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TiO_2-supported rhenium oxide catalysts for methanol oxidation: Effect of support texture on the structure and reactivity evidenced by an operando Raman study

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ABSTRACT

The methanol conversion to methylal over two TiO_2-anatase supported oxorhenate catalysts was investigated using *operando* Raman spectroscopy and compared to the catalytic activities afforded by a classical test. In dehydrated catalysts, two distinct structures were clearly identified and correlated to different catalytic behavior upon CH_3OH/He–CH_3OH/He/O_2–O_2 cycling. Such differences, intimately linked to the rhenium surface coverage, are proposed to reflect different degrees of polymerization.

1. Introduction

The unique performance of anatase TiO_2-supported rhenium oxide catalysts in direct methanol conversion to methylal (dimethoxymethane, DMM) has been emphasized by Iwasawa and co-workers [1]. This property is believed to be due to the redox capability of Re oxides, responsible for the selectivity oxidation of methanol to formaldehyde together with appropriate acidity of Re oxides allowing the acetalization of formaldehyde with methanol to form methylal [1,2]. The exact influence of the support on the structure of the active phase is a well-known concern in the field of heterogeneous catalysis. Although mandatory, the connections between the molecular structure of the supported phase and the catalyst activity still remain complicated to establish. With regards to oxide-based materials, the use of Raman spectroscopy has been shown to be relevant in identifying the structure of the supported phase [3,4]. One step more positive is the use of *in situ* and *operando* techniques devoted to real-time structure-reactivity connection and successfully applied to bulk [5], or supported metal oxides [6] like vanadates [7–9] or molybdates [10]. The supported rhenium oxide-based catalysts are believed to essentially hold a monomeric structure and therefore, the monolayer level cannot be reached [11,12]. This assumption was based on Raman characterizations and the high volatility of solid Re_2O_7. The mono-, di- or tri-oxo configuration of rhenium centers is still under debate and seems to be highly dependent on the support. We propose here an *operando* study of methanol conversion to methylal by anatase-TiO_2-supported rhenium oxide catalysts. A given rhenium content was added by incipient wetness impregnation of two commercially available anatase material, namely Hombikat K03 ($100\,m^2\,g^{-1}$) and F01 ($300\,m^2\,g^{-1}$) differing by their specific area. The corresponding supported catalysts will accordingly present two distinct surface coverage levels and will be denoted as ReK (high surface coverage) and ReF (low surface coverage).

The present work is devoted to a Raman study of Re/TiO_2 catalysts as only technique. Indeed, these solids cannot be directly analyzed by other classical techniques like UV–vis absorption or ESR spectroscopies because of the remarkable absorption of TiO_2 in the UV range and the presence of F centers, respectively.

2. Experimental and methods

2.1. Catalyst preparation

Titania-supported rhenium oxide catalysts were prepared by incipient wetness impregnation of TiO_2-anatase by a solution of perrhenic acid ($HReO_4$; Alfa Aesar, 75–80% purity). After impregnation, the samples have been aged for 2 h under ambient conditions and dried overnight in air at 373 K. Finally, the catalysts were calcined at 673 K for 6 h under N_2 flow (temperature increase rate = $1\,K\,min^{-1}$). Commercially available titanium oxides Hombikat K03 (porous volume: 0.71 mL) and Hombikat F01 (porous volume: 0.96 mL) provided by Sachtleben were used as supports. Before impregnation, these TiO_2 supports were thoughtfully rinsed

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in distilled water and calcined in air up to 673 K to remove any trace of contamination (surface and bulk purity checked using ICP and XPS). The BET surface areas of K03 and F01 supports were found to reach 93 and 254 $m^2 g^{-1}$, respectively, in as-modified materials. The rhenium loading in the impregnation solution was properly settled in order to yield a rhenium content of 7.4 wt% in the supported ReK and ReF catalysts. Nitrogen was preferred to oxygen as atmosphere for the calcination and pretreatment in order to minimize rhenium volatization as Re_2O_7. The analytical rhenium contents for ReK and ReF final materials were found to reach 7.1 and 7.0 wt%, respectively, corresponding to respective surface coverage reaching 2.7 and 1.0 Re nm^{-2}. Before reaction, the catalysts were pretreated 1 h at 623 K under 30 mL min^{-1} pure helium (temperature increase rate = 5 K min^{-1}).

2.2. Catalytic activity

We have compared the activity of both catalysts achieved by the *operando* apparatus to the one measured by means of a classical catalytic test [10] including a quartz fixed bed reactor. After due pretreatment at 623 K under pure helium flow, the powder catalyst was set to the reaction temperature, comprised between 473 and 553 K, and the gas feed was allowed through the catalytic bed. The products were subsequently analyzed using a μ-gas chromatograph (SRA) equipped with a Poraplot U and a 5 A molecular sieve columns and TCD detectors. The typical reaction conditions for both operando and classical catalytic test are the following: GHSV = 37500 mL $h^{-1} g^{-1}$ and He/O_2/CH_3OH = 80/16/4 (mol%) at 1 atm. In all cases, the carbon balance was comprised between 95 and 105%, which was considered as acceptable.

