assigned to the crystalline environment of the iron species in Fe-ZSM-5 samples [35,37]. In our case, given the amorphous nature of our sample, this assignment is not straightforward. When K or Ca are loaded on the Fe-SiO₂, a decrease in

intensity is observed for the 1080 and 1135 cm^{-1} bands (see Fig. 2) together with the appearance of a band located at 1000 cm^{-1} (1010 cm^{-1} for the $\text{K}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$ and 995 cm^{-1} for the $\text{Ca}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$). This new band was previously studied by Wang et al. [26,27] and could correspond to a tetrahedrally coordinated iron oxide “surrounded and stabilized by K^+ or Na^+ ” (K^+ or Ca^{2+} in this study) species. These K- or Ca-Fe species (such as ferrates [22,23]) can be formed during the calcination step after impregnation of the K or Ca salt, produced by its reactivity with the small particles/clusters of iron oxide on the silica surface. This hypothesis is also supported by the results showed in the UV-Vis analysis, where there was a reduction of the absorption corresponding to the small particles/clusters of iron oxide. The formation of these superficial species (K- and Ca-Fe species) with the well-dispersed iron into the silica framework, which occupies pseudotetrahedral positions cannot be ruled out in this respect. It is possible that the iron could migrate to extra-framework positions or could be covered (as was proposed by Horváth et al. [20]) by the alkali or alkaline earth oxide producing the decrease of its related bands at 1080 and 1135 cm^{-1} .

In order to determine the possible contribution of the K and Ca addition to other physicochemical properties of the materials, the normalized FTIR spectra of all the solids were analyzed and presented in Fig. 3.

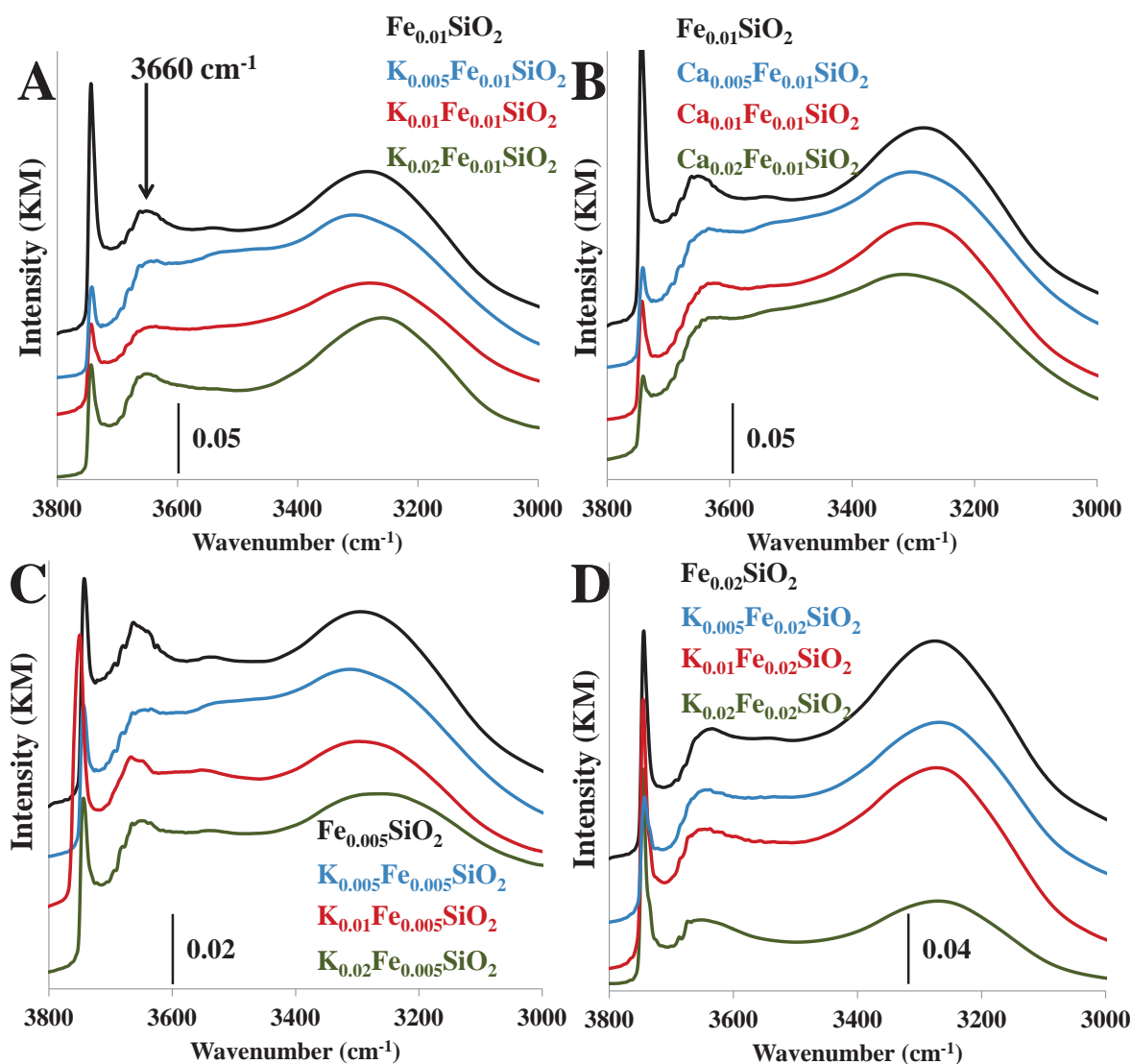


Fig. 3. Normalized FTIR spectra of the OH region (presented in Kubelka-Munk units) for all the catalysts prepared in this work. A) $\text{K}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, B) $\text{Ca}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, C) $\text{K}_{0.0x}\text{Fe}_{0.005}\text{SiO}_2$ and D) $\text{K}_{0.0x}\text{Fe}_{0.02}\text{SiO}_2$.

In Fig. 3 it is possible to compare the normalized (with respect to the most intense band at 1090 cm^{-1} , corresponding to the Si-O stretching) characteristic vibrations of the superficial OH

groups of this kind of materials. No significant modification of the fundamental framework vibration modes of the Fe-SiO₂ solids (810, 1000-1300 cm⁻¹) [19,36,38] is observed after the impregnation and calcination of the K or Ca-based salts. This fact reveals that the impregnation of the K or Ca nitrates only produces superficial modifications without affecting the Fe_{0.0x}-SiO₂ framework as it is previously discussed by UV-Raman spectroscopy. On the other hand, a significant modification in the OH vibration range occurs (Fig. 3) due to the K or Ca impregnation on the silica surface. When K or Ca are added with the lowest amounts (i.e., M_{0.005}Fe_{0.0x}SiO₂), there is a reduction in the intensity of the band corresponding to the bridged hydroxyls with Brønsted acid character (located at 3660 cm⁻¹) [36,39]. From our observations this reduction is not proportional to the K or Ca loading. This effect is also demonstrated by the normalized FTIR spectra corresponding to pyridine adsorption presented in Fig. S2 (See Supplementary Information). By this analysis it is possible to observe a proportional decrease in the intensity of the bands corresponding to adsorbed pyridine at 1446 and 1596 cm⁻¹ [40] as the K molar ratio increases (for the Fe_{0.005}SiO₂ catalyst) or when the K or Ca are added on the Fe_{0.001}SiO₂. In this sense, the addition of ions with a strong basic character on the silica surface reduces the amount of acid sites in the solid due to their exchange with the acidic proton neighbour to the iron atom. This fact could be beneficial for the epoxidation reaction due to the acidity reduction of the support. It is also possible to propose the blocking/covering of some iron sites of the silica framework due to the K or Ca oxide formation on the silica surface.

In this respect, the impregnation and calcination of the K or Ca salts produces the corresponding oxides deposited on the silica surface. For low loadings, the K or Ca ions interact with the acidic proton reducing its signal in all the catalysts (M_{0.005}Fe_{0.0x}SiO₂). Then, as the K or Ca loading increases, removal of the small clusters/particles (lower than 1 nm) takes place in the

Fe-SiO₂ samples, as observed by UV-Vis analysis [27–29]. This removal reduces the amount of the small iron oxide clusters/particles (responsible for the total oxidation of propylene) [20]. As it is mentioned above, this alkali or alkaline earth oxide can also cover the highly dispersed iron into the silica framework (which is the main species responsible for the propylene epoxidation reaction [19]).

As it is discussed in the spectroscopic techniques section, the addition of small amounts of K or Ca is a simple and useful way to reduce the amount or to remove the undesired iron oxide particles/clusters formed during the synthesis of the catalysts. However, this modification can also produce other different effects, like reducing the amount of bridged hydroxyls with Brønsted acid character located near the iron atom or blocking iron active sites, which is very interesting for this reaction due to their respective interaction with gaseous propylene or dioxygen in the propylene epoxidation reaction.

3.2 Propylene Epoxidation Reaction

The samples were tested under isothermal conditions (at 350, 400 or 450°C depending on the activity of the sample to ensure a significant value of propylene conversion) during at least 4 hours. However, the catalytic tests performed at 450°C for the Fe_{0.005}SiO₂ and Fe_{0.01}SiO₂ resulted in a fast deactivation of the catalysts due to carbon deposition on the surface. This effect was also observed in the Fe_{0.02}SiO₂ sample at 400°C. In all catalytic tests, except for those just mentioned, propylene conversion, PO yield, and PO selectivity remained constant during the reaction, and the values presented in this section correspond to the steady-state conditions. Analyzing all reaction products, it was possible to find out that the main by-product formed was CO₂, but in

some samples, acetaldehyde was also produced to a small extent (<1%). The results are shown in

Table 1.

Table 1
Catalytic performance of the samples prepared in propylene epoxidation by O₂ molecule under steady-state conditions

Catalyst	Temperature (°C)	C ₃ H ₆ Conversion (%)	PO Yield (%)	Selectivity (%)		
				PO	Others ^a	CO ₂
Fe _{0.01} SiO ₂	350	7.8	1.9	24.6	< 0.5	~75
	400	21.6	4.4	20.4	< 1.0	~78
K _{0.005} Fe _{0.01} SiO ₂	350	4.0	1.1	26.0	< 0.5	~74
K _{0.01} Fe _{0.01} SiO ₂	350	3.4	0.9	27.5	< 0.5	~72
K _{0.02} Fe _{0.01} SiO ₂	400	1.7	1.1	62.4	< 0.5	~37
Ca _{0.005} Fe _{0.01} SiO ₂	350	3.2	0.9	27.6	< 0.5	~72
Ca _{0.01} Fe _{0.01} SiO ₂	350	1.7	0.8	51.4	< 0.5	~48
Ca _{0.02} Fe _{0.01} SiO ₂	350	1.5	0.8	53.3	< 0.5	~46
Fe _{0.005} SiO ₂	350	5.5	1.8	33.6	< 0.5	~66
	400	19.1	5.1	26.7	< 1.0	~72
K _{0.005} Fe _{0.005} SiO ₂	350	2.0	0.6	33.8	< 0.5	~66
K _{0.01} Fe _{0.005} SiO ₂	450	2.2	1.3	58.8	< 0.5	~41
K _{0.02} Fe _{0.005} SiO ₂	450	1.4	0.9	65.5	< 0.5	~34
Fe _{0.02} SiO ₂	350	10.3	2.4	23.1	< 1.0	~76
K _{0.005} Fe _{0.02} SiO ₂	350	4.9	1.3	25.7	< 0.5	~74
K _{0.01} Fe _{0.02} SiO ₂	350	2.5	0.8	31.5	< 0.5	~68
K _{0.02} Fe _{0.02} SiO ₂	400	8.5	2.3	27.2	< 1.0	~63

^a Acetaldehyde is the main organic by-product obtained in the catalytic reaction.

The addition of the small amounts (only 0.005 molar ratios) of promoters (K or Ca) produces in the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst the decrease of the propylene conversion down to half of its initial activity. However, the PO yield is also halved since no significant modification of the PO selectivity is produced. Analyzing the addition of a larger amount of K on the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst it is possible to assess how the incorporation of an equimolar ratio of K/Fe ($\text{K}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$) produces a further reduction of both C_3H_6 conversion and PO yield also corresponding to a similar PO selectivity compared to the $\text{Fe}_{0.01}\text{SiO}_2$ sample. Nonetheless, when the K ratio is twice with respect to the Fe amount ($\text{K}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$) the C_3H_6 conversion is too low at 350°C and a temperature increase to 400°C is mandatory to obtain a significant conversion/yield value. At this new temperature, the C_3H_6 conversion is the lowest of this catalyst series (1.7%) but the PO yield is not reduced compared with the $\text{K}_{0.005}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$ catalysts. This results in a drastic increase of the PO selectivity from 24.6-27.5% to 62.4%. The catalytic activity corresponding to the non-promoted $\text{Fe}_{0.01}\text{SiO}_2$ at 400°C shows a quite high propylene conversion (21.6%) and very low PO selectivity (20.4%). In this sense, the addition of 0.02 molar ratio of K allows to control the propylene combustion at 400°C and to increase the PO selectivity.

