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Chapter

Application of Infrared Spectroscopy in Catalysis: Impacts on Catalysts' Selectivity

Patricia Concepción

Abstract

Catalysis plays an important role in sustainable chemistry, enabling the development of more efficient processes by minimizing the consumption of energy and reducing the generation of by-products. The design of efficient catalysts is a key point in this respect, where spectroscopy confers fundamental knowledge at the molecular scale. Among the different spectroscopies, infrared (IR) spectroscopy is of great interest, enabling information about the nature of active species and the reaction mechanism, leading to precise structure-activity correlations, which are a key point in the design of new catalysts. Moreover, the dynamic behavior of the catalysts under working conditions can be also monitored by IR spectroscopy, where structural modifications of working catalysts have strong repercussion in catalysis. In this chapter, interesting examples will be discussed, related to industrial relevant processes, like Fischer-Tropsch synthesis, ethylene oligomerization, synthesis of aniline from nitrocompounds, and the dehydration of aldoximes to nitriles.

Keywords: catalysis, Fischer-Tropsch, ethylene, nitrobenzene, aldoximes, CO

1. Introduction

One of the greatest challenges in the current chemical industry is the development of high-efficient processes with increased selectivity and reduced generation of by-products. This has motivated extensive research in the last years focused on the use of alternative renewable feedstocks and on the development of less energetic reaction pathways or radically new chemical processes [1]. Catalysis plays an important role in defining new eco-efficient processes, where improvements in catalyst design and in catalytic reactor engineering are key elements that have to be linked to each other. The rational development of catalysts with enhanced catalytic performance relays on a fundamental knowledge of the catalytic process encompassing the reaction mechanism, rate-limiting reaction step, and the nature of active sites of the catalyst, where spectroscopy and theoretical studies are key aspects [2, 3]. Among the different types of spectroscopies, infrared (IR) spectroscopy is one of the most powerful techniques for the characterization of catalytic systems. This is easily demonstrated by the high number of studies found in the literature focused on the characterization of catalysts involved in industrial relevant processes [4–8]. In recent years, thanks to the technological advances allowing enhanced spectral (signal/noise level), temporal (rapid scan and step scan), and

spatial (IR microscopy) resolution, with cutting-edge values in the μs and μm range, respectively, and by the development of new catalytic IR cells enabling transient studies in the μs range [9], a lot of interest has emerged in studying the catalyst under conditions resembling those encountered in catalysis, i.e., under "in situ" or "operando" conditions [10, 11]. In addition, extensive effort is being placed in coupling IR spectroscopy to other spectroscopies (UV–Vis, EXAFS, AP-XPS) [12, 13], expanding the information obtained for a given catalytic system. In the present chapter, the application of IR spectroscopy in catalysis is described providing interesting examples to illustrate how IR spectroscopy allows accurate characterization of catalyst surface sites and the identification of active sites in working catalysts enabling to establish structure-activity correlations, being this key point in the design of new catalysts. Moreover, the analysis of the reaction mechanism and rate-determining reaction steps by means of time- and temperature-resolved IR spectroscopy will also be discussed. Some examples related to relevant industrial processes like Fischer-Tropsch synthesis, ethylene oligomerization, dehydration of aldoxime compounds to their corresponding nitriles, and hydrogenation of nitrobenzene to aniline or azobenzene will be provided in order to illustrate the great potential of IR spectroscopy in the field of catalysis.

2. IR spectroscopy in catalyst characterization

IR spectroscopy provides detailed molecular information of the nature of adsorbed species on a catalyst surface, their interaction strength, and evolution under controlled atmospheres and temperatures. Using specific probe molecules, it allows to extract relevant information of the nature of surface sites on a catalyst, such as acid, base, and redox sites, surface defects, and the dynamic behavior of those sites under reaction conditions. Moreover, thermodynamic data such as entropy and enthalpy of molecular adsorption on a specific surface site [14, 15] and kinetic data can be accurately obtained. Altogether and comparing the IR data with macro-kinetic catalytic data, it assists in defining precise structure-activity correlations on a working catalyst, which is crucial in new catalyst designs. On the other hand, IR spectroscopy can be applied under a diverse set of environments: in air, in vacuum or in the presence of reactants under controlled low pressure, at cryogenic or high temperatures, and under more relevant catalytic conditions, including gases at atmospheric or even at higher pressures (20–30 bar) and liquids, allowing catalyst research to be performed under a wide range of reaction conditions. In the following sections, the application of IR spectroscopy in catalysis, especially in unraveling the nature of surface sites, discerning those who acts as active sites, and determining the reaction mechanism and rate-limiting step, will be discussed through selected illustrative examples.

2.1 Determination of the nature of surface sites

The surface of industrial catalysts is quite complex, comprising sites of different natures such as Brønsted (H^+) acid sites, Lewis acid and base sites, transition metals with redox properties, and surface defects. Due to this huge number of sites, it is sometimes hard to get information about the intrinsic properties of the surface sites present in a working catalyst and, more importantly, to identify those who are involved in the catalytic process, called active sites. In this direction, IR spectroscopy with the aid of probe molecules has been proven as a very powerful characterization technique. Such probe molecules interact with specific surface sites resulting in a shift of their characteristic vibrational mode providing information

about the chemical properties of the surface site (i.e., oxidation state, coordination, and chemical environment) and in the case that the adsorption coefficient of the corresponding IR mode is known, allowing their quantification. Many probe molecules are reported in the literature enabling information of specific aspects of the catalyst surface [16–18]. The choice of an appropriate molecule is a crucial point in the surface characterization, and often the combined use of several molecules is required for a comprehensive knowledge of the catalyst surface sites. Perhaps, the most widely known application of probe molecules in IR spectroscopy is related to the identification and quantification of acid sites (Lewis and Brønsted) in a catalyst [19, 20]. Several base molecules have been used for that purpose, where weak bases like H_2, N_2, CO, and NO have been proven as very sensitive to the local environment and oxidation state of the surface site [21, 22], while strong bases, like pyridine and ammonia, are less sensitive but very specific to the presence of Brønsted acid sites [23, 24]. The use of other probe molecules, like acetonitrile, alcohols, and thiols, has also been reported [25]. In this direction, an interesting example with important industrial repercussion is the search of efficient catalysts for the elimination of NO_x emissions, where the selective catalytic reduction (SCR) of NO_x with ammonia (NH_3-SCR) or hydrocarbons (HC-SCR) is today one of the most efficient technologies. In this context, Cu-exchanged zeolites have shown interesting catalytic performance, where the identification of the nature of copper species is clue but highly challenging due to the coexistence of many different species such as isolated Cu^{2+},Cu^+,$Cu(OH)^+$, dimeric [Cu-O-Cu], sub-nanometric Cu_xO_y clusters, and/or CuO and Cu_2O aggregates [26–28]. Despite the massive number of investigations on these systems, there is still controversy about the nature of active sites, mainly due to the wide range of catalysts explored in the literature containing a mixture of multiple copper sites. Therefore, one way to overcome the complexity of many industrial catalysts is to try to design catalysts containing well-defined uniform sites and use them as model systems in both catalytic and spectroscopic studies. Following this hint, Cu-exchanged zeolites with uniform isolated sites (Cu-SAPO-34 and Cu-SSZ-13) have been prepared in our group by a hydrothermal synthetic approach [29–31]. Both catalysts show high activity and stability in the NH_3-SCR reaction, making them interesting candidates for the investigation of active sites in the SCR reaction. IR spectroscopy of CO and NO adsorption as probe molecules, combined with theoretical modeling of the vibrational frequencies, has allowed precise identification of Cu^{2+}/Cu^+ species located either in the 8-ring or 6-ring of the zeolite structure, as well as the identification of Cu-O-Cu dimeric species, resolving some of the controversy in the assignation of IR band frequencies present in the literature and establishing the role of isolated Cu^{2+}/Cu^+ ions as active sites in the NH_3-SCR [32].

