Catalytically active species in new metathesis systems [W^{n+}(Mo^{n+})–ionic liquid–olefin]: A quantitative ESR study

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Abstract

For the first time, a quantitative approach is successfully used in the ESR study of new catalysts for olefin metathesis prepared by dissolution of WCl_6 and $MoCl_5$ in ionic liquids ($hmimBF_4$, $hpyrBF_4$, etc.). ESR monitoring of frozen probes taken upon interaction between the phases of an ionic liquid and hex-1-ene permits one to elucidate the key role of isolated paramagnetic complexes of W^{5+} and Mo^{5+} ions in catalysis. The use of $MoCl_5$ as a starting reagent opens a way for a quantitative observation of paramagnetic active species in two liquid phases. It is shown that the reaction in the biphasic system proceeds as a heterogeneous catalytic process: virtually all the isolated W^{5+} or Mo^{5+} species are located in the ionic liquid. The kinetics of formation/accumulation of the isolated paramagnetic W^{5+} species at the initial slow step of W^{6+} reduction by an olefin agrees closely with the kinetics of metathesis leading to the formation of a C_8 product. No induction period is observed in the case of Mo^{5+} ions. The number of the ESR-visible isolated paramagnetic Mo^{5+} complexes reaches ∼90% of the total number of molybdenum ions in the sample. Thus, the Mo(V) state of the active sites localized in ionic liquids is responsible for the further catalytic process. The same seems to be true for the W(V) species accumulated in the ionic liquid at the end of the first step of the reaction.
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1. Introduction

Ionic liquids attract growing attention as new media for diverse chemical reactions including catalytic processes. Surprisingly little is known, however, about the nature of catalytically active sites and active species formed in these specific "solvents". Spectral methods are not quite informative in the study of these moisture-sensitive and deeply colored liquids. Recently, it was demonstrated that WCl_6 being dissolved in ionic liquids forms an active species catalyzing metathesis of olefins at 20° C [1]. The aim of the present work is to monitor the formation of W(V) paramagnetic species in this process using ESR spectroscopy and to compare the behavior of the two catalytic systems: the first one prepared from WCl_6 and the second one originating from $MoCl_5$.

2. Experimental

2.1. Materials

As received WCl_6 and $MoCl_5$ (chemically pure grade) were used without further purification. Ionic liquids kindly donated by Merck KgaA as synthetic grade reagents were: tetrafluoroborates of 1-ethyl-3-methylimidazolium ($emimBF_4$); 1-hexyl-3-methylimidazolium ($hmimBF_4$); *N*-hexylpyridinium ($hpyrBF_4$); 1-butyl-3-methylimidazolium ($bmimBF_4$); trihexyl(tetradecyl)phosphonium; as well as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (emimOTf). Hex-1-ene (>99% purity) was purchased from Aldrich. High purity N_2 gas was used to provide the protective atmosphere upon catalyst preparation and study.

2.2. Catalyst preparation

The calculated amount of W(Mo) chloride was mixed with the ionic liquid (molar ratio ranging from 1/10 to 1/100) in

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a cylindrical 15 cm^3 vessel at 20 °C for 30 min under the N$_2$ flow. The probe of the solution/suspension formed was taken for an ESR testing.

2.3. Catalytic testing

Catalysts were tested at 20 °C in hex-1-ene metathesis [1]. A standard amount of hex-1-ene (0.3 cm^3; molar ratio olefin/catalyst 1/0.88) was added under N$_2$ to the catalyst in the reactor, the vessel was sealed and the reaction mixture was vigorously stirred (500–600 rpm) at 20 °C. After the specified time (5–120 min), the probes of the two layers (i.e., olefin and ionic liquid) were taken for analysis and ESR measurements.

The metathesis products were analyzed by GLC on a packed column (3 m × 3 mm) with SE-30 on Chromosorb; an SE-30 capillary column (30 m) and a Carbowax 20M capillary column (40 m) using the method of internal standards.

