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Synthesis of Ru, Rh and Pd complexes immobilized on modified supports. Investigation of the hydrogenation of cinnamaldehyde

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Summary — Cinnamaldehyde was hydrogenated over catalytic systems derived from Ru, Rh and Pd complexes immobilized on modified organic or mineral supports. It has been shown that selectivity for forming unsaturated alcohol could be improved by the use of weak base supports containing aliphatic or heterocyclic amino groups. The effect of the metal is also considered: the immobilized Ru complex shows a greater selectivity in the reduction of the carbonyl group than that obtained by catalytic systems containing Rh or Pd.

catalysis / hydrogenation / cinnamaldehyde / ruthenium catalyst / rhodium catalyst / palladium catalyst / silica support / resin support

Résumé — Préparation de catalyseurs à base de complexes du Ru, Rh et du Pd sur supports modifiés. Propriétés dans l'hydrogénation du cinnamaldéhyde. *L'hydrogénation de l'aldéhyde cinnamique a été effectuée en présence de catalyseurs à base de Ru, Rh, ou de Pd. Les solides ont été obtenus par fixation - échange de complexes organométalliques sur des supports organiques ou minéraux modifiés. Il a été montré que la sélectivité en alcool insaturé pouvait être augmentée par des supports à caractère basique contenant des groupements aminés, aliphatiques ou hétérocycliques. D'autre part, il a été observé que les complexes de ruthénium conduisent à des catalyseurs plus sélectifs que ceux obtenus à partir du rhodium ou de palladium.*

hydrogénation / cinnamaldéhyde / ruthénium catalyseur / rhodium catalyseur / palladium catalyseur / silice support / résine support

Introduction

The hydrogenation of α,β-unsaturated aldehydes into corresponding allyl alcohols is a topic of current interest in the field of metal catalysis. As a rule the heterogeneous catalytic systems are used in this process, but in some cases satisfactory results have been obtained with metal complexes. For instance, the hydrogenation of *trans*-retinal into *trans*-retinol was performed successfully over mononuclear hydridoruthenium complexes with triphenylphosphine and tris(*meta*-sulfophenyl)phosphine ligands [1, 2]. On the other hand many papers dealing with the application of metal complexes as catalytic precursors deal with the formation of metal particles on a support. For example, Blackmond et al [3] have used $[Ru(NH_3)_6Cl_3]$, $[Pt(NH_3)_4Cl_2]$ and $[Rh(NH_3)_5Cl]Cl_2$ complexes to disperse Ru, Rh, and Pt particles on activated carbons as well as on NaY and KY zeolites. These catalysts have been studied in the hydrogenation of cinnamaldehyde and 3-methylcrotonaldehyde [3]. Other catalysts for cinnamaldehyde reduction have been prepared from Ru-acetylacetonate impregnation on Al_2O_3 [4] or on carbon nanotubes [5]. This prompted us to investigate the catalytic behavior of hybrid catalysts prepared by linking metal complexes to solid supports.

It has been well established that the selectivity to unsaturated alcohols can be much improved by changing the supports. This is why the electronic and geometrical properties of the support are subject to extensive investigations [3, 6, 7]. This problem is more complicated in the case of catalysis with immobilized metal complexes. Since in many cases metal complexes are linked via chemical bonds to the support, the electronic donor-acceptor properties of the functional group of the support (which change the electronic density of the metal) must be taken into account. It is well known that the modification of supports by different ligands, in particular those with π-donor properties (amines, phosphines, etc), stabilizes complexes on the surface and prevents their degradation into metal species [8]. Moreover the results obtained by the modifications of the support can depend very much on the metal.

The aim of our work is to examine in detail the influence of the support on the catalytic behavior of the immobilized complexes in the hydrogenation of

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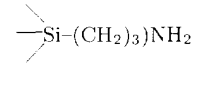
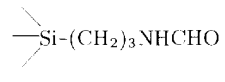
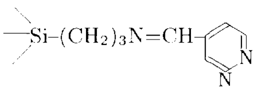
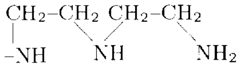
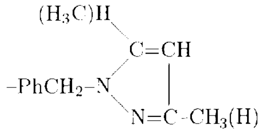
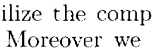
[*] Correspondence and reprints

Table I. Metal complexes and supports characteristics.