Among the different types of industrial catalysts, metal-based catalysts containing noble metals like Pt, Pd, and Rh and non-noble metals like Ni, Co, and Ru are used in many industrial processes. The catalytic activity and selectivity of this class of catalysts are strongly influenced by their particle size and morphology, electronic state of surface metal atoms, and metal interfaces or heterojunctions in the metal particle, where a comprehensive knowledge of these parameters is essential in understanding their catalytic performance. To achieve that, the combination of several spectroscopic tools is strongly required, being IR of CO as probe molecule of great interest. Based on the shift of the $\nu(C{\equiv}O)$ frequency, metal particles exhibiting different facets like the (111) (100) (110) crystallographic planes, as well as the presence of undercoordinated metal atoms located in steps and corners of the metal particle, can be easily detected [33, 34]. For example, by combining IR of CO as probe molecule with theoretical vibrational simulations obtained by the density functional theory (DFT) method, gold atoms of different natures have been

investigated in supported gold nanoparticle catalysts. Specifically, gold atoms with different coordination degrees (for instance, in the edge and corners of the particle), electron density (for instance, $Au^{\delta+}$ atoms located in the perimeter of the gold particle in close contact with the support), and oxidation state (Au^{3+}, Au^+ and Au^0) have been accurately defined [35].

Finally, the characterization of surface base sites in a catalyst using IR spectroscopy of probe molecules (like CO_2, trichloromethane, acetylene, and pyrrole) is less studied, mainly due to the complexity of some of the probe molecules when adsorbed on the catalyst surface [17, 36]. For example, CO_2 adsorption on basic surface sites leads to several types of carbonate species which hinder accurate identification of surface base properties [37].

2.2 Determination of the nature of active sites: structure-activity correlation

The main challenge in spectroscopy, and specifically in IR spectroscopy, is to differentiate the catalytic active sites which are directly involved in the reaction mechanism, from the rest of sites normally present on the surface of working catalysts. Only in this case, it is possible to define accurate structure-activity correlations, which allows to direct the synthesis of new catalysts. Identification of active sites is not always straightforward and requires a multidisciplinary approach, combining surface characterization with catalytic data and, if possible, with theoretical calculations. In the following subsections, we will provide some examples of our work where active sites have been accurately identified.

2.2.1 Nature of active sites in the dehydration of aldoximes to nitriles on heterogeneous ceria catalysts

Nitriles are precursors for a wide range of organic products like carboxylic acids, amines, ketones, and amides. The most efficient route for the synthesis of nitriles is the dehydration of aldoximes that can easily be obtained from the corresponding aldehydes. Homogeneous catalytic systems such as Pd(II) complexes with a phosphino-oxime ligand [38], Co(II)Cl$_2$ [39], Ga(OTf)$_3$ [40], and Fe(ClO$_4$)$_3$ [41] are employed with interesting performance but presenting important limitations such as catalyst recovery, use of hazardous organic solvents, and long reaction time. Therefore, a lot of attention is paid in developing alternative heterogeneous catalysts. Among the different heterogeneous catalysts reported in the literature [42, 43], nanocrystalline ceria (nCeO$_2$) stands as a very promising catalyst in the dehydration of a variety of aldoximes (including alkyl and cycloalkyl aldoximes) to the corresponding nitriles at moderate temperature (149°C) with yields around 80–97% [44]. The catalyst shows good stability and recyclability after several uses. While both acid and basic sites are discussed in the literature for aldoxime dehydration, there is no clear understanding about the role of each of them in the reaction mechanism. In order to shed light into the participation of acid and base sites in the reaction mechanism, we performed a detailed IR study on nCeO$_2$ compared with other catalysts (CeO$_2$, MgO, Al$_2$O$_3$, and TiO$_2$). The different catalysts are studied in the dehydration of 4-methoxybenzaldehyde oxime, where the initial reaction rate follows the order nCeO$_2$ > MgO > Al$_2$O$_3$ > CeO$_2$ > TiO$_2$. Surface characterization is done using CO and CHCl$_3$ as probe molecules. Based on the IR spectra of CO adsorption (**Figure 1A**), the acid strength of the different catalysts (being proportional to the red $\nu(C\equiv O)$ shift) can be ranked in the order Al$_2$O$_3$ > TiO$_2$ > MgO > nCeO$_2$ > CeO$_2$, while the number of surface acid sites (peak area normalized by the catalyst surface area), called surface acid density, follows a different order CeO$_2$ > TiO$_2$ > nCeO$_2$ > Al$_2$O$_3$ > MgO. In the same way, based on the
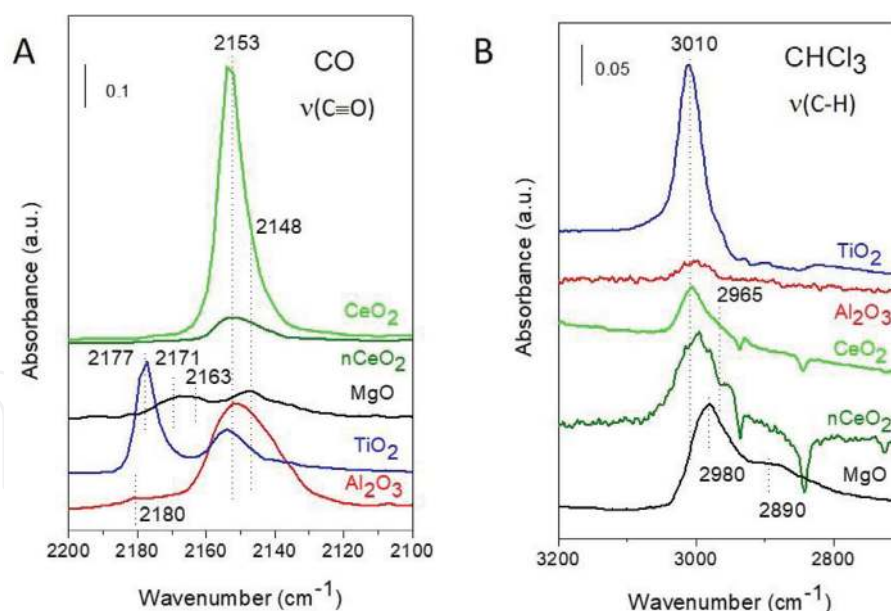
Figure 1.
(A) IR spectra of CO adsorption at saturation coverage on the different catalysts. (B) IR spectra of CHCl$_3$ adsorption at saturation coverage on the same catalysts. All spectra are normalized to sample weight.

