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Redox properties of Re_2O_7/Al_2O_3 as investigated by FTIR spectroscopy of adsorbed CO

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

This paper reports the first use of CO probe molecules in an IR investigation of the redox behaviour of alumina supported rhenium. After O_2 treatment the rhenium surface species are coordinatively saturated and do not allow the adsorption of CO. Treatment with H_2 at 823 K leads to the complete reduction of all rhenium species to rhenium metal. However, partially reduced rhenium Re^{x+} (where $0 < x < 7$) species can be generated through treatment with CO at 333 K, or similarly by exposure to isobutene at the same temperature. These results provide further evidence that partially reduced rhenium species are involved in the metathesis of alkenes.

Keywords: Rhenium; Alumina; FTIR; Carbon monoxide; Isobutene

1. Introduction

Alkene metathesis is a process that permits the synthesis of target alkenes to demand [1–3]. Unpromoted Re_2O_7/Al_2O_3 is an active catalyst for the metathesis of a wide range of alkenes and is active towards of propene even at room temperature [3]. Among other factors, the oxidation state of rhenium and its coordinative unsaturation play a determining role for the catalyst's activity and performance. It has been shown that Re_2O_7 forms a monolayer (∼18 wt.% Re_2O_7) on the alumina support surface [4]. The rhenium oxide species, and the possible active site precursors, appear to be monomeric tetrahedral ReO_4 moieties which are anchored to the support surface via Al–O–Re bonds, as shown by Raman spectroscopy [5–7]. At higher loadings two slightly different monomeric ReO_4-species are present both possessing three R=O bonds and one Al–O–Re anchoring bond [5,6].

The oxidation state of the rhenium under reaction conditions is still a matter of debate although using XPS analyses, Duquette et al. [8] reported the formation of Re^{6+} and Re^{4+} on exposure to 1-octene under reflux conditions, and Xu et al. [9] proposed the existence of rhenium in the oxidation states +7, +6, +4 and +3 after propene was flowed over the catalyst at 723 K. Yao and Shelef [10] detected the generation of Re^{2+} and Re^{4+} during H_2/O_2 redox cycles by ESR.

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The direct correlation of these oxidation states with catalytic properties suffers from two major drawbacks. Firstly, the physical characterisations are frequently carried out on samples which were pretreated at temperatures significantly higher than the typical reaction temperatures. Secondly, the number of active sites is typically only a small fraction of the total number of rhenium atoms in the sample [3,4,11].

Beside its redox properties, the strength of the catalysts' acid sites can also strongly influence the catalytic performance, since these sites may be responsible for undesired side reactions which would reduce the yields of the target products.

In the present paper we report on the redox and acid properties of a Re_2O_7/Al_2O_3 catalyst containing 9 wt.% Re_2O_7. This material was characterised by laser Raman spectroscopy (LRS) and temperature-programmed reduction (TPR) for comparison with reported data. Acid properties, rhenium oxidation states and coordinative unsaturation were then investigated by FTIR spectroscopy of CO adsorbed at low temperature after thermal treatments in N_2, O_2, CO, and H_2. In a final experiment, the state of the rhenium in the catalyst was probed by CO after exposure to isobutene at a typical reaction temperature of 333 K.

2. Experimental

2.1. Catalyst preparation

The Re_2O_7 catalyst was prepared by the incipient wetness method. One hundred grams of γ-Al_2O_3 (type D10-10 from BASF, Ludwigshafen, Germany) were impregnated with 74 ml of an aqueous perrhenic acid solution (Heraeus, Hanau, Germany) containing the appropriate amount of rhenium so as to yield a final material containing 9 wt.% Re_2O_7. The analytical value was 8.9 ± 0.2wt.%. The powder was then dried in air at 393 K for 16 h followed by thermal treatment at 823 K for 16 h in flowing N_2. The BET surface area of the resulting material was 200 $m^2\,g^{-1}$ (±5%). Assuming an area of 0.35 nm^2 per Re-atom [4], the Re_2O_7 loading of 9 wt.% corresponds to 50% of the theoretical monolayer capacity.

2.2. Temperature-programmed reduction (TPR)

The temperature-programmed reduction system comprised a TCD detector (GOW-MAC 24-550) with AuW-filaments, operating at 85 mA. The heating rate for the oven was 10 K min^{-1}, with an operating temperature range between 353 and 1173 K, measured with two Thermocoax (Phillips) type K thermocouples. The gas flow rate through the catalyst bed (0.1 ± 0.02 g powder) was 1.92 ml min^{-1} H_2 and 48.0 ml min^{-1} He. A quartz reactor with an outer diameter of 12 mm and an overall length of 250 mm was used for the measurements.

