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Thiophene as Internal Promoter of Selectivity for the Liquid Phase Hydrogenation of Citral Over Ru/KL Catalysts

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Abstract The effect of thiophene (Th) addition, in the concentration range 0–6 ppm, on the performance of Ru/KL catalysts is analyzed for the liquid phase hydrogenation of citral at 323 K and 4 MPa. The results show a promoter effect of thiophene on the overall hydrogenation activity of the catalysts, with a maximum at 3 ppm concentration of Th. Particularly, it is evidenced an increase in the selectivity towards the hydrogenation of the carbonyl group of citral.

Keywords Ru/KL catalysts · Citral hydrogenation · Thiophene as selectivity promoter

1 Introduction

Selective hydrogenation of citral is an important reaction in the sector of fine chemicals, unsaturated alcohols being the more valuable reaction products. In this line many research works have been published because, in addition to the importance of their hydrogenation products in the perfumes and pharmaceutical industries, this reaction is frequently used as a "reaction-model" to analyze new formulations for selective catalysts. The reaction pathway generally accepted for the hydrogenation of citral [1], including competitive parallel and consecutive reactions, is depicted in Fig. 1. Hydrogenation of C=O in Z and E isomers yields the unsaturated alcohols nerol and geraniol, respectively, whereas, hydrogenation of the conjugated C=C double bond produces citronellal. In addition, consecutive hydrogenation, isomerization and/or cyclization reactions of these primary products can occur, depending on the surface properties of the catalysts used. In general, ruthenium catalysts direct the reaction mainly to citronellal, and for this reason formulations of metal catalysts, highly selective toward unsaturated alcohols, are required.

The influence of the catalyst components and of the catalyst preparation method on the reaction selectivity is very well documented in the literature and reviewed by Kluson and Cerveny [2, 3]. In this sense several authors proposed addition of promoters such as Ge, Sn, Fe [4–6] and Cu [7], which can positively modify the selectivity toward unsaturated alcohols of the supported transition metals. On the other hand Hutchings [8] considers that organic sulfur compounds, added in very low concentration levels (1.8–2.7 × 10^{-3} S-atom/surface–Cu-atom), may be considered as promoters for hydrogenation of the C=O bond in the selective hydrogenation of α,β-unsaturated aldehydes using copper as catalyst, probably due to an inhibition of the C=C bond hydrogenation. Modification of selectivity induced by sulfur compounds for hydrogenation reactions over transition metal catalysts were early reported [9] and explained by an electron transfer from the metal to the sulfur, which affects the reaction mechanism at the surface [10]. Likewise, studies by Oudar [11] and Somorjai [12] demonstrated that sulfur is able to induce surface reconstruction, which can modify the selectivity in catalytic reactions.

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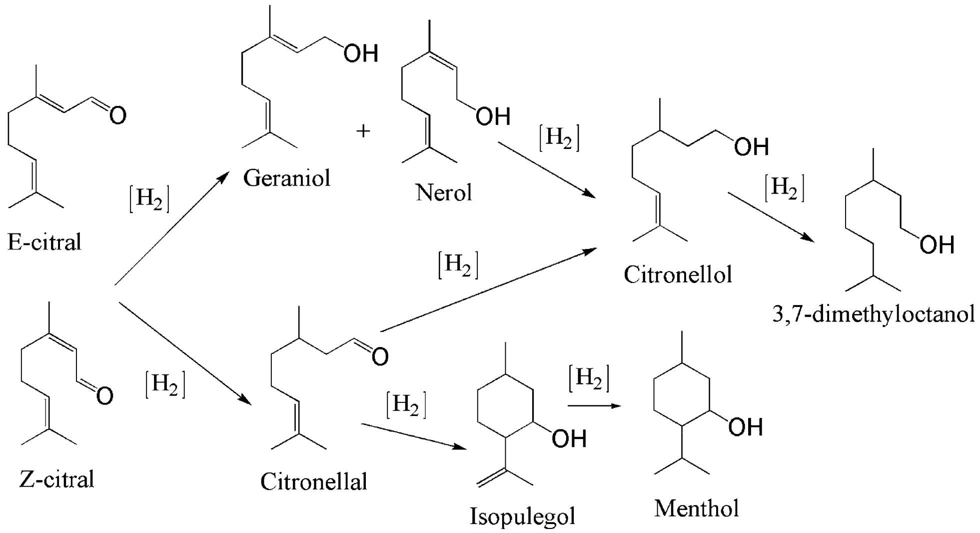