IR spectra of CHCl$_3$ adsorption (**Figure 1B**), the basic strength (being proportional to the blue ν(C-H) shift) can be ranked in the order MgO > nCeO$_2$ > CeO$_2$ > TiO$_2$ > Al$_2$O$_3$. The same order can be applied for the surface base density.

Once the catalyst acid and base sites are established, the "in situ" dehydration of propionaldehyde oxime is studied by IR spectroscopy in order to understand how the presence of those sites influences the reactivity of the samples. The observed IR red shift of both νC=N (from 1640 cm^{-1} in the gas phase to 1646 cm^{-1} on nCeO$_2$ and 1667 cm^{-1} on Al$_2$O$_3$) and νN-OH vibrations (1028 cm^{-1} in the gas phase to 1037 cm^{-1} on nCeO$_2$ and 1051 cm^{-1} on Al$_2$O$_3$), suggests a mechanism for which the activation of propionaldehyde oxime involves an N-bond complex to a surface Lewis acid site increasing in that way the C=N and N-OH bond strength [45], followed by N-OH bond elimination and C-H cleavage with subsequent water and nitrile formation (**Scheme 1**). This differs to the conventional oxidative dehydration mechanism (i.e., interaction of the oxygen of the oxime with Lewis acid sites) for which a blue shift of both vibrations would be expected [45].

In addition, notice that in general the shift in the IR vibration of an adsorbed molecule reflects the degree of bond activation which is proportional to their catalytic reactivity. However, such a correlation is not found in this case, where the observed shift of the N-OH vibration is proportional to the sample acid strength, but doesn't match to the catalyst activity. Thus, Lewis acid sites, while being involved in the reaction mechanism, seems not to be a determinant factor for the catalytic activity. On the contrary, considering that both nCeO$_2$ and MgO samples, with the highest basic strength, are the most active catalysts, surface basicity should
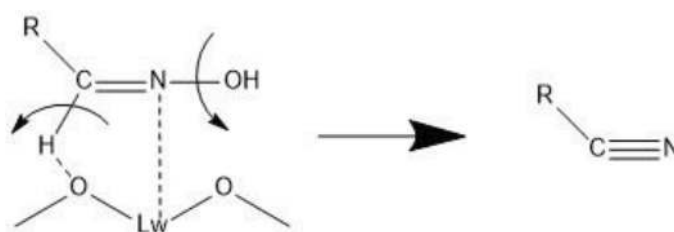
Scheme 1.
Proposed mechanism for the dehydrogenation of aldoximes to nitriles on metal oxide heterogeneous catalysts.

play a decisive role in the reaction mechanism. Basic sites are involved in the C-H bond cleavage, which from the IR and catalytic studies can be proposed as the rate-limiting step of the reaction. In conclusion, both Lewis acid sites and basic sites are involved in the reaction mechanism, being Lewis acid sites involved in the adsorption of the oxime, while strong basic sites are required for C-H activation.

In this way, combining IR data with catalytic data, the highest catalytic activity of the $nCeO_2$ can be ascribed to an appropriate number of surface acid sites enabling the activation of the oxime and strong basic sites favoring C-H cleavage. While similar strong basic sites are present on MgO, the lower surface density of acid sites explains its lower activity than $nCeO_2$. Moreover, owing to the basic character of both $nCeO_2$ and MgO, desorption of the nitrile from the catalyst surface is favored avoiding secondary reactions and enhancing catalyst stability.

2.2.2 Nature of active sites in ethylene oligomerization reaction

Ethylene oligomerization is an interesting chemical route of industrial importance for the production of linear and branched higher olefins. Those olefins, depending on their carbon number, show several applications, for example, comonomers in polyethylene industry (C_4–C_6), as plasticizer alcohols (C_8–C_{10}), as synthetic lubricants (C_{10}–C_{12}), in the detergent industry (C_{12}–C_{16}), and as lube oil components or in surfactant manufacture (C_{16}–C_{18}). Industrially, the process takes place in liquid phase using homogeneous transition metal complexes as catalysts and alkyl aluminum compounds as activators [46]. Owing to the limitations of the actual industrial process, such as difficulty to separate the catalyst from oligomers, increase of operational cost, and broad carbon number distribution of products, the search of alternative heterogeneous solid catalysts is very interesting from both economic and environmental points of view. In this sense, nickel loaded on acidic aluminosilicates such as zeolites and amorphous mesoporous supports has attracted great attention as efficient and environmentally friendly heterogeneous catalysts for ethylene oligomerization, although they suffered from catalyst deactivation with time of stream (TOS) [47]. Recently, our group developed a bifunctional catalyst comprised of Ni loaded on nanocrystalline zeolite HBeta (Ni-HBeta) with high catalytic activity and stability during the oligomerization process [48]. Ethylene conversions of ~90% at 2.5 wt% Ni loading in the Ni-HBeta catalyst under conventional reaction conditions (T = 120°C, P_{tot} = 35 bar, P_{C2H4} = 26 bar, WHSV = 2.1 h^{-1}) are obtained without apparent signs of deactivation within 1–9 h TOS. Despite the high promising features displayed by Ni-based catalysts, the nature of active sites (isolated Ni^+ and/or Ni^{2+}) remained under debate, being subject of intense research studies in the last years [49–52]. To this aim, catalytic studies with high temporal resolution in the earliest stage of the reaction monitored by a combined gas chromatograph (GC) and mass spectrometry (MS) analysis technique and coupled with "in situ" IR-CO surface titration spectroscopic studies are performed in our group in order to identify the nature of the active Ni sites for ethylene oligomerization in the Ni-HBeta catalyst [53]. Catalysts with different nickel loadings (1, 2.5, 5, and 10 wt%) are studied. Specification of the nature of nickel sites monitored by IR of CO as probe molecule shows in all samples isolated Ni^{2+} cations in ion exchange positions of the zeolite and isolated Ni^{2+} interacting with silanol groups of internal defects (hydroxyl nests) or stacking faults of the nanocrystalline beta zeolite. Indeed, the IR-CO spectra of the activated 5wt%Ni-HBeta catalyst show IR bands at 2214 and 2207 cm^{-1} assigned to carbonyls of isolated Ni^{2+} ion exchange cations [51, 54] and an IR band at 2196 cm^{-1} attributed to isolated Ni^{2+} interacting with silanol groups [55], in addition to IR bands at 2175, 2164, 2156, and 2143, 2131 cm^{-1}

attributed to CO interacting with Brønsted acid sites, aluminols, silanols, and physically adsorbed CO, respectively (**Figure 2**).

