

Radiation enhancement of the catalytic properties of three-dimensional coordination polymers of Ru(II) with diisocyanide ligands

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Abstract

Coordination polymers are drawing increasing attention due to their versatility in structure and function, and their potential applications as catalysts. These polymers may be synthesized by using aryldiisocyanides, which when coordinated to a d^6 metal such as Ru(II), act as bridges and give rise to two distinct types of three-dimensional polymeric networks. Polymer A, $[\text{Ru}(\text{1,4-diisocyanobenzene})_{4/2}^2(2\text{Cl})^{2-}]_n$, has a tetragonal geometry, having, most likely, Ru–Ru stacking interactions in the z direction, while polymer B, $[\text{Ru}(\text{1,4-diisocyanobenzene})_{6/2}^2(2\text{Cl})^{2-}]_n$, has a cubic geometry, having all the Ru atoms separated by the 1,4-diisocyanobenzene ligands. In the hydrogenation reaction of 1-hexene, polymer A is an efficient but a non-selective catalyst. The hydrogenation reaction is accompanied by isomerization, with *trans*-2-hexene as the leading isomer, which is hydrogenated as well after all the 1-hexene has been used up. The catalytic reaction proceeds with an induction period which suggests that polymer A in its original structure is not the actual catalyst. Irradiation of the reaction mixture with 350 nm UV light prior and during the catalytic reaction drastically reduces the induction period. This indicates that the energy of irradiation is sufficient to break the Ru–Ru stacking bonds, thus creating electron-deficient Ru sites prior to the addition of the olefin. An in-depth study of the influence of irradiation on the kinetics of the catalytic reaction is presented in this paper.

Keywords: Radiation; Polymers; Ruthenium; Diisocyanide ligands

1. Introduction

Coordination polymers have been attracting increasing attention in recent years due to their versatility in structure and function, and their potential applications in a variety of technologically relevant fields such as solid-state devices and catalytic processes [1]. Much attention has been devoted to the catalytic properties of polynuclear coordination species [2–4], since they have the ability to offer two or more sites of coordination by providing the stability for the

release of a site-holding ligand [5]. Of special interest are polymers which have metal atoms as an integral part of the polymer chain, since these polymers will provide multiple coordination centers bounded in the same complex. These types of materials are able to offer the advantages of both homogeneous and heterogeneous catalysts without exhibiting the disadvantages associated with each type of catalyst.

These polymers may be synthesized by utilizing multifunctional, nonchelating, rigid ligands, e.g. aryldiisocyanides [6–11], which when coor-

dinated to metal atoms, would act as bridges and would give rise to template polymerization [12,13], and result in one-, two- and three-dimensional materials. With Ru(II) as the d^6 metal of choice, it is possible, by using two different precursors, to obtain two distinctly different materials, both in their structure and in their catalytic properties [14,15]. The first compound, polymer A, with an empirical formula $[\text{Ru}(1,4\text{-diisocyanobenzene})_{4/2}^{2+}(2\text{Cl})^{2-}]_n$, has a three-dimensional structure with a tetragonal geometry, having Ru–Ru stacking interactions in the z direction. The second compound, polymer B, with an empirical formula $[\text{Ru}(1,4\text{-diisocyanobenzene})_{6/2}^{2+}(2\text{Cl})^{2-}]_n$, has a cubic geometry, having all the Ru atoms separated by the 1,4-diisocyanobenzene ligands [15].

Preliminary studies of the catalytic properties of polymer A in the hydrogenation reaction of 1-hexene show that the polymer is an efficient but a non-selective catalyst. The hydrogenation reaction is accompanied by isomerization, with trans 2-hexene as the leading isomer, which is hydrogenated as well after all the 1-hexene has been used up [14,16]. A closer examination of the initial period of the catalytic reaction depicts an induction period. This suggests that polymer A in its original structure is not the actual catalyst [17–20]¹. A possible hypothesis is that the two-dimensional layers of polymer A, which are held together by the Ru–Ru interaction, are undergoing separation due to the intercalation of the organic compound, resulting in the partial breakage of these bonds, and the formation of electron-deficient ruthenium sites [15,19]. These ruthenium sites are capable of coordinating the 1-hexene molecule, and perform the catalytic reaction. Irradiation of the reaction mixture with

350 nm UV light prior and during the catalytic reaction drastically reduces the induction period. This indicates that the energy of irradiation is sufficient to break the Ru–Ru stacking bonds, thus creating electron-deficient Ru sites prior to the addition of the olefin [14,21,22]. As expected, polymer B did not exhibit any noteworthy catalytic activity. In this paper, we shall examine qualitatively and in-depth the influence that irradiation has on the kinetics of the catalytic hydrogenation reaction.