On the other hand, in the Ca-promoted $\text{Fe}_{0.01}\text{SiO}_2$ series a different behaviour is observed when the Ca amount increases. The addition of 0.005 Ca/Si molar ratio produces the reduction of the propylene conversion and PO yield, more than half in both cases without any significant modification in the PO selectivity. However, when the Ca amount increases up to 0.01 and 0.02 ($\text{Ca}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{Ca}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$, respectively) a similar value of the C_3H_6 conversion and PO yield is observed (1.6% and 0.8%, respectively) obtaining PO selectivities around 52% without requiring a temperature increase. Analyzing the catalytic results of the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst

promoted with K or Ca it can be concluded that K-promotion produces higher selectivities towards PO despite of the higher temperatures required to reach significant propylene conversions.

For the $\text{Fe}_{0.005}\text{SiO}_2$ catalyst, the addition of the equimolar K/Fe ratio ($\text{K}_{0.005}\text{Fe}_{0.005}\text{SiO}_2$) produces the lessening of the C_3H_6 conversion and PO yield to 2.0% and 0.6%, respectively, with respect to the unpromoted catalysts. When the amount of potassium added after the synthesis of the $\text{Fe}_{0.005}\text{SiO}_2$ increases up to 0.01 and 0.02 ($\text{K}_{0.01}\text{Fe}_{0.005}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$, respectively) it is necessary to increase the reaction temperature up to 450°C to obtain significant conversion values. The temperature increase compensates the reduction in C_3H_6 conversion (which is not measurable at 350°C), obtaining values around 2.2 and 1.4% for the $\text{K}_{0.01}\text{Fe}_{0.005}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$ samples, respectively. In addition, the PO yield obtained in these catalytic tests is remarkably higher, reaching PO selectivities between 58.8% and 65.5% (under the same conditions, the unpromoted $\text{Fe}_{0.005}\text{SiO}_2$ catalyst gave 19.1% and 26.7% for propylene conversion and PO selectivity, respectively).

The catalysts prepared with the $\text{Fe}_{0.02}\text{SiO}_2$ sample present a different catalytic behaviour (in terms of PO selectivity) compared with the lower iron content. As it is possible to see in Table 1, as the K loading increases, the propylene conversion decreases to 2.5% for the $\text{K}_{0.01}\text{Fe}_{0.02}\text{SiO}_2$ catalyst with only a slight increase of the PO selectivity (31.5%). However, when the temperature reaction is increased at 400°C for the $\text{K}_{0.02}\text{Fe}_{0.02}\text{SiO}_2$ catalyst the propylene conversion increases up to 8.5%, diminishing the selectivity towards PO (27.2%).

Another important aspect that must be taken into account is the aforementioned carbon deposit produced during the reaction due to the propylene cracking on the catalysts surface. For the

catalysts without K or Ca, a small fraction of carbon deposit is observed after the reaction (less than a 3 wt. % determined by thermogravimetry). However, when K or Ca is added to the Fe-SiO₂ no carbonaceous deposit is obtained after the epoxidation reaction. Only for the K_{0.005}Fe_{0.02}SiO₂ and Ca_{0.005}Fe_{0.01}SiO₂ catalysts a slight deposit of carbon material is observed that results in a slight darkening of the materials. In this sense, the role of the alkali or alkaline earth promotion is very important because it allows to control the reactivity, decreasing the propylene conversion and its combustion and avoiding propylene cracking (and subsequent carbonaceous deposit) on the catalysts.

On the other hand, the catalysts prepared following the HCl treatment in order to remove the iron oxide particles present a different catalytic behaviour for the propylene epoxidation reaction. It must be previously mentioned that the HCl treatment (Fe_{0.005}SiO₂-HCl) was not enough for the complete elimination of the iron oxide particles (see Fig. S3 in Supplementary Information) but removes a significant portion of them. After the acidic treatment, the results from the propylene epoxidation reaction at 450°C (lower temperatures did not yield reliable results) for the Fe_{0.005}SiO₂-HCl catalyst were: 5.8% of propylene conversion, 2% of PO yield and a PO selectivity of 34.5% (with a 6 wt. % of carbonaceous deposit). These results mean that a large portion of the iron oxide particles were removed (compared with the 19.1% of propylene conversion for the raw Fe_{0.005}SiO₂) but there is no significant increase in the PO selectivity. Moreover, the high amount of carbonaceous deposit on the catalysts surface could be attributed to the acidity of the surface which favours propylene reactivity and cracking. For this reason, the propylene conversion of this sample is higher than the K-promoted Fe_{0.005}SiO₂. This catalyst was also treated with K (with a K molar ratio of 0.01) for its comparison with the K-promoted without the acidic treatment. As revealed by the UV-Vis analysis of the solid in Fig. S3, the

absorbance of this catalyst is quite similar to those obtained for the $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ without the HCl treatment. The resulting KNO_3 -treated catalyst presents a propylene conversion and a PO yield of 3.3 and 1.5%, respectively with a PO selectivity of 45%. However, no significant carbonaceous deposit is evidenced after the epoxidation reaction at 450°C. In this sense, it must be mentioned that it was not possible to achieve the selectivities of the $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ catalysts but the propylene conversion and PO yield were not so low.

The selectivities towards PO obtained for the $K_{0.02}Fe_{0.01}SiO_2$, $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ catalysts at 400 or 450°C presented in Table 1 (reaching values over 60%) are higher, but lower in propylene conversion (4-5%), than other promoted catalysts tested using O_2 as oxidant and based on transition metals such as Ag, Cu and/or Ru [11,22,41,42] and similar to other alkali promoted Cu [14,43] or Ag and Mo [44] catalysts.

Comparing the catalytic performance of our samples with similar catalysts (alkali or alkaline earth promoted iron based silica) reported in other studies, similar [26,27,29,45] or slightly lower [20,34] PO selectivities were obtained with similar values of propylene conversion in these cases. However, in these works the use of nitrous oxide was mandatory to produce the epoxidation of the propylene. In this sense, the replacement of nitrous oxide by molecular oxygen implies user-friendly reaction conditions.

According to the catalytic results and the characterization obtained for all the K- or Ca-promoted catalysts prepared in this work it is possible to propose which are the main changes produced by K or Ca in the iron species of the catalysts (Scheme 1). For the lowest K and Ca loadings, an important aspect that must be taken into account is the reduction in the PO yield but

with similar PO selectivities. As it was previously studied, the well-dispersed iron species incorporated into the silica framework (interacting with the molecular O₂) along with a neighbour acidic proton (interacting with gaseous propylene) are the main responsible species of the propylene epoxidation reaction in this kind of catalysts [19]. So the addition of this kind of promoters, even in the 0.005 molar ratios, is producing some changes in the well-dispersed iron species that diminishes the PO production. This catalytic behaviour can be explained through the FTIR and UV-Raman results. As the FTIR results shown, the addition of K or Ca modifies the surface properties of the silica. A significant reduction in the amount of acidic protons with Brønsted character located at 3660 cm⁻¹ is observed after the addition of the smallest K or Ca molar ratio. In this sense, its intensity decrease could be due to the substitution of the acidic proton by the K or Ca species during the thermal treatment after impregnation. This observation together with the PO yield decrease (see Table 1) suggests that there is a reduction of the number of sites that can interact with the propylene towards the epoxidation reaction. However, for these catalysts (with low K or Ca loadings) it is not possible to confirm the complete removal of the small iron oxide particles by either UV-Vis or UV-Raman (due to the formation of stabilized K- or Ca-Fe species). These particles are responsible for the total combustion of the propylene. From our observations, a graphical depiction of these catalysts is presented in Scheme 1 (upper right-hand side), where the number of acidic sites is reduced. The substitution of the acidic Brønsted proton by K or Ca oxide also produces a significant decrease of the propylene cracking on the catalyst surface thus resulting in lower carbon deposition during the epoxidation experiments.

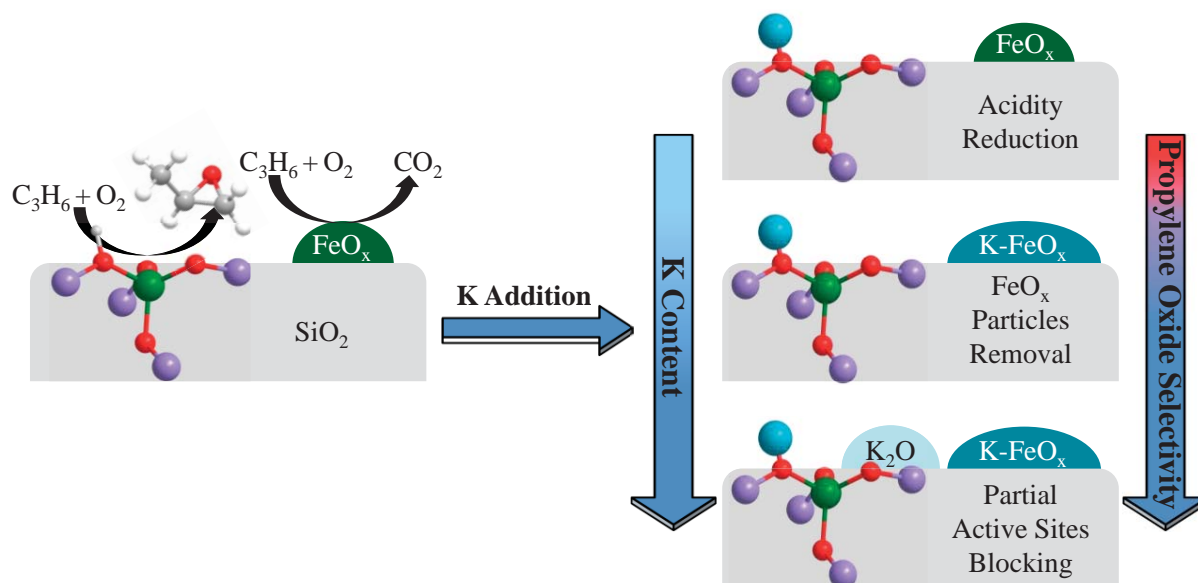
On the other hand, when the K or Ca loading increases different interactions can be produced on the Fe-SiO₂ surface. The picture in the middle right-hand side of Scheme 1 shows how as the

K content is increased K-Fe species are formed in addition to the substitution of the protons in the bridged hydroxyls with Brønsted acid character by K species. As it is commented by the UV-Vis characterization, the addition of the K precursor produces the dispersion of the iron oxide particles and the octahedral coordinated iron species. This fact is also supported by UV-Raman analysis, by the emergence of the band at 1010 cm^{-1} assigned to tetrahedrally coordinated iron oxide surrounded and stabilized by K^+ . In this sense, the reduction of the small particles/clusters of iron oxide determined by UV-Vis and TEM (which are the main responsible species for the total oxidation of the propylene towards CO_2) reduces the propylene conversion of the catalysts. Due to the fact that propylene epoxidation mainly occurs on the well-dispersed iron incorporated into the silica structure, the iron oxide particles removal produces an increase of the PO selectivity as a beneficial side effect. This behaviour is obtained for all the catalysts, where the propylene conversion progressively decreases when small loadings of K or Ca species are added. However, in order to achieve the complete elimination of the iron oxide particles, a higher amount of K (higher than the nominal Fe loading) is required. This is observed for samples $\text{Fe}_{0.005}\text{SiO}_2$ ($\text{K}_{0.01}$ and $\text{K}_{0.02}$) and $\text{Fe}_{0.01}\text{SiO}_2$ (only for the $\text{K}_{0.02}$ catalyst) which show similar E_g values around 4.50 eV. Using this kind of samples the propylene conversion and the PO selectivities are around 1.5% and 60%, respectively at their corresponding reaction temperature (see Table 1). The addition of Ca as a promoter does not produce the same efficiency (for the same promoter molar ratios) in removing the iron oxide particles (as confirmed by UV-Vis) despite the reaction temperature being 350°C in all cases. On the other hand, for the sample with the highest amount of iron oxide particles ($\text{Fe}_{0.02}\text{SiO}_2$), it has not been possible to remove all the iron clusters with the tested alkali molar ratio. By this way, the catalytic results obtained for this

sample show how the propylene conversion (up to 8.5% when the temperature is increased) is not as affected as in the other series.

