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CATALYTIC REACTION MECHANISMS

Influence of Molybdenum on Ceria Activity and CO_2 Selectivity in Propene Total Oxidation[1]

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Abstract—A total oxidation of propene into CO_2 is obtained on pure ceria at 673 K. However, in the presence of molybdenum, propene can be partially oxidized at room temperature. The Electron Paramagnetic Resonance (EPR) indicates changes in the oxidation state of molybdenum occurring upon interaction with propene. It has been found that the concentration of Mo(V) influences the propene conversion. The interaction between propene and molybdenum leads to the formation of surface species that, depending on the strength of their bonding to the surface, can be decomposed to ethene or coke. These results have been confirmed by infrared (FTIR) study. The oxidation reaction of propene is in competition with that of coke or ethene deposit on the catalyst surface, which can explain the decrease of the catalyst activity and selectivity in the presence of high molybdenum loadings.

1. INTRODUCTION

Catalysts based on pure or supported molybdenum MoO_3 are frequently used for a great number of different reactions, especially of the redox type, such as oxidation of hydrocarbons [1]. The condition for these reactions to occur is the activation of oxygen or hydrocarbon molecules [2]. It is known that if the reaction is ignited by the activated oxygen species, the organic molecule usually undergoes degradation, which leads to the total oxidation of hydrocarbons. If the oxidation of hydrocarbons starts with the activation of organic molecules, followed by a nucleophilic addition of the catalyst oxide ions, the formation of oxygenated compounds occurs. The subsequent reoxidation of the catalyst by gas phase oxygen completes the catalytic cycle. Partial oxidation is preferred for systems with a low thermodynamic stability of lattice oxygen, as MoO_3 oxide [3]. For this reason, molybdenum based catalysts are used in partial oxidation of propene [3, 4]. However, the redox couple Ce^{4+}/Ce^{3+} with the ability of ceria to shift between CeO_2 and Ce_2O_3, under oxidizing and reducing conditions, respectively [5] and mainly the ease of formation of labile oxygen vacancies [6, 7], make ceria a promising material for use either as a support or active catalyst in total oxidation reactions of hydrocarbons [8, 9]. A number of studies aimed to elucidate the propene adsorption on pure molybdenum oxide and molybdenum supported catalysts [10–16]. Davydov *et al.* [10, 11], on the ground of their IR and EPR studies, argued that interaction of MoO_3/Al_2O_3, MoO_3/MgO and gallium molybdate with propene led to the formation of σ-allylic complex bonded to the molybdenyl oxygen of MoO_3. Otherwise, Carrazan *et al.* [12] by means of their IR studies, mentioned that the adsorption of propene on molybdenum based catalysts gives rise to olefin/surface cation π-complex species with the formation of unsaturated aldehydes. This indicates the large selectivity of these species towards acrolein formation. It was proposed, that the first step of the reaction consists of the abstraction of α-hydrogen and the formation of π-allylic species attached to the metal centers. The next step is the insertion of lattice oxygen into these species [12–15]. It has been shown that molybdenum oxide contains active centers, which are able to perform the insertion of lattice oxygen into the propene molecules [13–15]. Anderson *et al.* [16] suggested that activation of propene molecules occured at the unsaturated Mo(VI) sites.

In the light of these results, concerning the nature of the interaction between propene and molybdenum, it seems of interest to investigate the catalytic oxidation and the adsorption of propene on molybdenum catalysts supported on ceria. Electron Paramagnetic Resonance (EPR) has been used for this purpose. This technique being very sensitive to the electronic structure and the symmetry of the surroundings of paramagnetic species, it is most suitable to investigate the centers during adsorption accompanied by electron transfer.

2. EXPERIMENTAL

2.1. Solid Synthesis

Cerium hydroxide $Ce(OH)_4$ was prepared by precipitation from cerium (III) nitrate hexahydrated

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[1] This article was submitted by the authors in English.

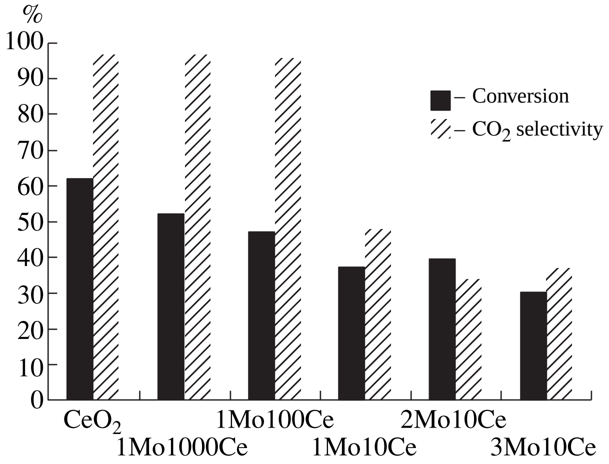

Fig. 1. Propene conversion and CO_2 selectivity of molybdenum-cerium catalysts in the oxidation of propene at 673 K.