2. Experimental

2.1. Synthesis of polymers A and B

The 1,4-diisocyanobenzene ligand was prepared by treating a boiling suspension of the corresponding diformylaminobenzene, $\text{C}_6\text{H}_4(\text{NHCHO})_2$, in a dichloromethane–triethylamine mixture, with diphosgene (best prepared by the photochlorination of methyl chloroformate) as the dehydrating agent, dissolved in dichloromethane. The detailed synthetic procedure is described elsewhere [23]. The polymerization reaction was carried out in a 3-neck, 100-ml round-bottom flask. One of the side necks of the flask was equipped with an Ar inlet, and the other side neck was sealed with a rubber stopper through which a syringe could be inserted for sample removal. 2.0 g (a fourfold excess) of 1,4-diisocyanobenzene was dissolved in 30 ml ethanol and placed in a dropping funnel attached to the central neck. The solution containing the ligand was then introduced dropwise into the main reaction flask at a rate of 3–5 ml/min, and the reaction was let to equilibrate for about an hour. The reaction mixture was then carefully filtered, and the remaining precipitate was dried in vacuum (0.1 torr) at 100°C for 7–8 days to eliminate traces of H_2O . The blue (resulting from the ‘red solution’ [24]) and the off-white (resulting from the ‘yellow solution’ [24]) precipitate were stored in the dark in small vials and under Ar atmo-

¹ The hydrogenation and hydroformylation reactions of alkenes are very similar in their initial mechanism. In both cases, the first step in the reaction is the formation of an empty coordination site on the metal atom, and the subsequent coordination of the alkene molecule. Therefore, some of the literature concerning the kinetics of the hydroformylation reaction may be relevant also for the hydrogenation reaction discussed in this paper.

sphere. The polymers were characterized by a variety of analytical methods, and the structures suggested in a previous publication [15] best fit the results of these analyses.

2.2. Heterogeneous catalytic experiments

The typical hydrogenation experiment was performed in a 100-ml glass autoclave, equipped

with a small side arm permitting the removal of samples during reaction. 40 mg polymer A was suspended in 10 ml methanol and 1 ml 1-hexene. The autoclave was pressurized to 2 atmospheres of H_2 , and the reaction was conducted at room temperature ca. 25°C. For the unaltered hydrogenation experiment, samples of 0.1 ml were removed initially every 30 min for the first 2 h, and thereafter every 3 h, and were analyzed by

