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Near- infrared spectroscopy of palladium-containing layered double hydroxides used as catalysts

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ABSTRACT

Three catalysts consisting of layered double hydroxides (LDHs) of magnesium and aluminium, and containing palladium in various forms, were synthesized and subsequently characterized by mid- and near-infrared spectroscopies. The results thus obtained are compared with those for a pure Mg/Al layered double hydroxide. The spectra for the Pd-containing LDHs (particularly the strength of the bands) were found to depend on the particular palladium form present. As a rule, the mid-infrared spectra contained a strong, broad band at $3800\text{--}2500\text{ cm}^{-1}$ due to stretching vibrations of the different types of hydroxyl groups present in the solids and another signal at ca. 1370 cm^{-1} due to the presence of carbonate ions in the interlayer region. These signals were the strongest in the near-infrared spectra, which were also quite similar, roughly, for all solids.

Keywords: LDH, Palladium catalysts, Mid-infrared spectroscopy, Near-infrared spectroscopy.

1. INTRODUCTION

Structurally, layered double hydroxides (LDHs) consist of brucite-like layers where a fraction of Mg^{2+} ions in the formula, $\text{Mg}(\text{OH})_2$, have been isomorphically substituted by a trivalent cation (usually Al^{3+}). The substitution causes an electron deficiency that is offset by anions occupying the interlayer region together with crystallization water [1]. The parent layered double hydroxide is the natural mineral hydrotalcite: $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. Their easy synthesis and flexible composition has fostered the preparation of a variety of LDHs, the general formula for which is $\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}[\text{A}_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, M(II) and M(III) denoting a divalent and a trivalent metal, respectively, and A an anion. A large number of LDHs containing diverse divalent and trivalent cations have been reported to date [2–4]. One of the divalent cations used to replace Mg^{2+} is Pd^{2+} . Solids containing variable proportions of this metal have been successfully used in various organic synthesis processes [5–8].

Layered double hydroxides can also be used to obtain catalysts containing palladium in various forms ranging from chelates to neutral species anchored or supported on the solid surface to negatively charged complexes occupying the interlayer region and offsetting the initial charge deficiency [11,12]. These catalysts have also been used, with variable success, in organic synthesis [9–12], and characterized by using a number of diffraction and spectroscopic techniques. However, Pd-containing LDHs have never to date been examined by near-infrared spectroscopy (NIRS). This technique essentially provides information about bonds involving a hydrogen atom (especially, O–H bonds). We therefore believed it of interest to use NIRS for the characterization of LDHs. In fact, NIR spectroscopy was previously used to examine various layered Mg(II)/M(III) double hydroxides with M(III) = Al, Ga or In, as well as Ni/Al, Ni/Fe and Mg/Fe [14,15] or Co/Al [16] LDHs.

The aim of this work was to use the NIRS technique to characterize three Mg/Al LDHs containing palladium in various forms. The solids had previously been used in the Suzuki cross-coupling reaction to obtain biphenyls [7]. Their results were compared with those for an Mg/Al LDH used as support for two of the catalysts. In addition, the solids were studied by mid-infrared spectroscopy in order to facilitate the unambiguous assignment of the NIR bands.

2. EXPERIMENTAL

2.1. Catalysts synthesis

The procedure used to synthesize the four Pd-containing Mg/Al LDHs studied is described elsewhere [17]. Briefly, the solids were prepared as follows: HT, which was used as support for the other three solids, was obtained by coprecipitation [18]; HT-Pd was prepared similarly to HT, but using 0.5% Pd to incorporate Pd^{2+} ions into the crystal network of the brucite-like layers [17]; HT-PdCl₄ was obtained by replacing the carbonate ions in HT with PdCl_4^{2-} [17]; finally, HT-PdAc₂Py₂ consisted of a Pd(II) acetate-pyridine chelate anchored on the surface of solid HT. The target solids were therefore three catalysts containing palladium in various forms and the starting Mg/Al LDH.

2.2 Catalyst characterization

As stated above, the studied solids were characterized for structure and surface properties by using various instrumental techniques as described elsewhere [10,16]. By way of summary, Table 1 gives the formula of each solid and its palladium content as determined by ICP-MS. The table also gives the lattice parameters for the solids as calculated from the

XRD patterns of Fig. 1. Fourier transform infrared (FT-IR) and magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopies had previously been used to characterize this type of catalyst, albeit as regards the interlayer ion only. In this work, we conducted a deeper FT-IR study of the solids that was completed by NIRS.