Thus, the addition of promoters (such as K or Ca) reduces the number of small iron oxide particles due to the formation of K- or Ca-Fe species during the calcination step after the nitrate impregnation. When the K molar ratio is higher than that of Fe ($K_{0.02}Fe_{0.01}SiO_2$, $K_{0.01}Fe_{0.005}SiO_2$, and $K_{0.02}Fe_{0.005}SiO_2$) the complete elimination of the iron oxide particles is possible. Under these conditions very promising PO selectivities (higher than 60%) by the oxidation of propylene with O_2 are obtained.

Finally, another undesirable scenario which cannot be ruled out when the promoter molar ratio is increased is that suggested by Horváth et al. [20] where there is a masking of the iron species due to its covering by K or Ca oxide (lower right-hand side in Scheme 1). The excess of alkali or alkaline-earth oxides or the formation of K- or Ca-Fe species on the catalysts surface could block the accessibility of the reactants to the active sites of the catalysts decreasing the catalytic behaviour of the materials. This effect is confirmed by the reduction in propylene conversion and PO yield between samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ measured at 450°C.



Scheme 1. Possible interpretation of the K effects on the Fe-SiO₂ surface and its influence on the PO selectivity.

4. Conclusions

Fe-SiO₂ catalysts modified with small loadings of K or Ca salts by impregnation methodology have been prepared and tested in the propylene epoxidation reaction in gas-phase using O₂ as oxidant. The addition of the promoters led to physicochemical changes of the surface of the iron-based catalysts, such as: the complete elimination of the small particles/clusters of iron oxide generated during the synthesis of the materials via the formation of superficial K- or Ca-Fe species, the substitution of the hydroxyls with Brønsted acid character by K or Ca species and the partial iron sites blocking. These modifications produced by the K or Ca incorporation are also reflected in the catalytic behaviour for the epoxidation of propylene. As a first consequence, the propylene conversion (towards CO₂) is drastically reduced due to elimination of the small

iron oxide particles. Furthermore, the acidity reduction and the blocking of the catalysts produce a reduction in the PO yield and avoids the cracking of propylene on the catalyst surface. As a result of these processes, a very promising PO selectivity (65.5%) is obtained using small loadings of Fe and K, and O₂ as oxidant without the production of many organic byproducts.

Author information

Corresponding Author

*E-mail: a.berenguer@ua.es (Ángel Berenguer-Murcia)

Acknowledgments

We thank the Spanish Ministry of Economy and Competitiveness (MINECO), Generalitat Valenciana and FEDER (CTQ2015-66080-R MINECO/FEDER and PROMETEOII/2014/010) for financial support. J.G.A. thanks the Spanish Ministry of Economy and Competitiveness (MINECO) for his fellowship (BES-2013-063678).

References

- [1] D. Kahlich, U. Wiechern, J. Lindner, *Ullmann's Encycl. Ind. Chem.* (2012) 313–335.
- [2] D. Trent, *Kirk-Othmer Encycl. Chem. Technol.* (2001) 1–26.
- [3] S.J. Khatib, S.T. Oyama, *Catal. Rev.* 57 (2015) 306–344.
- [4] K. Singh, K. Merchant, in: *Handb. Ind. Chem. Biotechnol.*, 2012, pp. 643–698.
- [5] S. Kanungo, D.M. Perez Ferrandez, F. Neira d'Angelo, J.C. Schouten, T.A. Nijhuis, *J. Catal.* 338 (2016) 284–294.
- [6] X. Feng, X. Duan, H. Cheng, G. Qian, D. Chen, W. Yuan, X. Zhou, *J. Catal.* 325 (2015) 128–135.
- [7] X.-Y. Chen, S. Chen, A. Jia, J. Lu, W. Huang, *Appl. Surf. Sci.* 393 (2017) 11–22.

- [8] A. Prieto, M. Palomino, U. Díaz, A. Corma, *Appl. Catal. A Gen.* 523 (2016) 73–84.
- [9] J. Chen, E.A. Pidko, V. V. Ordonsky, T. Verhoeven, E.J.M. Hensen, J.C. Schouten, T.A. Nijhuis, *Catal. Sci. Technol.* 3 (2013) 3042–3055.
- [10] D.O. Atmaca, D. Düzenli, M.O. Ozbek, I. Onal, *Appl. Surf. Sci.* 385 (2016) 99–105.
- [11] P. Phon-in, A. Seubsai, T. Chukeaw, K. Charoen, W. Donphai, P. Prapainainar, M. Chareonpanich, D. Noon, B. Zohour, S. Senkan, *Catal. Commun.* 86 (2016) 143–147.
- [12] S. Ghosh, S.S. Acharyya, R. Tiwari, B. Sarkar, R.K. Singha, C. Pendem, T. Sasaki, R. Bal, *ACS Catal.* 4 (2014) 2169–2174.
- [13] Q. Hua, T. Cao, X.-K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W.-X. Li, W. Huang, *Angew. Chem.*, 53 (2014) 4856–61.
- [14] J. He, Q. Zhai, Q. Zhang, W. Deng, Y. Wang, *J. Catal.* 299 (2013) 53–66.
- [15] W. Long, Q. Zhai, J. He, Q. Zhang, W. Deng, Y. Wang, *Chempluschem* 77 (2012) 27–30.
- [16] Q. Zhang, G. Chai, Y. Guo, W. Zhan, Y. Guo, L. Wang, Y. Wang, G. Lu, *J. Mol. Catal. A Chem.* 424 (2016) 65–76.
- [17] G. Jin, G. Lu, Y. Guo, Y. Guo, J. Wang, X. Liu, *Catal. Today* 93–95 (2004) 173–182.
- [18] X. Zheng, Q. Zhang, Y. Guo, W. Zhan, Y. Guo, Y. Wang, G. Lu, *J. Mol. Catal. A Chem.* 357 (2012) 106–111.
- [19] J. García-Aguilar, I. Miguel-García, J. Juan-Juan, I. Such-Basáñez, E. San Fabián, D. Cazorla-Amorós, Á. Berenguer-Murcia, *J. Catal.* 338 (2016) 154–167.
- [20] B. Horváth, M. Šustek, I. Vávra, M. Mičušík, M. Gál, M. Hronec, *Catal. Sci. Technol.* 4 (2014) 2664–2673.
- [21] Y. Yang, H. Xiang, Y. Xu, L. Bai, Y. Li, *Appl. Catal. A Gen.* 266 (2004) 181–194.
- [22] T. Chukeaw, A. Seubsai, P. Phon-in, K. Charoen, T. Witoon, W. Donphai, P. Prapainainar, M. Chareonpanich, D. Noon, B. Zohour, S. Senkan, *RSC Adv.* 6 (2016) 56116–56126.
- [23] Ş. Kalyoncu, D. Düzenli, I. Onal, A. Seubsai, D. Noon, S. Senkan, Z. Say, E.I. Vovk, E. Ozensoy, *Catal. Letters* 145 (2015) 596–605.
- [24] W. Yao, Y.L. Guo, X.H. Liu, Y. Guo, Y.Q. Wang, Y.S. Wang, Z.G. Zhang, G.Z. Lu, *Catal. Letters* 119 (2007) 185–190.
- [25] Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang, C. Li, *Microporous Mesoporous Mater.* 84 (2005) 41–49.
- [26] X. Wang, Q. Zhang, Q. Guo, Y. Lou, L. Yang, Y. Wang, *Chem. Commun.* 12 (2004) 1396–1397.
- [27] X. Wang, Q. Zhang, S. Yang, Y. Wang, *J. Phys. Chem. B* 109 (2005) 23500–23508.
- [28] S. Yang, W. Zhu, Q. Zhang, Y. Wang, *J. Catal.* 254 (2008) 251–262.
- [29] Q. Zhang, Q. Guo, X. Wang, T. Shishido, Y. Wang, *J. Catal.* 239 (2006) 105–116.
- [30] A. Held, J. Kowalska-Kuś, A. Łapiński, K. Nowińska, *J. Catal.* 306 (2013) 1–10.
- [31] Y. Wang, Q. Zhang, T. Shishido, K. Takehira, *J. Catal.* 209 (2002) 186–196.

- [32] M.S. Kumar, M. Schwidder, W. Grünert, A. Brückner, *J. Catal.* 227 (2004) 384–397.
- [33] J. Pérez-Ramírez, M.S. Kumar, A. Brückner, *J. Catal.* 223 (2004) 13–27.
- [34] B. Horváth, T. Soták, M. Hronec, *Appl. Catal. A Gen.* 405 (2011) 18–24.
- [35] F. Fan, Z. Feng, C. Li, *Acc. Chem. Res.* 43 (2010) 378–387.
- [36] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, G. Vlaic, *J. Catal.* 158 (1996) 486–501.
- [37] F. Fan, K. Sun, Z. Feng, H. Xia, B. Han, Y. Lian, P. Ying, C. Li, *Chem. - A Eur. J.* 15 (2009) 3268–3276.
- [38] D. Scarano, A. Zecchina, S. Bordiga, F. Geobaldo, G. Spoto, G. Petrini, G. Leofanti, M. Padovan, G. Tozzola, *J. Chem. Soc. Faraday Trans.* 89 (1993) 4123–4130.
- [39] J.P. Gallas, J.M. Goupil, A. Vimont, J.C. Lavalley, B. Gil, J.P. Gilson, O. Miserque, *Langmuir* 25 (2009) 5825–5834.
- [40] A. Penkova, L.F. Bobadilla, F. Romero-Sarria, M.A. Centeno, J.A. Odriozola, *Appl. Surf. Sci.* 317 (2014) 241–251.
- [41] J. Lu, M. Luo, H. Lei, C. Li, *Appl. Catal. A Gen.* 237 (2002) 11–19.
- [42] O. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R. Lambert, *J. Catal.* 236 (2005) 401–404.
- [43] A. Miller, B. Zohour, A. Seubsai, D. Noon, S. Senkan, *Ind. Eng. Chem. Res.* 52 (2013) 9551–9555.
- [44] A. Palermo, A. Husain, M.S. Tikhov, R.M. Lambert, *J. Catal.* 207 (2002) 331–340.
- [45] E. Ananieva, A. Reitzmann, *Chem. Eng. Sci.* 59 (2004) 5509–5517.

K- and Ca-promoted ferrosilicates for the gas-phase epoxidation of propylene with O₂

*Jaime García-Aguilar, Diego Cazorla-Amorós, Ángel Berenguer-Murcia**

Materials Science Institute and Inorganic Chemistry Department, Alicante University, Ap. 99, E-03080 Alicante, Spain.

Keywords: sol-gel, propylene epoxidation, alkali promotion, ferrosilicate, dioxygen.

ABSTRACT: In the propylene epoxidation reaction with Fe-SiO₂ catalysts the presence of iron oxide particles has a detrimental effect due to the total combustion of propylene on these iron species. Thus, the complete elimination of the iron oxide particles is presented as a preliminary strategy in order to increase the selectivity towards propylene oxide in iron-based catalysts. In this sense, a simple post-treatment of the catalysts with alkali or alkaline-earth elements (such as K or Ca, respectively) has proven effective in the total elimination of these iron oxide particles. Furthermore, the addition of K and Ca has modified the physico-chemical properties of the catalysts, decreasing their superficial acidity and (for higher K or Ca loadings) masking/blocking the active sites responsible for the catalytic reaction. With all this, it is shown that K has a higher efficiency removing the iron oxide particles compared with Ca (for the same molar ratios) and that a higher amount of K (compared to Fe) is required for the complete elimination of the iron oxide particles. A considerable propylene oxide selectivity enhancement

(up to 65%) has been obtained for the K-promoted $\text{Fe}_{0.005}\text{SiO}_2$ and $\text{Fe}_{0.01}\text{SiO}_2$ catalysts using O_2 as sole oxidant.

1. Introduction

The production of propylene oxide (PO) by gas-phase catalysis is one of the most important challenges for the chemical companies due to its commercial interest. PO is a precursor of polyether polyols for urethanes, propylene glycols, and glycol ethers. At present, the production of this compound is mainly performed in liquid phase carried out by the chlorohydrin (in which Cl_2 is used as oxidant) process with approximately 40% of PO production [1–3].

Performing the epoxidation of propylene by heterogeneous catalysis in gas phase is nowadays one of the most interesting research topics in order to obtain an industrial catalyst towards a more environmentally friendly and applicable PO synthesis [4]. Despite the high price of gold and the need to use H_2/O_2 gas mixtures to feed the reactor, the $\text{Au}/\text{Ti-SiO}_2$ based catalysts are still under intense study due to high selectivities towards PO (at relatively low temperatures). This has given rise to recent studies in which the researchers have paid special interest to the reaction mechanism using this type of catalysts [5–9]. Other studies were focused on the synthesis of PO using only O_2 and propylene in the gas stream composition aimed at avoiding the use of H_2 . However, it is mandatory to increase the reaction temperature (compared with the abovementioned $\text{Au}/\text{Ti-SiO}_2$ catalysts which requires H_2/O_2 mixtures) to activate the gas molecules and obtain the desired compound. In this sense, Khatib et al. [3] have recently reported a review summarizing the catalysts used for PO formation using gaseous O_2 . Pure Ru, Ag and Cu (or mixed with other metals)-based catalysts must be mentioned as thoroughly studied due to their similar or higher propylene conversion than $\text{Au}/\text{Ti-SiO}_2$ catalysts but with slightly lower PO selectivity [10–18].