2.3. Laser Raman spectroscopy (LRS)

Raman spectra were recorded with a Dilor (OMARS 89 triple monochromator) spectrometer, equipped with a thermoelectrically cooled charge-coupled device camera (Princeton Instruments). An Ar^+ ion laser (model series 2020, Spectra Physics) was used, and the sample, in air contact, was rotated during measurements. Dehydration of the samples and the subsequent measurement of the spectra was carried out in flowing dry oxygen in a quartz flow reactor which was heated from room temperature to 723 K. The temperature was then held constant for 30 min. The spectra were recorded with the scanning multichannel technique [12,13] with laser power of 5–50 mW at the sample position and an exciting wavelength of 488 nm for the hydrated and 514 nm for the dehydrated samples. The slit width was 150 μm and the scan time for a single spectrum was 10–90 s. The spectral resolution was 5 cm^{-1}.

2.4. FTIR spectroscopy

The IR spectra were recorded on a Bruker IFS-66 apparatus at a spectral resolution of 2 cm^{-1} accumulating 128 scans. Self-supporting wafers were prepared from the sample powders and treated directly in the purpose-made IR cell. The latter was connected to a vacuum-adsorption apparatus with a residual pressure below 10^{-3} Pa. The cell allowed the IR measurements to be performed both at ambient temperature and at 88 K. Prior to the adsorption measurements, the samples were activated and thermally treated under conditions outlined in the text (Section 3.2).

3. Results and discussion

3.1. Catalyst characterisation

The Raman spectrum of the as prepared sample recorded in the presence of adsorbed water is shown in Fig. 1, spectrum A. The bands detected at 334, 925 and 971 cm^{-1} clearly characterise monomeric tetrahedral ReO_4^- ions consistent with previous reports [5–7]. The broad shoulder below 925 cm^{-1} may be inferred to be caused by Al–O–Re bonds. After drying the catalyst in flowing O_2 at 573 K the signal-to-noise ratio decreases and the Re=O stretching bands shift to higher frequency at 968 and 998 cm^{-1}. This blue-shift after removal of adsorbed water is well-known for the oxo-vibrations of supported transition metal oxides [14]. The Al–O–Re band now appears as a broad and weak feature at ca. 870 cm^{-1}. The formation of the anchoring bonds was also proposed by Sibeijn et al. [15] who observed the erosion of free alumina O–H stretching bands because of their condensation with perrhenate acid. In conclusion, Raman spectroscopy suggests the presence of only one detectable isolated monometric ReO_4^- species in the present catalyst.

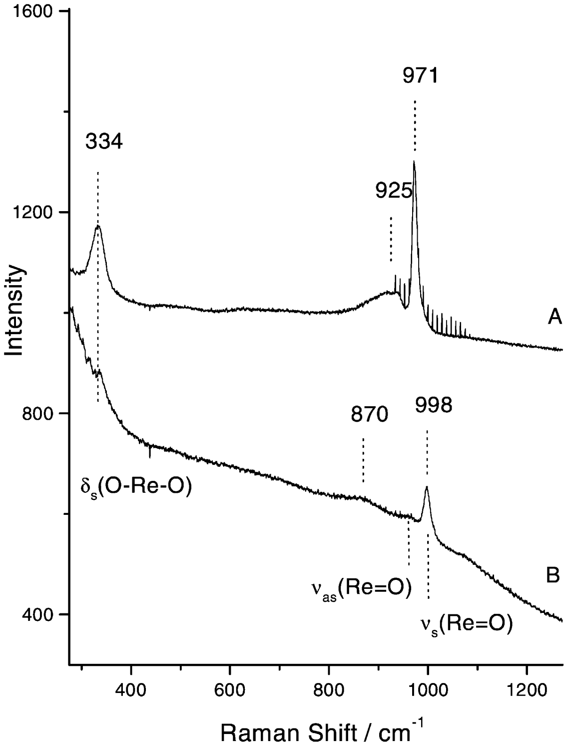

Fig. 1. Raman spectra (A) of hydrated as prepared Re_2O_7/Al_2O_3 and (B) of dehydrated Re_2O_7/Al_2O_3 after treatment in O_2 at 573 K.