FT-IR (MIR) spectroscopy. The Fourier transform infrared spectra for the catalysts were recorded over the wavenumber range 4000–400 cm^{-1} , using a spectral resolution of 4 cm^{-1} on a Perkin–Elmer Spectrum 100 FT-IR spectrophotometer. Samples were prepared by mixing the powdered solids with KBr (the blank) in a 18:85 ratio.

NIR spectroscopy. Near-infrared spectra were recorded on a Foss NIRSystems 6500 spectrometer. Individual spectra were obtained by co-adding 64 scans performed at a spectral resolution of 8 cm^{-1} over the range 11000–4000 cm^{-1} , using the DRIFT technique.

All spectral treatments applied (viz. baseline correction, smoothing, normalization and deconvolution) were done with the Peakfit v. 4.11 software package.

3. RESULTS AND DISCUSSION

3.1. Characterization of catalysts

Before discussing the MIR and NIR results obtained in this work, we believe it of interest to briefly comment on others reported in previous papers [10,17]. Table 1 shows the elemental composition of each solid. As can be seen, HT possessed a metal ratio identical with the theoretical value, which suggests that the cations were virtually completely incorporated into the solid phase. The amount of crystallization water present was estimated

from thermogravimetric data. That of palladium was equal or close to 0.5% by weight —by exception, the water content of the catalyst containing PdCl_4^{2-} ions was slightly higher than 10%. Figure 1 shows the XRD patterns for the catalysts. The pattern for HT (Fig. 1a) is typical of an LDH [18], and so are those for the other three solids, which only differ in signal strength and width (a result of the differences in crystallinity introduced by the synthetic procedures used). The lattice parameters shown in Table 1 are consistent with the reported values for LDHs consisting of Mg and Al in a ratio close to 2 [4].

Accurately assigning the signals in the NIR region, which contains overtones and combination bands for stretching and/or deformation vibrations, required the prior identification of the bands in the MIR region, which led us to examine the MIR spectra for the catalysts first.

3.1.1. MIR spectroscopy

The MIR spectrum for an LDH can usually be split into three distinct zones for easier study. The first zone, which essentially contains the bands for the fundamental stretching vibrations of hydroxyl groups, spans the wavenumber range $4000\text{--}2500\text{ cm}^{-1}$ and is usually that exhibiting the strongest bands for the LDH. The second, from 1800 to 1200 cm^{-1} , contains the signals for stretching vibrations of carbon–oxygen bonds in carbonate ions in the interlayer region in addition to deformation vibrations of water molecules. The third, which spans the range $1200\text{--}400\text{ cm}^{-1}$, contains the bands for deformation vibrations in carbonate and stretching vibrations in metal–oxygen bonds. A discussion of the bands observed in each zone follows.

Región MIR $4000\text{--}2500\text{ cm}^{-1}$: Figure 2 shows the MIR spectra for the three catalysts and the Mg/Al LDH in this zone. As can be seen, all solids exhibited four signals the exact wavenumbers for which are given in Table 2. The two signals observed at the greater wavenumbers can be assigned to stretching vibrations of hydroxyl groups directly bonded to

Al and Mg ions in octahedral brucite-like layers of the LDHs. The catalyst containing interlayer Pd^{2+} ions failed to give a third signal corresponding to Pd–OH groups owing to the low proportion of metal used (0.5%). The third component, observed at ca. 3100 cm^{-1} , can be assigned to hydroxyl groups in water molecules forming hydrogen bonds with interlayer carbonate ions [19]. This signal was also present, but ill-defined, in the spectrum for solid HT-PdCl₄, which should in theory have contained no carbonate but, as shown by its elemental composition, contained some —much less than the other LDHs, which obviously led to a highly attenuated signal in its FT-IR spectrum.

Region MIR 1800-1200 cm^{-1} : This spectral window (Fig. 3) typically contains the bands for fundamental stretching vibrations of carbonate (mode ν_3). Obviously, the spectrum for solid HT-PdCl₄ exhibited a much weaker signal than the others owing to its reduced carbonate content. Table 2 shows the exact wavenumbers for the normalized, deconvoluted bands. The presence of a shoulder above the signal for carbonate can be ascribed to a decreased symmetry in the ion activating vibrational mode ν_1 , which is inactive in symmetric carbonate molecules [20]. This second spectral zone also contained a well-defined band above 1600 cm^{-1} due to deformation vibrations of hydroxyl bonds in the water molecules [21].