2.4. ESR measurements

ESR spectra were taken in the X-band ($\lambda \cong 3.2$ cm) at −196 °C using a reflecting-type ESR spectrometer equipped with a 4104OR cavity and a quartz Dewar vessel. The ESR signals were registered in the absence of saturation in the field range of 2500–4000 G. The Excel program was used for spectra processing (baseline correction and double integration). DPPH and a frozen solution of MoCl$_5$ in CH$_3$OH were used as standards for g-factor calculation and quantitative Mo^{5+}-ESR analysis.

Samples of catalytic and olefin layers from the reactor were placed in identical quartz ampoules (3.5 mm diameter) to exceed the volume of the sample in the resonator (>30 mm height), purged with nitrogen, closed and immediately cooled to −196 °C by placing the ampoule in liquid nitrogen. ESR spectra were registered at −196 °C and normalized for the differences in the W(Mo) chloride concentration. Then, the closed ampoules were maintained at room temperature for several hours and ESR measurements at −196 °C were repeated. The solution of 1 mol.% MoCl$_5$ in absolute methanol was prepared as a standard for the comparative calculation of the "ESR-visible" fraction of Mo^{5+} and W^{5+} in our samples. Double integration of the ESR spectrum of this standard provided the absolute value for comparison with double integrals of signals under study. The shape of ESR lines was not playing a role and spectra simulation was not required. For the sake of accuracy, series of samples were measured consecutively, with ampoules placed in the same position inside the ESR resonator.

3. Results and discussion

In our preliminary ESR study, it was found that the samples of the W-containing ionic liquids taken from the reac-
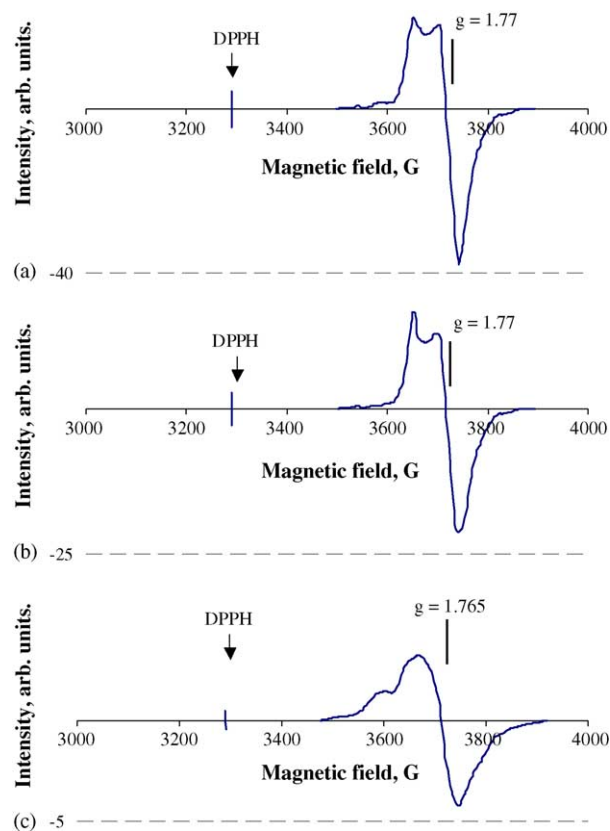

Fig. 1. ESR spectra recorded at −196 °C of the probes of the ionic liquid layers taken after 2 h of hex-1-ene metathesis at 20 °C: (a) 10% WCl$_6$ in hmimBF$_4$; (b) 10% WCl$_6$ in hpyrBF$_4$ and (c) 5% WCl$_6$ in emimBF$_4$.

tor after 2–2.5 h of metathesis give strong ESR signals at $g \cong 1.77$ (Fig. 1). These signals point unambiguously to the formation and accumulation of paramagnetic isolated W(V) species with unpaired electron located on the tungsten ion. Thus, a quite complex process of reorganization of the starting system, with W^{6+} to W^{5+} reduction, accompanies the interaction between the components in the original mixture. This behavior distinguishes the W-containing catalysts from another, better known metathesis system (Ru-complexes in neutral ionic liquids) [2–8]. From the recent study of Ru-containing samples, one can conclude that catalytically active Ru-complexes are created before the reaction and ionic liquid as the reaction medium does not differ essentially from traditional solvents [3–8].