Recently, our research group reported the synthesis of PO using dioxygen and ferrosilicate catalysts prepared in a sol-gel one-step synthesis of well-dispersed iron oxide species into the silica structure [19]. In these materials, the propylene epoxidation reaction took place on the iron sites dispersed into the silica framework while the total combustion (towards CO₂) was preferentially occurring on the small iron oxide particles/clusters decreasing the PO selectivity [20]. Due to the synthesis procedure, even when the iron loading is 0.005 (Fe/Si molar ratio), the formation of extra-framework small iron oxide particles cannot be avoided. Addition of some alkali and alkaline earth elements after the synthesis of the catalysts reduces the presence of iron oxide particles as reported in the literature [21]. This strategy was also used in the above-mentioned catalysts (Ag, Cu or Ru) to increase PO selectivity, reaching the best improvements with the K and Ca-based catalysts [11,22–24]. Even for Fe-SiO₂ catalysts (where N₂O is used as oxidant), this addition has beneficial effects in the selectivity towards PO in spite of a reduction in propylene conversion [25–29].

This work is focused on the reduction and/or removal of the small iron oxide particles /clusters observed in iron-based catalysts (Fe_{0.0X}SiO₂) in order to improve their catalytic performance. In order to increase the selectivity towards PO, the Fe_{0.0X}SiO₂ solids were impregnated after their synthesis with the nitrate salts of K and Ca to introduce the needed amount of the element. The removal of the small iron oxide particles was determined by different spectroscopy techniques such as UV-Vis, UV-Raman or FTIR. The promoted Fe_{0.0X}SiO₂ catalysts were tested in the propylene epoxidation reaction using O₂ as oxidant (avoiding the use of dangerous and harmful agents such as N₂O) with very promising results in terms of PO selectivity.

2. Experimental

2.1 Catalyst Preparation

2.1.1 Preparation of the $Fe_{0.0x}SiO_2$ Catalysts

Hierarchical Fe-doped silica catalysts were prepared following the synthesis described in [19]. In a typical synthesis, 0.400 g of surfactant (Pluronic® F127, Sigma-Aldrich), 0.452 g of urea (Sigma-Aldrich) and 5.052 g of an acetic acid solution (0.01 M) were mixed under vigorous stirring for 80 min, the final pH of the resulting solution being around 4. Then, the necessary amount of iron precursor (iron (III) nitrate nonahydrate, $(Fe(NO_3)_3 \cdot 9H_2O)$, 99.99%, Sigma-Aldrich) was added in the solution and the mixture was stirred for 1 h. Subsequently, the solution was cooled in an ice-water bath under stirring and the silica precursor was added dropwise (2.030 g Tetramethyl orthosilicate, TMOS, Sigma-Aldrich). This solution was kept under stirring for 40 min at 0°C.

Finally, the sol was introduced in a Teflon autoclave and heated at 40°C for 20 h to produce the aging of the sol (the pH after this step remained around 4). After this, the sample was submitted to a hydrothermal treatment at 120°C for 6 h, to decompose the urea (the final pH of the supernatant liquid being around 9-10). As a final step, the monolith was calcined at 550°C for 6 h under static atmosphere to eliminate the surfactant and the rest of unwanted precursors.

Three samples with different Fe/Si molar ratios were prepared $Fe_{0.005}SiO_2$, $Fe_{0.01}SiO_2$ and $Fe_{0.02}SiO_2$. The samples in this work were named according to the nominal molar Fe/Si ratio in each case, for example, $Fe_{0.01}SiO_2$ corresponds to the sample with 1 mol % Fe in the oxide (with respect to Si moles).

2.1.2 Preparation of the K and Ca-promoted $Fe_{0.0x}SiO_2$ Catalysts

Once the iron-based silica samples were calcined and milled, the samples were impregnated in excess volume using aqueous solutions containing the necessary amount of alkali (KNO_3) and alkaline earth ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) precursors. The stirring was maintained for 2 days, and then, the solvent was evaporated under stirring, heating the suspension at 80°C keeping the magnetic stirring until complete evaporation. Finally, the powder was calcined again in an oven at 550°C for 6 h. The samples are labelled as $\text{K}_{0.01}$, for the sample with a K/Si molar ratio of 0.01, before the $\text{Fe}_{0.0x}\text{SiO}_2$. For comparison purposes, Fe-free K and Ca-treated solids (with a molar ratio of 0.01) were prepared using pure silica and impregnating the alkali and alkaline earth salts as described above. In addition, a $\text{Fe}_{0.005}\text{SiO}_2$ sample was treated with a 1M HCl solution overnight, filtered the solid, washed until neutral pH and then dried at 100°C overnight. After the acidic treatment, a portion of the catalyst was treated with KNO_3 (using the necessary amount for a K molar ratio of 0.01) and calcined as described above.

2.2 Characterization

The catalysts were analyzed by Transmission Electron Microscopy (TEM, JEOL JEM-2010) with a coupled EDX detector. The microscope operates at 200 kV with a space resolution of 0.24 nm. For the TEM analysis, the sample was suspended in ethanol and sonicated for a few minutes. The suspension (one drop) was deposited onto a 300 mesh Lacey copper grid and left to dry at room temperature. This technique allows the observation of the iron particles in the catalysts and the detection of the metal (by EDX) if it is not possible to see the particles. The iron, potassium and calcium loadings were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Perkin–Elmer Optima 4300 system. A few milligrams of the catalyst were dissolved in 0.1 ml of HF (5 vol. %) at room temperature, in order to ensure the total dissolution of the catalyst, and then diluted to the linear element detection range (0.05–10

ppm). The untreated and K and Ca-treated iron based catalysts were also characterized by N₂ adsorption-desorption isotherm at -196°C and by CO₂ adsorption at 0°C (Quantachrome, Autosorb 6B) to analyze the porous texture of this kind of materials.

Some spectroscopic techniques were used to analyze the physicochemical properties of the catalysts after K and Ca modification. UV-Vis analysis (V-670, JASCO) equipped with a double monochromator system, a photomultiplier tube detector and an integrating sphere (ISN-723 UV-Visible-NIR, JASCO) was used in transmittance mode to determine the speciation of the iron. The incorporation of the iron was analyzed by UV-Raman (NRS-5100, Jasco). The catalysts were irradiated for 30 min with a UV laser (HeCd, 325 nm, 1mW). The equipment is fitted with a Thorlabs 20x UV objective. Fourier Transform Infrared Spectroscopy (FTIR-4100, JASCO) was also used. The catalysts were diluted (using 1:50 weight ratio) in KBr and dried at 120°C for 12 h before the analysis. Pyridine adsorption was performed in order to characterize the modification of the surface acidity using a reported procedure [30]. The catalysts, diluted in KBr using the same weight ratio, were calcined at 500°C. Then they were exposed to pyridine vapours for 3 days in a vacuum desiccator. After pyridine adsorption, the physically adsorbed pyridine was removed at 100°C for one day. The FTIR spectra presented are the result of the subtraction of the spectra of the pyridine-treated to the spectra of the untreated catalysts.

2.3 Propylene Epoxidation Tests

The catalysts were tested under steady-state conditions at ambient pressure for at least 4 hours. The standard temperature of the analysis was 350°C, but to obtain reliable catalytic results, in some catalysts it was necessary to increase the temperature up to 400 or 450°C. A WHSV of 10000 ml·g⁻¹·h⁻¹ and a gas composition of 10% C₃H₆, 10% O₂, 80% He was used in the catalytic

tests. The gas composition was analyzed with a GC chromatograph (Agilent 7820A) equipped with two columns, PoraBond Q (Agilent) and CTR-I (Alltech), for the separation of the organic (propylene, propane, propylene oxide, acetaldehyde, acetone) and the inorganic (mainly, O₂ and CO₂) compounds respectively. Propylene conversion, PO yield and PO selectivity were calculated using the following equations and with the respective calibration of each compound in order to describe the catalytic behaviour of the samples.

$$\text{Propylene Conversion (\%)} = \frac{C_{C_3H_6-in} - C_{C_3H_6-out}}{C_{C_3H_6-in}} \times 100$$

$$\text{PO Yield (\%)} = \frac{C_{PO-out}}{C_{C_3H_6-in}} \times 100$$

$$\text{PO Selectivity (\%)} = \frac{C_{PO-out}}{C_{C_3H_6-in} - C_{C_3H_6-out}} \times 100$$

3. Results and discussion

3.1 Characterization of the Catalysts

For all the catalysts prepared in this work, the metal loadings were analyzed by ICP-OES. As in the previous work [19], it was observed that in the one-step preparation of the catalysts, not all the iron can be incorporated into the silica framework. The real Fe/Si molar ratios for the prepared catalysts were 0.0043 (Fe_{0.005}SiO₂), 0.0095 (Fe_{0.01}SiO₂), and 0.0186 (Fe_{0.02}SiO₂). From our observations, approximately 7% of the iron was removed in the supernatant liquid at the end of the sol-gel process. On the contrary and due to the methodology employed for their addition, the real loadings for K and Ca calculated by ICP-OES were in all cases quite close to the desired nominal loadings.

TEM coupled with EDX characterization of the representative catalysts is presented in the Supplementary Information. From the TEM micrographs it is possible to see that no large iron oxide clusters/agglomerations are formed in most samples. Only for some samples in which the alkali loading is lower than that of Fe ($\text{K}_{0.005}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.005}\text{Fe}_{0.02}\text{SiO}_2$) some small particles can be observed. Despite the fact that it is not possible to see the possible K, Ca or Fe oxide species on the silica surface, the EDX analysis confirmed, in all cases, the presence of these elements. From the textural characterization of the samples (see Fig. S1 and Table S1 in the Supplementary Information) it is not possible to observe any significant modification in the N_2 isotherm shape or the textural properties (i.e., specific surface area, micropore volume or pore size distribution) after the treatment of the Fe-SiO₂ samples with K or Ca.

The spectroscopic techniques, such as UV-Vis, UV-Raman, and FTIR, are very useful to analyze the iron speciation in this kind of materials. Studying the UV-Vis absorption of the solid catalysts it is possible to determine the presence of iron incorporated into the silica framework and the existence of small particles of iron oxide deposited on the surface of the silica. In this sense, previous works reported the absorption of the incorporated iron in tetrahedral or pseudo-tetrahedral position into the silica framework in two bands located at around 220 and 260 nm (45000 and 38000 cm^{-1} , respectively). While the iron oxide particles present UV-Vis absorption near the 370 and 500 nm range (27000 and 20000 cm^{-1} , respectively). This effect allows the interpretation of the band gap energy (E_g) as a measure of the iron dispersion in this kind of materials [29,31]. It is very important to remark that some works attribute the absorption at around 280 nm to the octahedral coordinated Fe(III) species in this kind of materials [32–34]. The UV-Vis results (and each corresponding E_g values) of the K and Ca-promoted Fe-SiO₂ catalysts are presented in Fig. 1.