2.3. Operando Raman spectroscopy

After due catalyst pretreatment, the methanol was introduced in the spectroscopic cell by means of a He flow (typically 30 mL min^{-1}) bubbling in a saturator equipped with a condenser which temperature is set to 273 K to yield a methanol partial pressure of 3.91 kPa. The parameters were adjusted to reach a GHSV value similar to the one used for the classical test. After having passed through the catalytic bed, the reaction products were analyzed using the above-described μ-gas chromatograph. The *in situ* spectral analysis was allowed by using an environmental spectroscopic chamber developed by Harrick equipped with a new planar dome especially developed to permit Raman measurements in both UV and visible ranges [13]. Micro-Raman spectra were recorded in working conditions at different temperatures and under selected atmospheres using the 532 nm second harmonic line of a Nd:YAG laser (laser power on the sample: 5 mW). A 50× microscope objective was used to focus the excitation beam (13.6 μm spot) and collect the scattered light. The scattered light was collected through a confocal hole (150 μm) by a nitrogen cooled CCD (Labram Infinity, Jobin Yvon).

3. Results

3.1. Structure of the ReF and ReK catalysts before reaction

The Raman spectra of pretreated catalysts were collected at room temperature under dehydrated conditions and are presented in Fig. 1 along with those of perrhenic acid (Fig. 1a) and ReK material before calcination (Fig. 1b). The spectrum of ReK before calcination exhibits the remarkable structural features of well crystallized TiO_2-anatase phase at 396 (δ_{TiOTi}), 515 and 639 (ν_{TiO}) cm^{-1} together with a sharp line observed at 972 cm^{-1}. The latter positively resembles the one of perrhenic acid $HReO_4$, also observed at 972 cm^{-1}, as reminded in Fig. 1a, and is assigned to symmetric Re═O stretch vibration, ν_S(Re═O), of free perrhenate ion in non-distorted tetrahedral coordination. A weak contribution assigned to the asymmetric component is also observed at 920 cm^{-1} in both spectra. Accordingly, the dried catalyst consists in hydrated perrhenate ions freely dispersed inside the TiO_2 porosity.

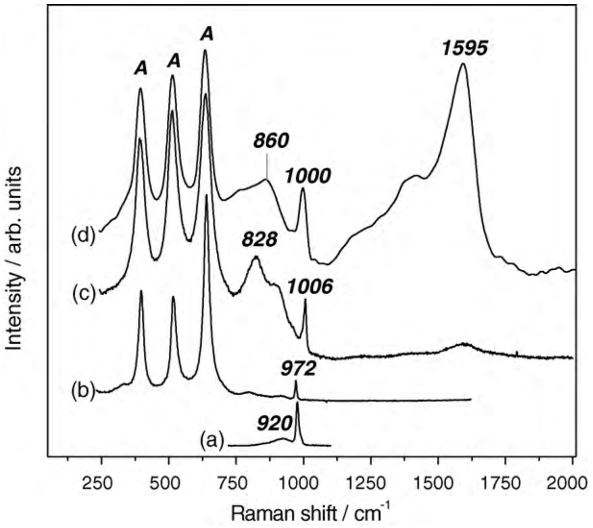


Fig. 1. Raman spectra of (a) perrhenate ion (ReO_4^-); (b) ReK catalyst before calcination; (c) pretreated ReF catalyst, dehydrated conditions; (d) pretreated ReK, dehydrated conditions.

Calcination of the catalyst at 673 K under pure N_2 and subsequent pretreatment at 623 K under helium flow produced significant changes in the structure of the ReK and ReF catalysts as depicted in Fig. 1c and d. In both cases, the features of anatase are broadened and the line previously observed at 972 cm^{-1} is shifted to 1006 (ReF) and 1000 cm^{-1} (ReK). Besides this mode, a broad additional scattering is observed in both cases between 800 and 900 cm^{-1}. Such modes certainly emerge from ν(Re–O) vibration in Re–O–Ti and/or Re–O–Re moieties. A remarkably broad and intense scattering between 1100 and 1750 cm^{-1} with a maximum at 1595 cm^{-1} is observed in the Raman spectrum of pretreated ReK catalyst prior to methanol exposure. This Raman signal is not observed anymore when the catalyst is brought back in air at room temperature, and its intensity seems to be strongly dependent of the excitation wavelength (not reported here).

The shift to higher wavenumbers of the $\nu(Re{=}O_t)$ mode observed around 1000 cm^{-1} in the spectrum of pretreated ReK catalyst usually accompanies the dehydration of supported oxides [10–12]. The molecular structure of dehydrated surface rhenium oxide based on the wavenumber of $\nu(Re{=}O_t)$ mode has been extensively discussed in the literature. Several works report on isolated tri-oxo Re species in C_3v symmetry [14–16], while earlier studies concluded on mono-oxo moieties [4,17–19] possibly embedding dimers or small aggregates [18,19]. The more realistic picture could eventually consist in a combination of different molecular structure, as suggested by Mitra et al. [15], which combination could be modified along surface coverage. In all cases, the wavenumber of the terminal Re═O vibration is found between 1000 and 1010 cm^{-1}.