In addition, olefins are poorly soluble in ionic liquids and the reaction takes place in the biphasic emulsion. In our search, in order to simplify the problem, we decided to start with another catalyst, namely MoCl$_5$. On one hand, molybdenum is known as a catalytically active substance for metathesis [9–11]. On the other hand, all the ions in the initial MoCl$_5$, being a pretty chemically stable compound, are in the paramagnetic Mo(V) state. Thus, a quantitative ESR monitoring of transformations in this simplified system becomes possible.
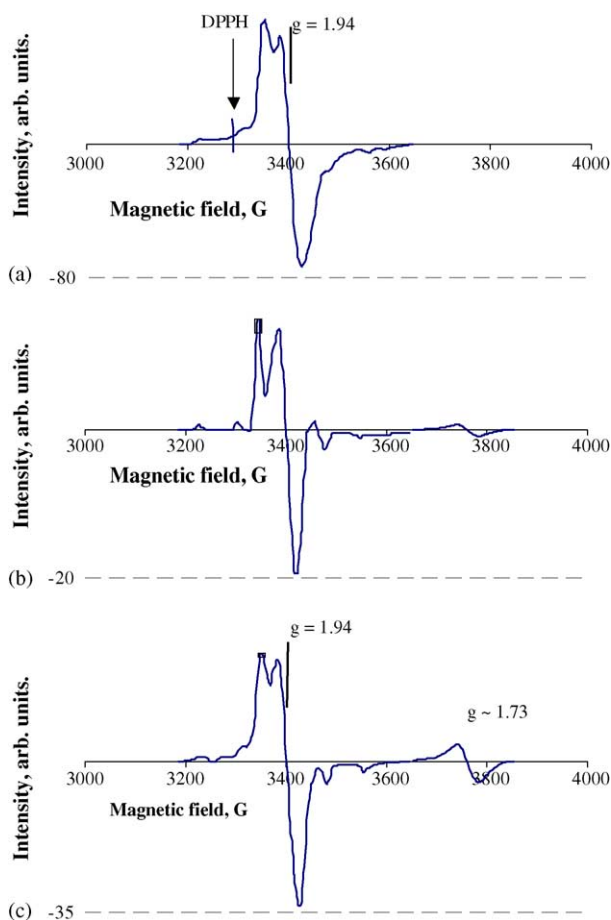
Fig. 2. ESR spectra recorded at –196 °C of the solutions of MoCl$_5$: (a) 1 mol.% MoCl$_5$ in absolute CH$_3$OH; (b) 1 mol.% MoCl$_5$ in hmimBF$_4$ and (c) 10 mol.% MoCl$_5$ in hmimBF$_4$.

3.1. Study of the [(Mo^{5+})–ionic liquid–hex-1-ene] system

3.1.1. Mo^{5+} as an absolute standard for quantitative ESR measurement

Pure bulk MoCl$_5$, in spite of the paramagnetic state of all Mo ions, shows no ESR signal. It is caused by a strong magnetic interaction between ions in the regular crystalline phase of the solid. Only dilution of Mo^{5+} ions by the inert matrix weakens this interaction and results in the appearance of Mo^{5+}-ESR signals from magnetically "isolated" ions and/or small irregular clusters with weakened interaction between Mo^{5+} ions. As to the linear dimension, an ∼1 nm distance provides sufficient magnetic isolation of the ions. Methanol, being a good solvent for MoCl$_5$, can be used for preparation of the Mo^{5+}-ESR standard.

Fig. 2a shows the ESR spectrum taken from the frozen diluted solution of Mo^{5+} in absolute methanol (1 Mo^{5+} ion per 100 molecules of CH$_3$OH). This narrow, asymmetric ESR signal with $g = 1.944$ is typical of isolated Mo^{5+} sites with the symmetry approximating the octahedral one. Similar ESR signals with $g = 1.95–1.945$ differing in the line shape

were observed earlier for isolated Mo^{5+} ions stabilized by matrices of different zeolites [12,13]. We assume that all the molybdenum ions in a diluted methanol solution of MoCl$_5$ are "ESR-visible" and contribute to the signal (Fig. 2a). Double integration of the spectrum gives us the absolute value for the sample containing the known amount of isolated Mo^{5+} ions. Thus, a direct comparison of double integrals of other ESR spectra with this standard permits a selective quantitation of Mo^{5+} active species in the ionic liquid and olefin layers of the reaction mixture.