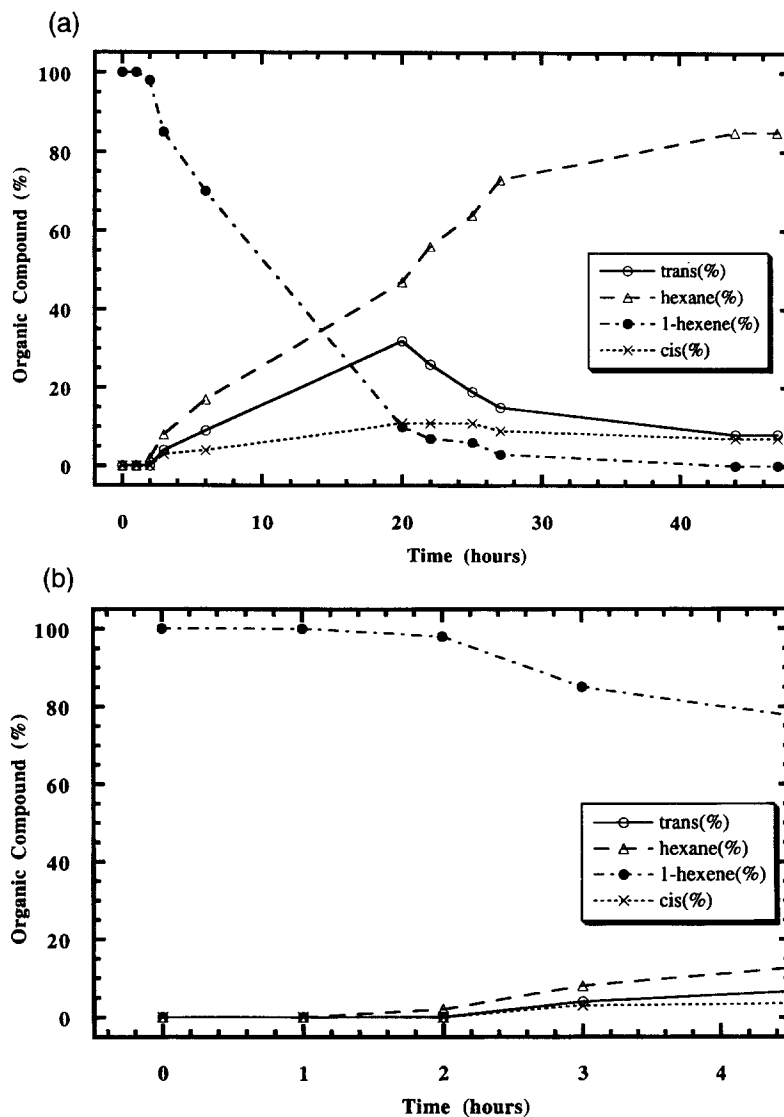


Fig. 1. (a) The relative concentrations of the organic compounds in the hydrogenation reaction of 1-hexene with $[Ru(1,4\text{-diiisocyanobenzene})_2^+2(2Cl)_2^-]_n$. The overall reaction time is ca. 45 h. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively. (b) The induction period observed in the hydrogenation reaction of 1-hexene with $[Ru(1,4\text{-diiisocyanobenzene})_2^+2(2Cl)_2^-]_n$. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively.

gas chromatography. Irradiation experiments were performed using a Hg lamp generating a 350 nm UV radiation. Irradiation was initiated at different times prior, during or both prior and during the course of the reaction. For the examination of the induction period under various conditions, sampling times varied depending on the reaction kinetics.

3. Results and discussion

The catalytic properties of polymer A were examined under various conditions in order to evaluate the relationship between the specific structure of the polymer and its ability to catalyze the hydrogenation of 1-hexene. The separation of the columnar interlayer Ru–Ru interactions [15], may create a coordination transition state able to undergo oxidative-addition reactions, and hence the polymer would act as a heterogeneous catalyst.

The results of the study of the catalytic properties of polymer A in the hydrogenation reaction of 1-hexene are shown in Fig. 1a. The polymer seems to be an efficient but a non-selective catalyst with a turn-over ratio of 1:100

(moles of Ru-atoms/1-hexene) within the experimental set-up used. The hydrogenation reaction is accompanied by the isomerization reaction, with the *trans* 2-hexene as the leading isomer, which in turn is hydrogenated as well after all the initial 1-hexene has been used up.

A closer examination of the initial period of the catalytic reaction, shown in Fig. 1b, depicts an induction period during which no reaction takes place. The regular mechanism offered in the literature for these types of hydrogenation reactions does not explain the presence of such an induction period, unless the polymer A in its original structure is not the actual catalyst [25,26]. A possible explanation for this phenomenon is that the two-dimensional layers of polymer A, which are held together by the Ru–Ru interaction, are undergoing separation due to the intercalation of the organic compound, resulting in the partial breakage of these bonds, and the formation of electron-deficient ruthenium sites. These ruthenium sites in turn are capable of coordinating the 1-hexene molecule, and perform the catalytic reaction.

Irradiation of the reaction mixture with 350 nm UV light prior and during the reaction eliminates the induction period, as shown in Fig. 2.

