Alkene hydrogenation catalyzed by rhenium carbonyls bonded to highly dealuminated Y zeolite: spectroscopic characterization of the working catalyst

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

Abstract

Rhenium carbonyls bonded to dealuminated zeolite Y calcined at 300 and at 500 °C were tested as catalysts for hydrogenation of ethylene and of propylene and characterized by infrared (IR) and extended X-ray absorption fine structure (EXAFS) spectroscopies, even under catalytic reaction conditions. The initially formed rhenium tricarbonyls bonded to the zeolite were converted into rhenium dicarbonyls during catalysis, as shown by IR and EXAFS spectra, and the coordination of the Re to the support changed, as shown by EXAFS results. Consequently, there were bonding positions on the Re centers for reactive ligands, including those identified by IR spectroscopy as alkyls and π-bonded alkenes. The catalysis is suggested to proceed via reaction of alkyl and hydride ligands on rhenium centers incorporating two CO ligands.
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1. Introduction

Supported mononuclear metal complexes are technologically important catalysts that present attractive opportunities for understanding the links between surface catalysis and purely molecular catalysis. Our goal was to determine the structure of a simple supported metal complex catalyst in the working state. We chose a supported rhenium carbonyl as the catalyst precursor because of the well-developed chemistry of such species (much of it contributed by Ugo and coworkers [1,2]) and because of their relative stability

[3]. We chose a nearly uniform crystalline support, dealuminated Y (DAY) zeolite [4], to simplify the structural characterization. We report infrared (IR) and extended X-ray absorption fine structure (EXAFS) spectra of the rhenium complex catalysts for alkene hydrogenation, providing evidence of hydrocarbon ligands formed from the reactants in addition to CO ligands remaining from the precursor.

2. Experimental methods

The zeolite-supported rhenium carbonyls were synthesized on a vacuum line and in a N_2-filled glovebox. The solvent *n*-hexane (99.0% purity, Aldrich) was purified by refluxing in N_2 in the presence of

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Na/benzophenone ketyl followed by sparging with dry N_2. Zeolite DAY (Degussa, Si:Al atomic ratio $\cong 100$) was calcined in flowing O_2, heated to 300 or 500 °C for 4 h, and evacuated for 12 h at 10^{-3} Torr to give samples denoted DAY_{300} and DAY_{500}, respectively. The precursor $HRe(CO)_5$ [5] was adsorbed on the zeolite by mixing in a slurry with *n*-hexane, stirred for 24 h, and evacuated at room temperature to remove the solvent. The resultant sample was treated in flowing H_2 at 80 °C for 4 h to form the supported rhenium tricarbonyl catalyst precursor [6]. The sample contained 1.0 wt.% Re.

Reactor feed gases ethylene (Matheson, 99.5%), propylene (Matheson, 99.5%), and He (Matheson, 99.999%) were purified by passage through traps containing zeolite 4A and activated γ-Al_2O_3 particles to remove oxygen and moisture. H_2 (99.99%) was prepared by electrolysis of water in a Balston generator. The supported complexes were tested as catalysts for reaction of a mixture of ethylene (or propylene) and H_2 in He. Reaction experiments were carried out at steady state in a temperature-controlled stainless-steel tubular flow reactor, with the effluent analyzed by gas chromatography. The reactor was loaded with 100–200 mg of catalyst, mixed with about 1 g of inert nonporous α-Al_2O_3 to minimize temperature gradients. Experiments were performed at various temperatures (25–300 °C) with volumetric feed flow rates of 63, 13, and 12 $cm^3\,min^{-1}$ of He, H_2, and alkene, respectively, and with various feed flow rates (63, 13, and 12 $cm^3\,min^{-1}$; 0, 13, and 12 $cm^3\,min^{-1}$; and 0, 49, and 24 $cm^3\,min^{-1}$ of He, H_2, and alkene, respectively) at 50 °C. Ethylene hydrogenation was investigated at room temperature and at 80 °C and propylene hydrogenation at room temperature and at 50 °C.

