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DRIFTS–XANES study of Pd-Ni/(Ce,Zr)O_x/Al_2O_3 model automotive catalysts

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Abstract

Pd-Ni catalysts supported on Al_2O_3 and (Ce,Zr)O_x/Al_2O_3, both in fresh and thermally aged states, were examined with the main aim of determining the effects of Ni and Ce-Zr mixed oxide on the catalytic activity for CO and C_3H_6 oxidation, and NO reduction reactions under stoichiometric conditions. For this purpose, catalytic activity results were analysed in conjunction with DRIFTS and XANES spectra recorded under reaction conditions to obtain information on the processes occurring in the catalysts during the course of the reactions. While a nickel-induced promotion of the formation of contacts between palladium and the Ce-Zr mixed oxides generally enhances the CO oxidation performance of the catalyst, it results detrimental to the NO reduction activity. This has been related to the higher difficulty in achieving the most active metallic palladium state for comparatively similar particle sizes in the presence of such contacts. Comparison of DRIFTS spectra under various reactant mixtures and between fresh and aged systems was shown to explain in a unique way the detrimental catalytic effects of hydrocarbon self-poisoning and sintering of the active components in the catalysts.

Keywords: Pd-Ni catalysts; TWC; CeO_2-ZrO_2; Al_2O_3; CO oxidation; NO reduction; C_3H_6 oxidation; Thermal aging; DRIFTS; Pd-K edge XANES

1. Introduction

Three-way catalysts (TWC) are widely used to diminish pollutant emissions (CO, NO_x and hydrocarbons) from gasoline engine powered vehicles [1–3]. Classical components of these systems usually include Rh, Pt and/or Pd as active metals, ceria as promoter and high surface alumina as the support [1,4]. In modern TWC formulations, the traditional promotion by ceria has been extended to other structurally related oxide systems in order to increase or maintain the durability of the TWC while enhancing oxygen storage capacity (OSC) properties of the catalyst [4,5]. In this respect, Ce-Zr mixed oxide systems, and in particular, in alumina supported Ce-Zr mixed oxide configurations, have been considered as optimum metal supports on the basis of their greater oxygen storage capacity after thermal sintering, which could potentially increase the useful lifetime of the catalytic system [5].

The increasingly stricter limits implanted worldwide for automobile toxic emissions have forced new aspects and requirements in three-way catalysts (TWC) to be considered. Among them, achievement of lower light-off temperature during the cold start phase is of the highest relevance, considering that the largest portion of the toxic emission is produced during that period [1,6]. In this sense, an approach of interest from an economical point of view consists in modifying the catalytic properties of palladium by introduction of a second base metal. Among these, in spite of legislative restrictions for its use in some countries, nickel has shown promising properties; thus, investigations by Nissan researchers have proposed that interactions between Pd and Ni can be beneficial for the light-off performance of the TWC [7,8]. This has been explained as a beneficial effect of the establishment of interactions between palladium and nickel aluminate crystals which apparently can enhance the NO reduction performance in catalysts with relatively high nickel loading [7,8].

Other beneficial effects of the presence of nickel have been recently discovered for samples with relatively low nickel contents [9,10]. It has been shown that the light-off

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performance, particularly CO oxidation, can be benefited by an apparent indirect nickel effect which favours the generation of contacts between active Pd and Ce-Zr mixed oxide components [9,10]. However, since this effect enhances the performance of fresh catalysts, it appears detrimental to the performance of thermally aged systems since the favoured formation of such contacts apparently leads to a higher degradation of active components [11]. In this respect, it must be noted that examination of the aging mechanisms of this kind of systems, and most specially thermal degradation [1], constitutes one of the most relevant aspects to be analysed for the next generation of TWC since system durability could strongly limit its practical application [12]. The present work aims to identify the main parameters that determine the catalytic activity of these systems (both in fresh and thermally aged states) by mainly examining the changes taking place in the catalysts under reaction conditions by DRIFTS and XANES spectroscopies, considering the significant detail of knowledge that could be achieved upon simultaneous monitoring of surface and bulk properties by employment of these two techniques [13,14].