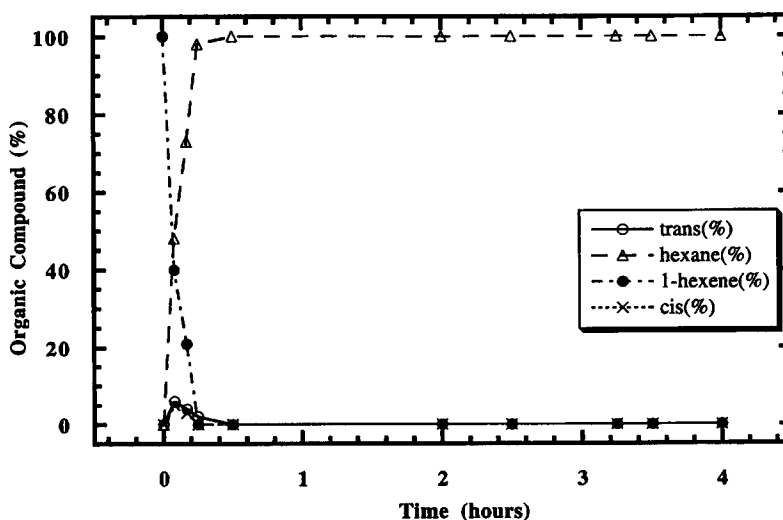


Fig. 2. The first 4 h in the hydrogenation reaction of 1-hexene with $[\text{Ru}(\text{1,4-diisocyanobenzene})_2^+ (2\text{Cl})_2^-]_n$ with 350 nm UV irradiation prior and during the reaction. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively.

This indicates that the energy of irradiation is sufficient to break the Ru–Ru stacking bonds and sustain the interlayer separation [27–29], thus creating electron-deficient Ru sites prior to and after the addition of the olefin. Moreover, the accompanying isomerization reaction, resulting in the formation of the *cis* and *trans* 2-hexene isomers, is greatly suppressed, being reduced to only 6% of the total organic products, and with a lifetime of only about 5 min. This indicates that the mechanism governing the hydrogenation reaction is greatly facilitated with the accelerated kinetics and the separation of the polymer layers prior to the addition of the olefinic substrate, and hence, the irradiation gives rise to the immediate dominance of the hydrogenation reaction.

The phenomena described above are further supported by the results shown in Figs. 3–5. Fig. 3 shows the evolution of the hydrogenation and the accompanying isomerization reactions with concomitant irradiation of the reaction mixture with 350 nm UV light. The induction period is considerably shortened from over 2 h to less than 15 min, and the reaction is completed in 4 h. The extent of the isomerization reaction is also reduced, from a combined 43% at maximum isomer content in the non-irradiated

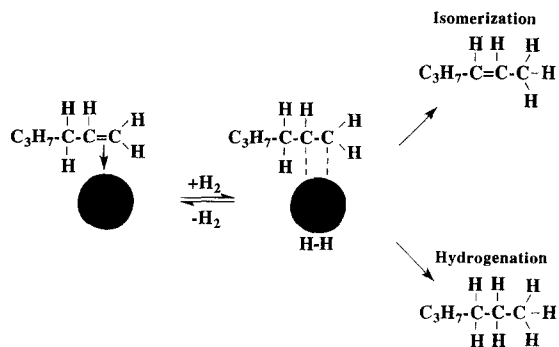


Fig. 4. The possible mechanistic pathway for the hydrogenation and isomerization reactions.

reaction mixture to a combined 13% maximum isomer content for the irradiated reaction mixture. As was the case for the conditions described in Fig. 2, the acceleration of the hydrogenation reaction causes a reduction in the extent of the accompanying isomerization reaction. This is most likely a result of the fast coordination of the olefin and the hydrogen to the electron-deficient ruthenium center [19], which is conducive to addition of the H_2 molecule to the olefin rather than the migration of the double bond to the neighboring position.

The possible mechanisms for the hydrogenation and isomerization processes are shown in Fig. 4. The first step in both processes is the

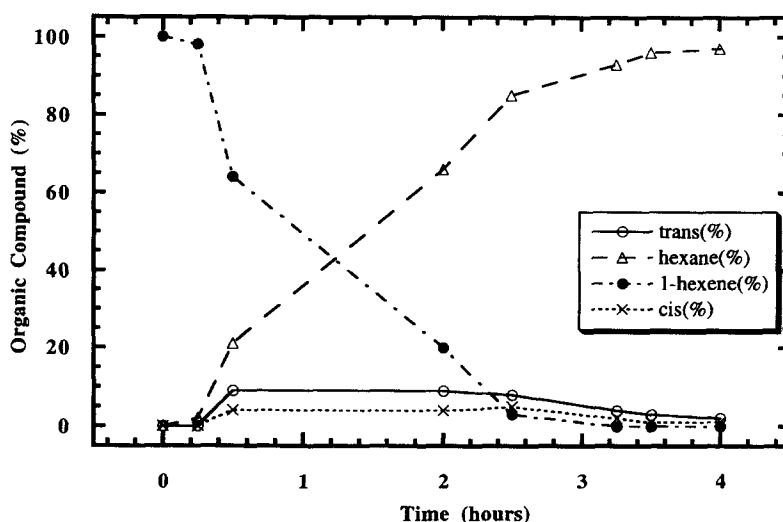


Fig. 3. The first 4 h in the hydrogenation reaction of 1-hexene with $[Ru(1,4\text{-diisocyanobenzene})_{4/2}^{2+}(2Cl)^{2-}]_n$ with 350 nm UV irradiation during the reaction. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively.