TPR analysis of the catalyst revealed two peaks at 616, 668 K and a weak broad feature at ca. 800 K (Fig. 2). According to the literature it is widely agreed that Re undergoes a one-step reduction from Re^{7+} species to Re^0, thus suggesting that the three peaks are due to different Re^{7+} species, although Raman spectroscopy detected only one monomeric tetrahedral species. The smaller high-temperature TPR peaks may then be attributed to a monomeric minority species which were not resolved in the Raman spectra. The presence of small and vibrationally undetected oligomeric rhenium oxo-surface species is not excluded. Although the exact positions of maximum reduction rates observed in the present work were not identical to those reported in the literature [5,16,17], there is qualitative agreement if the different experimental parameters are taken into account. In particular, our results support a reduction of Re^{7+} to Re^0 in H_2, when the cumulative experimental H_2-consumption is compared with the theoretically expected value. Both values were identical within the limits of accuracy of ±10% of the experiment. The contribution of the most intense low-temperature reduction peak at 616 K to the total H_2-consumption was 55 and 67% after pretreatment in flowing O_2 and N_2, respectively. Otherwise, no noticeable changes were observed in the TPR spectra after the different pretreatments.

3.2. FTIR spectroscopy of adsorbed CO

3.2.1. Alumina support

The alumina support was pretreated under N_2 at 823 K for 16 h, cooled under vacuum to 88 K and exposed to increasing partial pressures of CO. Both Lewis acid (LAS) and weak Brønsted acid (BAS) sites were detected in the material, the spectra being typical of Al_2O_3 reported in the literature [18,19]. LAS and BAS were characterised by carbonyl bands

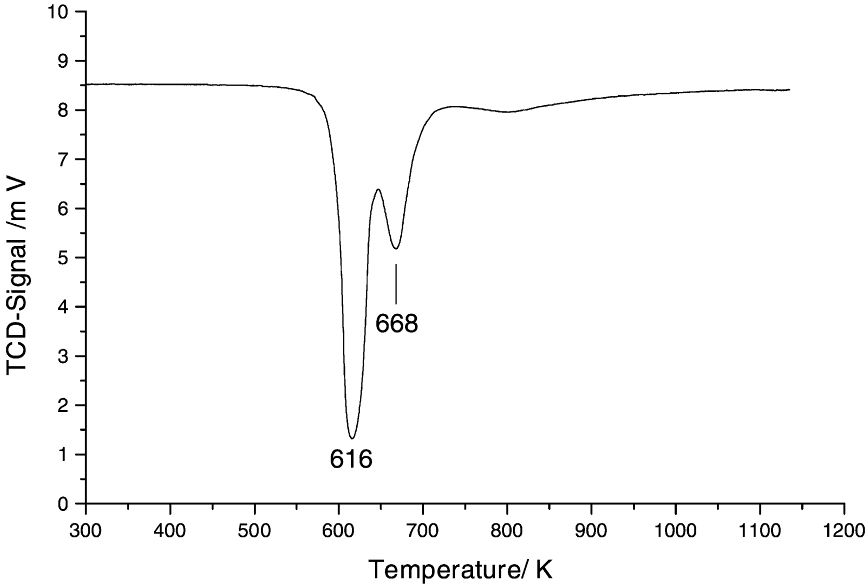

Fig. 2. TPR trace of Re_2O_7/Al_2O_3 after pretreatment in O_2 at 823 K for 1 h.

at 2180 and 2157 cm^{-1}, respectively, whereas the shoulder at 2143 cm^{-1} indicates physically adsorbed CO. The Lewis acidity was attributed to coordinatively unsaturated (cus) Al^{3+} cations occupying octahedral lattice sites (i.e. penta-coordinated). Three types (basic, neutral and acidic) of OH groups were detected in the infrared spectrum [20], all of which shifted to lower wavenumbers on interaction with CO. Shifts of 90–120 cm^{-1} were recorded, signifying weak Brønsted acidity.

3.2.2. Re_2O_7/Al_2O_3 catalyst

The Re_2O_7/Al_2O_3 catalyst underwent various pretreatments prior to CO adsorption at low temperature with the goal to investigate its redox properties.