IR spectra of powder samples were collected with a Bruker IFS 66v spectrometer with a spectral resolution of 4 cm^{-1}, as before [4]. To prepare an optically thin sample allowing the detection of minor bands, the powder was pressed between KBr windows.

EXAFS spectra at the Re L_{III} edge (10,535 eV) were collected at beam lines 2–3 and 4–1 of the Stanford Synchrotron Radiation Laboratory. The zeolite-supported rhenium complexes that had been tested as catalysts for propylene hydrogenation at 50 °C were pressed into self-supporting wafers (with masses of approximately 120 mg) under N_2 in a glove-box at the synchrotron. Each wafer was loaded into the EXAFS cell and sealed under a positive He pressure. The cell was aligned in the X-ray beam, and EXAFS spectra of functioning catalysts were recorded [6]; the zeolite-supported rhenium complexes during catalysis at 80 °C were also scanned in flowing mixtures of He, H_2, and ethylene at 1 atm and subsequently at room temperature in flowing He at 1 atm; some data were collected at liquid nitrogen temperature.

3. Analysis of X-ray absorption data

Details of the methods are as reported [4,6]. The phase shifts and backscattering amplitudes representing Re–Re and Re–O interactions were analyzed with EXAFS data characterizing Re powder and NH_4ReO_4 mixed with BN, respectively. $Os_3(CO)_{12}$ mixed with BN was used to represent phase shifts and backscattering amplitudes for analysis of the Re–C and Re–O* interactions (O* is carbonyl oxygen). Re–Si reference files were calculated with structural parameters representing a Re–Si alloy. A summary of parameters used to construct the reference files is given elsewhere [6].

4. Results

Table 1 is a summary of the ν_{CO} stretching frequencies characterizing rhenium carbonyls in the zeolite; data for comparable supported metal carbonyls are summarized elsewhere [6]. The ν_{CO} spectra characterize supported rhenium carbonyls under catalytic reaction conditions; the spectra recorded after catalysis had taken place in the flow system for 4 h at room temperature (2130 m, 2088 w, 2048 m, 2034 s, 2019 s, 1996 m, 1982 s, 1948 sh, 1924 sh cm^{-1}) and at 80 °C (2133 m, 2090 w, 2048 m, 2034 s, 2019 s, 1996 m, 1982 s, 1948 sh, 1924 sh cm^{-1}) include bands nearly matching those that were observed before catalysis, namely, 2133 w, 2056 m, 2036 vs, 2021 vs, 1984 vs, 1944 vs cm^{-1} (Table 1). The spectra of the used catalyst show an increased intensity of the 2050 cm^{-1} band and the appearance of weak bands at 2088 (and 2090), 1996, and 1925 cm^{-1}.

After propylene hydrogenation catalysis by the zeolite DAY_{500}-supported rhenium complex, a more marked change was observed in the IR spectra than

Table 1
Carbonyl stretching frequencies characterizing rhenium carbonyls on zeolite DAY after alkene hydrogenation

Zeolite support	Treatment	Stretching frequency (cm^{-1})
DAY_{300}	$C_2H_4 + H_2$ at 80 °C	2133 m, 2090 w, 2048 m, 2034 s, 2019 s, 1996 m, 1982 s, 1948 m, 1924 sh
DAY_{300}	$C_2H_4 + H_2$ at room temperature	2130 m, 2088 w, 2048 m, 2034 s, 2019 s, 1996 m, 1982 s, 1948 m, 1924 sh
DAY_{500}	$C_3H_6 + H_2$ at 50 °C	2088 w, 2052 s, 2031 m, 2017 w, 2008 w, 1981 m, 1932 s
DAY_{500}	$C_3H_6 + H_2$ at room temperature	2088 w, 2050 s, 2006 m, 1928 s

for the zeolite DAY_{300}-supported catalyst, regardless of the length of the catalytic test run (Fig. 1). Rhenium carbonyls in zeolite DAY_{500} after propylene hydrogenation at room temperature (Fig. 1) and at 50 °C are characterized by ν_{CO} bands at 2088 w, 2050 s, 2006 m, 1928 s cm^{-1} and 2088 w, 2052 s, 2031 m, 2017 w, 2008 w, 1981 m, 1932 s cm^{-1}, respectively (Table 1). The ν_{CO} bands characterizing zeolite DAY_{500}-supported rhenium carbonyls before catalysis (2133, 2055, 2036, 2021, 1984, 1946 cm^{-1}) had almost completely disappeared after the test, and two very strong new bands were observed, at 2050 and 1928 cm^{-1}.