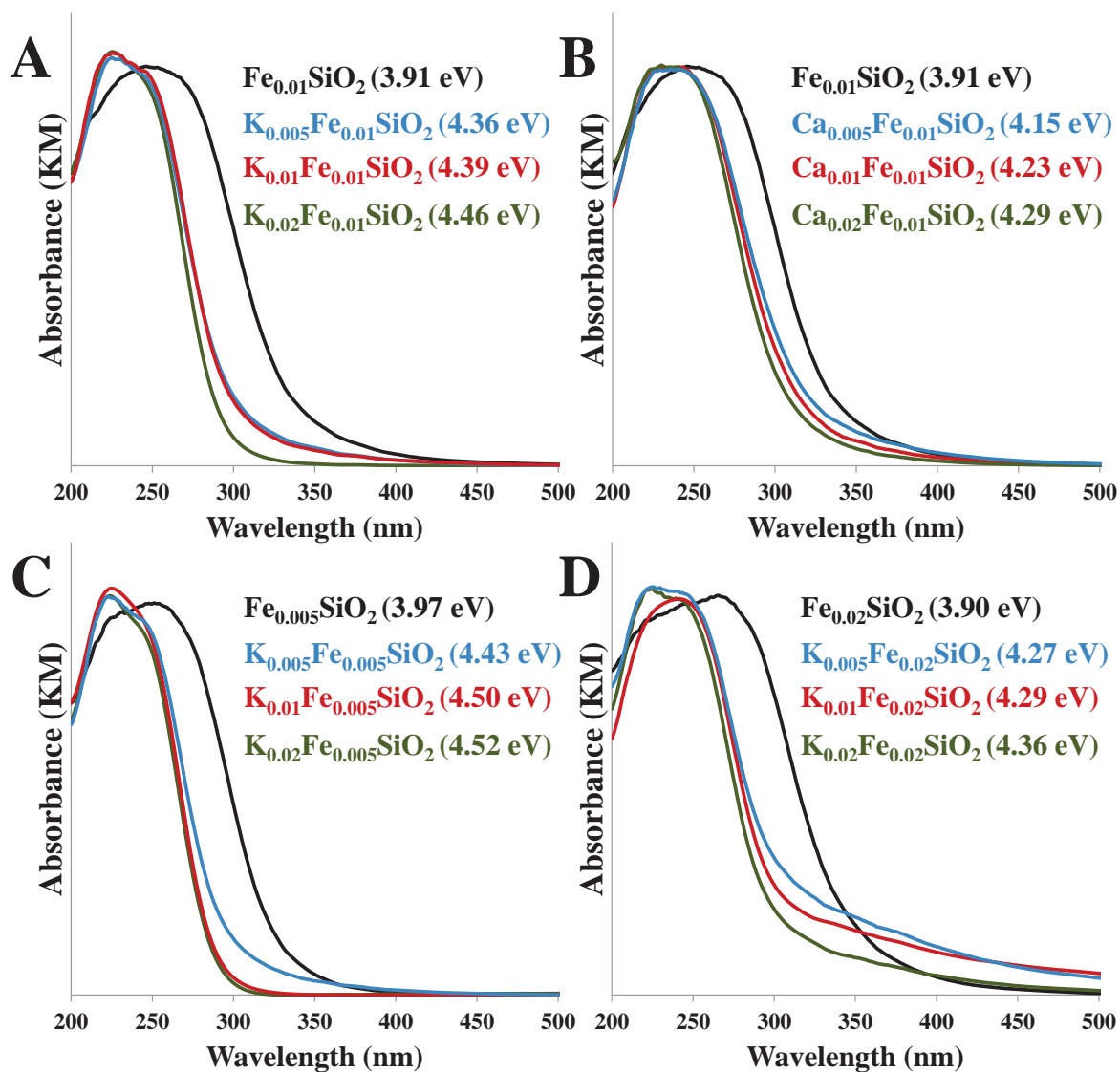


Fig. 1. Solid UV-Vis reflectance spectra (presented in Kubelka-Munk units) and their respective E_g value for the raw and post-K or Ca impregnation of the $\text{Fe}_{0.0x}\text{SiO}_2$ catalyst.

A) $\text{K}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, B) $\text{Ca}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, C) $\text{K}_{0.0x}\text{Fe}_{0.005}\text{SiO}_2$ and D) $\text{K}_{0.0x}\text{Fe}_{0.02}\text{SiO}_2$.

In order to select the appropriate promoter (K or Ca) which can yield a **better removal of** the iron particles and dispersion of the iron species, the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst was impregnated with the

3 different K or Ca/Si ratios (0.005, 0.01 and 0.02) and analyzed by UV-Vis reflectance (results presented in Fig. 1A and 1B). For the K-based catalysts, a substantial decrease in absorbance is observed for wavelengths above 300 nm. This can be associated to the removal of the iron oxide particles deposited on the silica surface. The total elimination of the iron oxide particles is reached for all samples in which the K content exceeded that of Fe. On the other hand, a reduction in the absorbance of the UV-Vis spectra near 280 nm after the addition of the alkali or alkaline earth based salts is also observed. This fact can be related to the removal of the small iron oxide clusters and/or extraction of the octahedrally coordinated iron species by the K treatment. These effects are observed also in the progressive increase of the E_g values obtained from the UV-Vis spectra, from the initial 3.91 eV for the raw $Fe_{0.01}SiO_2$ to the final 4.46 eV for the $K_{0.02}Fe_{0.01}SiO_2$ catalyst. In the case of Ca-based catalysts, the same trend is observed but it is not possible to remove all the particles of iron oxide produced during the synthesis of the material. All the samples, even the $Ca_{0.02}Fe_{0.01}SiO_2$, present a small but significant absorption at wavelengths higher than 300 nm and the increase of the E_g values is lower in the Ca samples than their K-based counterparts. The differences (in UV-Vis characterization) between the K and Ca-doped samples, when the small iron oxide particles and octahedral iron species removal is studied, allows us to confirm that for this kind of samples impregnation with K has a higher efficiency in reducing the number of iron oxide particles, as other authors have observed previously [27–29]. For this reason, the impregnation of the $Fe_{0.005}SiO_2$ and $Fe_{0.02}SiO_2$ samples was only studied with K.

The UV-Vis results of the K-impregnated catalysts in the $Fe_{0.005}SiO_2$ and $Fe_{0.02}SiO_2$ materials are presented in Fig. 1C and 1D, respectively. As it was previously studied, for all the raw catalysts, the amount of small iron oxide particles/clusters in extra-framework positions increases

with the Fe loading of the samples [19]. A progressive reduction in the absorption for the $K_{0.0x}Fe_{0.005}SiO_2$ series at 280 nm and above 300 nm (corresponding to the aforementioned species) is observed as the K content is increased in the catalysts. In the $K_{0.02}Fe_{0.01}SiO_2$ catalyst, when the K content is higher than the Fe molar content in the silica based catalysts (as with samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$), an almost total quenching of the absorption at wavelengths above 300 nm is observed, demonstrating the total removal of the iron oxide particles formed in the raw catalysts synthesis. The removal of the iron oxide particles produces the increase of the band gap energy up to 4.50 and 4.52 eV in the case of samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$, respectively. Finally, in the catalysts prepared with the highest iron content ($Fe_{0.02}SiO_2$) the addition of K has a different result, as it is possible to check in Fig. 1D. Even with the increase of the E_g up to 4.36 eV for the sample $K_{0.02}Fe_{0.02}SiO_2$ mainly due to the reduction in the absorption band located at 280 nm, there is a slight increase of the UV-Vis absorption in the 300-400 nm range. It is possible that the amount of iron oxide particles is too high for the K to remove all of them. All these UV-Vis results are corroborated by the colour of the catalysts and by the TEM micrographs presented in the SI. As K or Ca loading increases in the catalysts, the initial colour of the Fe-SiO₂ (slightly brown for $Fe_{0.01}SiO_2$ and $Fe_{0.02}SiO_2$) gradually disappears until total decolouration of the catalysts for all the $Fe_{0.005}SiO_2$ samples and the $K_{0.02}Fe_{0.01}SiO_2$.

Another complementary technique that can be used to analyze the structural modifications produced by the K and Ca addition is UV-Raman spectroscopy. The results of the prepared catalysts together with the blank silica and the K- and Ca-impregnated silica are shown in Fig. 2. Different regions of the spectra can be clearly distinguished depending on the species involved. The symmetric Si-O-Si stretching appears at 485 cm^{-1} for pure silica [35]. Close to this band, a

broad shoulder appears from 500 to 650 cm^{-1} , which we previously identified in bulk Fe_2O_3 and appears as a broad shoulder in samples $\text{Fe}_{0.01}\text{SiO}_2$ and $\text{Fe}_{0.02}\text{SiO}_2$ [19]. As it was previously reported, in the 800 cm^{-1} region for the pure SiO_2 sample it is possible to observe a low-intensity band that can be attributed to the vibration mode of siloxane linkage [25] or to the presence of defects [27]. In the 950-1150 cm^{-1} range three characteristic bands are observed in the SiO_2 and Fe-SiO_2 samples corresponding to different vibrations; 990 (Si-O-Si near iron species or other defect sites such as silanol groups) [25,27,35], 1080 (1016 cm^{-1} in [35], 1025 cm^{-1} in [36], 1074 cm^{-1} in [27] and 1090 cm^{-1} in [25]) and 1135 cm^{-1} (1115 cm^{-1} in [35], 1138 cm^{-1} in [27] and 1150 cm^{-1} in [36], not presented in ref. [25] maybe due to the use of a 244 nm laser irradiation), corresponding to vibrations of O_3SiO^- units with a very strong interaction with heteroatoms such as Fe-O-Si when the Fe is well-dispersed in isolated tetrahedral or pseudotetrahedral iron into the silica framework [19,25–27,36].

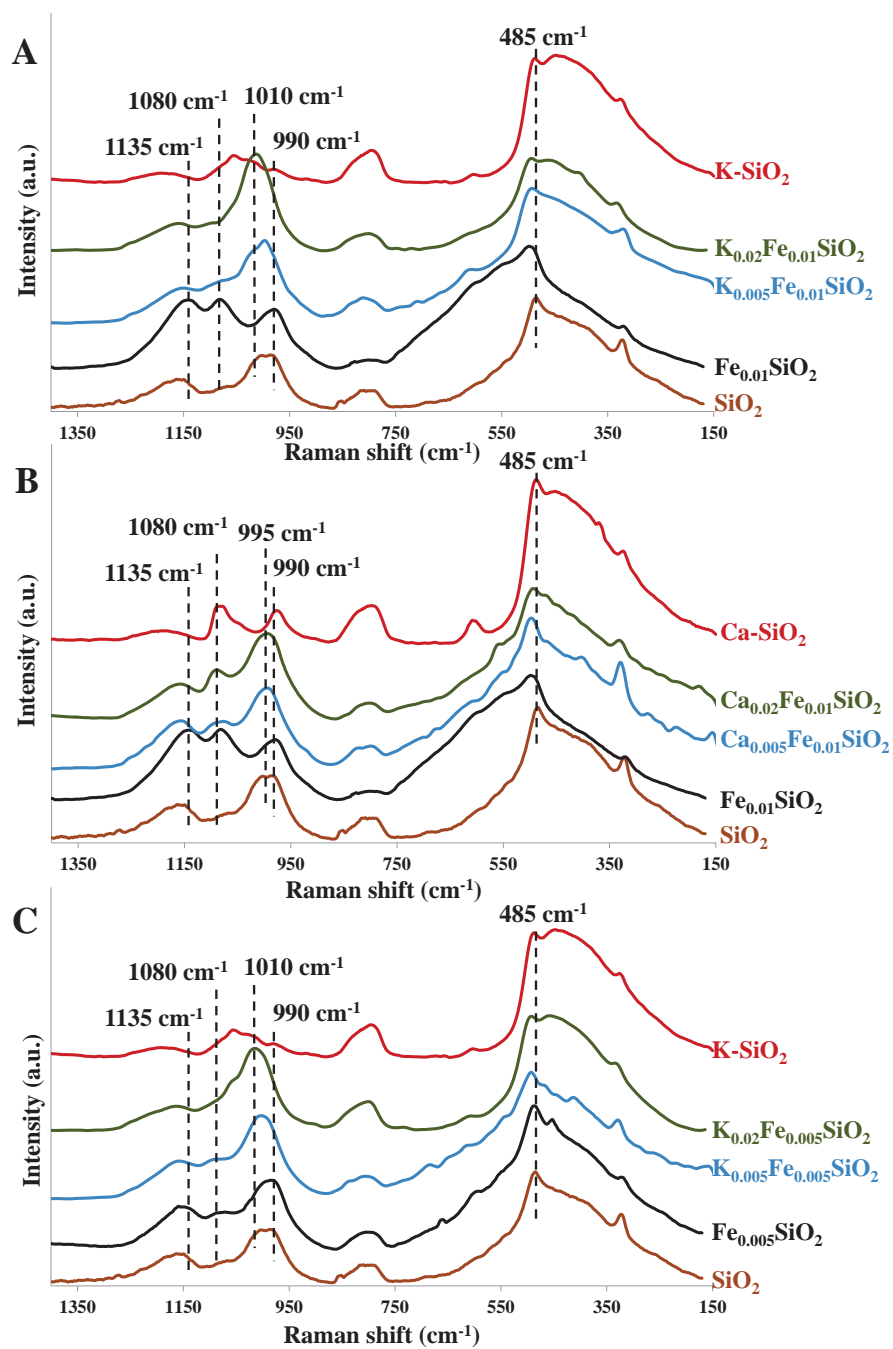


Fig. 2. Normalized UV-Raman analysis of representative catalysts prepared in this work.

A) $K_{0.0x}Fe_{0.01}SiO_2$, B) $Ca_{0.0x}Fe_{0.01}SiO_2$ and C) $K_{0.0x}Fe_{0.005}SiO_2$ series compared with the pure SiO₂ and its respective K or Ca-SiO₂ excited with a UV laser of 325 nm.