3.2.2.1. Pretreatment in oxygen. After O_2 pretreatment (overnight, 823 K) no Re-containing species were observed in the spectrum on admission of CO. TPR analysis suggests that the same Re species exist in materials pretreated under O_2 or N_2, and it is assumed that under oxidising conditions Re is coordinatively saturated (Re^{7+}) and therefore cannot adsorb CO, due to a lack of available coordination sites. Similar observations have been made for V, Cr, Mo, etc. where the element in its highest oxidation state does not form stable carbonyls [21].

3.2.2.2. Pretreatment in nitrogen. After 1 h under O_2 flow at 823 K, the standard catalyst was then heated overnight at the same temperature under N_2. On admission of CO at 88 K spectra very similar to those obtained for the alumina support were recorded with bands being observed at 2180, 2157 and 2143 cm^{-1} (see Fig. 3) which were assigned to CO coordinated to LAS, hydrogen-bonded to OH groups and to physically adsorbed CO. However, a shoulder at ca. 2200 cm^{-1} was detected, which was not observed in the support material. The assignment of this band is somewhat questionable, as it could be assigned to partially reduced Re^{x+} (where $x < 7$) species, but is equally likely assigned to penta-coordinated Al^{3+} sites which may be located in the vicinity of Re surface species, and hence, possess a different Lewis acid strength.

When compared with the support material itself, the OH region of the catalyst shows a loss of intensity in all OH groups, and an increase in intensity at ca. 3600 cm^{-1} as previously reported by Sibeijn et al. [15]. As with the alumina support itself, the

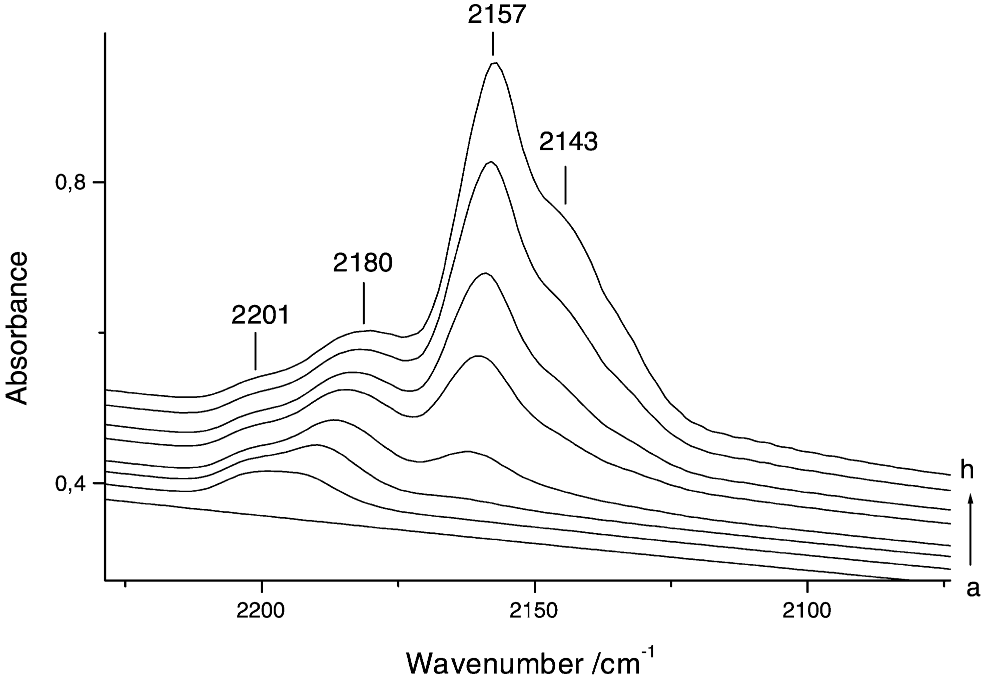

Fig. 3. FTIR spectra of CO adsorbed at 88 K on Re_2O_7/Al_2O_3 after pretreatment in N_2 at 823 K for 16 h: (a) background; (b)–(h) 0.1–5 kPa CO.

catalyst displays inhomogeneity of BAS, with shifts of 105–125 cm^{-1} being recorded.