The ν_{CH} bands (in the range of 2800–3100 cm^{-1}) characterizing adsorbates on zeolite DAY_{300}-supported rhenium carbonyls after ethylene hydrogenation catalysis are shown in Table 2 [7–9]. The supported rhenium carbonyls in the zeolite after catalysis at room temperature and at 80 °C are characterized by new
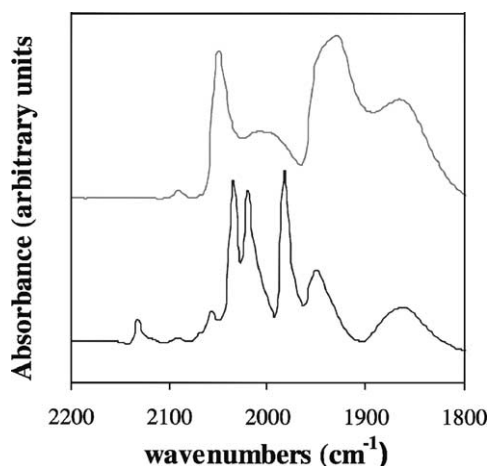

Fig. 1. IR spectra characterizing zeolite-supported rhenium carbonyls before (lower curve) and after (upper curve) propylene hydrogenation at room temperature.

Table 2
Stretching frequencies (from 2800–3100 cm^{-1}) characterizing zeolite-supported rhenium carbonyls and reference compounds incorporating ethylene-and propylene-derived adsorbates or ligands

Sample	Adsorbate or ligand	Stretching frequency (cm^{-1})	Reference
Rh(1 1 1)	π-Bonded ethylene	3060, 3000	[7]
Pt(1 1 1)	Di-σ-bonded propylene	2950, 2920, 2820	[8]
Pt(1 1 1)	π-Bonded propylene	3020–2880	[8]
CH_3CH_2Cl	Ethyl	2967, 2947, 2881	[9]
$Re(CO)_2$ on	Ethyl	2952, 2870	This work
zeolite DAY_{300}[a]	π-Bonded ethylene	3012	This work
$Re(CO)_2$ on	Ethyl	2955, 2920, 2896, 2867	This work
zeolite DAY_{300}[b]	π-Bonded ethylene	3029	This work
$Re(CO)_2$ on	Di-σ-bonded propylene	2964, 2927, 2856	This work
zeolite DAY_{500}[c]	π-Bonded propylene	3029	This work
$Re(CO)_2$ on	Di-σ-bonded propylene	2950, 2921, 2864	This work
zeolite DAY_{500}[d]	π-Bonded propylene	3018	This work

[a] Treated in $C_2H_4 + H_2$ at 80 °C.
[b] Treated in $C_2H_4 + H_2$ at room temperature.
[c] Treated in $C_3H_6 + H_2$ at 50 °C.
[d] Treated in $C_3H_6 + H_2$ at room temperature.

Table 3
Stretching frequencies (between 1000 and 1600 cm^{-1}) characterizing reference compounds having ethylene- and propylene-derived adsorbates or ligands

Sample	Adsorbate	Stretching frequency (cm^{-1})	Reference
Rh on alumina	Ethylene	1509, 1222	[9]
Pd on alumina	Ethylene	1513, 1188	[9]
Re(CO)$_2$ on zeolite DAY$_{300}$[a]	Ethylene	1537, 1456, 1367, 1153, 1091	This work
Re(CO)$_2$ on zeolite DAY$_{300}$[b]	Ethylene	1537, 1452, 1365, 1197, 1066	This work
CuO–MgO	Propylene	1510, 1440, 1400, 1350	[10]
Re(CO)$_2$ on zeolite DAY$_{500}$[a]	Propylene	1456, 1367, 1153, 1091	This work
Re(CO)$_2$ on zeolite DAY$_{500}$[b]	Propylene	1452, 1365, 1197, 1066	This work