reversible coordination of the double bond of the olefin to a vacant coordination site on the ruthenium (a site created by the separation of the polymer layers as a result of the Ru—Ru stacking bonds) [14,19]. At the same time, a hydrogen molecule is also reversibly activated on the remaining vacant coordination site of the ruthenium, but since this coordinative interaction is very weak, the equilibrium is considerably shifted toward the elimination of the free hydrogen molecule from the coordination sphere of the ruthenium center. Therefore, in order to achieve hydrogenation, it is necessary to have both the olefin and the hydrogen molecule in the coordination sphere of the ruthenium center at the same time. This is most likely to occur when the polymer layers have already been separated due to the breakage of the Ru—Ru interactions, as is the case in the reaction mixtures which have been irradiated.

A similar effect is observed also with reaction mixtures which were irradiated prior to the introduction of the olefin, but the reactions were conducted without irradiation as shown in Fig. 5. The reaction proceeds without any induction period, similar to the evolution of the reaction depicted in Fig. 2. However, unlike the latter,

the irradiation is stopped immediately prior to the introduction of the olefin, and the reaction is allowed to proceed in the 'dark', under conditions identical to those used in the initial catalytic experiments. Despite the initial fast kinetics, the reaction slows down after the first 10 min, accompanied by the formation of the *cis* and *trans* 2-hexene isomers to the extent of ca. 15% at their combined maximal concentration. For about 3 h, the concentration of both isomerization products is at an apparent steady state, followed by a slow decrease to yield the hydrogenation product. This experiment clearly illustrates the dramatic effect that irradiation has on the reaction kinetics. Irradiation of the catalyst prior to the introduction of the olefin essentially prepares the catalyst in its active form, and hence reaction starts immediately upon substrate addition, thus eliminating the presence of an induction period. However, the continuous separation of the polymer layers in order to sustain the catalyst in its active form is not possible due to the lack of irradiation during the reaction, and therefore the overall reaction slows down and becomes very similar to the non-treated reaction.

A combination of reaction conditions gives

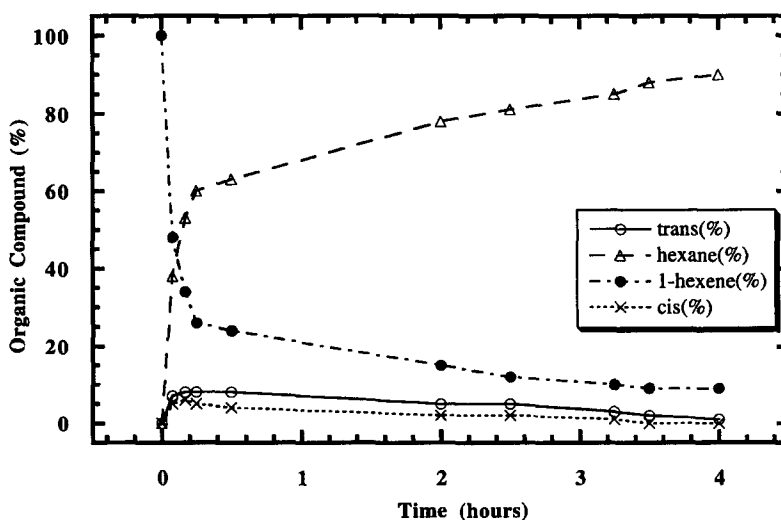


Fig. 5. The first 4 h in the hydrogenation reaction of 1-hexene with $[\text{Ru}(\text{1,4-diisocyanobenzene})_{4/2}^{2+}(\text{2Cl})^{2-}]_n$ with 350 nm UV irradiation prior to the reaction. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively.