Fig. 1 Reaction scheme for the hydrogenation of citral

During our research on Ru/KL catalysts for the liquid phase hydrogenation of citral we have verified that changes in the nature of the ruthenium precursor [13], the catalyst preparation method [14] and the copper addition [15] induce geometrical and/or electronic effects that substantially modify the adsorptive properties of the catalysts and consequently, the selectivity towards citronellal and geraniol + nerol. The aim of the present work is to enhance the selectivity towards the valuable unsaturated alcohols in the hydrogenation of citral, by introducing a modifier on the ruthenium surface such as thiophene, which was added in very low concentrations. For this purpose three very well characterized Ru/KL catalysts, with different surface structure were used. Namely two monometallic Ru/KL catalysts prepared from different metal precursors and a bimetallic RuCu/KL catalyst, where the existence of ruthenium and copper segregated phases was previously proved [15] have been tested with different concentrations of added thiophene in the reactant feed.

2 Experimental

2.1 Catalysts Preparation

The catalysts were prepared by incipient wetness impregnation using as support a KL zeolite (Carbide Union, SK-45, $K_9Al_9Si_{27}O_{72}$ in atoms per unit cell) with size of grain between 53 and 65 μm, previously calcined at 873 K for 3 h. Samples *Ru/KL-N* and *Ru/KL-C*, containing 2 wt% of Ru, were obtained by treating the zeolite with ruthenium (III) nitrosyl-nitrate in aqueous solution and triruthenium dodecacarbonyl in acetone solution, respectively. After drying at 393 K overnight, an aliquot of sample *Ru/KL-C* was impregnated with aqueous solutions of copper (II) nitrate trihydrate in an adequate concentration to obtain 0.5 wt% Cu on the zeolite (samples *RuCu/KL-C*) and thereafter dried at 393 K. All the catalysts were reduced at 673 K for 2 h under hydrogen flow (40 mL min^{-1}) heating at 5 K min^{-1} and after cooling down at RT under helium flow, each sample was suspended in 2-propanol under inert atmosphere and then transferred to the reaction flask containing a liquid mixture of citral and 2-propanol as solvent. Following this procedure one can assume that no oxidation of ruthenium surface occurs by effect of the atmospheric oxygen.

Metal dispersion of the catalysts (D_H) was calculated from the number of exposed Ru atoms per gram of catalyst, measured by hydrogen chemisorption, and the total number of Ru atoms per gram of catalyst, as determined by an inductively coupled plasma–atomic emission spectrometer (ICP–AES). Hydrogen chemisorption measurements were carried out in a conventional volumetric device at 373 K, due to the characteristic activated hydrogen chemisorption on ruthenium catalysts [16]. The catalyst samples (300 mg) previously reduced and outgassed, were contacted at 373 K with successive hydrogen pulses between 66 and 13.100 Pa and the loss of pressure measured. The hydrogen uptake was determined extrapolating to zero pressure the linear portion of the adsorption isotherm and the number of exposed metal atoms calculated assuming an atomic stoichiometry Ru/H = 1/1 [17].

Catalytic activity of the samples was evaluated in the hydrogenation of citral in the liquid phase at 323 K and 5 MPa. The reaction tests were performed in a three-phase bubble column slurry reactor operated in a semi-batch mode, with stationary liquid phase constituted by a mixture of 200 mL of 2-propanol and 1 mL of citral with 1 g of catalyst in suspension. The hydrogen flow (500 cm^3 min^{-1}) was continuously fed upstream through a sparger with holes of 0.05 cm diameter, located at the bottom of the reactor. The hydrogen flow rate acts in this case as stirrer.