3.1.2. Mo^{5+} dissolution in the ionic liquid

Fig. 2b and c shows ESR spectra taken from two frozen solutions [MoCl$_5$ + hmimBF$_4$] differing in the molybdenum concentration.

The spectrum of the diluted sample [1 mol.% MoCl$_5$ + hmimBF$_4$] (Fig. 2b) has a very well resolved fine structure, with relatively weak components originating from an additional splitting on Mo isotopes. Comparison of the integral intensity of this signal with the intensity of the standard (Fig. 2a) permits us to evaluate the fraction of "ESR-visible" Mo^{5+} ions in the sample as ∼80%. In addition to the strong specific signal from isolated Mo^{5+} ions ($g = 1.94$), a very weak unstructured line is observed in the high-field region ($g \sim 1.73$; $\Delta H \cong 75$ G). This line can be attributed to the admixture of species consisting of weakly aggregated Mo^{5+} ions.

A 10-fold increase in the molybdenum content in the sample [10 mol.% MoCl$_5$ + hmimBF$_4$] causes a ∼2-fold rise only of the intensity of the ESR signal from isolated Mo^{5+} ions and the signal becomes less resolved (Fig. 2c). At the same time, the intensity of the additional high-field line increases by a factor of ∼5 which agrees with the above assignment of this signal to the weakly aggregated Mo^{5+} ions. From the comparison with the standard, we can conclude that the fraction of "ESR-visible" Mo^{5+} ions in this case does not exceed ∼25% (∼20% of isolated Mo^{5+} ions plus ∼5% of weakly interacting ions). In fact, the brown opalescent mixture of 10 mol.% of MoCl$_5$ in hmimBF$_4$ does not look as a real solution. Anyway, mixing of 10% of MoCl$_5$ with the ionic liquid is accompanied by a very substantial dissipation of MoCl$_5$ in this specific "solvent", with stabilization of ∼1/4 of molybdenum(V) in a form of isolated ions. The rest of MoCl$_5$ remains undissolved.

3.1.3. Metathesis of hex-1-ene on the catalyst [(Mo^{5+})–ionic liquid]

The system [10 mol.% of MoCl$_5$ in hmimBF$_4$] demonstrates a high catalytic activity in hex-1-ene metathesis. As in the case of W-containing samples [1], oct-4-ene is formed as the main product of the reaction. It means that fast isomerization of the starting hex-1-ene to hex-2-ene takes place [1]. The kinetics of metathesis is presented in Fig. 3. No induction period is observed in the case of Mo^{5+} (Fig. 3). The lack of the induction period confirms that the number of catalytically
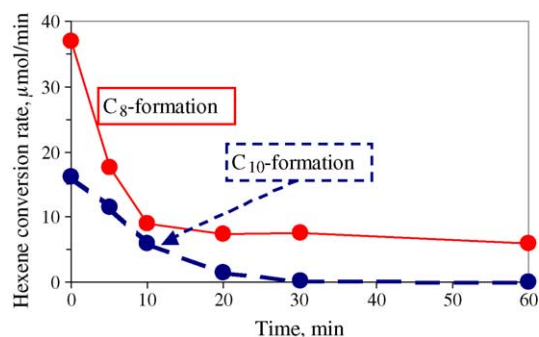
Fig. 3. Kinetics of hex-1-ene metathesis at 20 °C in the system [10 mol.% $MoCl_5$ + $hmimBF_4$].

active sites in the $MoCl_5$-based system is very considerable from the beginning of the reaction. The rate of transformation of the starting hex-1-ene to dec-5-ene, being relatively high at the beginning of the reaction, falls down to a negligible value after ∼25 min and hex-2-ene metathesis to oct-4-ene becomes highly selective in a further process.

ESR testing, with the highest possible amplification, of probes of the olefin layer taken in the course of the reaction show no signal from Mo^{5+} species. Therefore, the reaction in the biphasic system proceeds as a heterogeneous catalytic process: virtually all the isolated Mo^{5+} ions are located in the ionic liquid.