3.2.2.3. Pretreatment in hydrogen. Reduction of the catalyst was carried out in H_2 at three temperatures. At the lowest temperature (333 K) no reduction of the sample occurred, which was in agreement with the TPR results. A second reduction temperature (523 K for 2 h) was chosen which was more compatible with the TPR data, which resulted in the generation of Re metal (Re^0) characterised by a broad band at 2050 cm^{-1} (see Fig. 4). This observation was in agreement with the TPR data, suggesting a one-step reduction from Re^{7+} to Re^0. However, the shoulder at 2200 cm^{-1} was still visible, implying that partially reduced Re species could still be present, or that inhomogeneity exists within Al^{3+} LAS induced by the presence of the ReO_4^- species. A high temperature reduction at 823 K (2 h) was carried out in an attempt to resolve this ambiguity, which produced an intense band at 2045 cm^{-1} (Re^0) and removed the asymmetry in the band at 2200 cm^{-1}. The high reduction temperature suggests that all Re is now present as the metal, in which case all Re–O–Al bridging bonds have now been destroyed, thus resolving the inhomogeneous distributions of Al^{3+} LAS.

3.2.2.4. Pretreatment in carbon monoxide. In an attempt to generate partially reduced Re species reduction was carried out at moderate temperature (333 K) using CO. After evacuation of the cell and cooling to 88 K, small amounts of CO were admitted which led to five bands being observed in the carbonyl stretching region of the spectrum (see Fig. 5). Bands at 2186 and 2159 cm^{-1} were assigned to Al^{3+} LAS and Al–OH sites as in the support material and the distinctive shoulder at 2202 cm^{-1} was again attributed to Al^{3+} sites in the vicinity of Re oxo-species. The remaining two bands were observed at 2130 and 2080 cm^{-1}, respectively. The former was assigned to partially reduced Re (Re^{x+}, where $x < 7$), whereas the latter was assigned to isolated Re metal (Re^0) particles.

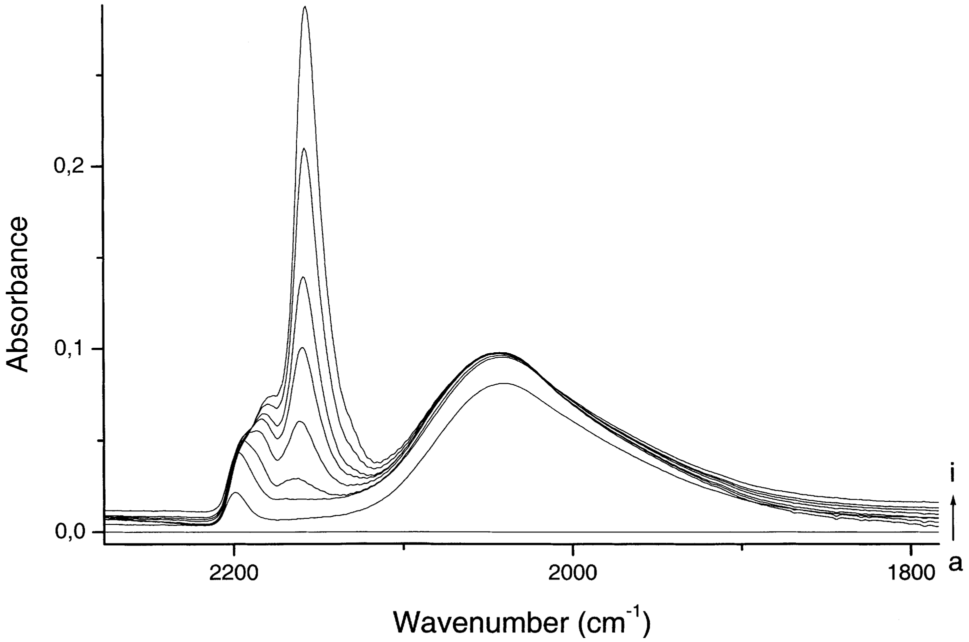

Fig. 4. FTIR spectra of CO adsorbed at 88 K on Re_2O_7/Al_2O_3 after reduction in H_2 at 523 K for 2 h: (a) background; (b)–(i) 0.1–2 kPa CO.