The column reactor consists of a 316 stainless steel tube, 22 in. length and 1 in. in nominal diameter, the catalyst particle/column diameter ratio being 0.0025. The liquid mixture, containing the catalyst, was charged into the reactor and after outgassing under helium flow, then the temperature was risen at 323 K and the pressure adjusted at 5 MPa. Longitudinal temperature profiles in the liquid are registered by means of three thermocouples located at different height in the reactor. When the reaction temperature is reached, the helium is switched by hydrogen and the pressure adjusted to the required value. At this moment, a liquid sample is collected and this is the zero time for the run. In all the runs the reaction progress with time was followed taking periodically liquid samples of the reactor, which were analyzed by gas-chromatography. In order to analyze the effect of sulfur compounds on the catalyst performance, several liquid mixtures were doped with different concentrations of thiophene in the range 0.3–6.0 ppm and the runs performed under similar conditions. Previously, it was verified the absence of external and internal mass transfer limitations under the fluidodynamic condition used [6]. From the reproducibility of the measurements the average standard deviation for citral conversion was estimated to be ±2.5%.

3 Results and Discussion

Chemical composition and metal dispersion of the catalysts are given in Table 1. In order to know the effect of sulfur on the performance of these catalysts in the liquid phase hydrogenation of citral, reaction tests were performed without and with 0.9 ppm of thiophene at 323 K and 4 MPa. Table 2 summarizes the conversion of citral (*X*) measured after 60 min of reaction, when the reaction is still under differential conditions and the secondary reactions are minimized. Hydrogenation activity of the catalysts after 60 min of reaction either without or with sulfur goes in the order *Ru/KL-N* > *Ru/KL-C* > *RuCu/KL-C* (Table 2). When comparing for any catalyst the reaction experiments with and without added thiophene, it can be noted a certain increase of the hydrogenation activity particularly for the monometallic catalysts. Thus, conversion of citral increases from 9.2 to 16.2% for *Ru/KL-N* and in a lower degree, from 10.1 to 11.9%, for *Ru/KL-C*, despite the very well known poisoning effect of thiophene on the supported metal catalysts [18]. In contrast, for *RuCu/KL-C* the conversion of citral is practically unaffected by the thiophene addition. In a similar way, thiophene improves the selectivity towards unsaturated alcohols (S_{UOL}) for the monometallic ruthenium samples in the detriment of that of citronellal (S_{Cal}), this being more perceptible for sample *Ru/KL-N*. With respect to *RuCu/KL-C*, thiophene does not substantially modifies the reaction product distribution. This latter result is comparable to that found by Ashour et al. [19] in the hydrogenation of crotonaldehyde in the gas phase over thiophene-modified Pd-Cu/SiO_2 catalysts.

Table 1 Composition and dispersion of the catalysts

Catalyst	Ru content (wt%)	Cu content (wt%)	*D* (%)
Ru/KL-N	2.03	0.00	25
Ru/KL-C	1.96	0.00	39
RuCu/KL-C	1.98	0.49	42

D, metal dispersion measured by hydrogen chemisoption

Table 2 Hydrogenation of citral over different Ru/KL catalysts at 323 K and 4 MPa after 60 min of reaction without and with 0.9 ppm of thiophene

Catalyst	*Th* (ppm)	*X* (%)	S_{Cal}	S_{OL}	S_{Col}	S_{DMO}
Ru/KL-N	0.0	9.2	60	20	11	9
Ru/KL-N	0.9	16.2	53	28	12	7
Ru/KL-C	0.0	10.1	74	15	7	4
Ru/KL-C	0.9	11.9	64	20	7	9
RuCu/KL-C	0.0	8.2	62	17	16	5
RuCu/KL-C	0.9	8.5	60	20	15	5