In the present study, two slightly different spectra evolving from Re/TiO_2 for two surface coverage values are observed under the same conditions. Besides the differences in $\nu(Re{=}O_t)$ shape and wavenumber, the broad lines between 780 and 950 cm^{-1} together with the 1300–1650 cm^{-1} region suggests two different structures or, in line with Mitra and co-workers, different structural distribution could be denoted.

Table 1
Catalytic activity in methanol conversion for ReF and ReK catalysts recorded during consecutive exposure to CH_3OH/He for 1 h at 473 and 513 K then 1 h $CH_3OH/He/O_2$ feeds measured using a classical catalytic reactor. In brackets: catalytic activity recorded under exposure to $CH_3OH/He/O_2$ without CH_3OH/He step.

Catalyst	Feed	*T* (K)	Conv. (%)	S_{DME} (%)	S_F (%)	S_{MF} (%)	S_{DMM} (%)	S_{CH4} (%)	S_{Cox} (%)
ReF	CH_3OH/He	473	2.2	8.2	0	69.5	0	0	22.3
	CH_3OH/He	513	6.7	13.7	0	58.8	0	11.3	16.2
	$CH_3OH/He/O_2$	513	12.8 (27.5)	5.2 (6.3)	15.8 (0.3)	15.0 (13.5)	64.0 (79.1)	0 (0)	0 (0.8)
ReK	CH_3OH/He	473	2.7	7.4	0	66.7	0	0	25.9
	CH_3OH/He	513	10.4	13.2	0	34.8	0	11.9	40.1
	$CH_3OH/He/O_2$	513	35.6 (28.7)	5.7 (5.0)	5.0 (0.3)	7.9 (10.5)	81.2 (83.7)	0 (0)	0.2 (0)

3.2. Methanol conversion

3.2.1. Compared activity evaluation between a classical reactor and the operando chamber

Together with the on-line analysis connected to the operando apparatus, the performances of the catalysts were measured at 513 K in a classical catalytic set up and reported in Table 1 in order to allow comparison. Rather low temperatures (<250 °C) were applied, and our tests all consisted in 1 h on stream, so that the rhenium volatilization, though not excluded, is rather limited. No loss of activity is observed under the selected conditions, indicating only little Re would be lost during reaction.

Under CH_3OH/He flow at 473 K, the methanol conversion and selectivities after 1 h on stream (reference time) are similar for both ReK and ReF catalysts.

After 1 h exposure, the main product is methyl formate, revealing a joint redox-acidic function of the catalysts [2]. Increasing the temperature produced an increase of the conversion in both cases, though more pronounced in the case of ReK catalyst (>10% conversion after 1 h). Part (20–30%) of the methyl formate is found to be decomposed into methane and CO_2. Considering the selectivities measured for comparable conversion levels, the two catalysts also significantly differ, in so far as the CO_x production is markedly increased in the case of ReK catalyst whereas slightly decreases for ReF. Allowing oxygen in the feed made the ReK material produce methylal with high levels of conversion and selectivities with regards to the literature [1]. Conversely, the methanol conversion in ReF catalyst is 2.8 times lower and the combination of redox and acidic functions do not allow an as good selectivity in methylal as found for ReK. This is with no doubt due to the prior step under CH_3OH/He. Indeed, direct reaction under $CH_3OH/He/O_2$ gave rise to activities comparable to those measured for ReK catalyst under the same conditions (values in brackets, Table 1).

The compared activities afforded by the two set ups are summarized in Fig. 2. It appears that the evolutions of selectivities according to the conversion level follow the same trends and reach close values. In general, taking into account the typical error made at low conversion rates, the catalytic operando cell appears to fairly reflect the real performances of a catalyst. Indeed, for a given conversion rate, the selectivities are highly similar. A practical comparison of the conversion values recorded after 1 h at the corresponding temperature under the same reacting conditions (GHSV) has evidenced the Harrick reactor under evaluates the conversion values. At 200 °C under CH_3OH/He, the conversion measured using the Harrick cell is found to be 2.7% instead of 3.8%, at 240 °C under CH_3OH/He, we have found 10.4% instead of 14.6% and finally, at 240 °C under $CH_3OH/He/O_2$, the conversion level was 35.6% instead of 38.1%. This comparison is effective for up flow configuration of the Harrick cell, equipped with a flat Raman dome, which makes the dead volume much lower than using the diffuse reflectance dome.

3.3. Operando Raman

3.3.1. ReF catalyst

The introduction of methanol carried by a helium flow without oxygen upon increasing temperature led to major structural changes in the Raman spectrum of ReF catalyst. Indeed, as soon as the methanol is allowed into the spectroscopic cell at 423 K, a severe loss of the initial Raman signal due to the oxide materials, including the support and the oxorhenate phase is observed as evidenced in Fig. 3b. Increasing the temperature produced no significant changes in the Raman spectra of catalyst under CH_3OH/He flow as shown in Fig. 3c and d. The disappearance of the Raman signal is critical enough to almost wipe away the structural bands of anatase. Simultaneously, two lines assigned to amorphous heavy carbon species are observed at 1324 and 1585 cm^{-1} [21].