Interestingly, independent of the nickel loading in the Ni-HBeta sample, the time-resolved GC–MS catalytic studies performed in a low-dead-volume catalytic setup, working at 1 bar, 120°C, and WHSV of 33 h^{-1} (**Figure 3A**), show a significant loss of ethylene conversion in parallel to a decrease in the butene concentration at the very early reaction stage (first 10 min) before achieving pseudo-steady-state activity at TOS of 30 min. The short time frame where the initial loss of activity occurs prevents their detection in a conventional high-pressure reactor setup, where all catalysts are shown to remain stable up to 9 h TOS. Coupled to the catalytic studies, IR studies at the same experimental conditions are performed using a low-volume IR catalytic cell. The "in situ" IR ethylene oligomerization reaction is stopped at different stages of the reaction (10 s, 8 min, 30 min, and 70 min) and the nature of Ni sites titrated by IR of CO as probe molecule. Since all catalysts displayed similar trends, the 5wt%Ni-HBeta catalyst is taken as representative in the following discussion. After "in situ" reaction with ethylene in the IR catalytic cell, a sharp reduction in the intensity of the IR bands related to the isolated Ni^{2+} ions is noticed even after only 10s of reaction (**Figure 3B**). The decrease in intensity is particularly significant for the higher frequency bands at 2214 and 2207 cm^{-1} related to the ion exchanged Ni^{2+} ions with stronger Lewis acid character, while that at 2196 cm^{-1} of less acidic isolated Ni^{2+} interacting with silanol groups is much less affected; meanwhile, Brønsted acid sites at 2175 cm^{-1} are also considerably reduced in intensity. In addition, dicarbonyl Ni$^+$ bands at 2138 and 2095 cm^{-1} [56] are clearly detected at low CO coverage since the very early reaction stage, increasing in intensity during the course of the reaction (spectra not shown).

Linking the IR and GC–MS data (**Figure 3C**), Ni$^+$ ions cannot be considered as active site since the intensity of the IR bands of Ni$^+$ ions increases with reaction time, while the catalytic activity decreases. Despite this, a clear parallelism between
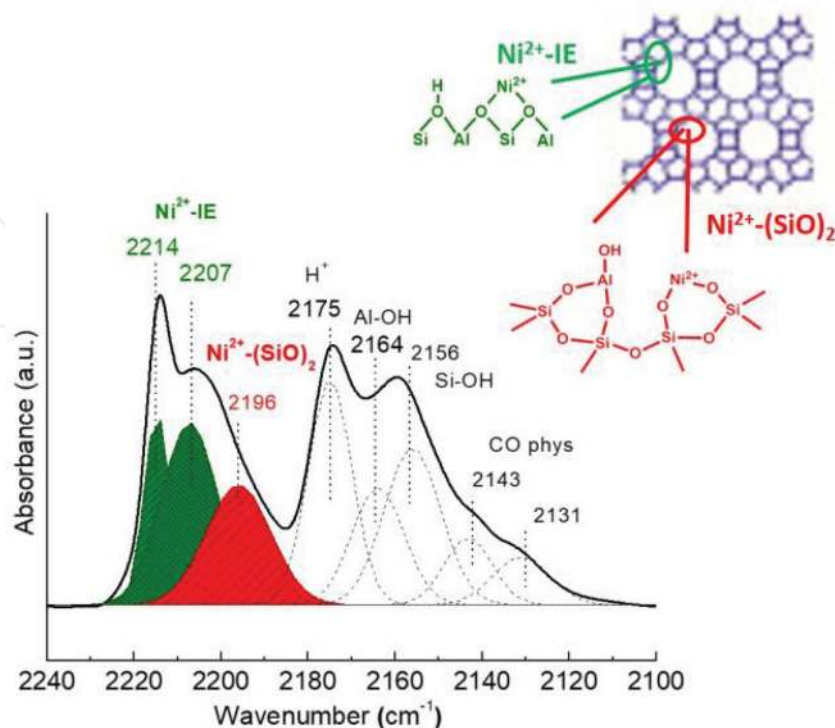