[a] Treated in C$_3$H$_6$ + H$_2$ at 50 °C.
[b] Treated in C$_3$H$_6$ + H$_2$ at room temperature.

bands at 3029, 2955, 2920, 2896, and 2867 cm^{-1} and 3012, 2952, and 2870 cm^{-1}, respectively, which suggest the presence of ligands on the rhenium formed from ethylene and H$_2$. Comparable data are summarized in Table 3 [9,10] for the catalysts used under other conditions. The data indicate propylene-derived adsorbates on the rhenium carbonyls used for propylene hydrogenation catalysis.

The EXAFS parameters characterizing the zeolite-supported rhenium carbonyls are summarized in Table 4, and those characterizing related rhenium carbonyls are summarized elsewhere [6]. The errors

Table 4
EXAFS results characterizing rhenium complexes in zeolite DAY[a]

Support	Treatment	Conditions of scan (gas, temperature)	Backscatterer	N	R (Å)	$10^3 \times \Delta\sigma^2$ (Å^2)	ΔE_0 (eV)
Zeolite DAY$_{500}$	C$_3$H$_6$ + H$_2$ at 50 °C	He, −196 °C	CO ligands				
			Re–C	1.8	1.95	−5.3	11.8
			Re–O*	2.3	3.05	−0.5	−0.1
			Support ligands				
			Re–O$_s$	1.6	2.04	−3.7	1.6
			Re–O$_l$	4.3	2.45	−4.2	7.1
			Re–Al	0.4	2.24	−5.8	−3.4
Zeolite DAY$_{300}$	C$_2$H$_4$ + H$_2$ at 80 °C	C$_2$H$_4$ + H$_2$, 80 °C	CO ligands				
			Re–C	1.8	1.96	−6.6	14.4
			Re–O*	2.3	3.17	−1.6	−1.2
			Support				
			Re−O$_s$	0.7	2.02	−8.0	14.2
			Re−O$_l$	4.3	2.44	−2.3	16.9
			Re–Al	0.4	2.25	−4.9	−4.5
Zeolite DAY$_{300}$	C$_2$H$_4$ + H$_2$ at 80 °C	He, room temperature	CO ligands				
			Re–C	1.8	1.95	−1.3	13.8
			Re–O*	2.3	3.06	1.3	2.5
			Support				
			Re–O$_s$	1.6	2.04	3.1	14.8
			Re–O$_l$	4.3	2.45	1.7	19.6
			Re–Al	0.4	2.30	2.8	9.3

[a] *Notation*: Re–O$_s$ and Re–O$_l$ represent Re–support oxygen contributions at relatively short and relatively long distances. O* represents carbonyl oxygen.

shown in Table 4, estimated from the data [11], represent precision, not accuracy. Estimated accuracies are as follows: coordination number (N), $\pm 30\%$; distance (R), $\pm 2\%$; Debye–Waller factor ($\Delta\sigma^2$), $\pm 30\%$; and inner potential correction (ΔE_0), $\pm 20\%$. The Nyquist theorem was used as before [4] to estimate the number of statistically justified fitting parameters (21), which exceeded the number used in the fits (20).