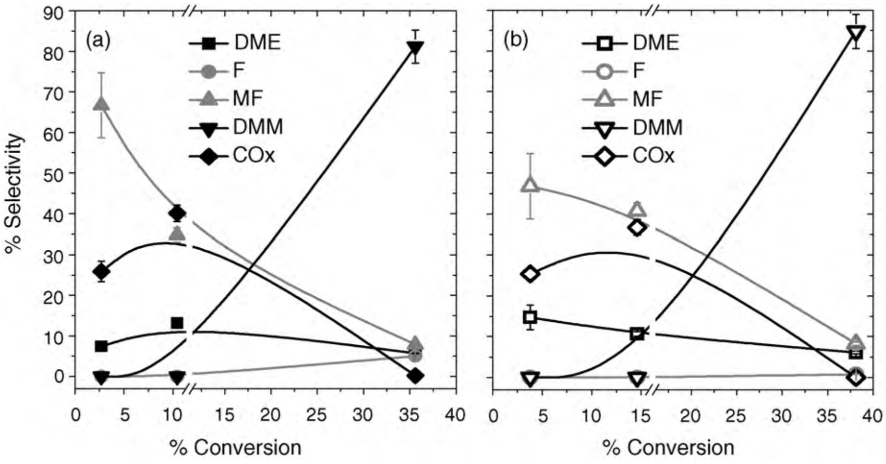


Fig. 2. Compared conversion-selectivity curves for (a) a classical fixed bed reactor and (b) the spectroscopic «operando» chamber used in the present work in the case of ReK catalyst; the break symbolizes the steps without oxygen (left) and with oxygen (right).

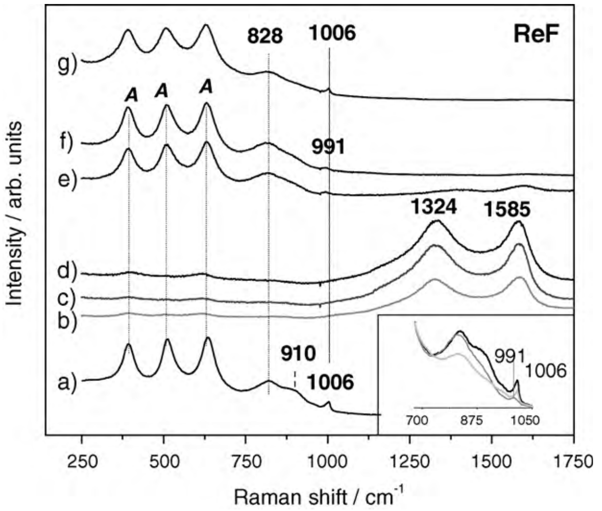


Fig. 3. Evolution of the Raman spectrum of ReF catalyst upon successive treatments (a) + black line in insert: activated catalyst; (b) CH_3OH/He, 423 K; (c) CH_3OH/He, 473 K; (d) CH_3OH/He, 513 K; (e) $CH_3OH/He/O_2$, 513 K (30 min); (f) $CH_3OH/He/O_2$, 513 K (1 h); (g)pure O_2, 513 K (30 min).

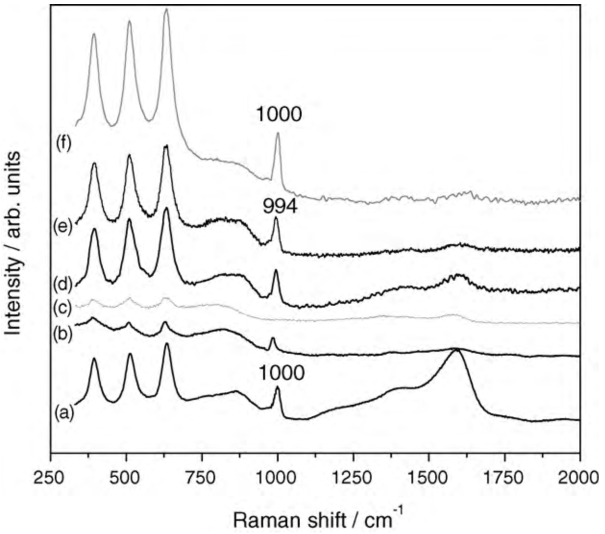


Fig. 4. Evolution treatments (a) Dehydrated catalyst; (b) CH_3OH/He 473 K; (c) CH_3OH/He 513 K; (d) $CH_3OH/He/O_2$ 513 K, 30 min; (e) $CH_3OH/He/O_2$ 513 K, 1 h; (f) O_2, 513 K, 30 min.

The light absorption of such a coke layer could be responsible for the observed loss of Raman signal.