rise to the kinetics shown in Fig. 6. 15 min after the addition of the olefin to the reaction mixture, while still in the induction period, a 10 s UV pulse was applied to the reaction vessel, followed by the 'dark' period in which the reaction was allowed to proceed undisturbed. Several such UV pulses were applied at different times. Immediately following a pulse, the reaction kinetics accelerated and then slowed down to reach an apparent steady state. The hydrogenation reaction reached completion after 8 h, while the combined maximal concentration of the *cis* and *trans* 2-hexene isomers reached after 4 h, did not exceed 13%. Once again, the activation of polymer A proves to be a key element in the mechanistic aspects of the hydrogenation reaction. When polymer A is in its active form, i.e. when the layered structure created by the Ru–Ru inter columnar interactions is broken and the ruthenium centers become electron deficient, as shown in Fig. 7, the catalytic reaction does not exhibit any induction period. Since the separation of the layers is reversible, irradiation of the reaction mixture prior to the introduction of the olefinic substrate is not sufficient to maintain polymer A in its active form, and therefore the reaction slows

down during the 'dark' periods. When the reaction mixture is irradiated prior and during the reaction, the hydrogenation of the substrate is completed after only 15 min.

The results presented so far may be explained in terms of the structural changes that occur in polymer A as a result of its exposure to UV radiation in the presence of 1-hexene. In the absence of irradiation prior and/or during the catalytic reaction, the driving force for the separation of the two dimensional polymeric layers and the intercalation of the olefin in the coordination sphere of an electronically deficient ruthenium center is the olefin itself. Since the three-dimensional structure of polymer A suggests a porous network, there is a considerable concentration gradient between the concentration of the olefin in solution and its concentration inside the network. Hence, the olefin osmotic pressure will essentially break the weak Ru–Ru interactions, and 'push' the polymer layers apart in order to make room for the bulky 1-hexene molecule. This mechanism is shown in Fig. 8. Once the layers are separated, the olefin molecules penetrate between the opening layers and coordinate to the ruthenium centers. If polymer A is irradiated prior to the addition

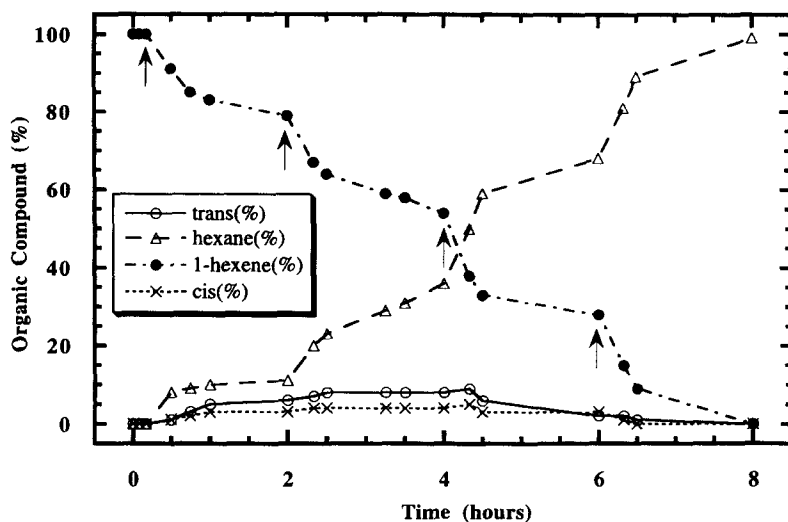


Fig. 6. The first 4 h in the hydrogenation reaction of 1-hexene with $[\text{Ru}(\text{1,4-diiisocyanobenzene})_{4/2}(\text{2Cl})^{2-}]_n$ with 350 nm UV irradiation pulses of 10 s during the reaction. The catalytic suspension was not irradiated prior to the addition of the olefin. The 'cis' and 'trans' notation indicates *cis* 2-hexene and *trans* 2-hexene, respectively.