Analysis of the EXAFS data characterizing the catalyst after propylene hydrogenation, with the sample scanned at liquid nitrogen temperature, was performed first because the data quality was highest, and the results were used to guide the analysis of results representing the other samples, which were investigated at higher temperatures and were thus characterized by lower-quality data. The EXAFS data characterizing rhenium complexes on zeolite DAY_{500} after propylene hydrogenation catalysis at $50\,^{\circ}C$ (Table 4) include no Re–Re contributions, indicating that the rhenium species were mononuclear and site isolated. Re–C and Re–O* contributions were found at distances of 1.95 and $3.05\,\text{Å}$, respectively, consistent with CO ligands coordinated to Re (Table 5 [6,12,13]). The coordination numbers of 1.8 and 2.3 for the Re–C and Re–O* shells, respectively, indicate that each Re atom was bonded to two CO ligands. A Re–O_s contribution (the subscript refers to short) was found with a coordination number of 1.6 and a (bonding) distance of $2.04\,\text{Å}$, consistent with other metal–support-oxygen bond distances typically found in the range of 2.04–$2.18\,\text{Å}$ [12,13]. Two other Re–support contributions were determined, Re–O_l (l refers to long) and Re–Al, with coordination numbers of 4.3 and 0.4 and at distances of 2.45 and $2.24\,\text{Å}$, respectively. These distances are too long to be bonding distances; the latter contribution is identified only tentatively.

The EXAFS data characterizing rhenium carbonyls in zeolite DAY_{300} undergoing ethylene hydrogenation catalysis are summarized in Table 4. Fitting of the data was attempted with both di- and tricarbonyls of rhenium, and only the former provided satisfactory fits.

Following the EXAFS measurements characterizing rhenium carbonyls in zeolite DAY_{300} during ethylene hydrogenation at $80\,^{\circ}C$, the sample was cooled to room temperature in flowing He and characterized again. No Re–Re contribution was found. The Re–C ($N = 1.8$, $R = 1.95\,\text{Å}$) and Re–O* ($N = 2.3$, $R = 3.06\,\text{Å}$) contributions are consistent with values reported for the sample mentioned immediately above and for other supported metal dicarbonyls, e.g. $Os(CO)_2$ on γ-Al_2O_3 and $Rh(CO)_2$ in zeolite DAY (Table 5). A Re–O_s contribution ($N = 1.6$, $R = 2.04\,\text{Å}$) matches that mentioned above. Two other contributions were determined, Re–O_l and Re–Al, with N equal to 4.3 and 0.4 and R equal to 2.45 and $2.30\,\text{Å}$, respectively, nearly matching the values reported for the above-mentioned sample (Re–O_l, $N = 4.3$, $R = 2.45\,\text{Å}$; Re–Al, $N = 0.4$, $R = 2.24\,\text{Å}$).

Kinetics data were collected for ethylene hydrogenation catalyzed by rhenium complexes in zeolite DAY_{300}. The conversions at $50\,^{\circ}C$ were about 1%. The apparent activation energy, determined from the temperature dependence of the rate determined from differential conversion data, was $56\,\text{kJ/mol}$. From a plot of conversion versus inverse space velocity [6], the turnover frequency, TOF, at $50\,^{\circ}C$ was found to

Table 5
EXAFS results characterizing supported metal carbonyls[a]

Support	Precursor	Structure or structural model	EXAFS contribution						Reference
			M–C		M–O*		M–O_s		
			N	R (Å)	N	R (Å)	N	R (Å)	
MgO_{390}	$[Re_2(CO)_{10}]$	$[Re(CO)_3\{OMg\}_x\{HOMg\}_{3-x}]$	2.8	1.88	2.9	3.08	3.1	2.18	[12]
Zeolite DAY_{500}	$[HRe(CO)_5]$	$[Re(CO)_3\{O_{R4}{}^{2-}\}_2\{O_{R6}{}^{2-}\}]$	2.8	1.96	3.3	3.14	3.3	2.09	[6]
Zeolite DAY_{300}	$[HRe(CO)_5]$	Mixture of rhenium carbonyls	4.2	1.96	4.7	3.09	3.3	2.18	[6]
Zeolite DAY_{300}	$[Rh(CO)_2(acac)]$	$[Rh(CO)_2]$	2.2	1.86	2.3	2.96	1.9	2.15	[6]
γ-Al_2O_3	$[Rh_4(CO)_{12}]$	$[Rh(CO)_2]$	–	1.81	–	3.00	7.0	2.04	[13]
SiO_2	$[Ru_3(CO)_{12}]$	$[Ru(CO)_2]$	–	1.87	–	3.01	4.9	2.08	[13]