Allowing oxygen in the feed according to a ratio CH_3OH/O_2 of 0.25 (Fig. 3e), led to a rapid, though incomplete recovering of the Raman features of the catalyst. The intensity of the lines at 1300 and 1600 cm^{-1} is lowered and the structural bands of anatase are detected yet again. However, the intensity of the $Re^{VII} = O_t$ – where t stands for terminal – vibration is severely weakened compared to the spectrum of the pretreated catalyst while the broad line around 828 cm^{-1} remains quite intense. The Raman lines at 1324 and 1585 cm^{-1} progressively vanish so that after 30 min O_2 flow introduction, a small contribution is still observed, which is not observed anymore after 1 h (Fig. 3f). This suggests the coke-like layer was re-oxidized in presence of oxygen. The structure of the catalyst is observable again and a weakened $\nu_S(Re = O_t)$ contribution is observed at 991 cm^{-1}. This shift to lower wavenumbers while working is typical [22] and reflects a modification of the Re environment along the reaction After subsequent treatment in pure oxygen flow 30 min at 513 K, the wavenumber of the terminal Re═O stretching vibration is yet again detected at 1006 cm^{-1} and the area of the $\nu(Re{=}O_t)$ line normalized with regards to the area of the 250–750 cm^{-1} range of the spectrum is twice smaller than before reaction. In addition, the broad scattering observed under He after pretreatment around 910 cm^{-1} is not observed anymore under O_2.

3.3.2. ReK catalyst

A similar procedure was applied to the K03-supported material and the structural evolutions of the active phase are presented in Fig. 4. After 1 h exposure to pure CH_3OH/He flow at 473 K, the features of anatase are hardly detected, however the hindrance of the Raman signal is not as severe as what was observed in the case of ReF catalyst (Fig. 4b and c). At 473 K under CH_3OH/He, the Raman line characteristic of the terminal $Re{=}O_t$ vibration is still observed around 995 cm^{-1} after 1 h at 473 K (Fig. 4b) then disappeared after 1 h at 513 K (Fig. 4c). This time, no additional Raman line is detected in the 1100–1800 cm^{-1} range during the CH_3OH/He step. In this case, the loss of Raman signal cannot be assigned to the optical absorbance of a coke-like layer. Conversely, the broad features observed in the pretreated catalyst under helium flow are not longer observed when methanol is allowed in the feed. The introduction of O_2 in the mixture produces the reverse process: the Raman spectrum of anatase is currently recovered and the $\nu(Re{=}O_t)$ vibration is detected at 994 cm^{-1}. A broad line centered around 1590 cm^{-1} is observed during the first 30 min exposure to the $CH_3OH/He/O_2$ feed. Regeneration of the catalyst treatment at 513 K under pure O_2 allowed almost complete recovery of the Raman features of both the support and the active phase. However, the broad components detected around 1595 cm^{-1} in the pretreated catalyst are severely reduced while the $\nu(Re{=}O_t)$ mode is fully recovered. Simultaneously, the contribution of the scattering observed between 750 and 950 cm^{-1} is significantly weakened upon exposure to pure O_2.

4. Discussion

4.1. Structure of dehydrated catalysts

In the previous section, we have pointed out significant little structural differences in the structures of the two catalysts under dehydrated conditions according to the surface coverage of the catalyst. After removal of the anatase contribution by spectral difference, the extra scattering was decomposed into Gauss curves as presented in Fig. 5.

4.2. 950–1010 cm^{-1}

The spectra of dehydrated ReK and ReF catalysts in helium both exhibit a rather sharp line at ca 1000 cm^{-1} assigned to the $\nu(Re{=}O_t)$ mode, in good agreement with previous observations in dehydrated catalysts [6,14–19]. The terminal Re═O stretch vibration in low coverage ReF gives rise to a quite sharp line observed at 1006 cm^{-1} and the presence of a $\nu_{AS}(Re{=}O_t)$ mode observed around 966 cm^{-1} assigned to the anti-symmetric component suggests presence of isolated tri-oxo species in ReF material. This observation is in line with the recent findings of Lee and Wachs according which surface isolated tri-oxo rhenium species are predominant at low rhenium content [16].

In the case of high surface coverage ReK material, the relative broadness of the Raman lines makes it difficult to draw a final structural depiction. Based on the work of Weckhuysen et al. [19], the presence of small Re_xO_y clusters is plausible in this case.