Region MIR 1200-400 cm^{-1} : Carbonate ions in the interlayer region of an LDH possess planar symmetry typical of D_{3h} groups [22] and are spectroscopically identical to free carbonate ions, which exhibit three active modes in the IR region. The first such mode, ν_3 , is described above and appears at ca. 1360 cm^{-1} . The second appears at ca. 860 cm^{-1} and can be assigned to out-of-plane deformation vibrations (ν_4). Finally, the third active mode (ν_2) also corresponds to in-plane deformation vibrations but appears at ca. 675 cm^{-1} . Table 2 shows the exact wavenumbers for each normalized, deconvoluted band obtained from the spectra of Fig. 4. The spectra additionally contained bands which can be assigned to translational modes of hydroxyl groups under the influence of trivalent aluminium atoms (signals at 780 and 550 cm^{-1}), together with the respective deformation modes at 1030 and

950 cm^{-1} . Finally, the band at the smallest wavenumber (450 cm^{-1}) can be assigned to backbone vibrations of oxygen-bonded octahedral aluminium atoms (Al–O).

3.1.2. NIR spectroscopy

As previously done with the FT-IR spectra, the NIR spectra for the catalysts were also split into three different zones for easier study, namely: 11000–9000, 8000–6000 and 5500–4000 cm^{-1} .

Región 11000-9000 cm^{-1} : This spectral zone contained a strong band that was deconvoluted into the signals shown in Fig. 5, the exact wavenumbers for which are given in Table 3. The zone exhibited the bands corresponding to the second overtone of stretching vibrations of the different types of O–H bonds present in the solids. A solid containing a transition metal such as palladium can additionally give electronic bands, as previously reported for Ni and Co [16], and Fe [23]. The spectrum for the solid containing no palladium, HT, was that exhibiting the greatest number of signals and deconvoluted into four bands. The two bands at the greater wavenumbers (10452 and 10373 cm^{-1}) can be assigned to the second overtone of stretching vibrations of O–H bonds in the hydroxyl groups forming the brucite-like octahedral layers, which appeared at 3598 and 3499 cm^{-1} in the MIR spectrum. The third signal in the spectrum, observed at 10150 cm^{-1} , corresponds to the second overtone of stretching vibrations of OH groups in water (the band at 3340 cm^{-1} in the MIR spectrum). Finally, the fourth band (9692 cm^{-1}) can be assigned to the second overtone of stretching vibrations of O–H bonds in water molecules bonded to carbonate ions in the interlayer region. As can be seen, none of the wavenumbers for the NIR spectra coincided exactly with three times the values for the MIR signals owing to the anharmonic nature of the vibrations. The catalysts containing palladium also gave the previous four signals, which differed in strength and were due to their octahedral layer structure. However, they additionally exhibited a signal at a greater wavenumber that can be assigned to electronic transitions between *d* orbitals in the palladium atoms. This was the sole difference in this spectral region other than signal strength between the Pd-containing catalysts and the pure LDH.

Also, the presence of the metal outside the octahedral layers resulted in substantially stronger signals.

Región 8000-6000 cm^{-1} : This zone contained four signals essentially due to the first overtone of stretching vibrations of O–H bonds; hence, they were the strongest signals in the NIR spectrum (Fig. 6). The signals were somewhat weaker for the catalyst containing platinum in complexed form, whether intercalated (HT-PdCl₄) or supported (HT-PdAc₂Py₂). Irrespective of signal intensity, all spectra contained an asymmetric component centred at ca. 7000 cm^{-1} that was deconvoluted into three bands. Similarly to the previous zone, these three signals can be assigned to the first overtone of vibrations of the different types of O–H bonds present in the solids (see Table 3). Also, some solids exhibited a fourth, very weak band above 7500 cm^{-1} due to the addition or subtraction of the deformation mode for the split first overtone of the fundamental stretching vibration of the OH group (i.e. $2\nu_1 + \delta\nu$).

Región 5500-4000 cm^{-1} : This spectral zone contained two strong signals centred at ca. 5200 and 4400 cm^{-1} that were deconvoluted into several bands as shown in Fig. 7. The signal at the smaller wavenumber, which was deconvoluted into two bands, was a combination of several bands in the MIR region and is difficult to assign unambiguously. On the other hand, the bands at the greater wavenumber can be assigned to overtones of O–H bonds in water and to carbonate combination bands that result from splitting of the symmetric and anti-symmetric stretching vibrations for the anion [$2(\nu_1 + \nu_3)$].