[a] *Notation*: Re–O_s represents contributions from support oxygen atoms. M represents metal; O* represents carbonyl oxygen. The braces denote groups that are part of a support surface.

be $3.1 \times 10^{-3}\,s^{-1}$ when H_2 and ethylene were fed in a 1:1 molar ratio. The catalytic activity of the support in the absence of rhenium was found to be at most 8% of the activity of the supported rhenium complex (and the reported rates were corrected for the relatively small activity of the support itself). The catalysis data are similar to those reported [3] for propylene hydrogenation catalyzed by a rhenium complex supported on MgO.

5. Discussion

Re(I), with a d^6 electron configuration, forms a saturated complex with 18 electrons, [Re(I)(CO)$_3$ $\{O_{R4}^{2-}\}_2\{O_{R6}^{2-}\}$] (Fig. 2) [6]. During alkene hydrogenation the structure of [Re(I)(CO)$_3\{O_{R4}^{2-}\}_2$ $\{O_{R6}^{2-}\}$] changed so that each rhenium atom was coordinated to four oxygen atoms at a distance of approximately 2.45 Å (nonbonding contribution), while an oxygen atom at 2.04 Å (bonding contribution) was found (Table 4), consistent with EXAFS and IR data suggesting the formation of [Re(I)(CO)$_2\{O^{2-}\}$]. The

loss of a CO ligand and two surface ligands causes the rhenium complex to become unsaturated and activated for catalysis.

The ν_{CO} IR and EXAFS spectra characterizing the working catalysts are consistent with the presence of only two of the initial three CO ligands remaining on each Re center; in the section that follows, we work from the hypothesis that these complexes and not undetected minority species were the catalytically active species. The removal of a CO ligand from the precursor rhenium tricarbonyl on the support is inferred to have provided a bonding site for reactants on the Re center. Furthermore, additional bonding sites were opened up by the change in coordination of the rhenium to the support; the EXAFS-derived coordination numbers characterizing the Re–O$_s$ contribution decreased from about 3 to about 1 (or 2), indicating the formation of rhenium dicarbonyl complexes bonded to single oxygen atoms of the support (or perhaps to two). Thus, the spectroscopic data indicate rhenium carbonyls with sufficient bonding sites to accommodate the hydride and hydrocarbon ligands expected for catalytic hydrogenation of alkenes.
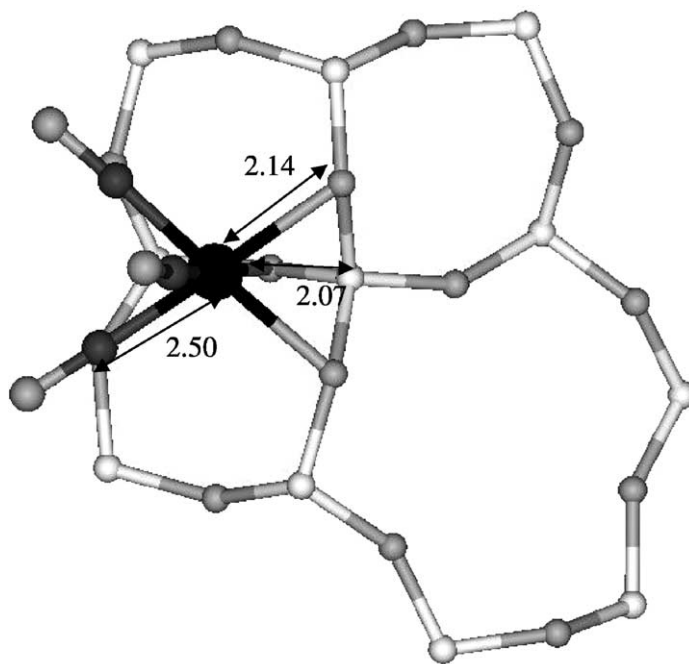

Fig. 2. Bonding position of Re(CO)$_3$ in the supercage of zeolite DAY$_{773}$ at a T5 (three-hollow) site: (A) site I and (B) site II. Key: O, light gray; C, dark gray; Re, black; Si, Al, white. Distances are given in Å.