Figure 2.
IR spectra of CO adsorption at saturation coverage and at −175°C on the 5wt%Ni-HBeta sample activated in N$_2$ flow (20 ml/min) at 300°C for 3 h.
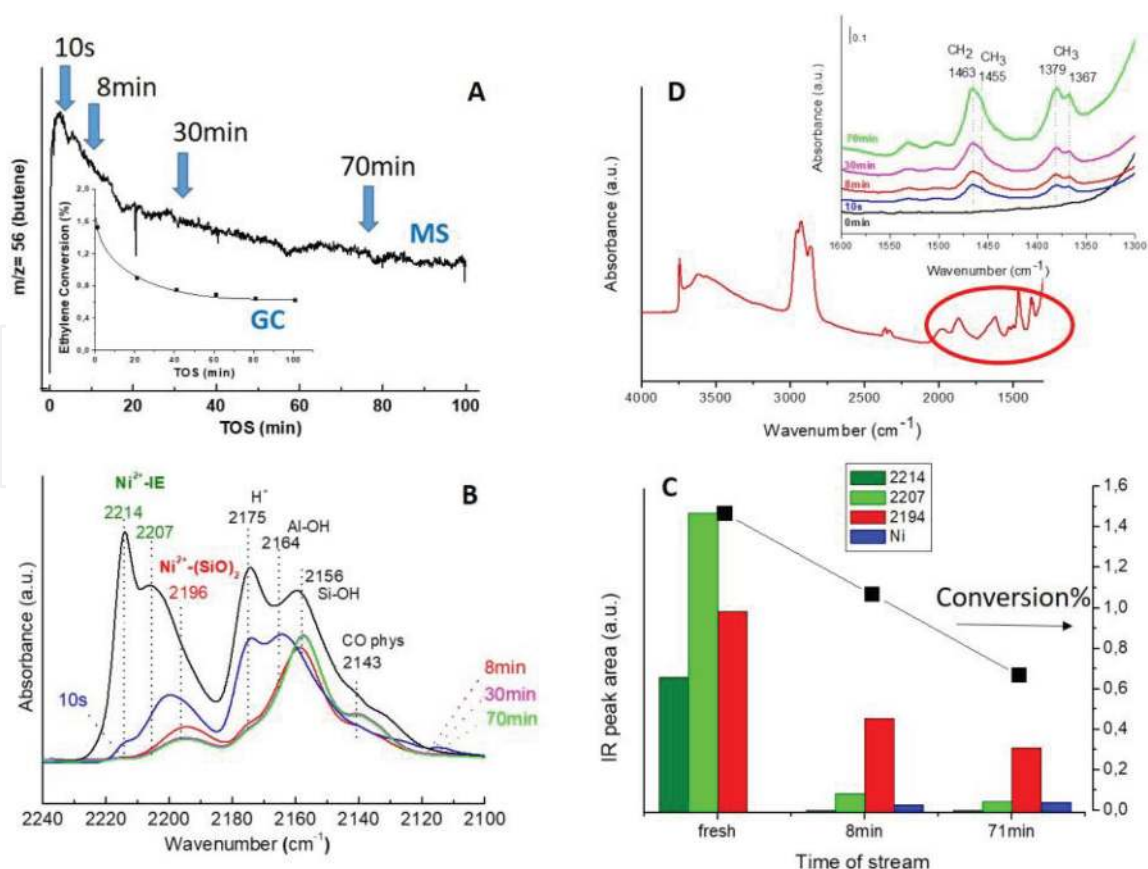
Figure 3.
(A) Time-resolved GC–MS analysis in the ethylene oligomerization reaction performed at 1 bar and 120°C on the 5wt%Ni-HBeta sample. The arrows correspond to the reaction stages where surface titration by IR-CO is performed. (B) IR spectra of CO adsorption at −175°C and at saturation coverage on the 5wt%Ni-HBeta sample stopped at selected reaction times. (C) Evolution in the concentration of the different nickel sites in the working 5wt%Ni-HBeta sample and their correlation with catalytic data (conversion). (D) The "in situ" IR spectra under ethylene oligomerization reaction at 1 bar and 120°C and at different TOS highlighting hydrocarbon formation.

the reduction in intensity of the IR bands of isolated Ni^{2+} ions and the initial decline in ethylene conversion rate is observed, implying that the two phenomena should be closely related. Significantly, while isolated ion exchange Ni^{2+} ions (IR bands at 2214 and 2207 cm^{-1}) become almost totally blocked in the first seconds of the reaction, Ni^{2+} ions interacting with silanol groups (IR band at 2196 cm^{-1}) remain accessible under reaction conditions and can accordingly be considered as the true catalytic active sites under steady-state conditions. The blocking of the most acid Ni^{2+} and Brønsted acid sites under reaction conditions is due to irreversibly adsorbed hydrocarbons formed from the very early stages of reaction as detected in the "in situ" IR spectra (**Figure 3D**). In conclusion, these results highlight the importance of nickel sites of intermediate Lewis acid strength in order to design efficient ethylene oligomerization catalysts.

2.2.3 Nature of active sites in the Fischer-Tropsch reaction

The Fischer-Tropsch (FT) reaction has gained renewed interest in the last years as an alternative route to produce high-quality liquid fuels from alternative sources to petroleum, such as natural gas, coal, and biomass [57]. In the FT process, cobalt-based catalysts have preferentially been employed due to their high stability, low activity for the competitive reverse water gas shift reaction (WGSR), and high selectivity to long-chain n-paraffins compared to alternative catalysts based on

iron [58]. Due to the interest in this process, a lot of research has been devoted to prepare novel catalysts with improved catalytic behavior. One conventional way to improve the catalytic activity is increasing the metal dispersion (i.e., decreasing particle size), but unexpectedly a low reaction rate and a low selectivity to the desired long-chain hydrocarbons have been observed in the FT process when decreasing the cobalt particle size below 8–9 nm [59, 60]. This trend differs from the classical structure sensitivity behavior, and the reason behind has been a long-lasting debate in the literature. Particularly, the presence of unreduced Co species due to the lower reducibility of small Co nanoparticles and the reoxidation of Co sites under reaction conditions in highly dispersed catalysts [60–64] have been the most widely discussed issues. In order to understand this nonclassical particle size-dependent activity, cobalt nanoparticles with a homogenous particle size distribution from 5.6 to 10.4 nm are prepared in our laboratory using a reverse micellar synthesis procedure and deposited onto a surface-silylated ITQ-2 delaminated pure silica zeolite [65]. As reference, a Co/SiO_2 catalyst with Co particle size of 141 nm is also studied. The metal loading in all samples is 10 wt%. The high reducibility of the catalysts and their homogeneous particle size distribution make them ideal candidates as model systems for investigating the aforementioned catalytic behavior. Spectroscopic studies combined with catalytic studies under FT conditions (P = 20 bar and T = 220°C) are performed. In the catalytic studies, the intrinsic catalytic activity (TOF) decrease with decreasing Co particle size from 10.4 to 5.6 nm remains constant for particle sizes above 10.4 nm, according to the literature. The evolution of the cobalt sites under FT reaction conditions is nicely followed in the "in situ" IR studies performed at ambient pressure under syngas flow and at increasing temperatures (25–220°C) (**Figure 4**). All samples show similar trend, where at 25°C two IR bands at 2048 cm^{-1} associated with linearly CO adsorbed on fcc Co^0 sites [66] and at 1625 cm^{-1} due to adsorbed water are observed. Increasing the temperature to 150 and 200°C, there are no bands observed in the Co-carbonyl region, probably due to a complete blockage of the surface sites and due to CO dissociation and the growth of adsorbed H_xC intermediate species. Indeed, a band at 612 cm^{-1} is observed in the low-frequency range, associated with adsorbed oxygen atoms (i.e., Co-O) [67]. Finally, increasing the temperature to
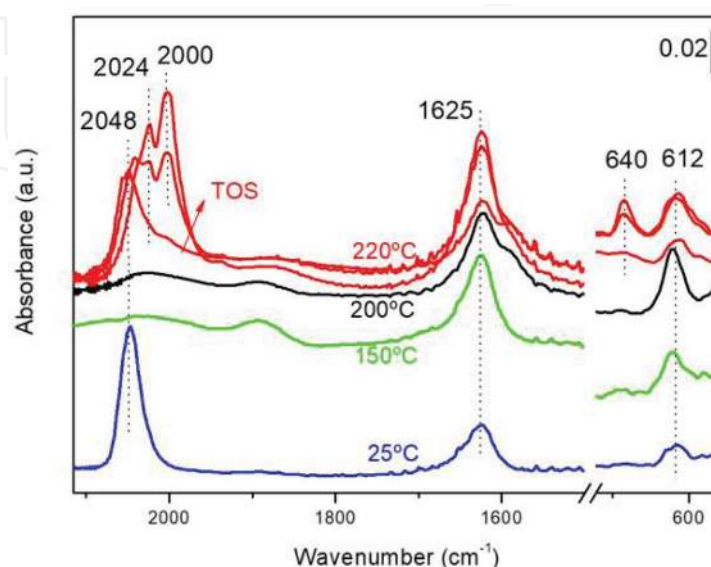

Figure 4.
FTIR spectra of the Co/ITQ-2 sample with 10.4 nm Co particle size under FT reaction conditions at 1 bar and at 25, 150, 200, and 220°C. Each spectrum is recorded after 45 min at each temperature. At 220°C the IR spectra are recorded at 120, 210, and 240 min time on stream (TOS).