In all the studied series presented in Fig. 2, deposition of the K or Ca salt on the Fe-SiO₂ solids does not produce any important change in the band located at 485 cm⁻¹ corresponding to the symmetric Si-O-Si stretching. This band is slightly shifted to higher wavenumbers due to the incorporation of iron into the silica framework [19,35] and is not affected by the deposition of the K and Ca oxides on the silica (K-SiO₂ and Ca-SiO₂) indicating that post-impregnation does not produce modifications in the silica framework and the oxides are only deposited on the silica surface. Important changes in the UV-Raman spectra are observed after the modification of the iron-based catalysts. In the raw Fe_{0.01}SiO₂, a shoulder is observed from 500 to 650 cm⁻¹ (Fig. 2A and 2B) which is not observed for the SiO₂ and K or Ca-treated materials. As the K or Ca loading increases, this band reduces its intensity down to values similar to the pure silica solid. It is possible to assign this shoulder to the small iron oxide clusters/particles or iron in octahedral coordination in the original Fe-SiO₂ materials which are dispersed and removed after K or Ca impregnation [27–29].

In the 800 cm⁻¹ region, a weak signal is observed for the pure silica and the raw Fe-SiO₂ samples. However, when the K or Ca oxides are loaded on the silica surface the band becomes more intense and its shape is modified. The same band is obtained for the samples with the highest K loading (0.02), especially for the Fe_{0.005}SiO₂ sample. This fact might be due to the excess potassium used in the impregnation producing potassium oxide (as observed for the K-SiO₂ sample). This was also observed for the Ca-containing sample.

The assignation of each band within the 990-1135 cm⁻¹ region might be done with existing literature. The band at 1165 cm⁻¹ has been assigned to the crystalline environment of the iron species in Fe-ZSM-5 samples [35,37]. In our case, given the amorphous nature of our sample, this assignment is not straightforward. When K or Ca are loaded on the Fe-SiO₂, a decrease in

intensity is observed for the 1080 and 1135 cm^{-1} bands (see Fig. 2) together with the appearance of a band located at 1000 cm^{-1} (1010 cm^{-1} for the $\text{K}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$ and 995 cm^{-1} for the $\text{Ca}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$). This new band was previously studied by Wang et al. [26,27] and could correspond to a tetrahedrally coordinated iron oxide “surrounded and stabilized by K^+ or Na^+ ” (K^+ or Ca^{2+} in this study) species. These K- or Ca-Fe species (such as ferrates [22,23]) can be formed during the calcination step after impregnation of the K or Ca salt, produced by its reactivity with the small particles/clusters of iron oxide on the silica surface. This hypothesis is also supported by the results showed in the UV-Vis analysis, where there was a reduction of the absorption corresponding to the small particles/clusters of iron oxide. The formation of these superficial species (K- and Ca-Fe species) with the well-dispersed iron into the silica framework, which occupies pseudotetrahedral positions cannot be ruled out in this respect. It is possible that the iron could migrate to extra-framework positions or could be covered (as was proposed by Horváth et al. [20]) by the alkali or alkaline earth oxide producing the decrease of its related bands at 1080 and 1135 cm^{-1} .

In order to determine the possible contribution of the K and Ca addition to other physicochemical properties of the materials, the normalized FTIR spectra of all the solids were analyzed and presented in Fig. 3.

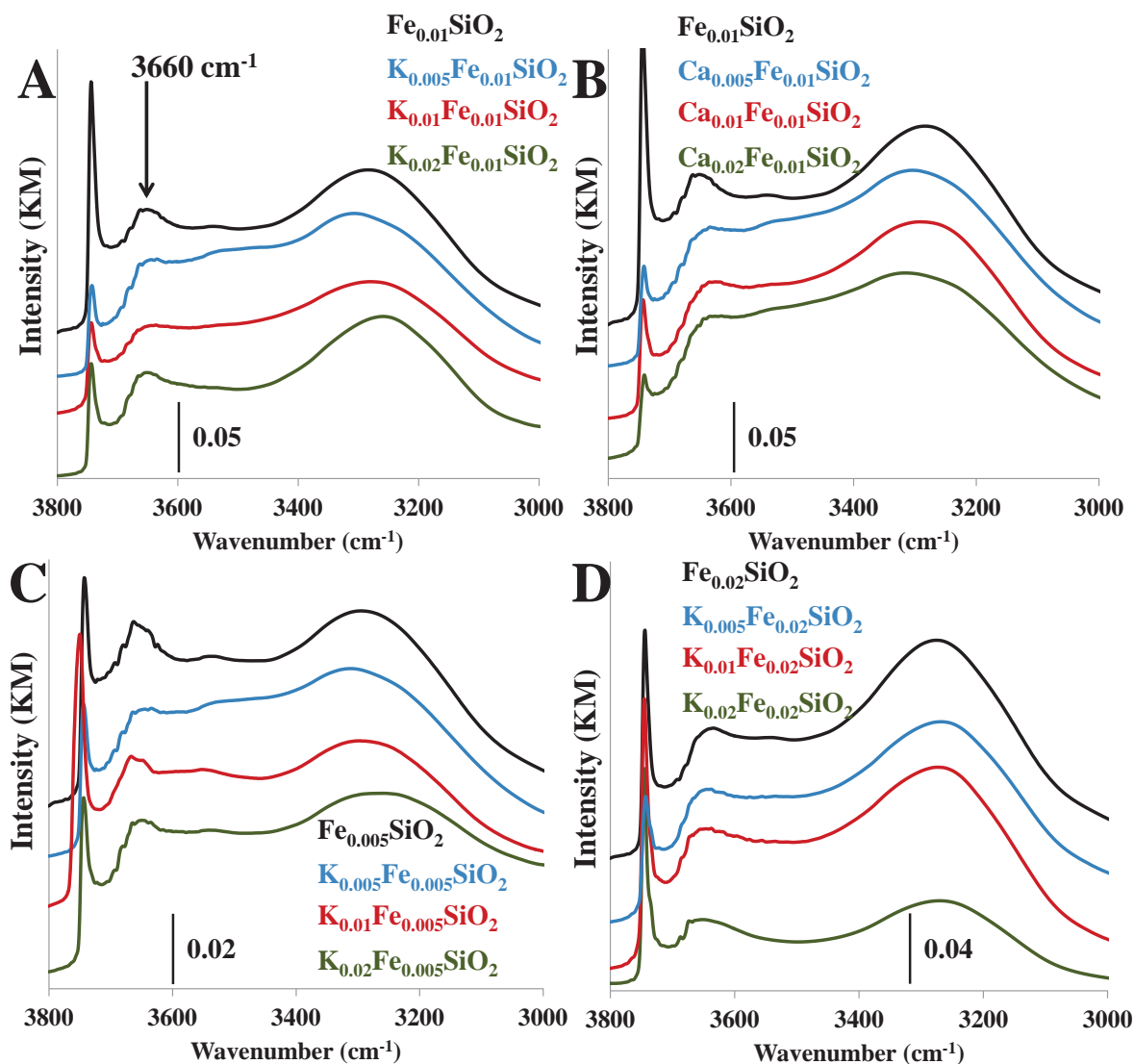


Fig. 3. Normalized FTIR spectra of the OH region (presented in Kubelka-Munk units) for all the catalysts prepared in this work. A) $\text{K}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, B) $\text{Ca}_{0.0x}\text{Fe}_{0.01}\text{SiO}_2$, C) $\text{K}_{0.0x}\text{Fe}_{0.005}\text{SiO}_2$ and D) $\text{K}_{0.0x}\text{Fe}_{0.02}\text{SiO}_2$.

In Fig. 3 it is possible to compare the normalized (with respect to the most intense band at 1090 cm^{-1} , corresponding to the Si-O stretching) characteristic vibrations of the superficial OH

groups of this kind of materials. No significant modification of the fundamental framework vibration modes of the Fe-SiO₂ solids (810, 1000-1300 cm⁻¹) [19,36,38] is observed after the impregnation and calcination of the K or Ca-based salts. This fact reveals that the impregnation of the K or Ca nitrates only produces superficial modifications without affecting the Fe_{0.0X}-SiO₂ framework as it is previously discussed by UV-Raman spectroscopy. On the other hand, a significant modification in the OH vibration range occurs (Fig. 3) due to the K or Ca impregnation on the silica surface. When K or Ca are added with the lowest amounts (i.e., M_{0.005}Fe_{0.0X}SiO₂), there is a reduction in the intensity of the band corresponding to the bridged hydroxyls with Brønsted acid character (located at 3660 cm⁻¹) [36,39]. From our observations this reduction is not proportional to the K or Ca loading. This effect is also demonstrated by the normalized FTIR spectra corresponding to pyridine adsorption presented in Fig. S2 (See Supplementary Information). By this analysis it is possible to observe a proportional decrease in the intensity of the bands corresponding to adsorbed pyridine at 1446 and 1596 cm⁻¹ [40] as the K molar ratio increases (for the Fe_{0.005}SiO₂ catalyst) or when the K or Ca are added on the Fe_{0.001}SiO₂. In this sense, the addition of ions with a strong basic character on the silica surface reduces the amount of acid sites in the solid due to their exchange with the acidic proton neighbour to the iron atom. This fact could be beneficial for the epoxidation reaction due to the acidity reduction of the support. It is also possible to propose the blocking/covering of some iron sites of the silica framework due to the K or Ca oxide formation on the silica surface.

In this respect, the impregnation and calcination of the K or Ca salts produces the corresponding oxides deposited on the silica surface. For low loadings, the K or Ca ions interact with the acidic proton reducing its signal in all the catalysts (M_{0.005}Fe_{0.0X}SiO₂). Then, as the K or Ca loading increases, removal of the small clusters/particles (lower than 1 nm) takes place in the

Fe-SiO₂ samples, as observed by UV-Vis analysis [27–29]. This removal reduces the amount of the small iron oxide clusters/particles (responsible for the total oxidation of propylene) [20]. As it is mentioned above, this alkali or alkaline earth oxide can also cover the highly dispersed iron into the silica framework (which is the main species responsible for the propylene epoxidation reaction [19]).

As it is discussed in the spectroscopic techniques section, the addition of small amounts of K or Ca is a simple and useful way to reduce the amount or to remove the undesired iron oxide particles/clusters formed during the synthesis of the catalysts. However, this modification can also produce other different effects, like reducing the amount of bridged hydroxyls with Brønsted acid character located near the iron atom or blocking iron active sites, which is very interesting for this reaction due to their respective interaction with gaseous propylene or dioxygen in the propylene epoxidation reaction.

3.2 Propylene Epoxidation Reaction

The samples were tested under isothermal conditions (at 350, 400 or 450°C depending on the activity of the sample to ensure a significant value of propylene conversion) during at least 4 hours. However, the catalytic tests performed at 450°C for the Fe_{0.005}SiO₂ and Fe_{0.01}SiO₂ resulted in a fast deactivation of the catalysts due to carbon deposition on the surface. This effect was also observed in the Fe_{0.02}SiO₂ sample at 400°C. In all catalytic tests, except for those just mentioned, propylene conversion, PO yield, and PO selectivity remained constant during the reaction, and the values presented in this section correspond to the steady-state conditions. Analyzing all reaction products, it was possible to find out that the main by-product formed was CO₂, but in

some samples, acetaldehyde was also produced to a small extent (<1%). The results are shown in

Table 1.

Table 1
Catalytic performance of the samples prepared in propylene epoxidation by O₂ molecule under steady-state conditions

Catalyst	Temperature (°C)	C ₃ H ₆ Conversion (%)	PO Yield (%)	Selectivity (%)		
				PO	Others ^a	CO ₂
Fe _{0.01} SiO ₂	350	7.8	1.9	24.6	< 0.5	~75
	400	21.6	4.4	20.4	< 1.0	~78
K _{0.005} Fe _{0.01} SiO ₂	350	4.0	1.1	26.0	< 0.5	~74
K _{0.01} Fe _{0.01} SiO ₂	350	3.4	0.9	27.5	< 0.5	~72
K _{0.02} Fe _{0.01} SiO ₂	400	1.7	1.1	62.4	< 0.5	~37
Ca _{0.005} Fe _{0.01} SiO ₂	350	3.2	0.9	27.6	< 0.5	~72
Ca _{0.01} Fe _{0.01} SiO ₂	350	1.7	0.8	51.4	< 0.5	~48
Ca _{0.02} Fe _{0.01} SiO ₂	350	1.5	0.8	53.3	< 0.5	~46
Fe _{0.005} SiO ₂	350	5.5	1.8	33.6	< 0.5	~66
	400	19.1	5.1	26.7	< 1.0	~72
K _{0.005} Fe _{0.005} SiO ₂	350	2.0	0.6	33.8	< 0.5	~66
K _{0.01} Fe _{0.005} SiO ₂	450	2.2	1.3	58.8	< 0.5	~41
K _{0.02} Fe _{0.005} SiO ₂	450	1.4	0.9	65.5	< 0.5	~34
Fe _{0.02} SiO ₂	350	10.3	2.4	23.1	< 1.0	~76
K _{0.005} Fe _{0.02} SiO ₂	350	4.9	1.3	25.7	< 0.5	~74
K _{0.01} Fe _{0.02} SiO ₂	350	2.5	0.8	31.5	< 0.5	~68
K _{0.02} Fe _{0.02} SiO ₂	400	8.5	2.3	27.2	< 1.0	~63

^a Acetaldehyde is the main organic by-product obtained in the catalytic reaction.