Fig. 4 demonstrates the transformation of the Mo^{5+}-ESR signal accompanying the catalytic reaction. The integral intensity of the signal from isolated Mo^{5+} ions in the ionic liquid increases drastically and the high-field line from inter-
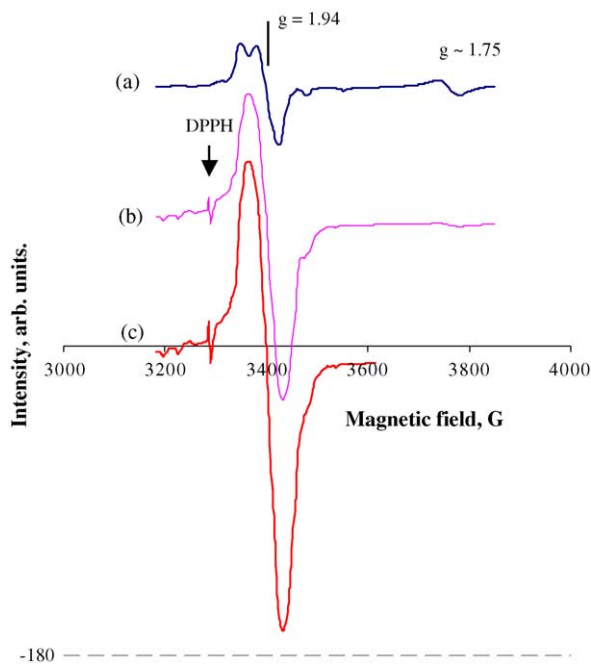

Fig. 4. ESR spectra recorded at −196 °C of the probes of the [10% $MoCl_5$ + $hmimBF_4$] layer taken at different steps of hex-1-ene metathesis at 20 °C: (a) before the reaction; (b) after 10 min of the reaction and (c) after 60 min of the reaction.

acting ions disappears completely in the course of the reaction (Fig. 4). During the first 10 min of the reaction, the fraction of ESR-visible isolated Mo(V) species increases from 25 to ∼60% and after 1 h, it reaches ∼90% of the total number of molybdenum ions in the sample. So, in the presence of an olefin, 100% dissolution of $MoCl_5$ takes place and virtually all atoms of the catalytically active component are stabilized in a working catalyst as isolated paramagnetic complexes of Mo^{5+} ions. Fractions of other valence states of molybdenum (Mo^{4+} and Mo^{6+}) in the active catalyst are negligible.

A visual change of the ionic liquid layer is also clearly seen after the reaction: an originally brown opalescent liquid becomes a clear solution with a bright green-blue color. Thus, interaction with the olefin causes further dissolution and stabilization of isolated paramagnetic Mo^{5+} complexes in the layer of the ionic liquid. One can assume that organic fragments are included in the coordinative sphere of the formed paramagnetic species. At the same time, no other ESR signals attributable to organic radicals can be detected in the course of the reaction. Therefore, the formation of additional paramagnetic species is not accompanied by the charge transfer and the density of the unpaired electron in the paramagnetic complex formed remains located completely on the Mo^{5+} ion.

Thus, the Mo(V) state of the active sites localized in the ionic liquid seems to be entirely responsible for the catalytic metathesis of hex-1-ene to a C_8 product.

It is interesting to compare our results with the data received earlier by Kazansky and co-workers for heterogeneous supported catalysts MoO_3/SiO_2 [14,15] and WO_3/SiO_2 [16,17] activated by γ- or UV-irradiation in presence of CO and alkanes. It was demonstrated that these catalysts, with partially reduced Mo and W sites, are very active in metathesis of propene and hexene. ESR monitoring confirmed an accumulation of Mo(V) ions as a result of the reductive pre-treatment [15]. In discussion of the reaction mechanism, the activity was related with formation of ions with (IV) rather than (V) valence state. From the other hand, it was supposed that the pre-reduced ions interacted with olefin with formation of the carbenic complexes being active sites for further chain metathesis and formally, the ion in such complex had the (V) valence state. Our data shows unambiguously that the paramagnetic (V) state of the Mo ions in active complexes localized in the ionic liquid is predominant and fractions of other valence states of molybdenum {(VI) and (IV)} in the active catalyst are negligible.