$Ce(NO_3) \cdot 6H_2O$ 1 M with an alkali solution NaOH 2 M. The resulting hydroxide $Ce(OH)_4$ was filtered, washed, and dried for about 20 h at 373 K. Ceria is obtained after calcination of this latter at 773 K for 4 h under a flow of air (75 mL min^{-1}) with a temperature rate of 0.5 K min^{-1}. Molybdenum-cerium catalysts 1Mo1000Ce, 1Mo100Ce, 1Mo10Ce, 2Mo10Ce, and 3Mo10Ce have been prepared by impregnation of different solutions of ammonium heptamolybdate $Mo_7O_{24}(NH_4)_6 \cdot 4H_2O$ at $Ce(OH)_4$ support ($S = 138$ m^2 g^{-1}; $V_{porous} = 0.44$ mL g^{-1}). These solids have respectively the following atomic ratios (Mo/Ce = 0.001, 0.01, 0.1, 0.2, 0.3). After drying at 373 K for about 20 h, solids were stabilized by calcination under dried air (4 L h^{-1}) at 773 K for 4 h. The temperature was raised at a rate of 0.5 K min^{-1}.

2.2. Propene Oxidation

The propene (C_3H_6) oxidation was realized in a catalytic microreactor coupled to a Varian 3600 gas chromatograph using a double detection FID and TCD. The catalysts were reactivated at 723 K for 1 h under a flow of dried air 4 L h^{-1} × 100 mg of these catalysts were tested in the presence of a mixture (2.27% propene-97.73% air). The propene conversion (%) at 673 K is given by the following relation: $[(CO + CO_2)_{673\,K}/(CO + CO_2 + 3C_3H_6)_{673\,K}] \times 100$. The selectivity of the catalysts towards the formation of CO_2 was obtained from the ratio $[CO_2/(CO + CO_2)]$.

2.3. EPR Analysis

The EPR measurements were carried out on molybdenum-cerium catalysts after treatment under a flow of propene (2.27 ml min^{-1}) from room temperature to 373 K. Before treatment, catalysts have been activated at 723 K for 1 h. EPR studies were carried out also on 3Mo10Ce catalyst initially evacuated in a vacuum (3×10^{-5} mbar) for 1 h at 573 K and subjected to propene adsorption at different pressures for 30 min in the temperature range of 298–573 K. The temperature was raised with 2 K min^{-1} from 298 K to the desired temperature and was maintained for 30 min. The EPR spectra were recorded at liquid nitrogen temperature 77 K on a EMX BRUKER spectrometer with a cavity operating at a frequency of ~9.5 GHz (X band). The magnetic field was modulated at 100 kHz. The g values were determined from precise frequency and magnetic field values. The relative concentration of paramagnetic sites I_{int} was determined as normalized double integrals of EPR spectra using Bruker's WINEPR program.

2.4. FTIR Analysis

The FTIR studies, were carried out using Perkin-Elmer FTIR spectrum 2000. 20 mg of each catalyst was pressed into self-supported wafers under a pressure of 8000 kg cm^{-2}, and then placed with a sample holder inside a Pyrex cell with NaCl windows, which allowed pre-treatment under vacuum, introduction of reactants and recording of the spectra. After pre-treatment under vacuum (3×10^{-5} mbar) of 3 Mo10Ce catalyst at 573 K for 1 h, 500 mbar of propene gas was introduced into the cell which was cooled in nitrogen liquid for 30 min. The spectra were recorded at room temperature 10 min after the cell was taken out of the nitrogen liquid.

3. RESULTS AND DISCUSSIONS

3.1. Catalytic Oxidation of Propene

Figure 1 shows the catalytic activity and the selectivity in CO_2 of molybdenum-cerium catalysts towards the oxidation reaction of propene at 673 K (maximum value reached in the exhaust steam). The propene conversion ratio is about 62% for pure ceria catalyst, with a high selectivity in CO_2 ($CO_2/(CO + CO_2) = 97\%$). Similar activity and selectivity in CO_2 were obtained when the reaction is performed in the presence of catalysts with small amounts of molybdenum (1Mo1000Ce, 1Mo100Ce). Whereas, for catalysts with higher molybdenum loadings, a lower activity is obtained with the formation of a large quantity of CO during the propene oxidation. Only 30% of propene is decomposed in the presence of 3Mo10Ce with the formation of 63% of CO ($CO/(CO + CO_2) = 63\%$). Thus, the presence of molybdenum decreases the catalytic activity and lowers its selectivity in CO_2 with respect to the propene oxidation reaction.