The addition of the small amounts (only 0.005 molar ratios) of promoters (K or Ca) produces in the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst the decrease of the propylene conversion down to half of its initial activity. However, the **PO yield** is also halved since no significant modification of the PO selectivity is produced. Analyzing the addition of a larger amount of K on the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst it is possible to assess how the incorporation of an equimolar ratio of K/Fe ($\text{K}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$) produces a further reduction of both C_3H_6 conversion and **PO yield** also corresponding to a similar PO selectivity compared to the $\text{Fe}_{0.01}\text{SiO}_2$ sample. Nonetheless, when the K ratio is twice with respect to the Fe amount ($\text{K}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$) the C_3H_6 conversion is too low at 350°C and a temperature increase to 400°C is mandatory to obtain a significant **conversion/yield value**. At this new temperature, the C_3H_6 conversion is the lowest of this catalyst series (1.7%) but the **PO yield** is not reduced compared with the $\text{K}_{0.005}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{K}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$ catalysts. This results in a drastic increase of the PO selectivity from 24.6-27.5% to 62.4%. The catalytic activity corresponding to the non-promoted $\text{Fe}_{0.01}\text{SiO}_2$ at 400°C shows a quite high propylene conversion (21.6%) and very low PO selectivity (20.4%). In this sense, the addition of 0.02 molar ratio of K allows to control the propylene combustion at 400°C and to increase the PO selectivity.

On the other hand, in the Ca-promoted $\text{Fe}_{0.01}\text{SiO}_2$ series a different behaviour is observed when the Ca amount increases. The addition of 0.005 Ca/Si molar ratio produces the reduction of the propylene conversion **and PO yield**, more than half in both cases without any significant modification in the PO selectivity. However, when the Ca amount increases up to 0.01 and 0.02 ($\text{Ca}_{0.01}\text{Fe}_{0.01}\text{SiO}_2$ and $\text{Ca}_{0.02}\text{Fe}_{0.01}\text{SiO}_2$, respectively) a similar value of the C_3H_6 conversion and **PO yield** is observed (1.6% and 0.8%, respectively) obtaining PO selectivities around 52% without requiring a temperature increase. Analyzing the catalytic results of the $\text{Fe}_{0.01}\text{SiO}_2$ catalyst

promoted with K or Ca it can be concluded that K-promotion produces higher selectivities towards PO despite of the higher temperatures required to reach significant propylene conversions.

For the $\text{Fe}_{0.005}\text{SiO}_2$ catalyst, the addition of the equimolar K/Fe ratio ($\text{K}_{0.005}\text{Fe}_{0.005}\text{SiO}_2$) produces the lessening of the C_3H_6 conversion and PO yield to 2.0% and 0.6%, respectively, with respect to the unpromoted catalysts. When the amount of potassium added after the synthesis of the $\text{Fe}_{0.005}\text{SiO}_2$ increases up to 0.01 and 0.02 ($\text{K}_{0.01}\text{Fe}_{0.005}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$, respectively) it is necessary to increase the reaction temperature up to 450°C to obtain significant conversion values. The temperature increase compensates the reduction in C_3H_6 conversion (which is not measurable at 350°C), obtaining values around 2.2 and 1.4% for the $\text{K}_{0.01}\text{Fe}_{0.005}\text{SiO}_2$ and $\text{K}_{0.02}\text{Fe}_{0.005}\text{SiO}_2$ samples, respectively. In addition, the PO yield obtained in these catalytic tests is remarkably higher, reaching PO selectivities between 58.8% and 65.5% (under the same conditions, the unpromoted $\text{Fe}_{0.005}\text{SiO}_2$ catalyst gave 19.1% and 26.7% for propylene conversion and PO selectivity, respectively).

The catalysts prepared with the $\text{Fe}_{0.02}\text{SiO}_2$ sample present a different catalytic behaviour (in terms of PO selectivity) compared with the lower iron content. As it is possible to see in Table 1, as the K loading increases, the propylene conversion decreases to 2.5% for the $\text{K}_{0.01}\text{Fe}_{0.02}\text{SiO}_2$ catalyst with only a slight increase of the PO selectivity (31.5%). However, when the temperature reaction is increased at 400°C for the $\text{K}_{0.02}\text{Fe}_{0.02}\text{SiO}_2$ catalyst the propylene conversion increases up to 8.5%, diminishing the selectivity towards PO (27.2%).

Another important aspect that must be taken into account is the aforementioned carbon deposit produced during the reaction due to the propylene cracking on the catalysts surface. For the

catalysts without K or Ca, a small fraction of carbon deposit is observed after the reaction (less than a 3 wt. % determined by thermogravimetry). However, when K or Ca is added to the Fe-SiO_2 no carbonaceous deposit is obtained after the epoxidation reaction. Only for the $\text{K}_{0.005}\text{Fe}_{0.02}\text{SiO}_2$ and $\text{Ca}_{0.005}\text{Fe}_{0.01}\text{SiO}_2$ catalysts a slight deposit of carbon material is observed that results in a slight darkening of the materials. In this sense, the role of the alkali or alkaline earth promotion is very important because it allows to control the reactivity, decreasing the propylene conversion and its combustion and avoiding propylene cracking (and subsequent carbonaceous deposit) on the catalysts.

On the other hand, the catalysts prepared following the HCl treatment in order to remove the iron oxide particles present a different catalytic behaviour for the propylene epoxidation reaction. It must be previously mentioned that the HCl treatment ($\text{Fe}_{0.005}\text{SiO}_2\text{-HCl}$) was not enough for the complete elimination of the iron oxide particles (see Fig. S3 in Supplementary Information) but removes a significant portion of them. After the acidic treatment, the results from the propylene epoxidation reaction at 450°C (lower temperatures did not yield reliable results) for the $\text{Fe}_{0.005}\text{SiO}_2\text{-HCl}$ catalyst were: 5.8% of propylene conversion, 2% of PO yield and a PO selectivity of 34.5% (with a 6 wt. % of carbonaceous deposit). These results mean that a large portion of the iron oxide particles were removed (compared with the 19.1% of propylene conversion for the raw $\text{Fe}_{0.005}\text{SiO}_2$) but there is no significant increase in the PO selectivity. Moreover, the high amount of carbonaceous deposit on the catalysts surface could be attributed to the acidity of the surface which favours propylene reactivity and cracking. For this reason, the propylene conversion of this sample is higher than the K-promoted $\text{Fe}_{0.005}\text{SiO}_2$. This catalyst was also treated with K (with a K molar ratio of 0.01) for its comparison with the K-promoted without the acidic treatment. As revealed by the UV-Vis analysis of the solid in Fig. S3, the

absorbance of this catalyst is quite similar to those obtained for the $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ without the HCl treatment. The resulting KNO_3 -treated catalyst presents a propylene conversion and a PO yield of 3.3 and 1.5%, respectively with a PO selectivity of 45%. However, no significant carbonaceous deposit is evidenced after the epoxidation reaction at 450°C. In this sense, it must be mentioned that it was not possible to achieve the selectivities of the $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ catalysts but the propylene conversion and PO yield were not so low.

The selectivities towards PO obtained for the $K_{0.02}Fe_{0.01}SiO_2$, $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ catalysts at 400 or 450°C presented in Table 1 (reaching values over 60%) are higher, but lower in propylene conversion (4-5%), than other promoted catalysts tested using O_2 as oxidant and based on transition metals such as Ag, Cu and/or Ru [11,22,41,42] and similar to other alkali promoted Cu [14,43] or Ag and Mo [44] catalysts.

Comparing the catalytic performance of our samples with similar catalysts (alkali or alkaline earth promoted iron based silica) reported in other studies, similar [26,27,29,45] or slightly lower [20,34] PO selectivities were obtained with similar values of propylene conversion in these cases. However, in these works the use of nitrous oxide was mandatory to produce the epoxidation of the propylene. In this sense, the replacement of nitrous oxide by molecular oxygen implies user-friendly reaction conditions.

According to the catalytic results and the characterization obtained for all the K- or Ca-promoted catalysts prepared in this work it is possible to propose which are the main changes produced by K or Ca in the iron species of the catalysts (Scheme 1). For the lowest K and Ca loadings, an important aspect that must be taken into account is the reduction in the **PO yield** but

with similar PO selectivities. As it was previously studied, the well-dispersed iron species incorporated into the silica framework (interacting with the molecular O₂) along with a neighbour acidic proton (interacting with gaseous propylene) are the main responsible species of the propylene epoxidation reaction in this kind of catalysts [19]. So the addition of this kind of promoters, even in the 0.005 molar ratios, is producing some changes in the well-dispersed iron species that diminishes the PO production. This catalytic behaviour can be explained through the FTIR and UV-Raman results. As the FTIR results shown, the addition of K or Ca modifies the surface properties of the silica. A significant reduction in the amount of acidic protons with Brønsted character located at 3660 cm⁻¹ is observed after the addition of the smallest K or Ca molar ratio. In this sense, its intensity decrease could be due to the substitution of the acidic proton by the K or Ca species during the thermal treatment after impregnation. This observation together with the **PO yield** decrease (see Table 1) suggests that there is a reduction of the number of sites that can interact with the propylene towards the epoxidation reaction. However, for these catalysts (with low K or Ca loadings) it is not possible to confirm the **complete removal of** the small iron oxide particles by either UV-Vis or UV-Raman (due to the formation of stabilized K- or Ca-Fe species). These particles are responsible for the total combustion of the propylene. From our observations, a graphical depiction of these catalysts is presented in Scheme 1 (upper right-hand side), where the number of acidic sites is reduced. The substitution of the acidic Brønsted proton by K or Ca oxide also produces a significant decrease of the propylene cracking on the catalyst surface thus resulting in lower carbon deposition during the epoxidation experiments.

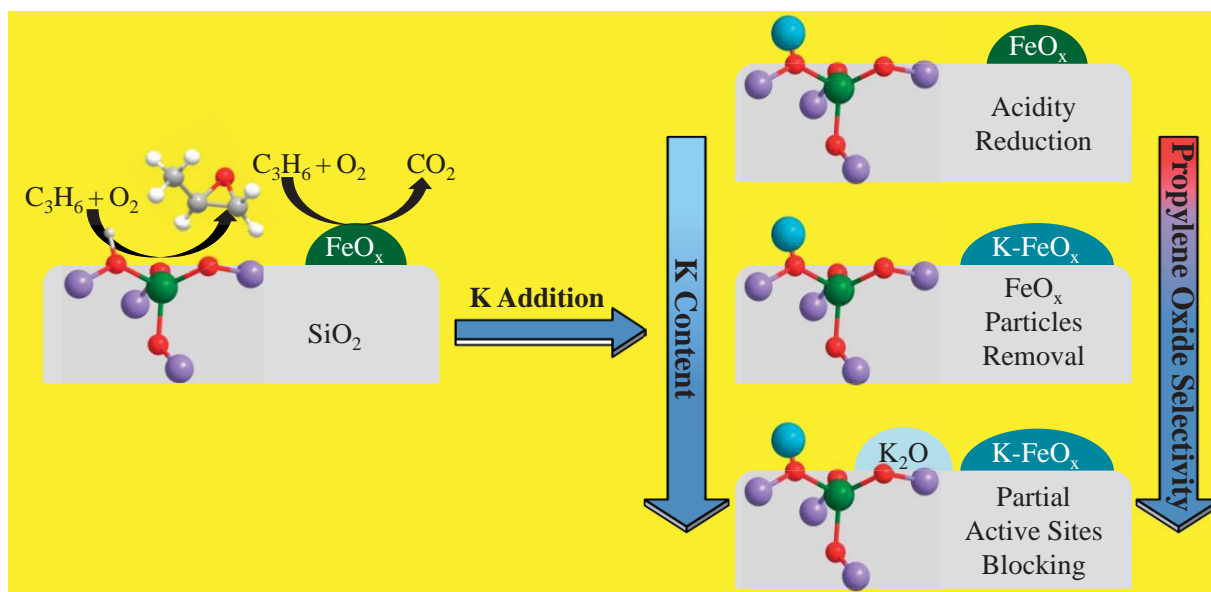
On the other hand, when the K or Ca loading increases different interactions can be produced on the Fe-SiO₂ surface. The picture in the middle right-hand side of Scheme 1 shows how as the