220°C, Co-carbonyls are rapidly restored, due to desorption of reaction intermediate species leaving free cobalt metal sites for CO adsorption. Concomitantly, a progressive shift in the Co-carbonyl IR band is observed from 2048 cm^{-1} to 2024 and 2000 cm^{-1} with increasing reaction time at 220°C, where the 2024 and 2000 cm^{-1} IR bands are related to unsaturated or low coordinated cobalt surface sites located in defect sites or on more open crystallographic cobalt planes [68, 69]. Being this shift in the IR bands irreversible, it is ascribed to cobalt surface reconstruction from an fcc structure to a more open crystallographic structure, the last one behaving as the true active site under working conditions [65]. Notice the parallel appearance of an IR band at 642 cm^{-1} ascribed to cobalt-carbon species [70, 71] which provides the first experimental evidence for the role of carbon atoms in promoting surface reconstruction of the cobalt particle under FT conditions, in agreement to previous DFT calculations [72].

Notoriously, on the sample with the smallest Co particle size (5.6 nm) and lower catalytic activity (**Figure 5A**), a band at 2060 cm^{-1}, not observed on the other samples, is detected in the "in situ" IR spectra (**Figure 5B**). This band, already observed in their reduced state prior to FT reaction, increases in intensity under FT conditions and has been ascribed to Co$^{\delta+}$ sites in the cobalt-support interface [73]. While those interface sites are mayoritary in particles of small size, their increase under FT reaction conditions results from morphological changes in the small cobalt nanoparticle, as already detected by HRTEM, where a flattening of the cobalt particle is observed after FT reaction, enhancing the amount of metal interface sites. Since the electropositive character of the Co$^{\delta+}$ sites inhibits CO dissociation, a higher amount of these sites turn out in a lower FT activity, explaining in that way the lower FT catalytic activity observed at small Co particle sizes. This result is interesting from a fundamental point of view explaining the nonclassical particle size-dependent FT activity and more importantly from a scientific point of view, highlighting the dynamism of catalysts under reaction condition and their impact on their catalytic performance, which has been underestimated in many studies. In this context, thanks to the recent development of advances of the spectroscopic tools with "in situ" capabilities, a lot of progress has been done in this direction, not only in the FT reaction but also in other catalytic processes, revealing a highly dynamic behavior of the catalysts at working conditions [74, 75].
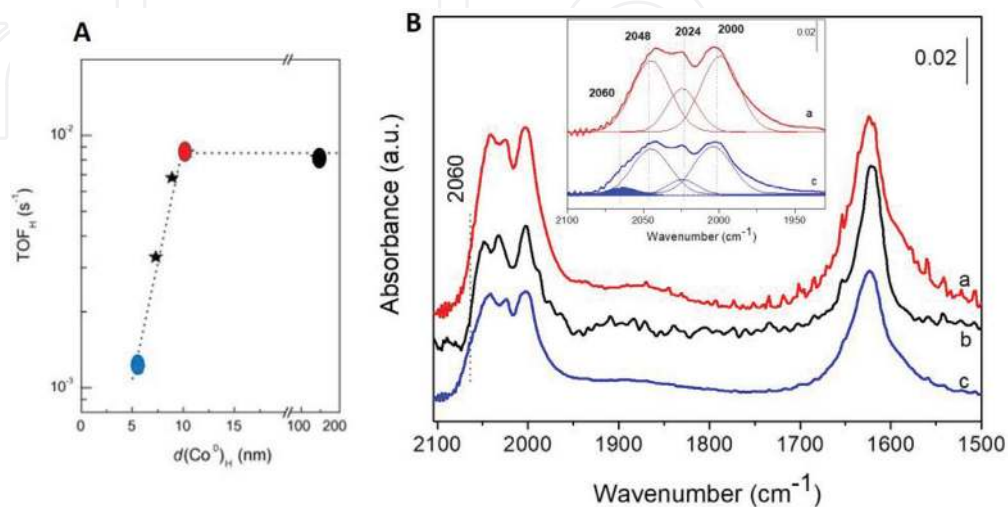

Figure 5.
(A) Variation of the turnover frequency (TOF) in FT at 220°C and 20 bar with the cobalt particle size. (B) IR spectra after 4 h on stream in FT (220°C, 1 bar) for (a) Co-ITQ-2 with 10.4 nm Co particle size, (b) Co/SiO₂ with 141 nm Co particle size, and (c) Co-ITQ-2 with 5.6 nm Co particle size samples. In the inset the deconvolution of the Co-carbonyl region highlighting the presence of the 2060 cm^{-1} IR band.

2.3 Determination of reaction mechanism and rate-limiting reaction step

Besides the characterization of catalyst surface sites, the identification of reaction intermediate species and reaction mechanism in a catalytic process is of great interest. It allows to define the rate-limiting reaction step, which coupled to a fundamental knowledge of the nature of active sites involved in each elementary step, enables a rational design of industrial catalysts. However, due to the transient nature of reaction intermediates, differentiating them from other species present in the catalyst but not being involved in the catalytic process (called as spectators) is often difficult. Ways to do it are following the evolution of surface species during time- and temperature-resolved IR experiments and combining the IR data with catalytic data obtained either "in situ" in coupled GC–MS analysis or in "ex situ" studies. The same can be done performing pressure-dependent IR studies. Next, an example will be presented that is supported by temperature-resolved IR studies, and different reaction mechanisms are established depending on the catalyst properties.