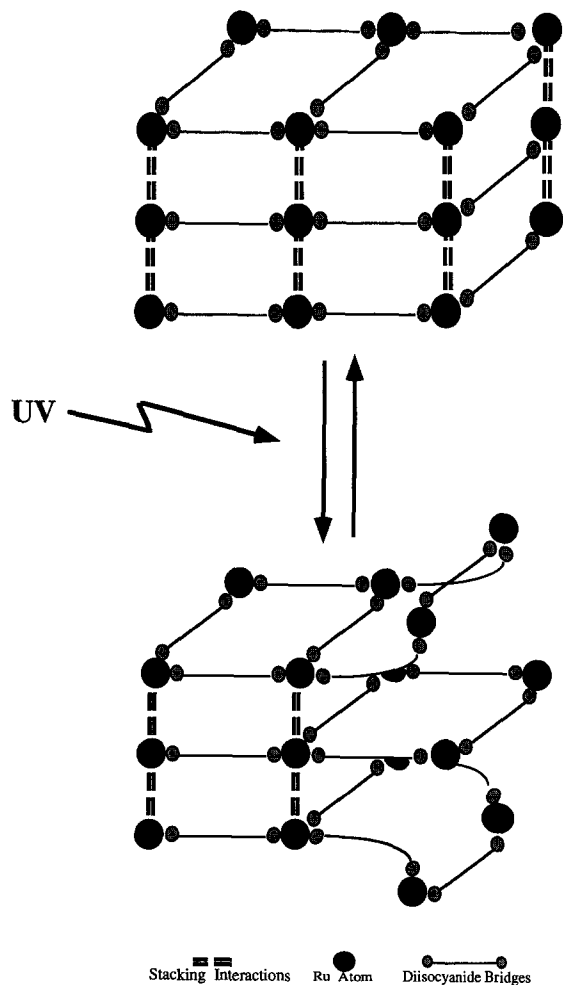


Fig. 7. Schematic description of the influence of the 350 nm UV irradiation on the stability of the Ru—Ru weak stacking interactions and the consequences of their reversible breakage.

of the olefin, the layers are already separated and the intercalation process may occur instantaneously, as shown in Fig. 9. This mechanism explains the lack of an induction period when the reaction mixture was irradiated prior to olefin addition, but the reaction was carried in the absence of UV.

The overall kinetics of the reaction system is dependent upon the amount of energy needed to break the Ru—Ru stacking interactions, separate the polymer layers and allow for the coordination of the olefin molecules. There is no doubt that the energy which the UV irradiation provides is very effective in creating the crucial

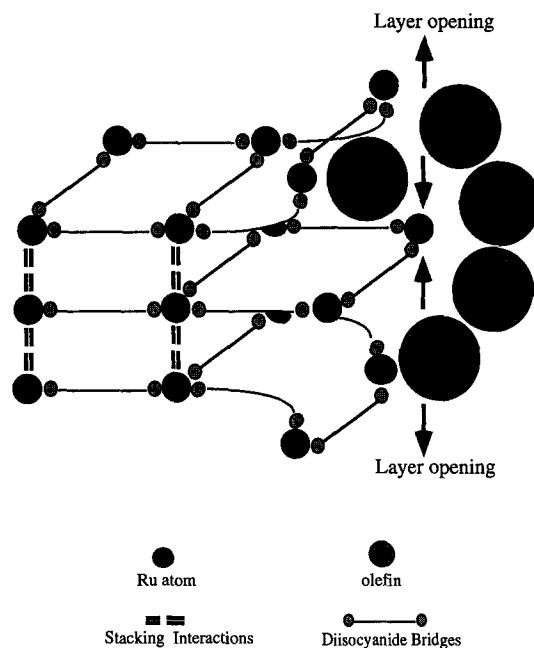


Fig. 8. Schematic description of the 'layer opening' mechanism in polymer A, generated by the addition of 1-hexene to the catalyst suspension

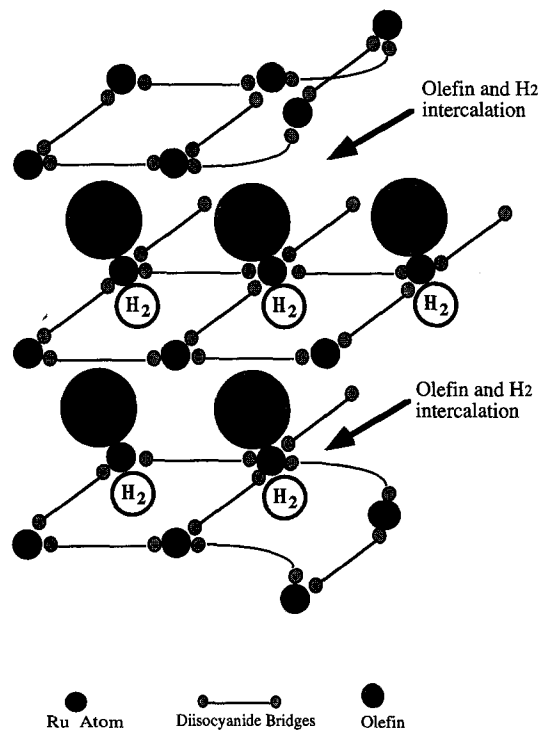


Fig. 9. Schematic description of the intercalation and the coordination of the olefin molecules to the electron-deficient ruthenium centers, and the activation of hydrogen in the hydrogenation reaction.

coordination-deficient metallic center necessary for the progress of the catalytic reaction. A detailed quantitative study of the kinetics of the hydrogenation reaction with polymer A as catalyst is underway.