2. Experimental

Pure alumina (γ-Al_2O_3 Condea Puralox) and ceria-zirconia/alumina with 10 wt.% of Ce-Zr mixed oxide content (expressed, in accordance with ICP-AES analysis, as $Ce_{0.5}Zr_{0.5}O_2$) were employed as supports. The latter was prepared by equimolar cerium-zirconium coprecipitation within a reverse microemulsion containing the appropriate amount of alumina, followed by separation of the solid, rinsing with methanol, drying overnight at 393 K and calcining under air at 773 K for 2 h. Full details of the procedure and materials employed in this microemulsion preparation can be found elsewhere [9,15]. The supports were coimpregnated (incipient wetness method) with aqueous solutions of Pd(II) and Ni(II) nitrates (in order to achieve 1 wt.% loadings for each of the metals in the final catalysts) followed by overnight drying at 393 K and calcination under air at 773 K for 2 h. Supported monometallic Pd reference catalysts (with 1 wt.% loading) were prepared by the same method. S_{BET} values obtained for these catalysts were in all cases close to that of the parent alumina (ca. 200 $m^2\,g^{-1}$). The catalysts will be referred to as PdNiA and PdNiCZA (or using only a Pd prefix for the monometallic references) for the systems supported on alumina or ceria-zirconia/alumina, respectively. These catalysts were subjected to an accelerated aging treatment in a muffle furnace under air at 1273 K for 16 h. These latter will be denoted with a suffix—a. S_{BET} values obtained for the aged catalysts were 84 and 83 $m^2\,g^{-1}$ for PdNiA-a and PdNiCZA-a, respectively. More details on the preparation or characterization of these catalysts can be found elsewhere [9,11].

The catalysts pretreated under diluted O_2 flow at 773 K were analysed with respect to their light-off activity for model CO-O_2 (1% CO + 0.5% O_2), CO-O_2-NO (1% CO + 0.45% O_2 + 0.1% NO) and CO-O_2-NO-C_3H_6 (1% CO + 0.1% C_3H_6 + 0.9% O_2 + 0.1% NO) stoichiometric reactions (N_2 balance) at a space velocity of $3 \times 10^4\ h^{-1}$ in a pyrex glass fixed-bed flow reactor. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) analysis of adsorbed species present on the catalyst surface under reaction conditions was carried out using a Perkin-Elmer 1750 FTIR fitted with an MCT detector. On-line analysis of the NO concentration at the outlet of the IR chamber was performed by chemiluminescence (Thermo Environmental Instruments 42C). The DRIFTS cell (Harrick) was fitted with CaF_2 windows and a heating cartridge that allowed samples to be heated to 773 K. Samples of ca. 65 mg were pretreated in situ under a diluted O_2 flow (in a similar manner described above for the catalytic tests), before introducing the reaction mixture and heating at 2 K min^{-1} from 298 to 673 K, recording one spectrum (4 cm^{-1} resolution, average of 50 scans) generally every 20–30 K. The gas mixture (similar to that employed for catalytic tests) was prepared using a computer-controlled gas-blender with 80 $cm^3\,min^{-1}$ passing through the catalyst bed. X-ray absorption near edge structure (XANES) experiments at the Pd-K edge were performed at station 9.3 of the SRS synchrotron. A Si(1 1 1) double-crystal monochromator was used in conjunction with a rejection mirror to minimise the harmonic content of the beam. Transmission experiments were carried out using Kr/Ar-filled ionisation chambers. The energy scale was simultaneously calibrated by measuring a Pd foil using a third ionisation chamber. Samples were self-supported (absorbance 0.5–1.0) and placed in a controlled-atmosphere cell for treatment. XANES spectra were taken every 15 K in the presence of the CO + NO + O_2 flowing mixture (similar to the one employed for catalytic activity tests) during a 5 K min^{-1} temperature ramp up to 673 K. The series of spectra were analysed by using principal factor analysis (PCA), details of which can be found elsewhere [16].

3. Results and discussion

Table 1 summarizes catalytic activity results obtained for the different reactions and catalysts. Different effects are noteworthy from these results. First, regarding fresh catalysts, it is clear that the presence of both nickel and Ce-Zr mixed oxide (CZ) enhances the CO oxidation activity in any of the reactions while a higher NO reduction activity is achieved when CZ is not present in the catalyst. The enhancement in the CO oxidation activity induced by both Ni and CZ can be explained by the presence of a greater amount of contacts between Pd and CZ in the presence of nickel, as demonstrated in a previous work by mainly X-ray energy dispersive spectroscopy (XEDS) [9]. It must be noted in this sense that CZ is a significant promoter of Pd CO oxidation activity mainly because it can open a new low activation energy reaction path in which interfacial oxygens could act as active species [17,18]. Other possible effects of a predominant presence of such contacts can be related to an enhanced dispersion of palladium considering the known ability of ceria-related materials to facilitate supported metals dispersion [17]; this could itself explain the enhanced CO oxidation performance. However, as analysed in detail in a former contribution [9], no apparent Pd particle size differences were noted during comparison of high resolution electron microscopy results for PdNiA and PdNiCZA.