### 2.3.1 Hydrogenation of nitroaromatics on supported gold catalysts

Experiments performed in our laboratory have shown that under the same reaction conditions (T = 120°C, P = 4 bar H_2, [Au] = 1%mol, Nitrobenzene = 0.25 M), Au nanoparticles of 2.5–3.5 nm particle size deposited on ceria (Au/CeO$_2$) and on titania (Au/TiO$_2$) display different selectivities in the hydrogenation of nitrobenzene. Thus, aniline is predominately formed on Au/TiO$_2$ ($\sim$90% selectivity at 97% conversion), while azobenzene ($\sim$99% selectivity at 100% conversion) is formed on the Au/CeO$_2$ catalyst [76]. Both aniline and azobenzene are valuable intermediates in the industrial production of pharmaceuticals, agrochemicals, pigments, dyes, and food additives, conferring high interest in the possibility to tune in a rational way the selectivity to the desired product by modifying the nature of the catalyst. If one considers the general reaction scheme proposed by Haber to reduce nitroaromatics (**Scheme 2**), it seems that the different catalytic performance of both Au/TiO$_2$ and Au/CeO$_2$ catalysts has to be related to a different reaction route (direct route versus condensation route), but the question is why both catalysts follow different reaction paths, and why in the case of the condensation route aniline is not formed as the final product. In order to answer this question, IR studies combined with micro-kinetic studies have been performed on both catalysts.

2.3.1.1 IR studies of the hydrogenation of nitrobenzene on Au/TiO$_2$ catalysts

The hydrogenation of nitrobenzene is followed by IR on the Au/TiO$_2$ catalysts performing temperature-dependent studies. In the IR spectra (**Figure 6A**), simultaneous to the consumption of nitrobenzene (IR bands at 1523 cm^{-1}), nitrosobenzene (1483, 1475 cm^{-1}), phenylhydroxylamine (1489 cm^{-1}), and aniline (1495 cm^{-1}) are formed [77, 78]. The micro-kinetic data IR displayed in **Figure 6B** shows a low surface concentration of nitrosobenzene and a high amount of phenylhydroxylamine. Being phenylhydroxylamine an intermediate compound (see **Scheme 2**), its high surface concentration indicates a low hydrogenation rate to aniline and the coexistence of an additional parallel direct reaction path of phenylhydroxylamine formation starting from nitrobenzene in which nitrosobenzene formation is circumvented (**Figure 6C**). These results and the absence of IR bands of azoxy and/or azocompounds help to propose a direct hydrogenation route. Moreover, it is shown that the low surface concentration of nitrosobenzene during nitrobenzene hydrogenation is clue in this reaction path.
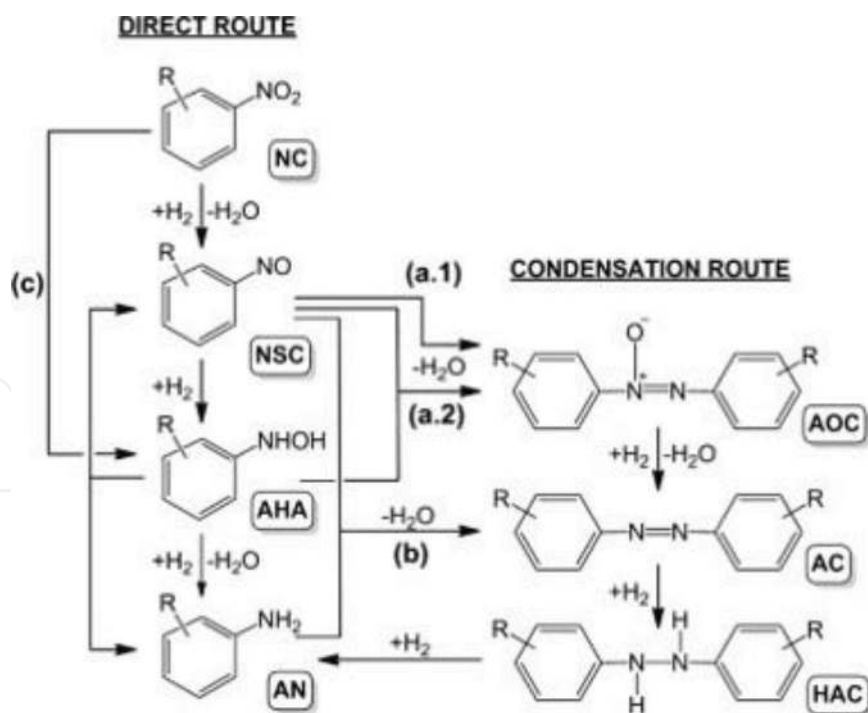
Scheme 2.
Reaction pathways in the hydrogenation of nitrocompounds to anilines. NC = nitrocompound,
NSC = nitrosocompound, AHA = aromatic hydroxylamine, AN = aniline, AOC = azoxycompound,
AC = azocompound, HAC = hydrazocompound [76].
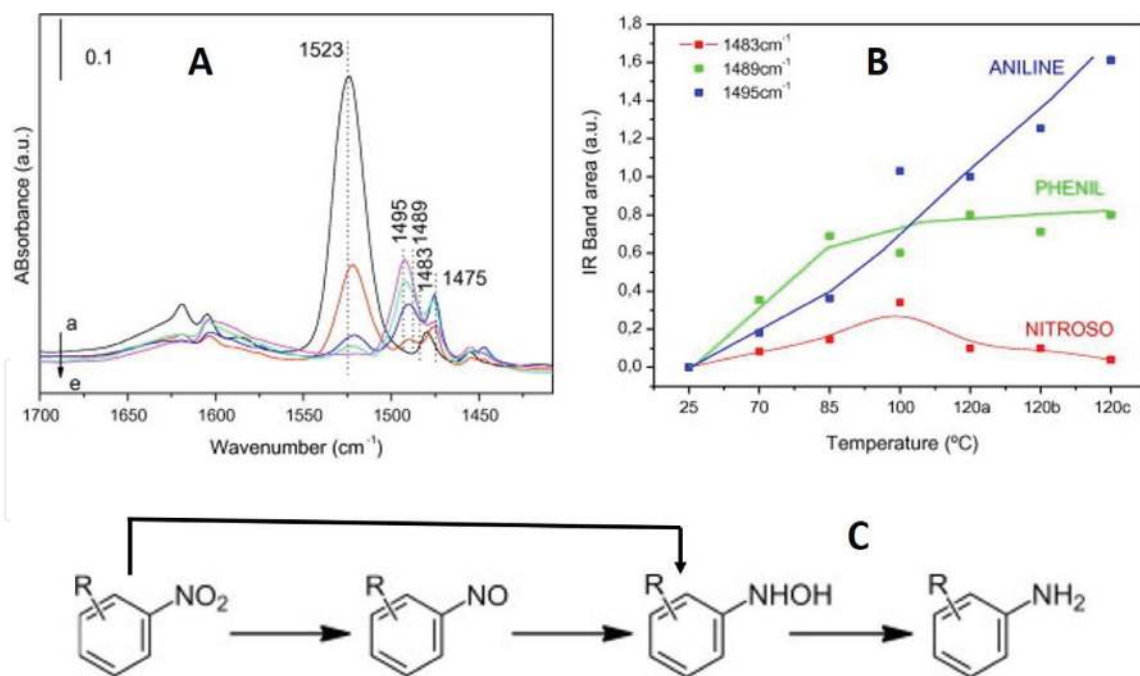
Figure 6.
(A) IR spectra in the hydrogenation of nitrobenzene on Au/TiO$_2$ catalyst at (a) 25°C, (b) 70°C, (c) 85°C, (d)
100°C, and (e) 120°C (0.5 mbar NB and 8 mbar H$_2$). (B) Evolution of the IR surface reaction intermediates
species with temperature. (C) Proposed reaction path.