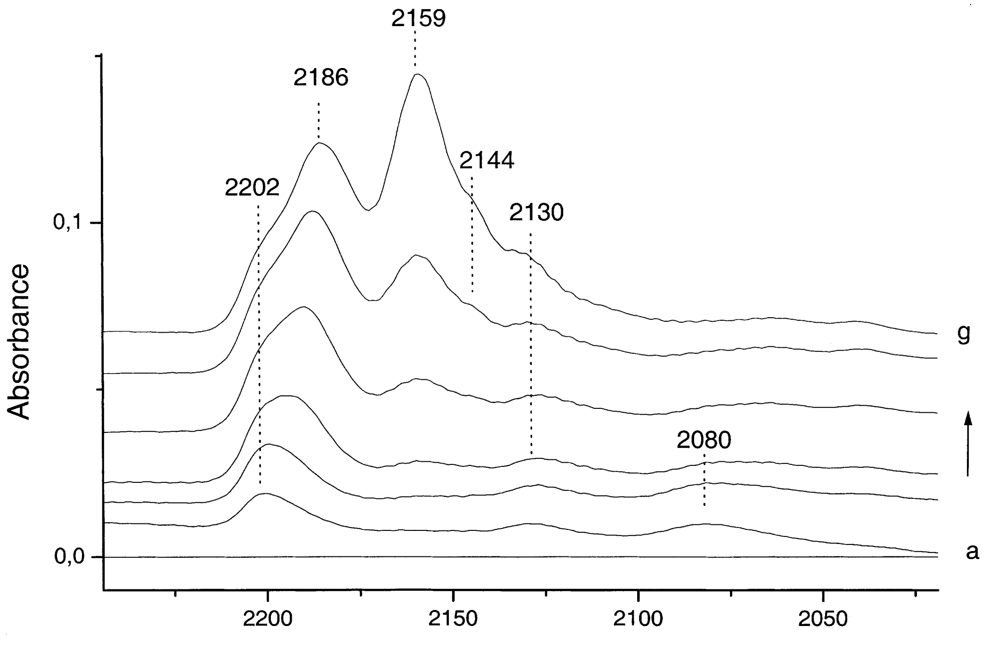

Fig. 5. FTIR spectra of CO adsorbed at 88 K on Re_2O_7/Al_2O_3 after pretreatment in CO at 333 K for 1 h: (a) background; (b)–(g) 2 kPa and 233–133 K.

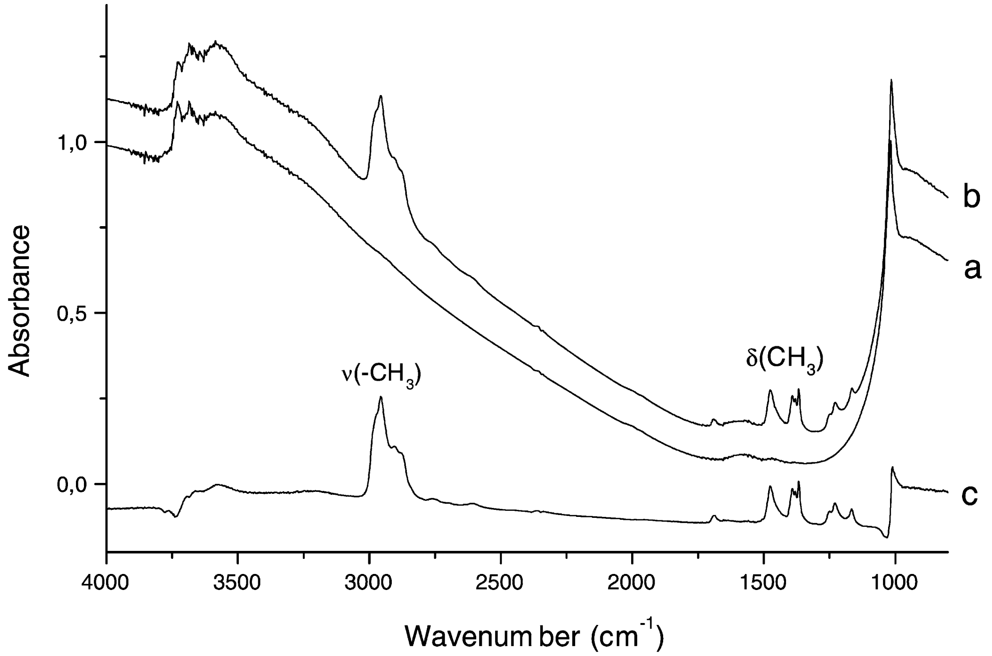

Fig. 6. FTIR spectra of isobutene adsorbed on Re_2O_7/Al_2O_3: (a) catalyst after pretreatment in N_2 at 823 K for 16 h; (b) after exposure to flowing isobutene at 333 K and evacuation at 333 K for 1 h; (c) difference spectrum.