It is well-known that during oxidation reaction of hydrocarbons, oxide catalysts are subjected to a reduction after oxidation of hydrocarbon molecules. The more the catalyst is reduced, the more the hydrocarbon molecules are oxidized. Otherwise, it is well-known that ceria is easily reduced at elevated temperatures in non-stoichiometric oxides CeO_{2-x} ($0 < x < 0.5$) rich in

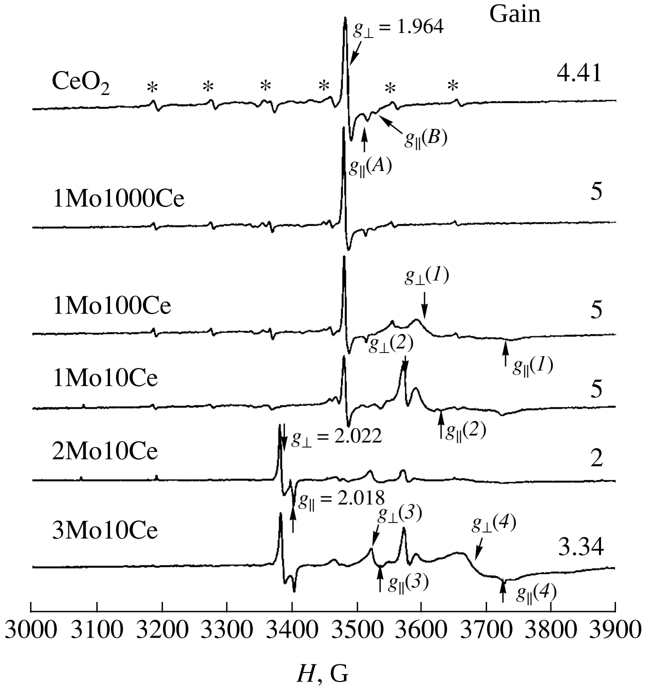

Fig. 2. EPR spectra, recorded at 77 K, of molybdenum–cerium catalysts treated under vacuum at 573 K for 1 h.

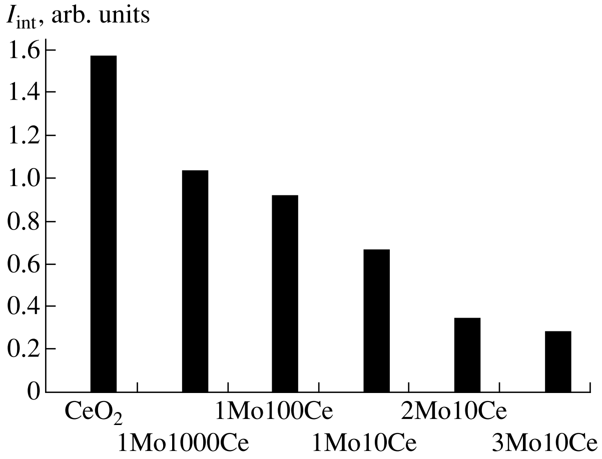

Fig. 3. Variation of superposed (Ce^{3+}) signal intensity with the increase of molybdenum loading.

oxygen vacancies [5–7]. The latter are responsible for oxygen mobility on ceria surface, which is favorable for the oxidation reactions [9]. It might be possible then, that the reduction of ceria is more difficult in the presence of molybdenum, which can decrease the number of oxygen vacancies on the surface and consequently its activity with respect to propene oxidation. Otherwise, the catalytic activity is related to the affinity of the oxide towards the reactant [17]. The nature of the intermediate products reversibly or irreversibly adsorbed on the catalysts surface, plays a crucial role in the behavior and the performance of the catalysts during the oxidation reaction [17]. Thus, the oxidation ability of the samples, has been checked by the redox behavior of the catalysts under reduced atmospheres and through the study of propene adsorption on the surface. The Electron Paramagnetic Resonance has been used for these studies for further understanding of the catalytic results.

3.2. EPR Study of Molybdenum-Cerium Catalysts

The treatment under vacuum of the catalyst at high temperatures can induce a partial reduction of the solid comparable to that occurred during the combustion cycle. The EPR technique has been used to study the catalysts after thermal treatment under vacuum and after interaction with propene at room temperature.