3.2. Study of the [(W^{6+})–ionic liquid–hex-1-ene] system

The starting pure WCl_6 powder shows a weak, slightly asymmetric, low-field ESR line, with $g \cong 2.25$ and $\Delta H \sim 130$ G. This signal can be attributed to a small admixture of paramagnetic W(V) ions in the matrix of bulk WCl_6. Any details of paramagnetic sites coordination and location cannot be determined, yet this specific signal is simply indicative of the presence (if so) of the starting solid WCl_6
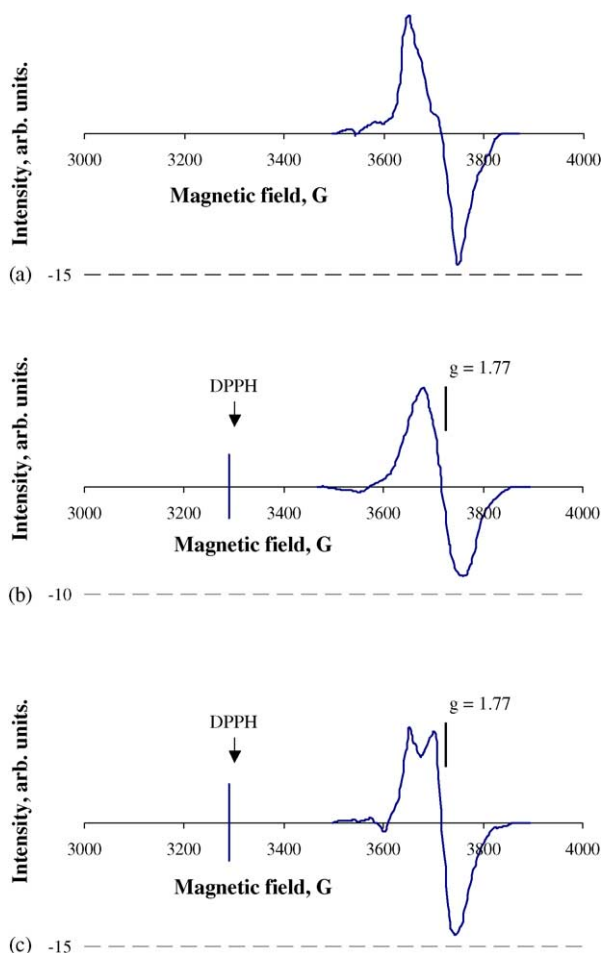
Fig. 5. ESR spectra recorded at $-196\,^{\circ}C$ of the probes of the ionic liquid layers taken after 2 h of hex-1-ene metathesis at $20\,^{\circ}C$: (a) 10% WCl_6 in emimOTf; (b) 10% WCl_6 in bmimBF$_4$ and (c) 2% WCl_6 in hmimBF$_4$.

Table 1
Fraction of ESR-visible W^{5+} in different ionic liquids after hex-1-ene metathesis at $20\,^{\circ}C$ for 2–2.5 h

Ionic liquid	Starting amount of WCl_6 in ionic liquid (mol.%)	Fraction of tungsten ions detected as ESR-visible W^{5+} (%)
hmimBF$_4$	10	20
hmimBF$_4$	2[*]	38
hmimBF$_4$	0.5[**]	~60
hpyrBF$_4$	10	11
emimBF$_4$	5	11
bmimBF$_4$	10	5
emimOTf	10	9
Trihexyl(tetradecyl)-phosphoniumBF$_4$	10	0

[*] After 18 h of the reaction.
[**] After 2 h at $55\,^{\circ}C$.

fractions of W^{5+} accumulated in different ionic liquids after a long-term metathesis of hexene are calculated in the above-mentioned assumption and given in Table 1.