Th, thiophene concentration; *X*, conversion of citral; S_{Cal}, selectivity towards citronellal; S_{OL}, selectivity towards unsaturated alcohols; S_{Col}, selectivity towards citronellol; S_{DMO}, selectivity towards 3,7-dimethyl-octanol

The differences in performance of the ruthenium catalysts for the citral hydrogenation under thiophene free conditions were already discussed in terms of a different location of the metal particles in the zeolite framework [13] and of decoration/encapsulation phenomena in the *RuCu/KL-C* sample [15]. In the presence of thiophene (*Th*) the differences observed in Table 2 can be associated to the same factors above mentioned, whatever the specific effect of sulfur on the metal. Thus, since the population of metal particles outside the zeolite exhibited by *Ru/KL-N* is higher than that found for *Ru/KL-C*, it seems that the *Th*↔Ru interaction, responsible of the observed changes, should be more favored for the more accessible larger particles in the former catalyst. In fact adsorption of thiophene is a structure-sensitive process that preferentially occurs on large particles [20] where the surface ensembles of adjacent metal atoms enable the multiple anchoring of the molecules, a prerequisite for breaking the C–S bond. In addition, the higher electron-donor character of the metal site the stronger the metal sulfur bond and the easier the sulfur compound hydrogenolysis. In a similar way, the negligible effect of thiophene on *RuCu/KL-C* is consistent both with the existence of segregated copper and ruthenium phases previously proposed for this sample [15] and with the fact that electronegativity of copper (1.90) is lower than that of ruthenium (2.20). Under these conditions thiophene, due to its electron-acceptor character, will be preferentially adsorbed on the segregated copper which, moreover, does not play any significant role in hydrogenation reaction.

Hutchings et al. [21, 22], in early works about hydrogenation of crotonaldeyde in the gas phase, observed that very low levels of sulfur enhance the selectivity towards the unsaturated alcohols over Cu/Al_2O_3 catalysts, in spite of the fact that the catalysts were partially deactivated along the time. Based on a detailed CO-FTIR study [23] they concluded that the promotional effect observed was electronic in nature, with formation of new Cu^+–S selective hydrogenation sites. More recently [24] it has been also found that thiophene modifies the selectivity towards dimethylcyclohexane isomers in the hydrogenation of *o*-xylene over Pd/Al_2O_3 and Ru/Al_2O_3 catalysts and it has been demonstrated that this phenomenon is quantitatively influenced by both the concentration of thiophene in the liquid feed and the deactivation degree of the catalysts. Such effects were attributed to changes in the electronic state of the remaining active metal sites produced by the chemisorbed thiophene.

Since the major improvements in catalytic performance were obtained with the *Ru/KL-N* catalyst, in order to get a better insight about the effect of thiophene on the ruthenium surface and its ascendancy on the catalyst selectivity, different runs were carried out with this catalyst using reaction mixtures, where 0.3, 0.9, 1.8, 3.0, 4.5 and 6.0 ppm of thiophene were added. These concentrations are those required to cover 2, 6, 12, 20, 30 and 40%, respectively, of the total catalyst metal surface (25% dispersion) assuming a molar adsorption stoichiometry *Th*/Ru = 1/1. Figure 2 shows the thiophene concentration effect on the catalytic activity. Note that the increase in the thiophene added enhances the catalytic activity, which reaches a maximum value for thiophene concentration of around 1.8 ppm.