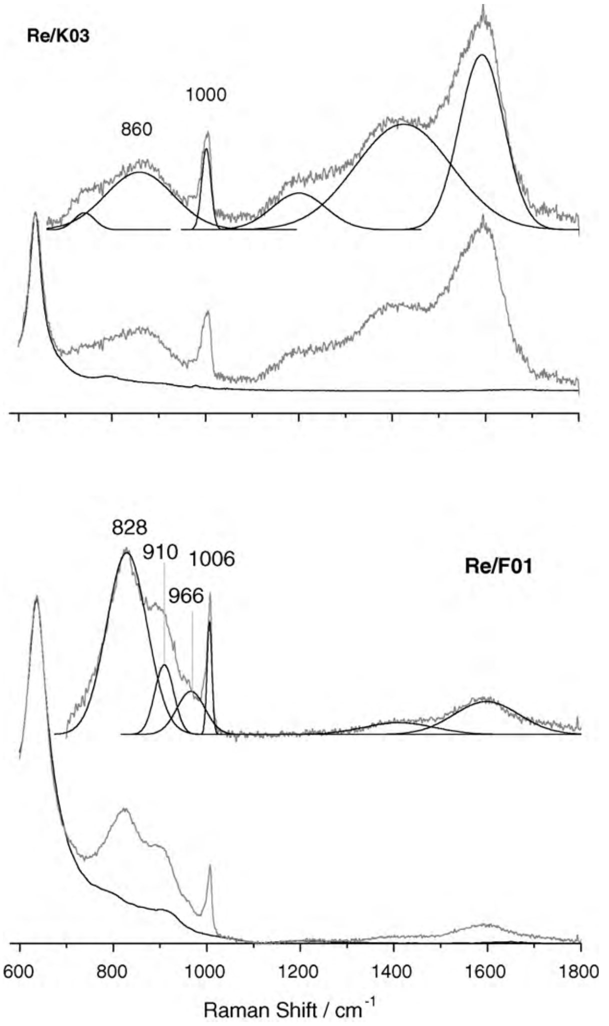


Fig. 5. Structure of ReK (top) and ReF (bottom) catalysts under dehydrated conditions and difference deconvolution.

4.3. 750–950 cm^{-1}

Between 950 and 1050 cm^{-1}, the Raman spectra of ReK and ReF catalysts are essentially related to those described in literature. On the opposite, the broad lines observed in the *in situ* spectra of pretreated catalysts between 800 and 950 cm^{-1} were never reported in literature under similar conditions (before reaction and visible Raman). Based on a thoughtful comparison with the literature, we suggest these modes could be related to the inert atmosphere used for both calcination and dehydration steps. Indeed, most of the spectra reported for supported ReO_x materials usually refer to catalysts which were calcined and/or dehydrated in dry air or oxygen prior to reaction. The new features mentioned above consist in a broad line detected around 860 cm^{-1} in ReK catalyst which can be deconvoluted into two components at 828 and 910 cm^{-1} in the case of ReF material (Fig. 5). These modes do correspond to either ν_{as}(M–O–M′) or ν_s(–O–M–O–) vibrations [22] where M = Re or Ti. These vibrations are sensitive to Raman enhancement by resonance effect as recently proposed by Chua et al. [17]. Having in mind that such modes can also already be observed in partially reduced transition metal oxides under *in situ* conditions using a visible excitation [10], one can propose these new components are probably the result of an enhancement of the Raman scattering cross section in the visible range (532 nm in the present case) when a fraction of the rhenium is reduced to Re^{VI}. Indeed, Re^{VI} oxides exhibit an absorption band around 520 nm [23]. This assumption is also suggested by XPS and diffuse reflectance UV–vis spectra (not reported here) collected on similar samples though prepared using another technique [24].

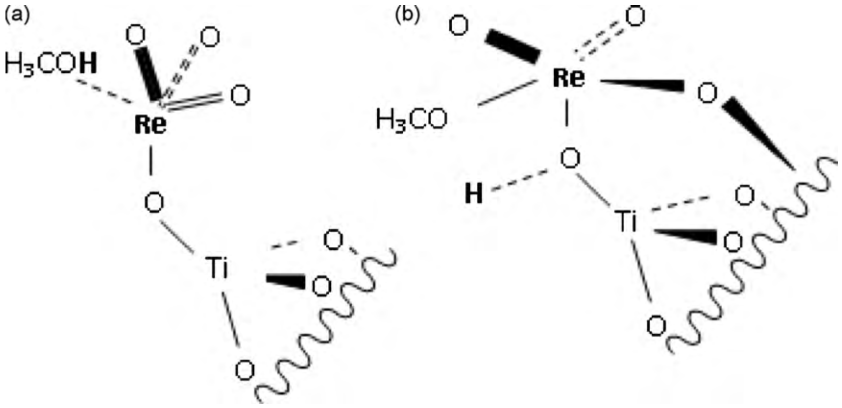
At this point, it is however impossible to conclude whether the lines observed around 750–850 cm^{-1} evolve from stretching vibrations of simply bonded Re–O in (Ti–O–Re), or (Re–O–Re) bridging oxygen in Re_xO_y clusters. Indeed, the Re–O simple bond is very sensitive to the coordination and gives rise to a broad range of lengths and wavenumbers. As an example, the Re–O bond length in ReO_3 where the rhenium stands in octahedral coordination is located around 1.87 Å (wavenumber: 905 cm^{-1}) [24] whereas the Re–O bond distances in Re_2O_7 retaining both tetra- and octahedrally coordinated Re according to [26] are distributed from 1.8 to 2.05 Å (wavenumber: 780–1010 cm^{-1}) [27]. Eventually, the observation of such modes is in good agreement with the Raman signature of mixed valence rhenium oxides reported by Purans et al. [28]. In that study, the authors report on a vibration at 880 cm^{-1} in partially oxidized ReO_3 which they assigned to the Re–O stretch vibration for oxygen ions shared between ReO_4 tetrahedra and ReO_6 octahedra.