The data obtained demonstrates that the number of isolated W^{5+} species accumulated in the layer of the ionic liquid after the reaction can reach a very considerable value (Table 1). As in the case of Mo-containing mixtures, a visual change of the ionic liquid layer takes place as a result of the reaction: the ionic liquid becomes a solution with a deep blue-green color. Thus, interaction with an olefin causes a partial dissolution/reduction of tungsten, with stabilization of isolated paramagnetic W^{5+} complexes in the ionic liquid. On the other hand, in ESR spectra of the probes taken after the reaction, a rather weak low-field ESR line at $g \cong 2.25$ can be still detected. The presence of this line being typical of the WCl_6 phase points to preservation of a noticeable part of the parent WCl_6 in the ionic liquid in a form of undissolved bulk particles.

No ESR signals from W^{5+} species can be detected for the olefin layer taken in the course of the reaction. Again, the reaction in the biphasic system prepared from WCl_6 proceeds as a heterogeneous catalytic process: isolated W^{5+} species are located in the ionic liquid solely.

No transformation of hex-1-ene takes place after 2.5 h of the reaction when the phosphonium ionic liquid is used. In parallel, no ESR signal from paramagnetic W^{5+} ions appears in these reaction mixtures (Table 1). By analogy with Mo(V), the W(V) state of the active sites localized in the ionic liquid seems to be responsible for the catalytic metathesis of hex-1-ene to the C_8 product.

In a preliminary study, the reaction was carried out for 2–2.5 h and only the resulting reaction mixture was analyzed [1]. In testing the system [2% WCl_6–hmimBF$_4$–hex-1-ene], with a reduced WCl_6 content, it was found that no products and no W^{5+} ions were formed after 2 h. However, an overnight mixing of this system resulted in the appearance of both reaction products and paramagnetic W^{5+} species in large quantities (Table 1). So, an induction period lasts hours in this diluted system.
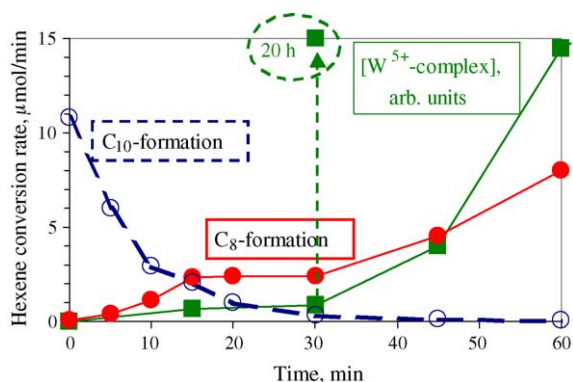
in our reacting mixtures. Really, mixing of 10 mol.% of WCl_6 with ionic liquids results in the formation of muddy, brown suspensions. ESR spectra of these suspensions consist of a weak low-field line mentioned above and a very weak high-field signal, at $g \sim 1.75$, from a trace amount of isolated W^{5+} species. Preservation of the low-field ESR line after mixing the components points to the preservation of the bulk WCl_6 particles being suspended in the ionic liquid.

Subsequent long-term reaction in the triple mixture [(WCl_6)–ionic liquid–hex-1-ene] at room temperature is accompanied by the appearance of strong high-field ESR signals, as shown in Fig. 1. ESR spectra of other systems are additionally presented in Fig. 5. The problem of the quantitative measurement of these signals is the lack of the appropriate W^{5+}-ESR standard. However, we still can evaluate the number of W^{5+} ions in our probes using the molybdenum(V)-ESR standard as a rather close analogue of the tungsten(V)-containing system. Thus, double integrals of the signals shown in Figs. 1 and 5 are compared with the double integral of the Mo^{5+}-ESR standard (Fig. 2a). The

Fig. 6. Kinetics of hex-1-ene metathesis at $20\,^\circ$C in the system [10 mol.% $WCl_6 + bmimBF_4$].

Fig. 7. Kinetics of hex-1-ene metathesis at $20\,^\circ$C in the system [10 mol.% $WCl_6 + hpyrBF_4$]: (a) first testing and (b) second testing, with the same ionic liquid layer.

For the low-loaded reaction mixture [0.5% (WCl_6)–hmim–hex-1-ene], the induction period lasts even days: neither reaction products nor W^{5+} species can be detected after 36 h of the interaction at $20\,^\circ$C. Subsequent treatment of the mixture at $55\,^\circ$C for 2 h leads, however, to appearance of the C_8 product and reduction of a big fraction ($\sim$60%) of W^{6+} ions to isolated W^{5+} species (Table 1).