Table 1
Isoconversion temperatures (in K) at 50% conversion for the three pollutants obtained during light-off tests under stoichiometric conditions at 3×10^4 h^{-1} GHSV for the reactions A = CO + O_2, B = CO + O_2 + NO and C = CO + O_2 + NO + C_3H_6 over the indicated catalysts (values in parentheses correspond to the monometallic Pd reference)

	T_{50} (CO)			T_{50} (NO)		T_{50} (C_3H_6)
	A	B	C	B	C	C
PdNiCZA	334 (404)	403 (433)	482 (503)	455 (456)	524 (536)	511 (534)
PdNiA	447 (447)	479 (479)	526	408 (410)	531	528
PdNiCZA-a	463	518	581 (519)	525	595 (536)	576 (524)
PdNiA-a	469	518	588	533	584	577

It appears more complicate to explain the decreased performance of the Ni- and CZ-containing system for NO reduction (Table 1). Former work on this reaction evidenced opposite effects of the establishment of contacts between Pd and CZ entities in this type of systems. On the one hand, it appeared that dispersed CZ entities could facilitate the NO reduction activity of metallic Pd by providing new active interfacial sites in the form of surface oxygen vacancies able to reductively activate NO [18–21]. However, difficulties could also appear in the presence of such contacts, and in contrast to cerium-free supported systems [14,24], for generating metallic palladium surfaces [22]; these latter are known to be most active for such process [23,24]. In order to investigate this phenomenon, it becomes necessary to monitor the evolution of the systems under reaction conditions, as can be provided by XANES and DRIFTS techniques.

PCA analysis of the Pd-K edge XANES spectra of PdNiCZA and PdNiA under CO + O_2 + NO suggests the presence of only two different chemical species during the course of the runs (Fig. 1). Comparison of the XANES spectra of the two species with reference compounds indicates that the palladium appears to be present initially in the form of an oxidised Pd^{2+} species with a local symmetry similar to that shown by PdO (D_{2h} symmetry group). The second Pd-containing species is readily ascribed to a zero-valent Pd^0 fcc phase by comparison with a Pd foil. These results discard in turn the formation of Pd-Ni alloys as responsible of any of the observed catalytic effects; this is in agreement with maintenance of an oxidised state of nickel in the course of the reaction according to parallel Ni-K edge experiments (not shown), and also in agreement with previous ferromagnetic resonance results [9]. Fig. 2 shows the evolution of the fraction of each of these species as a function of the reaction temperature. The concentration of the Pd^{2+} species decreases gradually from ca. 400 K with concomitant formation of reduced Pd^0 being produced; the reduction process becomes apparently complete between 570 and 650 K. Noteworthy, a slightly greater facility for bulk reduction is apparent for the PdNiA system. This contrasts with previous results in which the CZA-supported catalyst was compared with an alumina-free CZ-supported one [10]. However, a significant difference in palladium particle size was also noticed in that case (in contrast to the one analysed here, as