3.2.1. EPR study after thermal treatment under vacuum of the catalysts. Figure 2 shows the EPR spectra recorded at 77 K of molybdenum-cerium catalysts treated under vacuum (3×10^{-5} mbar) at 573 K for 1 h. The EPR spectra recorded at 77 K for pure ceria, 1Mo1000Ce and 1Mo100Ce catalysts, present a superposition of two signals (A) and (B) having the same axial symmetry. These signals can be attributed to the presence of two different sites of Ce^{3+} in the solid [electron configuration f^1, $g_e > g_\perp > g_\parallel$], or more exactly to the presence of electrons trapped in the free orbital (4*f*) of Ce^{4+} ions [5–7]. Moreover, according to the literature [5–7], signal (A) characterized by $g_\perp = 1.964$; $g_\parallel = 1.939$ and $g_{iso} = 1.955$ is due to Ce^{3+} ions in the bulk of the solid, stabilized by some lattice defects and oxygen vacancies favorable for oxidation reactions [18]. Whereas, signal (B) ($g_\perp = 1.964$; $g_\parallel = 1.946$; $g_{iso} = 1.958$) corresponds to Ce^{3+} ions with easily removable ligands. As shown in Fig. 3, the intensity of these signals, calculated by double integration (DI) of the EPR signals, decreases progressively with the increase of molybdenum loading in the solid. It can be deduced then, that the presence of Ce^{4+}/Ce^{3+} redox couple which is favorable for the oxidation reaction also decreases in the presence of molybdenum. Thus, the presence of molybdenum implies a decrease of the number of anionic vacancies present on the surface. This can be related to the low activity and selectivity in CO_2 of the catalysts containing higher quantity of molybdenum with respect to propene oxidation reaction. Otherwise an axial signal characterized by $g_{\perp(1)} = 1.899$; $g_{\parallel(1)} = 1.839$ and $g_{iso} = 1.879$ is observed for 1Mo100Ce catalyst (Fig. 2). In addition to this signal, another signal with axial symmetry ($g_{\perp(2)} = 1.915$; $g_{\parallel(2)} = 1.889$; $g_{iso} = 1.906$) appeared in the EPR spectra of 1Mo10Ce, 2Mo10Ce, and 3Mo10Ce catalysts (Fig. 2). These signals are characteristic of the d_1 configuration and can be attributed to the presence of two different sites of molybdenum (V) [Mo^{5+}(*1*) and Mo^{5+}(*2*)] stabilized with oxygen ligands ($g_\perp > g_\parallel$) [19]. In fact, similar spec-

EPR signals recorded at 77 K for molybdenum-cerium catalysts after treatment under vacuum at 573 K

Signal	$g_\perp$	$g_\parallel$	g_{iso}	α
Ce^{3+}(*A*)	1.964	1.939	1.955	–
Ce^{3+}(*B*)	1.964	1.946	1.957	–
Mo^{5+}(*1*)	1.899	1.839	1.879	1.58
Mo^{5+}(*2*)	1.915	1.889	1.906	1.29
Mo^{5+}(*3*)	1.943	1.929	1.938	1.23
Mo^{5+}(*4*)	1.862	1.841	1.855	1.15
O^- species	2.022	2.018	2.020	–