For better understanding of the [(WCl_6)–ionic liquid–hex-1-ene] system transformation during the reaction, the kinetics of both product formation and W^{5+} species accumulation were monitored in parallel.

Fig. 6 shows the kinetics of hex-1-ene metathesis at $20\,^\circ$C with the catalyst [10 mol.% WCl_6–$bmimBF_4$], with an overlapped curve presenting the process of W^{5+} species accumulation in the $bmimBF_4$ layer. Both C_8 formation and W^{5+} accumulation curves show a similar S-shape behavior with a noticeable induction period. The repeated ESR testing of the sample taken during the induction period and placed into the closed ampoule shows a sharp increase of the W^{5+}-ESR signal after the additional ampoule exposure at $20\,^\circ$C for 20 h (Fig. 6, arrow). Therefore, the slow reduction of W(VI) by the olefin dissolved in the ionic liquid layer lasts in a closed ampoule.

Fig. 7a demonstrates that the same type of the process, with induction period, takes place in the system [10 mol.% WCl_6–$hpyrBF_4$–hexene]. After 2 h of the reaction, the layer of the ionic liquid was retained in the reactor and the catalytic reaction was repeated with a fresh portion of hexene. The kinetics of the product formation in this second test is presented in Fig. 7b. No induction period is seen in the second test, as distinct from the first one (Fig. 7). These data confirms once more that the catalytic formation of the C_8 product is governed by the presence of paramagnetic W(V) species in the ionic liquid layer. The formation/accumulation of these catalytically active species occurs rather slowly at the first step of the process started from the W(VI) state (Figs. 6 and 7a). It is reasonable to assume that for the sample of the ionic liquid which accumulated a maximum amount of the active W(V) species as a result of the first test, the repeated reaction proceeds without any induction period (Fig. 7b).
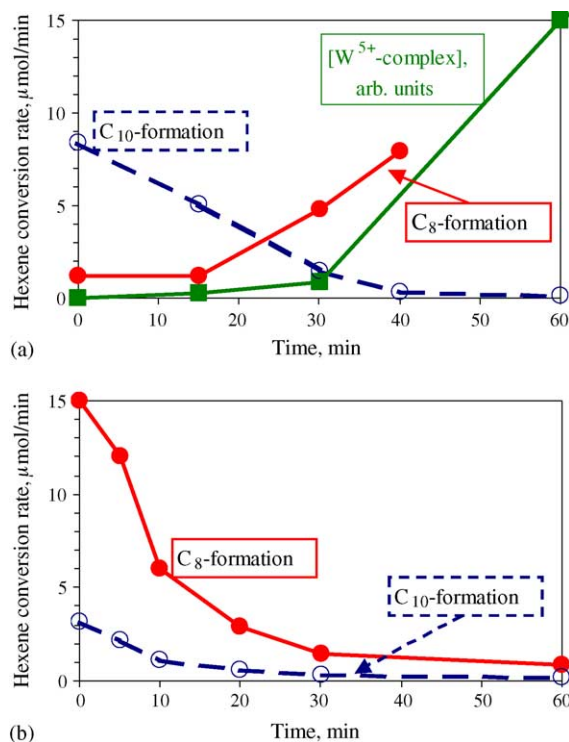
4. Conclusions

1. A quantitative approach is successfully used for the first time in the ESR study of catalysts prepared by dissolution of WCl_6 and $MoCl_5$ in ionic liquids.
2. The key role of isolated paramagnetic complexes of W^{5+} and Mo^{5+} ions in the catalytic metathesis of hex-1-ene is demonstrated. The number of ESR-visible isolated paramagnetic Mo^{5+} complexes in the ionic liquid reaches $\sim$90% of the total number of molybdenum ions in the sample.
3. It is shown that the reaction in the biphasic system proceeds as a heterogeneous catalytic process: virtually all isolated W^{5+} or Mo^{5+} species are located in the ionic liquid.
4. The kinetics of formation/accumulation of isolated paramagnetic W^{5+} species at the first slow step of W^{6+} reduction by an olefin agrees closely with the kinetics of metathesis to the C_8 product.

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