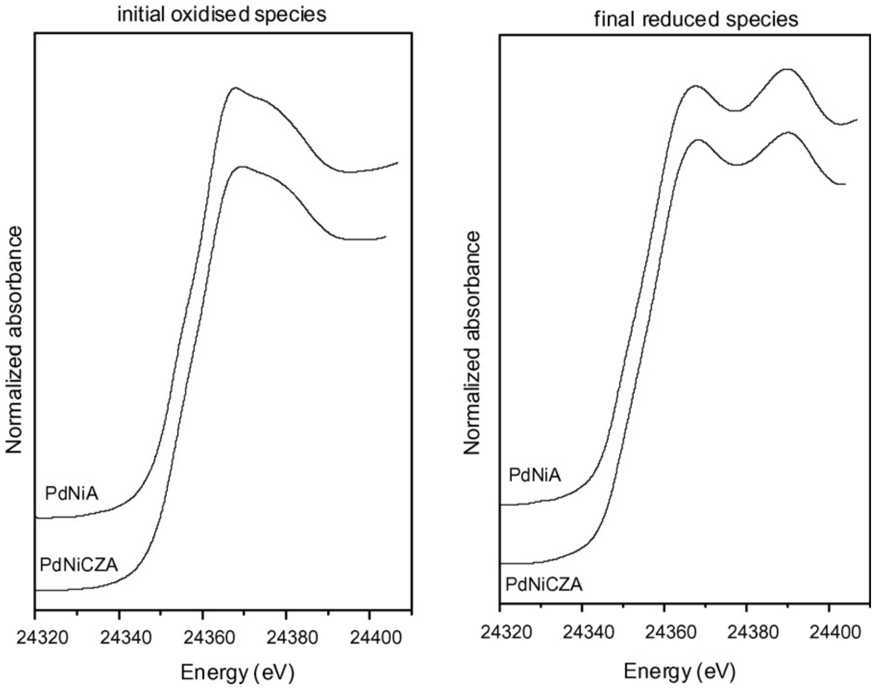

Fig. 1. XANES spectra for the indicated catalysts: (left) Pd initial, oxidised species; (right) Pd final, reduced species (see text for details).

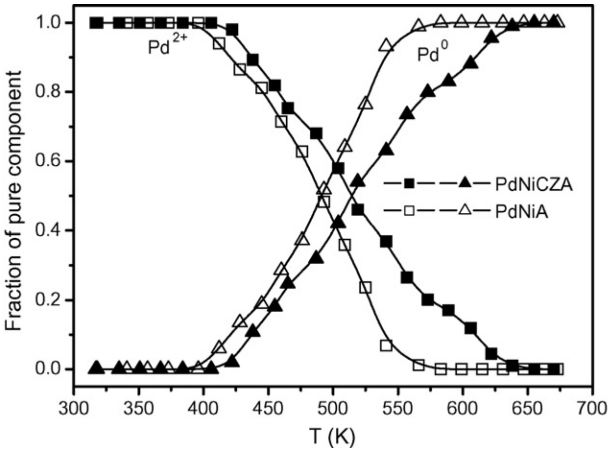

Fig. 2. Concentration profiles of species detected by XANES during the run under CO-O_2-NO for the indicated catalysts.

mentioned above) since apparently higher palladium dispersion was observed for the CZ-supported catalyst [9].

The higher difficulty observed for palladium reduction in the CZA-supported system may explain its lower NO reduction activity, taking into account that most active sites for that reaction involve metallic palladium particles [24,25]. This result is consistent with the evolutions observed for the species chemisorbed on the sample surface under reaction conditions, as detected by DRIFTS (Fig. 3). Different chemisorbed species are observed to be formed upon chemisorption of the various reactants and/or of intermediates/products formed. CO chemisorption is responsible of bands attributable to atop (band at 2100–2060 cm^{-1}) or bridging (or bridging and three-fold coordinated, respectively; bands at ca. 1970 and a broader one centred at ca. 1920 cm^{-1} and extending down to ca. 1800 cm^{-1}, respectively) carbonyl species chemisorbed on metallic palladium [23,24,26–28]. Carbonyl species resulting from CO adsorption on oxidised Pd^{n+} sites (bands at ca. 2160–2130 cm^{-1} [18,26]) are also apparent. Noteworthy, the presence of CZ significantly promote formation of this latter species. This is in accordance with XANES results evidencing the higher difficulty for reduction of palladium particles in the PdNiCZA system. Other bands which are observed in these spectra, and are not considered of relevancy to the catalytic processes [10,24], are related to adsorbed isocyanate species (at ca. 2250 and 2231 cm^{-1} [24,27]) and a band at ca. 1850 cm^{-1} that is assigned to nitrosyl species chemisorbed on Ni^{2+} cations [10,29].

As noted in Table 1, the presence of hydrocarbon in the reactant mixture appreciably decreases the activity for either CO oxidation or NO reduction reactions while differences as a function of the presence of CZ in the catalyst become considerably minimised. This is uniquely explained by DRIFTS comparison of the spectra detected in the presence (Fig. 4) and absence (Fig. 3) of the hydrocarbon in the reactant mixture. The presence of C_3H_6 in the reactant mixture considerably hinders the generation of chemisorbed carbonyl species, in particular those formed over metallic palladium particles. This evidences a hydrocarbon self-poisoning effect due to the stronger chemisorption of this reactant (and/or of fragments derived from its dissociation/activation) on the active metallic particles, which considerably retards activation and reaction of the other pollutants (CO and NO) [30]. Note that selection rules for the hydrocarbon-derived species