4. CONCLUSIONS

Mid- and near-infrared spectroscopies were used here to characterize palladium-containing Mg/Al layered double hydroxides (LDHs). The palladium was either inserted into the brucite-like layers of the LDH, intercalated as PdCl₄²⁻ in the interlayer region of the solid or supported as PdAc₂Py₂ on its surface. The catalysts, which were synthesized in previous work, exhibited a layered structure containing carbonate ions in the interlayer

region; by exception, the presence of PdCl_4^{2-} in one of the solids dramatically reduced the amount of intercalated carbonate. The MIR spectra for the solids exhibited three distinct zones exhibiting marked differences in fundamental stretching vibrations of hydroxyl groups present in the catalysts ($3800\text{--}2500\text{ cm}^{-1}$ zone); such differences testify to the reduction in the amount of carbonate present in the catalyst containing palladium as an anionic chelate. This is also apparent from the decreased strength of the band for the stretching vibration of C–O bonds, which appears at ca. 1370 cm^{-1} . The NIR region allowed the pure LDH to be discriminated from the Pd-containing catalysts on the basis of the presence of electronic bands due to the metal, which appeared at ca. 10700 cm^{-1} (especially in the catalyst containing Pd as a chelate). Finally, the bands in the remainder of the NIR region exhibited significant differences in strength between catalyst types.

5. ACKNOWLEDGEMENTS

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Table 1. Experimentally determined chemical composition and lattice parameters of the catalysts (from reference 17).

Catalyst	Formulae ^a	%Pd ^b	<i>a</i> (Å) ^c	<i>c</i> (Å) ^c
HT	Mg _{0.670} Al _{0.330} (OH) ₂ (CO ₃) _{0.165} ·0.68H ₂ O	—	3.042	22.701
HT-Pd	Mg _{0.630} Pd _{0.040} Al _{0.330} (OH) ₂ (CO ₃) _{0.165} ·0.54H ₂ O	0.5	3.030	22.173
HT-PdCl ₄	Mg _{0.670} Al _{0.330} (OH) ₂ (CO ₃) _{0.072} (PdCl ₄) _{0.094} ·0.68H ₂ O	10.25	3.050	23.589
HT-PdAc ₂ Py ₂	Mg _{0.670} Al _{0.330} (OH) ₂ (CO ₃) _{0.165} ·0.72H ₂ O	0.6	3.040	22.548

^aChemical formula of the LDHs. ^bPercent weight of palladium. ^cLattice parameters.

Table 2. Infrared spectral analysis of synthesized catalysts (in cm^{-1}).

HT	HT-Pd	HT-PdCl ₄	HT-PdAc ₂ Py ₂	Assignment
3598	3571	3584	3601	MO-H stretching
3499	3449	3464	3460	MO-H stretching
3340	3316	3323	3324	Water O-H stretching
3095	3071	3121	3070	Water O-H stretching bonding to carbonate
1615	1638	1630	1579	Water O-H bending
1406	1435	1451	1410	CO ₃ stretching (reduced symmetry)
1363	1366	1372	1360	CO ₃ antisymmetric stretching (mode ν_3)
1032	1030	1016	1022	Al-OH deformation
951	946	934	948	Al-OH deformation
856	862	833	852	CO ₃ bending out-of-plane (mode ν_4)
782	784	739	779	Al-OH traslation
676	675	648	677	CO ₃ bending in-plane (mode ν_2)
550	555	559	554	Al-OH traslation
450	453	448	452	Al-O skeleton

Table 3. Near infrared spectral analysis of synthesized catalysts (in cm^{-1}).

HT	HT-Pd	HT-PdCl ₄	HT-PdAc ₂ Py ₂	Assignment
	10777	10763	10727	Electronic bands
10542	10578	10476	10557	2 nd overtone of M-OH stretching
10373	10341	10301	10273	2 nd overtone of M-OH stretching
10150	10146	10094	9997	2 nd overtone of water O-H stretching
9692	9629	9751	9657	2 nd overtone of water stretching bonding to CO ₃
7855			7540	2 $\nu_1 + \delta\nu$
7146	6997	7076	7035	1 st overtone of M-OH stretching
6991	6859	6917	6880	1 st overtone of M-OH stretching
6709	6576	6612	6590	1 st overtone of water O-H stretching

Figure 1. XRD patterns for the catalysts.

Figure 2. 4000-2500 cm^{-1} spectral region for the catalysts studied.

Figure 3. 1800-1200 cm^{-1} spectral region for the catalysts studied.

Figure 4. 1200-400 cm^{-1} spectral region for the catalysts studied.

Figure 5. NIR spectra of synthesized catalysts in the 11000-9000 cm^{-1} region.

Figure 6. NIR spectra of synthesized catalysts in the 8000-6000 cm^{-1} region.

Figure 7. NIR spectra of synthesized catalysts in the 5500-4000 cm^{-1} region.

RESEARCH HIGHLIGHTS

► We use for the first time the NIR spectroscopy to characterize palladium supported over hydrotalcites catalysts. ► The catalysts exhibited three distinct zones with marked differences in fundamental stretching vibrations of OH groups. ► The NIR region allowed the pure LDH to be discriminated from the Pd-containing catalysts on the basis of the presence of electronic bands due to the metal.