tra have been observed for these species (Mo^{5+}) in different matrix [20–22]. According to the literature, the Mo^{5+}(*1*) ions can be attributed to the reduction of Mo^{6+} species dispersed on ceria surface. However, Mo^{5+}(*2*) ions observed in the presence of high molybdenum loadings are due to the reduction of octahedral Mo^{6+} species polymerized on ceria. Moreover, the EPR spectra of 1Mo10Ce, 2Mo10Ce, and 3Mo10Ce recorded at room temperature have shown the presence of only the signal characteristic of Mo^{5+}(*2*) ions ($g_{\perp(2)} = 1.915$; $g_{\parallel(2)} = 1.889$ and $g_{iso} = 1.906$). Thus, these ions Mo^{5+}(*2*) are more probably located in octahedral sites with a weak tetrahedral distortion. In fact, Shelimou *et al.* [21], have attributed the absence of this EPR signal at room temperature to Mo^{5+} ions with tetrahedral symmetry which is due to the fact that the spin-lattice relaxation is too short at room temperature. However, Martini [22] confirms that Mo^{5+} ions in tetrahedral sites cannot be detected by EPR even at 77 K. In addition, Che *et al.* [20] have shown that strong distortions of Mo^{5+} ions can be observed in EPR spectra. Thus, it is very probable that Mo^{5+}(*1*) present a strong tetrahedral distortion. Whereas Mo^{5+}(*2*) ions are located in weakly distorted octahedral sites. Nevertheless, for d^1 ions located in octahedral sites with tetragonal deformation, the value of the g tensor corresponds to the α ratio [$\alpha = (g_e - g_\parallel)/(g_e - g_\perp) = 4\,\delta/\Delta$]. This α ratio characterizes the amplitude of the tetragonal distortion (δ) relatively to that of the octahedral axial field Oh(Δ) [23]. α is respectively equal to 1.58 and 1.29 for Mo^{5+}(*1*) and Mo^{5+}(*2*) ions. This indicates also that Mo^{5+}(*1*) ions are strongly distorted, whereas, Mo^{5+}(*2*) ions are octahedral with a weak tetrahedral distortion. At least two other axial signals characterized respectively with $g_{\perp(3)} = 1.943$; $g_{\parallel(3)} = 1.929$ and $g_{iso} = 1.938$ and $g_{\perp(4)} = 1.862$; $g_{\parallel(4)} = 1.841$ and $g_{iso} = 1.855$ can be identified for the catalysts 2Mo10Ce and 3Mo10Ce. Similar spectra have been observed in the literature and have been attributed to hexacoordinated Mo^{5+} ions typical of MoO_6 octahedral in MoO_3 lattice [24, 25]. Additionally, the value of a ratio relative to these species is equal to 1.23 [Mo^{5+}(*2*)] and 1.15 [Mo^{5+}(*4*)]. This further indicates the location of these species in octahedral sites with a very weak tetragonal distortion. The presence of reduced Mo^{5+} ions confirms that during treatment under vacuum, the catalysts can be partially reduced. It can be deduced that, the Mo^{6+}/Mo^{5+} redox couple is less active with respect to propene oxidation than the Ce^{4+}/Ce^{3+} redox couple, which can affect the catalytic activity of the oxide. In addition to molybdenum V signals, an axial signal with a very high intensity characterized by $g_\perp = 2.022$; $g_\parallel = 2.010$ and $g_{iso} = 2.018$ is observed for 2Mo10Ce and 3Mo10Ce treated under vacuum at 573 K (Fig. 2). This signal is characteristic of paramagnetic oxygen species in interaction with the solid. A similar signal has been observed in the literature and attributed to O^- species adsorbed on magnesium oxide partially reduced [26, 27]. Such O^- species are in interaction with molybdenum oxide, since this signal is not observed for pure ceria. Furthermore, this signal characteristic of O^- species was not observed at room temperature which can be related to spin-lattice relaxation time that is too short at room temperature. Thus, it can be deduced that a modification of oxygen lattice arrangement can occur in the presence of molybdenum. This modification can play an important role in the variation of the selectivity and the activity of catalytic system containing a high amount of molybdenum, during propene oxidation. The different signals observed after thermal treatment of molybdenum-cerium catalysts are reported in table.

3.2.2. EPR study of the catalysts after interaction with propene. The molybdenum-cerium catalysts have been studied in EPR after treatment under a flow of propene (2.27 ml min^{-1}) from room temperature to 373 K. The rate of temperature is 5 K min^{-1}. As for propene catalytic test, the catalysts were preliminarily reactivated for 1 h at 773 K under a flow of dried air (30 ml min^{-1}). No change has been observed for pure ceria, 1Mo1000Ce, 1Mo100Ce, and 1Mo10Ce catalysts after treatment under propene flow. However, for 2Mo10Ce and particularly 3Mo10Ce, a new signal noted (S) with isotropic symmetry ($g_{iso} = 2.0034$) and a very weak intensity has been detected at room temperature. This signal is associated with reduced molybdenum Mo^{5+} signals. The presence of this signal is due to propene interaction with molybdenum oxide since it was not observed for pure ceria. In order to confirm that, different pressures of propene have been introduced on 3Mo10Ce for 30 min at room temperature after being treated under vacuum at 573 K for 1 h. Vacuum treatment of the catalyst can induce more active vacancies on the solid surface favorable for more interaction of propene with the solid. The resulting EPR spectra recorded at room temperature (Fig. 4a) and 77 K