Since hydrogenation of citral follows two parallel ways followed of successive reactions (see reaction scheme in Fig. 1) additional information about the effect of thiophene on the catalysts can be drawn from Fig. 3, where selectivity towards the main reaction products for conversion levels around 15% is depicted. It is observed that citronellal is the major reaction product for thiophene concentrations lower than 1.8, while for higher concentrations (3, 4.5 ppm) the formation of geraniol and nerol is remarkably favored, in such a way that these products are majority. In absence of thiophene, the selectivity towards citronellal ($S_{Cal} = 60\%$) is higher than that of the unsaturated alcohols ($S_{OL} = 20\%$), due to the fact that hydrogenation of the C=C conjugated bond is thermodynamically favored over than of C=O by ca. 100 kJ mol^{-1} [25] and, moreover, it is kinetically preferred on ruthenium catalysts [26]. When comparing the results of the doped runs with the preceding one, it is seen that S_{UOL} initially increases with thiophene concentration, reaches a maximum (46%) for 3.0 ppm of thiophene and then decreases to 30% when this latter is 6.0 ppm. Selectivity towards citronellal follows the opposite trend, whereas, selectivity towards the more hydrogenated products, citronellol and 3,7-dimethyloctanol, is less affected although maxima are observed for these products by using 4.5 and 6.0 ppm of thiophene, respectively. Since these selectivities are the result of the overall balance of the competitive parallel and successive hydrogenation reactions of citral, and they depend in turn on the physicochemical properties of the surface, evolution of selectivities values in Fig. 3 denotes important surface changes, depending on the thiophene loading. Hence, from

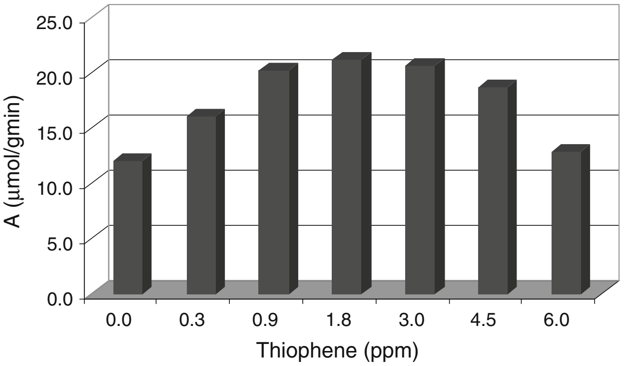

Fig. 2 Effect of the thiophene concentration on the hydrogenation activity of the Ru/KL-N catalyst at 323 K and 5 MPa

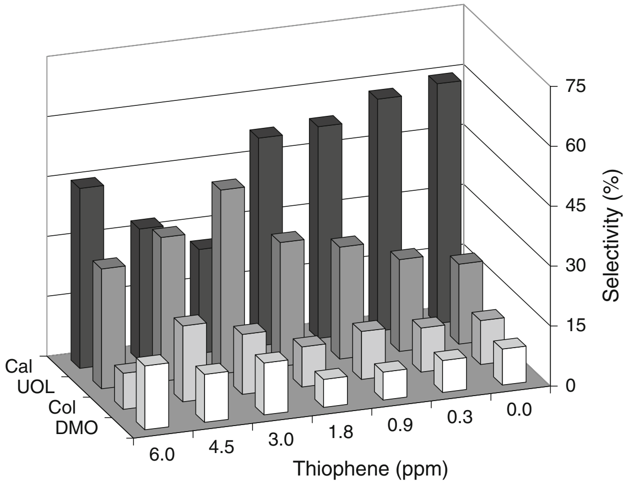

Fig. 3 Selectivity towards the main hydrogenation products of citral over Ru/KL-N catalyst as a function of the thiophene concentration at conversion levels of around 15%: Cal, citronellal; UOL, α, β-unsaturated alcohols; Col, citronellol and DMO, 3,7-dimethyl-octanol

the analyzed results it can be suggested that thiophene produces a promoter effect on Ru/KL supported catalysts that affects to both activity and selectivity.