4.4. 1300–1700 cm^{-1} range

The changes occurring in the 1300–1700 cm^{-1} wavenumber region of the Raman spectra of ReK are of peculiar interest. They clearly differ from the coke that was observed at the surface of the ReF catalyst under methanol and do not impediment the catalyst activity. Noticeable is the fact these broad lines were present prior to methanol introduction and they are not stable in oxygen at room temperature. The relative intensity and the width of these modes are quite remarkable and their intensity is much dependent on the excitation wavelength. The assignment of these features is not straightforward; however, based on the previous discussion, we propose here that these modes can be more or less directly related to the presence of rhenium oxide small clusters embedding several oxidation states, possibly correlated with structural defects (oxygen vacancies, as an example) in TiO_2 structure. For rhenium oxide compounds, this wavenumber range is rather rare. Indeed, such features are not expected for $Re^{(VII)}O_4$ and no first order Raman is allowed for ReO_3 moieties. However, Ishii and co-workers have observed second-order Raman scattering on bulk ReO_3, which gave rise to numerous lines between 200 and 2000 cm^{-1} [27], which could support the presence of Re^{VI} in the present case. This peculiarity certainly deserves a complete investigation of the electronic structure of supported mixed valence oxides and currently justifies a specific study.

4.5. Operando Raman

In the two studied cases, the modification of the Raman signal is very fast, which illustrates the enhanced ability of the active phase to be reduced by methanol. Such a decrease of the overall Raman signal upon catalyst reduction has already been observed under reducting conditions [11]. Indeed, a significant quenching of Raman signal can be caused by color centers, classically observed in reduced transition metal oxides. Iwasawa and co-worker has proposed the Re^{VI}/Re^{IV} redox couple is responsible of methanol conversion to methylal [1], making sense to the presence of Re^{IV} under these conditions. An experience run by Kuzmin et al. on WO_3–ReO_2 mixtures has shown a dramatic loss of Raman signal upon increasing $Re^{(IV)}O_2$ content [29]. Despite the hindrance of Raman spectrum is no direct evidence, our results are in line with the findings of Iwasawa and rapid reduction of rhenium to Re^{IV} is to be considered upon CH_3OH/He treatment. The main product of ReF reduction in CH_3OH is methyl formate (Table 1), which involves a 4



Scheme 1. Proposition for methanol-to-TiO_2 proton transfer.

electrons oxidation of methanol, attesting effective reduction of the catalyst. In addition, the Raman spectra of ReF catalyst under CH_3OH/He flow rapidly exhibit lines at 1324 and 1585, indicating coke accumulation that poisons the surface and impediment further activity. Concerning the ReK catalyst, two products are detected: carbon dioxide and methylformate. Both require high reduction level of the catalyst as discussed above.

4.6. ReF catalyst

As described in the previous section, the introduction of oxygen in the feed led to an incomplete recovering of the initial structure: a modification of the broad scattering between 750 and 966 cm^{-1} is observed, as the sub-band at 828 cm^{-1} is increased at the expense of the one located around 910 cm^{-1}. The line characteristic of the terminal Re═O stretch vibration is detected yet again and shifted from 1006 cm^{-1} before reaction to 991 cm^{-1}. Based on the previous discussion, this result is a sign of rhenium partial re-oxidation and changes in its coordination sphere. These observations support the proposition according which tetrahedrally coordinated rhenium comes to an octahedral-like coordination during reaction. The adsorption of methanol and, along reaction, the presence of a mobile hydrogen atom located at the vicinity of the Re–O–Ti bond can be responsible of the shift to lower wavenumbers observed while operating as depicted in Scheme 1.

The oxidation of methanol in presence of O_2 was limited to a 2 electrons one since the main products formed were methylal and formaldehyde, and the Raman spectra of the working catalyst reveal re-oxidation of Re to Re^{VII}. The conversion level almost reaches 13% (Table 1), which is 2.8 times smaller than the one reported for the ReK catalyst (Table 1). This difference is clearly due to the reducing step under pure methanol in helium since the removal of the CH_3OH/He step revealed a normal activity. Accordingly, this reducing step is responsible of a poisoning coke layer and prevents rhenium regeneration as an active site. Re-oxidation test of the catalyst under pure oxygen feed at 240 °C flow conditions could not yield a complete re-oxidation of rhenium sites. Indeed, the area of the Re═O vibration normalized with respect to the anatase contribution is divided by 2. Thus, a correlation between the structure of the rhenium phase, the surface coverage, the re-oxidation of rhenium sites and the catalytic activity loss can be done.

4.7. ReK catalyst

The structure of the ReK catalyst under working conditions ($CH_3OH/He/O_2$) after a reducing step in CH_3OH/He exhibits an intermediate state while the catalyst is being partially re-oxidized. After 40 min under reaction conditions, the Raman spectrum of the working catalyst remains stable and exhibits lines characteristic of terminal Re^{VII}═O bonds at 994 cm^{-1}. Concerning the catalytic activity, we have observed an effective methanol conversion to methylal featured by due conversion (35%) and high selectivity (80%) levels. The activity level is better than the one measured without prior CH_3OH/He reducing step, indicating the latter has a beneficial effect on the catalyst activity. This accounts for the enhanced ability of reduced Re sites to be efficiently re-oxidized by oxygen in ReK catalyst. The reversibility of the ReK catalyst is fairly confirmed after re-oxidizing step in pure oxygen, as the initial intensity of the terminal Re═O stretching vibration in ReK catalyst is positively recovered. Considering the surface coverage of ReK catalyst (2.7 at. Re nm^{-2}) and having in mind the previous discussion, we can propose the re-oxidation of Re and the release of products from the catalyst surface could be assisted by an oligomeric structure.