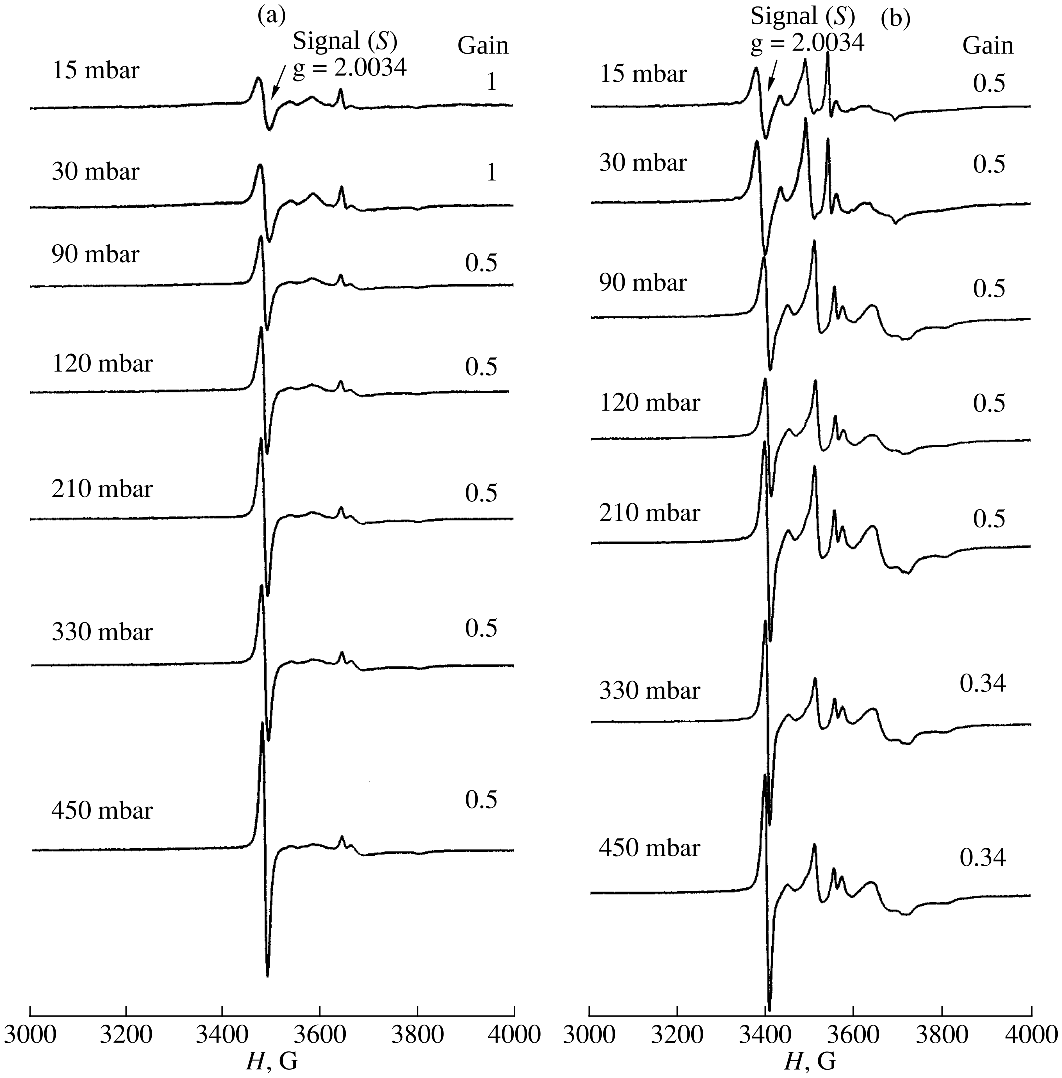

Fig. 4. EPR spectra of 3Mo10Ce after adsorption of different pressures of propene at room temperature, (a) recorded at 298 K and (b) at 77 K.

(Fig. 4b) for 3Mo10Ce catalyst, show the presence of this signal with a very high intensity for a low propene pressure (15 mbar). It is important to notice that the very low intensity observed for signal (*S*) after treatment of 3Mo10Ce under a flow of propene is due to the fact that the catalyst was activated under air before treatment under propene and the surface is not completely free of water molecules and other residual species that can delay the interaction of propene with molybdenum oxide. In addition, an increase of signal (*S*) intensity has been observed for 3Mo10Ce with the increase of propene pressure (Fig. 5). This variation indicates that the signal (*S*) is produced after interaction of propene with molybdenum oxide. Furthermore, the isotropic symmetry and the *g* value permit one to attribute this signal (*S*) either to trapped electron in the lattice MoO_3 or to organic unsatured hydrocarbon species or coke. In order to explain the nature of the species related to this signal, experiments on the reduction of pure molybdenum oxide (MoO_3) with hydrogen or propene were performed. This signal (*S*) appeared only during interaction of MoO_3 with propene and disappeared after prolonged oxidation at a higher temperature; it was not observed on interaction with hydrogen at the same conditions. Such behavior indicates that the signal (*S*) is more probably due to paramagnetic hydrocarbon species attached to molybdenum centers of the catalysts surface. In fact, Carrazan *et al.* [12] have evidenced a partial oxidation of propene to acrolein after its adsorption on the surface of molybdenum supported catalysts at room temperature. Moreover, a lot of studies were aimed at elucidating the mechanism of the redox processes occurring during selective oxidation of propene to acrolein using molybdenum based catalysts [1–4, 10–16]. However, no acrolein was found in the products for our catalytic test. The single electron is

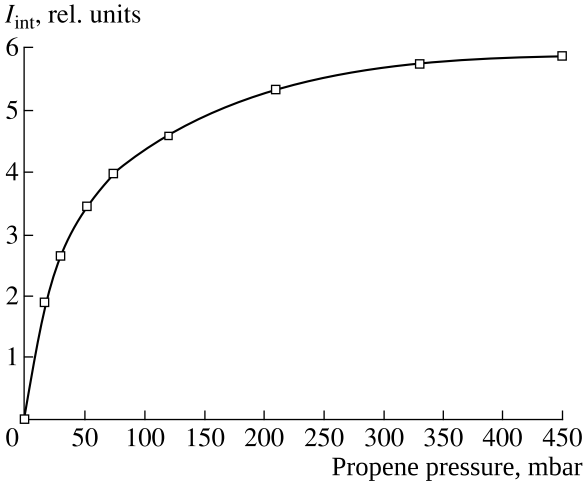

Fig. 5. Variation of signal (S) intensity for 3Mo10Ce catalyst with the increase of propene pressure.