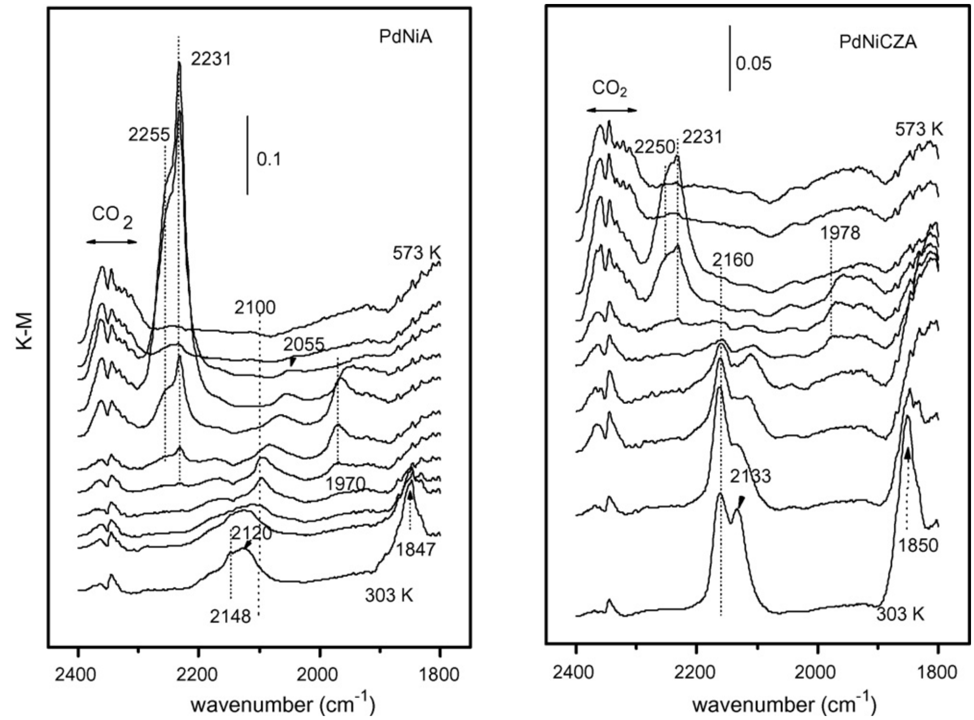

Fig. 3. *Operando* DRIFTS spectra obtained during the course of the CO-O_2-NO reaction for the indicated catalysts. Spectra taken every 30 K from 303 up to 573 K (from bottom to top).

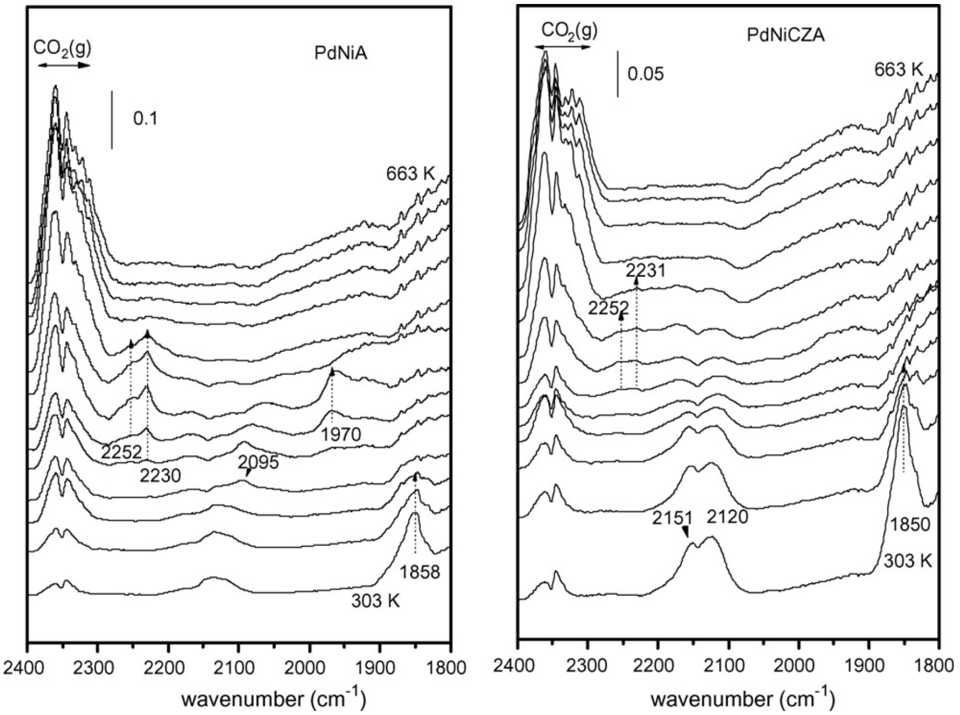

Fig. 4. *Operando* DRIFTS spectra obtained during the course of the CO-O_2-NO-C_3H_6 reaction for the indicated catalysts. Spectra taken every 30 K from 303 up to 663 K (from bottom to top).