5. Conclusion

The present work has pointed out two slightly distinct structures for Re/TiO_2 materials according to the surface coverage. Observation of modes between 700 and 950 cm^{-1} was related to the use of inert atmosphere for both calcination and pretreatment steps. This procedure could restrain rhenium volatilization as Re_2O_7 during high temperature steps of catalyst preparation and we have proposed that a part of rhenium stands as Re^{VI} in the pretreated catalysts. Both studied materials were shown to be active in direct methanol conversion to methylal and are both rapidly reduced under CH_3OH/He flow. Conversely, this reducing step was found to be partly non-reversible in the case of the low coverage catalysts whereas has exerted a beneficial influence on the activity of the high coverage one. This suggests that an oligomeric structure improves the Re^{IV} re-oxidation while operating. Eventually, the commercial Raman cell reactor developed by Harrick® was shown in the present study to be relevant for steady-state operando Raman studies. Because of its easy adaptation to numerous spectroscopic techniques, the use of this operando reactor appears to be suitable, from the catalytic activity point of view, for non-coupled though complementary techniques.

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References

[1] Y. Yuan, T. Shido, Y. Iwasawa, Chem. Commun. (2000) 1421–1422.
[2] J.M. Tatibouët, Appl. Catal. A: Gen. 148 (1997) 213–252.
[3] J.A. Moulijn, J.C. Mol, J. Mol. Catal. 46 (1988) 1–14.
[4] I.E. Wachs, Catal. Today 27 (1996) 437–455.
[5] I.E. Wachs, J.-M. Jehng, G. Deo, B.M. Weckhuysen, V.V. Guliants, J.B. Benziger, Catal. Today 32 (1996) 47–55.
[6] E.L. Lee, I.E. Wachs, J. Phys. Chem. C 111 (2007) 14410–14425.
[7] A. Brückner, U. Bentrup, M. Fait, B. Kubias, Catal. Today 99 (2005) 123–129.
[8] M.D. Argyle, K. Chen, A.T. Bell, E. Iglesia, J. Catal. 208 (2002) 139–149.
[9] M.V. Martìnez-Huerta, G. Deo, J.L.G. Fierro, M.A. Bañares, J. Phys. Chem. C 112 (30) (2008) 11441–11447.
[10] M. Brandhorst, S. Cristol, M. Capron, C. Dujardin, H. Vezin, G. Le Bourdon, E. Payen, Catal. Today 113 (2006) 34–39.
[11] H. Hu, I.E. Wachs, J. Phys. Chem. B 99 (1995) 10911–10922.
[12] J. Okal, J. Baran, J. Catal. 203 (2001) 466–476.
[13] X. Sécordel, E. Berrier, M. Clément, Application Note # 701204, Harrick Scientific Products, 2008.
[14] M.A. Vuurman, D.J. Stufkens, A. Oskam, I.E. Wachs, J. Mol. Catal. 76 (1992) 263–285.
[15] B. Mitra, X. Gao, I.E. Wachs, A.M. Hirt, G. Deo, Phys. Chem. Chem. Phys. 3 (2001) 1144–1152.
[16] E. Lee, I.E. Wachs, J. Phys. Chem. C 112 (2008) 6487–6498.
[17] Y.T. Chua, P.C. Stair, I.E. Wachs, J. Phys. Chem. B 105 (2001) 8600–8606.
[18] N. Escalona, J. Ojeda, R. Cid, G. Alves, A. López Agudo, J.L.G. Fierro, F.J. Gil Llambías, Appl. Catal. A 234 (2002) 45–54.
[19] B.M. Weckhuysen, J.-M. Jehng, I.E. Wachs, J. Phys. Chem. B 104 (2000) 7382–7387.
[21] J. Liu, Z. Zhao, P. Liang, C. Xu, A. Duan, G. Jiang, W. Lin, I.E. Wachs, Catal. Lett. 120 (2008) 148–153.
[22] M.A. Bañares, in: B.M. Weckhuysen (Ed.), In Situ Spectroscopy of Catalysts, vol. 5, ASP, 2004, p. 59.
[23] R.M. Edreva-Kardjeva, A.A. Andreev, J. Mol. Catal. 46 (1988) 201–207.
[24] X. Sécordel, E. Berrier, S. Cristol, C. Dujardin, M. Capron, M.-A. Languille, A. Brückner, J.-F. Paul, in preparation.
[26] F.D. Hardcastle, I.E. Wachs, J.A. Horsley, G.H. Via, J. Mol. Catal. A: Chem. 46 (1988) 15.
[27] M. Ishii, T. Tanaka, T. Akahane, N. Tsuda, J. Phys. Soc. Jpn. 41 (1976) 908–912.
[28] J. Purans, A. Kuzmin, E. Cazzanelli, G. Mariotto, J. Phys.: Condens. Matter 19 (2007) 226206.
[29] J. Kuzmin, E. Purans, C. Cazzanelli, G. Vinegoni, Mariotto, J. Appl. Phys. 84 (10) (1998) 5515–5524.