In order to evaluate the kinetic effect of thiophene on the hydrogenation of both unsaturated C=C and C=O bonds, yields to citronellal (Y_{Cal}) and unsaturated alcohols (Y_{OL}) versus the reaction time are plotted in Fig. 4 for the different concentrations of thiophene. In presence of low concentrations of thiophene (<3 ppm) formation of citronellal is enhanced, while for the higher concentrations its yield decreases, although it always remains higher than in the run without thiophene. In contrast, yield to unsaturated alcohols continuously increases with thiophene content, reaching the maximum value for 3.0–4.5 ppm, when the effect of thiophene on the hydrogenation of the C=C double bond is rather negligible. Thus, from a practical point of view, it is interesting to remark that e.g., after 60 min of reaction and in comparison with the sulfur free experiment, Y_{OL} increases from 3 to 7.2% by effect of 3 ppm of thiophene, while Y_{Cal} only increases from 4.5 to 5%, i.e., hydrogenation of the carbonyl group is preferentially promoted.

In our knowledge the above described kinetic effect of thiophene has to be related to the fact that thiophene acts as an adsorbate in competition with citral, modifying the electronic properties of the metal surface. In addition, taking into account the shape of the graphs in Fig. 2, the hydrogenation of citral in presence of thiophene can be considered a volcano-type reaction, in agreement with the rules of electrochemical promotion established by Brosda et al. [27] i.e., citral and thiophene are strongly adsorbed on supported ruthenium. Although in this competitive process thiophene deactivates the surface metal sites on which adsorbs and probably hydrogenolyses, as a consequence an electron deficient field over the neighboring metal atoms may be originated [9] and then catalytic properties are greatly affected. This phenomenon, however, does not seem to occur on the *RuCu/KL-C* sample.

Two modes of adsorption, in a planar orientation to the surface, blocking the surface active sites, and in perpendicular form by means of sulfur atom anchorage, have been established for thiophene on transition metals [28]. In both cases thiophene would be in competition with the citral molecule, as it is schematized in Fig. 5. For the non-planar adsorption, due to the free rotation of the thiophene molecule, the hydrocarbon chain can inhibit adsorption of other molecules over the whole adjacent surface. In ref [24] we found that toxicity of thiophene with respect to ruthenium, in the liquid phase *o*-xylene hydrogenation at 333 K, is $T = 2$ Ru-atom/*Th*-molecule, indicating that thiophene is perpendicularly bonded to the ruthenium surface by means of sulfur atom anchorage [29]. In the present work, however, the results shown in Figs. 3 and 4 suggest the occurrence of both forms of adsorption. Thus, for 0.3–1.8 ppm of thiophene the increase of the yield to citronellal may be related to the preferential planar adsorption of thiophene, (scheme A in Fig. 5) where the π-electrons of the aromatic thiophene ring interacts with the valence band of ruthenium, forming donor-acceptor complexes which favor the hydrogenation of the C=C bond over the remaining free ruthenium atoms. For higher thiophene coverage (3–4.5 ppm) preferential adsorption of the sulfur compound by S-anchorage form, with a strong Ru–S bond and probable formation of Ru^{+}–S sites, can occur. In such a case a decrease in the electronic density of the surrounding ruthenium atoms free of sulfur can be expected, this is, electron deficient $Ru^{\delta+}$ species will be in coexistence with Ru^{0}. From the point of view of activity and selectivity we can say that thiophene, together with a poisoning effect, modifies the adsorptive properties of the remaining free ruthenium atoms, but in a different way