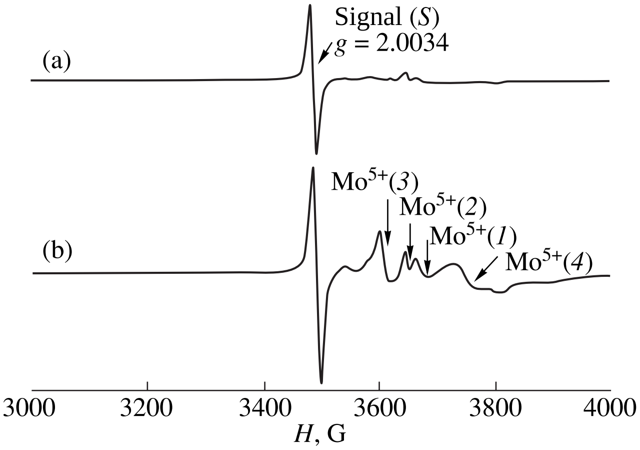

Fig. 6. EPR spectra of 3Mol0Ce catalyst treated under 450 mbar of propene recorded at (a) 298 and (b) 77 K. DI/N: double integral/normalized.

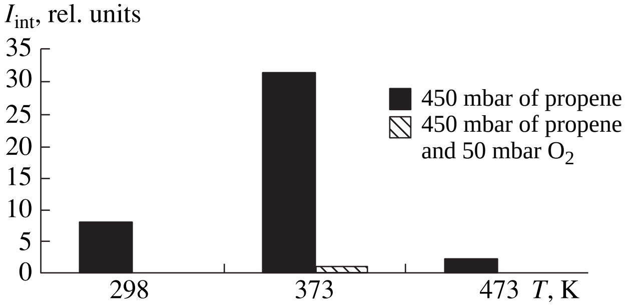

Fig. 7. Variation of signal (*S*) intensity with the increase of the temperature for the catalyst 3Mo10Ce.

polarized and in interaction with Mo^{6+} centers, since no hyperfine structure was observed for the EPR signal (*S*) recorded at room temperature. Moreover, when the spectrum of 3Mo10Ce treated under 450 mbar of propene is recorded at 77 K, the intensity of signal (*S*) increases slightly and does not follow the Curie law, while the intensity of the reduced molybdenum signal Mo^{5+} increases considerably, particularly that of $Mo^{5+}(3)$ species (Fig. 6). Such behavior indicates, that at a low temperature, the single electron is more polarized and shifted towards molybdenum (VI) centers, which are further reduced to Mo^{5+} ions. Based on these results, it can be deduced then, mat after adsorption, propene molecules are activated on the surface of molybdenum oxides leading to the formation of surface species which, depending on the strength of its bonding to the surface, may be decomposed to ethene or coke. Nevertheless, it seems important to notice that the axial signal ($g_\perp = 2.022$, $g_\| = 2.010$, $g_{iso} = 2.018$) characteristic of O^- oxygen species, which has been observed after treatment of 3Mo10Ce at 573 K (Fig. 2), disappears completely in the presence of propene (Fig. 6). This can be related to the modification of lattice and surface oxygen arrangement of 3Mo10Ce. Moreover, the EPR study of 3Mo10Ce catalyst after interaction with propene at higher temperatures, have shown a modification of signal (*S*) intensity with temperature. A higher intensity of this signal is observed at 373 K (Fig. 7). The more the temperature increases, the easier the activation of propene is. When the temperature reaches 473 K, the intensity of this signal decreases considerably, which implies a further oxidation of propene. Otherwise, the intensity of the signal (*S*) decreases in the presence of oxygen (Fig. 7). In fact, this signal was not observed at room temperature when the 3Mo10Ce catalyst is treated under a mixture of propene (450 mbar) and oxygen (50 mbar). Thus, the presence of oxygen enhances the decomposition of propene to oxygenated species at room temperature. Finally, this signal is due to propene interaction with molybdenum oxide and could be attributed to the presence of organic unsatured hydrocarbon species or coke.