The ν_{CH} bands in the IR spectra indicate alkene-derived ligands on the Re center during catalysis. (As expected, no EXAFS contributions were found that could be attributed to alkene-derived ligands, probably because the Re–alkene contributions were not separable from the various Re–O contributions.)

In the IR spectra characterizing rhenium carbonyls in zeolite DAY$_{300}$, the increase in intensity of ν_{CO} bands at 2090, 2048, 1996, and 1924 cm^{-1} (Table 1) after ethylene hydrogenation at room temperature (similar results were observed at 80 °C) indicates the structural change of the rhenium carbonyls under catalytic reaction conditions. The structural changes were more pronounced in the case of propylene hydrogenation at room temperature (similar results were observed at 50 °C) for the zeolite DAY$_{500}$-supported catalyst, with the sample being characterized by very strong ν_{CO} bands (the main bands) at 2050 and 1928 cm^{-1} (Table 1, Fig. 1). Two main ν_{CO} bands are consistent with a rhenium dicarbonyl with C$_{2v}$ symmetry.

The appearance of these two main ν_{CO} bands 2050 and 1928 cm^{-1} (Table 1) characterizing the zeolite DAY$_{500}$-supported rhenium carbonyls after propylene hydrogenation is in accord with the spectra of other metal dicarbonyl species, which also are characterized by two main absorption bands (Table 6), including [Rh(I)(CO)$_2$], [Ru(CO)$_2$], *trans*-[Re(III)(CO)$_2$I$_4$]$^-$, and [CpRe(CO)$_2$C$_5$H$_8$], where Cp refers to cyclopentadienyl (species with C$_{2v}$ symmetry allow two main ν_{CO} bands in the IR spectrum [16]).

The ν_{CH} bands characterizing rhenium carbonyls after ethylene hydrogenation catalysis are consistent with the formation of the ethylene-derived ligands on the Re centers in the zeolite DAY$_{300}$-supported sam-

ples. We cannot determine the identities of these ligands with the greatest confidence, but the data suggest that they were π-bonded ethylene and ethyl, as follows: the following ν_{CH} bands were observed in the spectrum of zeolite DAY$_{300}$-supported rhenium carbonyls after ethylene hydrogenation at 80 °C: 3012, 2952, and 2870 cm^{-1}. The 2952 and 2870 cm^{-1} bands are consistent with ethyl ligands on the Re center (Table 2). For example, CH$_3$CH$_2$Cl is characterized by ν_{CH} bands at 2967 (CH$_2$ symmetric), 2947 (CH$_3$ antisymmetric), and 2881 (CH$_3$ symmetric) cm^{-1}, similar to the ν_{CH} bands representing our rhenium carbonyl. A band similar in frequency to the 2967 cm^{-1} band of CH$_3$CH$_2$Cl was not observed in the spectrum of the catalyst; it might have been obscured by the broad band at 2952 cm^{-1} (FWHM approximately 15 cm^{-1}), or it may not be active for this sample as a result of the symmetry of the ligand on rhenium [6,16,17]. The 3012 cm^{-1} band (suggested to represent a C=C–H stretch) is weak and comparable to the 3015 cm^{-1} band observed for ethylene π-bonded to Pt(111), consistent with the presence of π-bonded ethylene on the Re center in the working catalyst.

Rhenium carbonyls in zeolite DAY$_{300}$ after ethylene hydrogenation at room temperature are characterized by ν_{CH} bands at 3029, 2955, 2920, 2896, and 2867 cm^{-1}. Those at 2955, 2920, 2896, and 2867 cm^{-1} suggest the formation of ethyl, consistent with the IR bands characterizing CH$_3$CH$_2$Cl (2967, 2947, 2881 cm^{-1}, Table 2). The 3029 cm^{-1} band is consistent with the formation of π-bonded ethylene, as observed for ethylene adsorbed on Pt(111) (3015 cm^{-1}, Table 2).