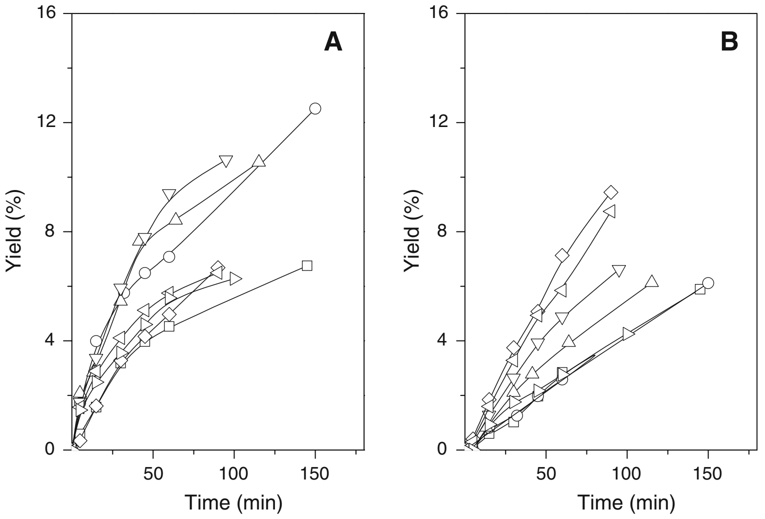

Fig. 4 Yields to citronellal (**a**) and, α, β-unsaturated alcohol (**b**) as a function of the time of reaction (up to 100 min) for the different thiophene concentrations over Ru/KL-N (□) 0 ppm, (○) 0.3 ppm, (△) 0.9 ppm, (▽) 1.8 ppm, (◇) 3.0 ppm, (◁) 4.5 ppm, (▷) 6.0 ppm

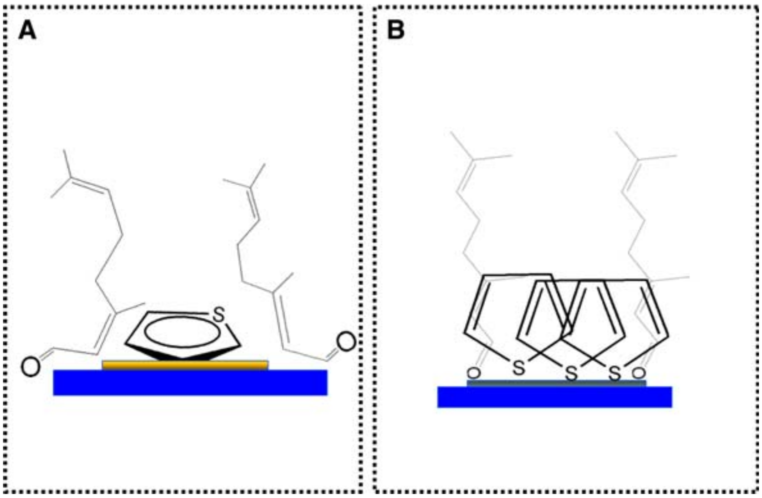

Fig. 5 Adsorption of thiophene on metal surfaces: **a** planar mode, **b** perpendicular mode by sulfur atom anchorage

depending on the surface coverage. That is, the thiophene concentration induces a balanced proportion of species adsorbed through the two modes, planar and non-planar. It is evident that the surface coverage by perpendicular anchored species and the $Ru^{\delta+}/Ru^{0}$ ratio increase with the increasing thiophene concentration. Under these conditions citral can preferentially chemisorbs on $Ru^{\delta+}$ through the more nucleophilic C=O bond, leading to the activation of the carbonyl group, which is hydrogenated by hydrogen activated on Ru^{0} in the close vicinity. Thus, the positive effect of $Ru^{\delta+}$ species, for unsaturated alcohols production, overcomes the negative effect of loss of active metal sites whenever, the thiophene content is lower than 4.5 ppm. For higher concentrations of poison, the overall balance of both effects is the progressive loss of activity and selectivity towards alcohols.

4 Conclusions

The effect of thiophene on the activity and on selectivity of Ru/KL and RuCu/KL catalysts for the selective hydrogenation of citral at 323 K and 4 MPa, is analyzed in the liquid phase, in a three-phase bubble reactor. Thiophene poisons the ruthenium atoms on which chemisorbs, but enhances the hydrogenation activity of the remaining free metal sites. Selectivity to the main reaction products is consistent with a competitive citral-thiophene adsorption, where the adsorption mode of thiophene seems to govern the preferential hydrogenation of either the C=O or the C=C conjugated bonds. Formation of $Ru^{\delta+}$ species, by effect of the electrophilic thiophene, in association with the reduced Ru^{0} enhances the hydrogenation of the carbonyl group to produce unsaturated alcohols, geraniol and nerol. This positive effect is maximum for thiophene concentration in the range 3.0–4.5 ppm.

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