This is confirmed by additional IR experiments where the surface coverage of
nitrosobenzene on the Au/TiO$_2$ catalyst is modified and the evolution of surface
species under hydrogenation conditions monitored. Thus, at low surface coverage, a
fast hydrogenation of nitrosobenzene to phenylhydroxylamine is observed,

followed by further hydrogenation to aniline, whereas at high nitrosobenzene coverage, azoxybenzene is mainly formed [76].

2.3.1.2 IR studies of the hydrogenation of nitrobenzene on Au/CeO₂ catalysts

In the temperature-dependent nitrobenzene hydrogenation IR studies performed on the Au/CeO₂ catalyst, nitrobenzene (IR bands at 1509 and 1343 cm^{-1}) disappears slowly, followed by nitrosobenzene formation (1540, 1491, and 1398 cm^{-1}) (**Figure 7A**). Nitrosobenzene is stabilized on the catalyst surface until 100°C, temperature at which azoxybenzene (IR bands at 1546, 1372, and 1357 cm^{-1}) is formed. Increasing temperature to 120°C azobenzene (IR bands at 1303 and 1566 cm^{-1}) is formed, showing a maximum at 21 min of reaction and then starting to decrease. This is associated to desorption of azobenzene to the gas phase, avoiding in that way a progressive hydrogenation to aniline and explaining the high selectivity to azobenzene displayed by the Au/CeO₂ catalyst [76]. These results are in line with a condensation route favored by an accumulation of nitrosobenzene on the catalyst surface. Moreover, previous IR results show a very fast reactivity of nitrosobenzene with phenylhydroxylamine, even at 25°C, giving azoxybenzene. Based on it, the surface accumulation of nitrosobenzene in the hydrogenation of nitrobenzene on the Au/CeO₂ catalyst, the absence of phenylhydroxylamine in the IR spectra, and the onset of azoxybenzene formation at 100°C indicate that the hydrogenation rate of nitrosobenzene to phenylhydroxylamine is low, being this the rate-limiting step. In conclusion, from these results, the different reaction pattern observed on the Au/CeO₂ catalysts is related to the stabilization of nitrosobenzene on the CeO₂ surface, which is ascribed to their basic properties compared to the TiO₂ as support.

Accordingly, these results show that it is possible to modulate the selectivity in the one-step nitroaromatic hydrogenation by adjusting the catalyst properties modulating in that way the concentration of nitrosobenzene on the catalyst surface.
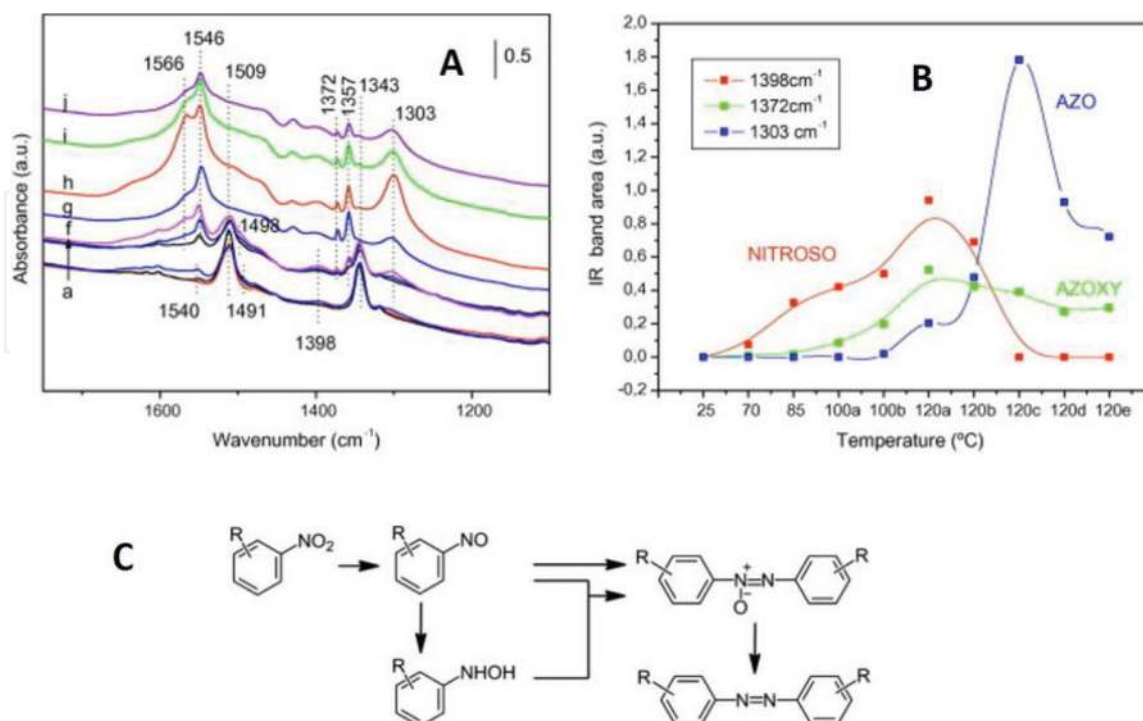

Figure 7.
(A) IR spectra in the hydrogenation of nitrobenzene on Au/CeO₂ catalyst at (a) 25°C, (b) 70°C, (c) 85°C, (d) 100°C 10 min, (e) 100°C 30 min, (f) 120°C 7 min, (g) 120°C 17 min, (h) 120°C 21 min, (i) 120°C 26 min, and (j) 120°C 46 min (0.5 mbar NB and 8 mbar H₂). (B) Evolution of the IR surface reaction intermediates species with temperature. (C) Proposed reaction path.

3. Conclusion

IR spectroscopy has been shown as a very powerful technique in the field of catalysis, enabling important information difficult to obtain with other techniques. Thus, surface sites and active species can be properly analyzed, which combined with the analysis of the reaction mechanism and the rate-limiting step are key points to direct the synthesis of catalysts with improved selectivity. Moreover, the dynamism of catalyst surfaces under reaction conditions monitored by IR spectroscopy has been highlighted, a fact usually underestimated but with strong repercussion on the catalytic performance.

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Conflict of interest

There is no conflict of interest in this publication.

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