chemisorbed on the metallic particles can prevent their observation in the spectra [30].

On the other hand, spectra similar to those presented in Figs. 3 and 4 were recorded under the same conditions for the two aged catalysts (results not shown). In contrast to results observed for the fresh catalysts, bands attributable to species chemisorbed on the palladium particles were barely observable in the spectra, as expected given the strongly sintered state of the catalysts. This affects to both palladium and CZ active components of the catalysts, as previously evidenced mainly by XRD [11], and explains in a general way the significant catalytic activity decrease observed for the aged catalysts. In particular, the palladium sintering produced by aging is nicely illustrated by experiments of CO chemisorption at room temperature on the catalysts at the end of the reaction. As shown in Fig. 5, bands due to carbonyls chemisorbed on metallic palladium particles are mainly observed for the two fresh systems (atop carbonyls at 2092 cm^{-1} and bridging carbonyls at ca. 1983 and 1920 cm^{-1}) while weaker bands due to carbonyls chemisorbed on oxidised palladium (bands at 2149 or 2141 cm^{-1}) show contributions to the spectra (particularly for PdNiCZA). These spectra reveal that in these catalysts palladium forms predominantly metallic palladium particles at the end of the reaction, which are partially oxidised mainly as a consequence of interaction with NO [10,11,18]. Stabilization of a partially oxidised state of palladium in PdNiCZA can also be a consequence of the presence of propene and its influence over particles in contact with the CZ component [31]. In contrast, the aged systems display carbonyl bands of very low intensity, which are a consequence of the sintering of palladium. In particular, chemisorbed carbonyls are barely observable for PdNiCZA-a, which is also a consequence of a certain CZ encapsulation of palladium particles upon aging in this system, as recently demonstrated by electron microscopy [11].

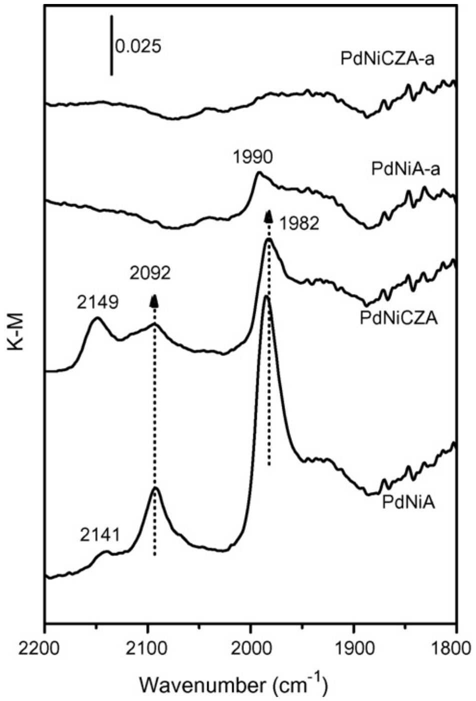

Fig. 5. DRIFTS spectra of the indicated catalysts recorded after cooling to 303 K under nitrogen at the end of the CO + O_2 + NO + C_3H_6 reaction, followed by treatment under a flow of 3% CO in nitrogen and final purging under nitrogen at 303 K.

4. Conclusions

DRIFTS and XANES analyses of model Pd-Ni TWC under reaction conditions provide important details to explain their catalytic behaviour. The effects of Ni presence are essentially related to a Ni-favoured generation of contacts between Pd and Ce-Zr mixed oxide components [9]. This phenomenon can apparently contribute to retard palladium reduction under reaction conditions, being of relevancy to explain a lower NO reduction activity in samples of comparable palladium particle size. Effects of competition between reactants (particularly, self-poisoning effects induced by propene presence in the mixture) are uniquely explained by DRIFTS comparison of the evolution of chemisorbed species under the various reaction atmospheres.

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