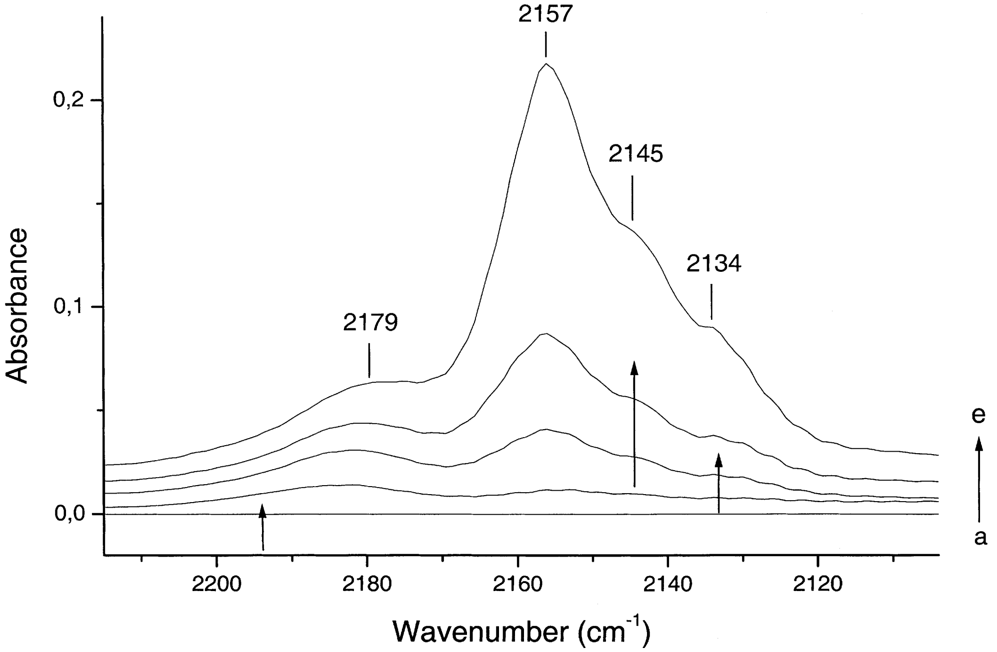

Fig. 7. FTIR spectra of CO adsorbed at 88 K on Re_2O_7/Al_2O_3 after pretreatment in isobutene (conditions see caption to Fig. 6): (a) background; (b)–(e) 2 kPa and 183, 163, 143 and 123 K, respectively.

3.2.2.5. Pretreatment in isobutene. In an attempt to monitor the redox properties of Re after exposure to a reactant gas, isobutene was flowed over the surface at 333 K for 1 h. Following evacuation at 333 K, the surface was left with hydrocarbon fragments (see Fig. 6) that were only removed by calcination at 673 K. Similar behaviour had been previously reported for *n*-butene adsorption on Re-alumina catalysts [22]. An identical procedure was carried out on the support material alone, and resulted in very similar hydrocarbon fragments being detected in the spectrum. Remarkably bands that could be assigned to unsaturated hydrocarbon deposits were not unequivocally detected. Admission of CO after evacuation led to bands at 2200, 2190, 2160 and 2135 cm^{-1} being observed (see Fig. 7), the latter being attributed to partially reduced Re. No metallic Re was detected, so it would appear that only partially reduced Re species (Re^{x+}, where $0 < x < 7$) are generated on contact with isobutene at 333 K. This observation is in agreement with previous work reporting the generation of Re^{x+} species after reaction with octene [8] and propene [9].

4. Conclusions

This paper has examined the oxidation state of alumina supported rhenium under a variety of redox treatments. After an oxidative pretreatment the surface rhenium species are coordinatively saturated and hence do not interact with CO probe molecules. Overnight treatment under N_2 produces a similar effect, though an inhomogeneity in the Al^{3+} LAS was detected, most likely caused by the presence of rhenium surface species. Metallic rhenium (Re^0) was generated on reduction with H_2 at temperatures of 523 K and above, though the inhomogeneity of the Al^{3+} site was only resolved after high temperature reduction. Via reduction with CO at 333 K it was possible to generate a partially reduced rhenium Re^{x+} ($0 < x < 7$) species in addition to the metal. This partially reduced species was also detected after exposure to isobutene at 333 K for 1 h, though after this treatment the formation of metallic rhenium was not observed. These results further support the hypothesis that partially reduced rhenium species are involved in alkene metathesis.

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