K content is increased K-Fe species are formed in addition to the substitution of the protons in the bridged hydroxyls with Brønsted acid character by K species. As it is commented by the UV-Vis characterization, the addition of the K precursor produces the dispersion of the iron oxide particles and the octahedral coordinated iron species. This fact is also supported by UV-Raman analysis, by the emergence of the band at 1010 cm^{-1} assigned to tetrahedrally coordinated iron oxide surrounded and stabilized by K^+ . In this sense, the reduction of the small particles/clusters of iron oxide determined by UV-Vis and TEM (which are the main responsible species for the total oxidation of the propylene towards CO_2) reduces the propylene conversion of the catalysts. Due to the fact that propylene epoxidation mainly occurs on the well-dispersed iron incorporated into the silica structure, the iron oxide particles removal produces an increase of the PO selectivity as a beneficial side effect. This behaviour is obtained for all the catalysts, where the propylene conversion progressively decreases when small loadings of K or Ca species are added. However, in order to achieve the complete elimination of the iron oxide particles, a higher amount of K (higher than the nominal Fe loading) is required. This is observed for samples $\text{Fe}_{0.005}\text{SiO}_2$ ($\text{K}_{0.01}$ and $\text{K}_{0.02}$) and $\text{Fe}_{0.01}\text{SiO}_2$ (only for the $\text{K}_{0.02}$ catalyst) which show similar E_g values around 4.50 eV. Using this kind of samples the propylene conversion and the PO selectivities are around 1.5% and 60%, respectively at their corresponding reaction temperature (see Table 1). The addition of Ca as a promoter does not produce the same efficiency (for the same promoter molar ratios) in removing the iron oxide particles (as confirmed by UV-Vis) despite the reaction temperature being 350°C in all cases. On the other hand, for the sample with the highest amount of iron oxide particles ($\text{Fe}_{0.02}\text{SiO}_2$), it has not been possible to remove all the iron clusters with the tested alkali molar ratio. By this way, the catalytic results obtained for this

sample show how the propylene conversion (up to 8.5% when the temperature is increased) is not as affected as in the other series.

Thus, the addition of promoters (such as K or Ca) reduces the number of small iron oxide particles due to the formation of K- or Ca-Fe species during the calcination step after the nitrate impregnation. When the K molar ratio is higher than that of Fe ($K_{0.02}Fe_{0.01}SiO_2$, $K_{0.01}Fe_{0.005}SiO_2$, and $K_{0.02}Fe_{0.005}SiO_2$) the complete elimination of the iron oxide particles is possible. Under these conditions very promising PO selectivities (higher than 60%) by the oxidation of propylene with O_2 are obtained.

Finally, another undesirable scenario which cannot be ruled out when the promoter molar ratio is increased is that suggested by Horváth et al. [20] where there is a masking of the iron species due to its covering by K or Ca oxide (lower right-hand side in Scheme 1). The excess of alkali or alkaline-earth oxides or the formation of K- or Ca-Fe species on the catalysts surface could block the accessibility of the reactants to the active sites of the catalysts decreasing the catalytic behaviour of the materials. This effect is confirmed by the reduction in propylene conversion and PO yield between samples $K_{0.01}Fe_{0.005}SiO_2$ and $K_{0.02}Fe_{0.005}SiO_2$ measured at 450°C.



Scheme 1. Possible interpretation of the K effects on the Fe-SiO₂ surface and its influence on the PO selectivity.

4. Conclusions

Fe-SiO₂ catalysts modified with small loadings of K or Ca salts by impregnation methodology have been prepared and tested in the propylene epoxidation reaction in gas-phase using O₂ as oxidant. The addition of the promoters led to physicochemical changes of the surface of the iron-based catalysts, such as: the complete elimination of the small particles/clusters of iron oxide generated during the synthesis of the materials via the formation of superficial K- or Ca-Fe species, the substitution of the hydroxyls with Brønsted acid character by K or Ca species and the partial iron sites blocking. These modifications produced by the K or Ca incorporation are also reflected in the catalytic behaviour for the epoxidation of propylene. As a first consequence, the propylene conversion (towards CO₂) is drastically reduced due to elimination of the small

iron oxide particles. Furthermore, the acidity reduction and the blocking of the catalysts produce a reduction in **the PO yield** and avoids the cracking of propylene on the catalyst surface. As a result of these processes, a very promising PO selectivity (65.5%) is obtained using small loadings of Fe and K, and O₂ as oxidant without the production of many organic byproducts.

Author information

Corresponding Author

*E-mail: a.berenguer@ua.es (Ángel Berenguer-Murcia)

Acknowledgments

We thank the Spanish Ministry of Economy and Competitiveness (MINECO), Generalitat Valenciana and FEDER (CTQ2015-66080-R MINECO/FEDER and PROMETEOII/2014/010) for financial support. J.G.A. thanks the Spanish Ministry of Economy and Competitiveness (MINECO) for his fellowship (BES-2013-063678).

References

- [1] D. Kahlich, U. Wiechern, J. Lindner, *Ullmann's Encycl. Ind. Chem.* (2012) 313–335.
- [2] D. Trent, *Kirk-Othmer Encycl. Chem. Technol.* (2001) 1–26.
- [3] S.J. Khatib, S.T. Oyama, *Catal. Rev.* 57 (2015) 306–344.
- [4] K. Singh, K. Merchant, in: *Handb. Ind. Chem. Biotechnol.*, 2012, pp. 643–698.
- [5] S. Kanungo, D.M. Perez Ferrandez, F. Neira d'Angelo, J.C. Schouten, T.A. Nijhuis, *J. Catal.* 338 (2016) 284–294.
- [6] X. Feng, X. Duan, H. Cheng, G. Qian, D. Chen, W. Yuan, X. Zhou, *J. Catal.* 325 (2015) 128–135.
- [7] X.-Y. Chen, S. Chen, A. Jia, J. Lu, W. Huang, *Appl. Surf. Sci.* 393 (2017) 11–22.

- [8] A. Prieto, M. Palomino, U. Díaz, A. Corma, *Appl. Catal. A Gen.* 523 (2016) 73–84.
- [9] J. Chen, E.A. Pidko, V. V. Ordonsky, T. Verhoeven, E.J.M. Hensen, J.C. Schouten, T.A. Nijhuis, *Catal. Sci. Technol.* 3 (2013) 3042–3055.
- [10] D.O. Atmaca, D. Düzenli, M.O. Ozbek, I. Onal, *Appl. Surf. Sci.* 385 (2016) 99–105.
- [11] P. Phon-in, A. Seubsai, T. Chukeaw, K. Charoen, W. Donphai, P. Prapainainar, M. Chareonpanich, D. Noon, B. Zohour, S. Senkan, *Catal. Commun.* 86 (2016) 143–147.
- [12] S. Ghosh, S.S. Acharyya, R. Tiwari, B. Sarkar, R.K. Singha, C. Pendem, T. Sasaki, R. Bal, *ACS Catal.* 4 (2014) 2169–2174.
- [13] Q. Hua, T. Cao, X.-K. Gu, J. Lu, Z. Jiang, X. Pan, L. Luo, W.-X. Li, W. Huang, *Angew. Chem.*, 53 (2014) 4856–61.
- [14] J. He, Q. Zhai, Q. Zhang, W. Deng, Y. Wang, *J. Catal.* 299 (2013) 53–66.
- [15] W. Long, Q. Zhai, J. He, Q. Zhang, W. Deng, Y. Wang, *Chempluschem* 77 (2012) 27–30.
- [16] Q. Zhang, G. Chai, Y. Guo, W. Zhan, Y. Guo, L. Wang, Y. Wang, G. Lu, *J. Mol. Catal. A Chem.* 424 (2016) 65–76.
- [17] G. Jin, G. Lu, Y. Guo, Y. Guo, J. Wang, X. Liu, *Catal. Today* 93–95 (2004) 173–182.
- [18] X. Zheng, Q. Zhang, Y. Guo, W. Zhan, Y. Guo, Y. Wang, G. Lu, *J. Mol. Catal. A Chem.* 357 (2012) 106–111.
- [19] J. García-Aguilar, I. Miguel-García, J. Juan-Juan, I. Such-Basáñez, E. San Fabián, D. Cazorla-Amorós, Á. Berenguer-Murcia, *J. Catal.* 338 (2016) 154–167.
- [20] B. Horváth, M. Šustek, I. Vávra, M. Mičušík, M. Gál, M. Hronec, *Catal. Sci. Technol.* 4 (2014) 2664–2673.
- [21] Y. Yang, H. Xiang, Y. Xu, L. Bai, Y. Li, *Appl. Catal. A Gen.* 266 (2004) 181–194.
- [22] T. Chukeaw, A. Seubsai, P. Phon-in, K. Charoen, T. Witoon, W. Donphai, P. Prapainainar, M. Chareonpanich, D. Noon, B. Zohour, S. Senkan, *RSC Adv.* 6 (2016) 56116–56126.
- [23] Ş. Kalyoncu, D. Düzenli, I. Onal, A. Seubsai, D. Noon, S. Senkan, Z. Say, E.I. Vovk, E. Ozensoy, *Catal. Letters* 145 (2015) 596–605.
- [24] W. Yao, Y.L. Guo, X.H. Liu, Y. Guo, Y.Q. Wang, Y.S. Wang, Z.G. Zhang, G.Z. Lu, *Catal. Letters* 119 (2007) 185–190.
- [25] Y. Li, Z. Feng, Y. Lian, K. Sun, L. Zhang, G. Jia, Q. Yang, C. Li, *Microporous Mesoporous Mater.* 84 (2005) 41–49.
- [26] X. Wang, Q. Zhang, Q. Guo, Y. Lou, L. Yang, Y. Wang, *Chem. Commun.* 12 (2004) 1396–1397.
- [27] X. Wang, Q. Zhang, S. Yang, Y. Wang, *J. Phys. Chem. B* 109 (2005) 23500–23508.
- [28] S. Yang, W. Zhu, Q. Zhang, Y. Wang, *J. Catal.* 254 (2008) 251–262.
- [29] Q. Zhang, Q. Guo, X. Wang, T. Shishido, Y. Wang, *J. Catal.* 239 (2006) 105–116.
- [30] A. Held, J. Kowalska-Kuś, A. Łapiński, K. Nowińska, *J. Catal.* 306 (2013) 1–10.
- [31] Y. Wang, Q. Zhang, T. Shishido, K. Takehira, *J. Catal.* 209 (2002) 186–196.

- [32] M.S. Kumar, M. Schwidder, W. Grünert, A. Brückner, *J. Catal.* 227 (2004) 384–397.
- [33] J. Pérez-Ramírez, M.S. Kumar, A. Brückner, *J. Catal.* 223 (2004) 13–27.
- [34] B. Horváth, T. Soták, M. Hronec, *Appl. Catal. A Gen.* 405 (2011) 18–24.
- [35] F. Fan, Z. Feng, C. Li, *Acc. Chem. Res.* 43 (2010) 378–387.
- [36] S. Bordiga, R. Buzzoni, F. Geobaldo, C. Lamberti, E. Giamello, A. Zecchina, G. Leofanti, G. Petrini, G. Tozzola, G. Vlaic, *J. Catal.* 158 (1996) 486–501.
- [37] F. Fan, K. Sun, Z. Feng, H. Xia, B. Han, Y. Lian, P. Ying, C. Li, *Chem. - A Eur. J.* 15 (2009) 3268–3276.
- [38] D. Scarano, A. Zecchina, S. Bordiga, F. Geobaldo, G. Spoto, G. Petrini, G. Leofanti, M. Padovan, G. Tozzola, *J. Chem. Soc. Faraday Trans.* 89 (1993) 4123–4130.
- [39] J.P. Gallas, J.M. Goupil, A. Vimont, J.C. Lavalley, B. Gil, J.P. Gilson, O. Miserque, *Langmuir* 25 (2009) 5825–5834.
- [40] A. Penkova, L.F. Bobadilla, F. Romero-Sarria, M.A. Centeno, J.A. Odriozola, *Appl. Surf. Sci.* 317 (2014) 241–251.
- [41] J. Lu, M. Luo, H. Lei, C. Li, *Appl. Catal. A Gen.* 237 (2002) 11–19.
- [42] O. Vaughan, G. Kyriakou, N. Macleod, M. Tikhov, R. Lambert, *J. Catal.* 236 (2005) 401–404.
- [43] A. Miller, B. Zohour, A. Seubsai, D. Noon, S. Senkan, *Ind. Eng. Chem. Res.* 52 (2013) 9551–9555.
- [44] A. Palermo, A. Husain, M.S. Tikhov, R.M. Lambert, *J. Catal.* 207 (2002) 331–340.
- [45] E. Ananieva, A. Reitzmann, *Chem. Eng. Sci.* 59 (2004) 5509–5517.

Supplementary Material

[Click here to download Supplementary Material: SI_EPOX_ALK_FINAL.docx](#)