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References

- [1] R. Hoffmann, *Solids and Surfaces: a Chemist's View of Bonding in Extended Structures*, VCH Publishers, New York, 1988, and pertinent references therein.
- [2] P. Chini, *Pure Appl. Chem.*, 23 (1970) 489.
- [3] A.L. Robinson, *Science*, 194 (1976) 1150.
- [4] E.L. Muetterties, *Science*, 196 (1977) 839.
- [5] R.M. Laine, *J. Mol. Catal.*, 14 (1987) 137.
- [6] M.S. Lewis, K.R. Mann, J.G. Gordon II and H.B. Gray, *J. Am. Chem. Soc.*, 98 (1976) 7461.
- [7] J. Powell, *J. Organometal. Chem.*, 179 (1979) 101.
- [8] A. Efraty, I. Feinstein, F. Frolow and L. Wackerle, *J. Am. Chem. Soc.*, 102 (1980) 6341.
- [9] A. Efraty, I. Feinstein and F. Frolow, *Inorg. Chem.*, 21 (1982) 485.
- [10] I. Feinstein-Jaffe, F. Frolow, L. Wackerle, A. Goldman and A. Efraty, *J. Chem. Soc. Dalton Trans.*, 2 (1988) 469.
- [11] I. Feinstein-Jaffe and S.E. Maisuls, *J. Organometal. Chem.*, 350 (1988) 57.
- [12] J.T. Mague and J.P. Mitchener, *Inorg. Chem.*, 8 (1969) 119.
- [13] M. Hanack, S. Deger and A. Lange, *Coord. Chem. Rev.*, 83 (1988) 115.
- [14] I. Feinstein-Jaffe and A. Efraty, *J. Molec. Cat.*, 40 (1987) 1.
- [15] R. Tannenbaum, *Chem. Mater.*, 6 (1994) 550.
- [16] B.R. James, *Homogeneous Hydrogenation*, Wiley, New York, 1973.
- [17] P. Pino, R. Ercoli and F. Calderazzo, *Chim. Ind. (Milan)*, 37 (1955) 782.
- [18] J. Azran and M. Orchin, *Organometallics*, 3 (1984) 197.
- [19] C.D. Hoff, F. Ungváry, R.B. King and L. Markó, *J. Am. Chem. Soc.*, 107 (1985) 666, and pertinent references therein.
- [20] I. Kovács, F. Ungváry and L. Markó, *Organometallics*, 5 (1986) 209.
- [21] M.B. Simpson, M. Poliakoff, J.J. Turner, W.B. Maier II and J.G. McLaughlin, *J. Chem. Soc. Chem. Commun.*, 1355 (1983).
- [22] K. Yasufuku, H. Noda, J-i. Iwai, H. Ohtani, M. Hoshino and T. Kobayashi, *Organometallics*, 4 (1985) 2174.
- [23] A. Efraty, I. Feinstein, L. Wackerle and A. Goldman, *J. Org. Chem.*, 45 (1980) 4059.
- [24] R. Tannenbaum, *Inorg. Chim. Acta*, 130 (1987) 49.
- [25] P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds.), *Organic Synthesis via Metal Carbonyls*, Vol. II, Wiley, New York, 1977, pp. 74–88.
- [26] A.J. Birch and I.D. Jenkins, in H. Alper (Ed.), *Transition Metal Organometallics in Organic Synthesis*, Vol. I, Academic Press, New York, 1976, pp. 49–55.
- [27] K.R. Mann, J.G. Gordon II and H.B. Gray, *J. Am. Chem. Soc.*, 97 (1975) 3553.
- [28] H. Isci and W.R. Mason, *Inorg. Chem.*, 14 (1975) 913.
- [29] A.E. Underhill and D.M. Watkins, *Inorg. Nucl. Chem. Lett.*, 13 (1977) 235.