In order to confirm these results, the structures formed during adsorption of propene on 3Mo10Ce catalyst were studied by means of IR spectroscopy.

3.3. IR Study of 3Mo10Ce Catalyst after Interaction with Propene

The IR spectra, recorded at room temperature, of 3Mo10Ce catalyst treated under vacuum at 573 K after adsorption and desorption of propene (500 mbar at 77 K) are presented in Fig. 8. Propene adsorption on 3Mo10Ce catalyst produces two series of bands in the 3100 to 2700 cm^{-1} and in the 1800–1200 cm^{-1} regions (Fig. 8, spectrum *2*). The presence of IR band at 3092 cm^{-1} indicates that a certain portion of propene molecules are adsorbed on the surface without breaking the double bond. This band is characteristic of $\nu_{=CH}$ stretching vibration of physisorbed propene [10, 12]. The bands observed at 2972, 2932, and 2896 cm^{-1} can be assigned

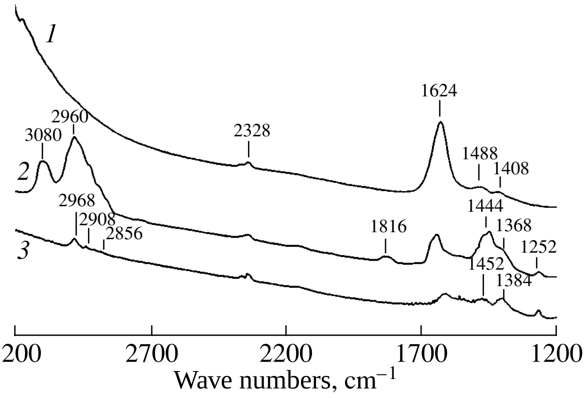

Fig. 8. IR spectra, recorded at room temperature, of 3Mo10Ce catalyst (*1*) treated under vacuum for 1 h at 573 K (*2*) after adsorption of propene (500 mbar at 77 K) and (*3*) after propene desorption at room temperature.

to stretching and deformation vibration of C–H bond in CH, CH_2, or CH_3 groups. In fact, it has been shown by spectral analysis of individual propene complexes [28] that it is difficult to elucidate differences between various complexes via $\nu_{=CH}$ stretching and deformation vibrations because of the overlap of the frequency ranges. According to the literature [10, 28], the band observed at about 1625 cm^{-1} should be attributed to stretching vibration of C=C bond. However, the band observed at about 1624 cm^{-1} for the untreated sample with propene (Fig. 8, spectrum *1*) should be due to physisorbed H_2O and the treatment with propene should remove with water. The frequencies at about 1400 cm^{-1} are characteristic of C–H deformation vibrations. The other bands observed at 1828 and 1264 cm^{-1} are due to the vibrations of C–O bond in CO_2 and CO_3 carbonate species. In addition, after propene desorption the bands due to propene chemisorbed on the surface remain stable, whereas that of physisorbed molecules of propene disappears (3092 cm^{-1}) (Fig. 8, spectrum *3*). Thus, the IR results seem to evidence the formation of organic unsatured hydrocarbon species or coke during propene chemisorption with 3Mo10Ce catalyst.

According to these observations and taking into account that the catalytic oxidation of propene was realized in the presence of oxygen (2.27% of propene in air) at 673 K, it can be deduced then, that at the beginning of the catalytic test and at low temperatures (<373 K), a partial oxidation of propene could occurred on molybdenum oxide MoO_3 for 1Mo10Ce, 2Mo10Ce, and 3Mo10Ce catalysts. This reaction leads to the formation of surface species that, depending on the strength of its bonding to the surface, can be decomposed to ethene or coke [12]. This process is easier in the presence of oxygen and at higher temperatures. It can induce a modification of catalyst surface structure and a modification of oxygen arrangement in the solid that can affect the activity and selectivity of the catalytic system in the presence of molybdenum. Moreover, the oxidation reaction of propene is in competition with that of coke or ethene deposit on the catalyst surface, which can explain the decrease of the catalyst activity and selectivity in the presence of high molybdenum loadings.

4. CONCLUSION

This work has shown the relation between the catalytic properties of the catalysts with respect to the propene oxidation reaction both with its redox behavior and its interaction with propene molecules. The decrease of the catalyst activity in the presence of molybdenum can be explained by the decrease of the number of anionic vacancies on the surface, which can be due to the reduction of ceria that might be difficult in the presence of molybdenum. Otherwise, the strong interaction of propene with molybdenum and its partial oxidation at room temperature can affect the catalysts activity and selectivity during the oxidation of propene. Thus, a competition of partial oxidation of propene on MoO_3 can be produced with a complete oxidation of propene on ceria, during the catalytic oxidation of propene in the presence of catalysts with high molybdenum loadings.

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