The IR bands in the region of 1000 and 1600 cm^{-1} characterizing ethylene-derived ligands on rhenium

Table 6
Reference literature summary of ν_{CO} bands characterizing metal carbonyls on supports and in solution

Support or solution	Precursor	Structural	CO stretching frequency (cm^{-1})	Reference
SiO$_2$	[Ru$_3$(CO)$_{12}$]	Ru(CO)$_2$	2050, 1985	[13]
CS$_2$, CCl$_4$		CpRe(CO)$_2$C$_5$H$_8$	1973 s, 1893 s	[14]
CH$_2$Cl$_2$		*trans*-[Re(III)(CO)$_2$I$_4$]$^-$	2050 s, 1995 s	[15]
CH$_2$Cl$_2$		*trans*-[Re(II)(CO)$_2$I$_4$]$^{2-}$	1915 s, 1875 s	[15]
THF		Rh(CO)$_2$(acac)	2081 s, 2010 vs	[4]
Zeolite DAY$_{120}$	[Rh(CO)$_2$(acac)]	Rh(I)(CO)$_2$	2115 s, 2049 vs	[4]
Zeolite DAY$_{300}$	[Rh(CO)$_2$(acac)]	Rh(I)(CO)$_2$	2116 s, 2050 vs	[4]
Zeolite DAY (T4)		Rh(I)(CO)$_2$	2114, 2060	[4]

carbonyls in zeolite DAY_{300} provide additional evidence of the formation of ethyl and π-bonded ethylene on the rhenium (Table 3). The spectra recorded after ethylene hydrogenation catalysis at room temperature (1537, 1066, 1452, 1365, and $1197\,cm^{-1}$) and $80\,^\circ C$ (1537, 1091, 1456, 1367, and $1153\,cm^{-1}$) suggest the formation of π-bonded ethylene as indicated by the 1153 and $1197\,cm^{-1}$ bands characterizing the respective samples; the bands are similar to those characterizing ethylene π-bonded to metal surfaces and supported metals (Table 3) [9].

The IR bands in the range $2800–3100\,cm^{-1}$ characterizing zeolite DAY_{500}-supported rhenium carbonyls used for propylene hydrogenation suggest the formation of π-bonded propylene. The spectra observed after catalysis at room temperature (3029, 2964, 2927, and $2856\,cm^{-1}$) and $50\,^\circ C$ (3018, 2950, 2921, and $2864\,cm^{-1}$) are similar to each other. The band at wavenumbers $>3000\,cm^{-1}$ is indicative of π-bonded propylene, as observed for propylene on Pt supported on SiO_2 [8] and on Pt(1 1 1) [10].

The IR bands characterizing propylene-derived adsorbates in the region of $1000–1600\,cm^{-1}$ lead to a similar interpretation (Table 3). The 1456 and $1367\,cm^{-1}$ and the 1452 and $1365\,cm^{-1}$ bands characterizing the samples after propylene hydrogenation at $80\,^\circ C$ and room temperature, respectively, are consistent with the presence of π-bonded propylene [9].

In summary, the data clearly show changes in the supported rhenium tricarbonyl precursor as a result of its coming in contact with catalytically reacting mixtures of H_2 and an alkene, with the changes providing bonding positions on the Re centers for reaction intermediates, identified by the IR spectra as hydrocarbons, likely alkyls and π-bonded alkenes. Although we do not have sufficient data to determine how the amounts of these intermediates depend on the reaction conditions, the results are sufficient to suggest that the catalysis likely proceeds via π-bonding of an alkene, bonding of hydrogen, reaction to form alkyl, and further reaction to form alkane.

6. Conclusions

The results presented here for supported metal complex catalysts that are simple enough to be considered molecular analogues demonstrate the value of using the combination of IR and EXAFS spectroscopies to track structural changes in working catalysts, with specific information about the ligands provided by the IR spectra and specific information about the metal–support interface provide by the EXAFS spectra. Metal carbonyl catalysts offer the advantage of the structural information in the spectra provided by the CO ligands.

Acknowledgements

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