Complex immobilized	*Support*	*Functional group of the support*	*Parameters of support*
$[Rh_2(O_2CCH_3)_4]$ or $[Ru_2(O_2CCH_3)_4]$ or $[Pd(NH_3)_4Cl_2]$ or $PdCl_2$	γ-AMPS, weak base silica gel	 $Si-(CH_2)_3)NH_2$	$S = 120\ m^2 \cdot g^{-1}$ $NH_2 = 7 \times 10^{-4}$ groups·mg^{-1} macroporous
$[Ru_2(O_2CCH_3)_4]$	γ-PAS, weak acid silica gel	 $Si-(CH_2)_3NHCHO$	$S = 120\ m^2 \cdot g^{-1}$ $NH_2 = 7 \times 10^{-4}$ groups·mg^{-1} macroporous
$[Ru_2(O_2CCH_3)_4]$	γ-CAS, weak base silica gel	 $Si-(CH_2)_3N=CH-$	$S = 120\ m^2 \cdot g^{-1}$ $NH_2 = 7 \times 10^{-4}$ groups·mg^{-1} macroporous
$[Ru_2(O_2CCH_3)_4]$ or $[Rh_2(O_2CCH_3)_4]$ or $[Pd(NH_3)_4Cl_2]$	AN-511, granules, weak base resin		macroporous Gr = 0.65 mm, CN = 20%
$[Ru_2(O_2CCH_3)_4]$ or $[Pd(NH_3)_4Cl_2]$	MP-6204, weak base resin	$-Ph-CH_2-N(CH_3)_2$	macroporous, Gr = 0.47 mm, CN = 20%
$[Ru_2(O_2CCH_3)_4]$ or $[Pd(NH_3)_4Cl_2]$	MP-500, weak base resin	$-Ph-CH_2-N^+(CH_3)_3Cl^-$	macroporous Gr = 0.47 mm, CN = 20%
$Ru_2(O_2CCH_3)_4]$ or $[Rh_2(O_2CCH_3)_4]$	Polyorgs-IV, weak base resin		macroporous Gr = 0.54 mm, CN = 12%
$[Pd(NH_3)_4Cl_2]$	Amberlyst 31 Wet, strong acid	$-Ph-SO_3^- H^+$	gel, Gr = 0.76 mm, CN = 4%
$Ru_2(O_2CCH_3)_4]$ or $[Pd(NH_3)_4)Cl_2]$	K 2641, strong acid	$-Ph-SO_3^- H^+$	macroporous, Gr = 0.84 mm, CN = 20%

Gr: Granulometry, CN: crosslinker number.

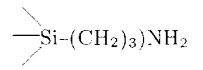
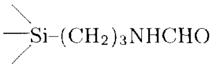
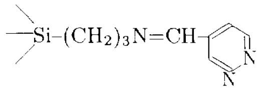
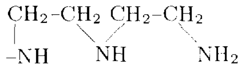
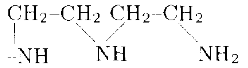
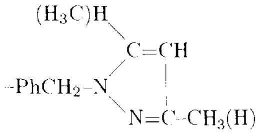
α,β-unsaturated carbonyl compounds (cinnamaldehyde), in particular the nature and the acid–base properties of functional groups of the support. The effect of the metal has been also studied via the grafting of Ru, Rh or Pd complexes on ion-exchange resins containing aliphatic or heterocyclic aminogroups as well as silica gels containing $-(CH_2)_3NH_2$; $-(CH_2)_3NHCHO$ and $-(CH_2)_3N=CH-$ N.

As for the metal precursor, the $[Pd(NH_3)_4Cl_2]$ complex can easily be transformed into Pd metal particles in the presence of usual supports. On the other hand polymers can stabilize the complex species without metal formation [9]. Moreover we have shown [10, 11], that the binuclear structure, as well as the acetate ligands Rh and Ru of tetraacetate complexes, were kept after fixation on supports containing amines. Due to bridging acetate groups and to the functional groups of the support, these immobilized complexes are stable even during the reduction step and represent convenient models of supported clusters.

We have also shown that Wilkinson-type Rh and Ru complexes ($MCl(PPh_3)_3$) are inert in the hydrogenation of the carbonyl group [12]. Moreover these complexes are able to react with the aldehyde carbonyl group according to the reaction

$$MCl(PPh_3)_3 \xrightarrow{R-CHO} M(CO)Cl(PPh_3)_2 + PPh_3 + RH$$

Table II. Activity of $[Ru_2(O_2CCH_3)_4]$ fixed on different and modified supports. S:Ru = 200:1, reaction temperature *T*r = 130 °C; activation temperature *T*a = 130 °C.

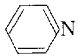
Support	*Functional group of the support*	*Wo, mol/mol·h*	*Conv (%)*
γ-AMPS, weak base silica gel	 $Si-(CH_2)_3NH_2$	9.7×10^{-2}	100 (23 h)
γ-PAS, weak acid silica gel	 $Si-(CH_2)_3NHCHO$	2.3×10^{-3}	10.2 (26 h)
γ-CAS, weak base silica gel		1.2×10^{-3}	10.0 (70 h)
AN-511, granules, weak base resin		5.6×10^{-3}	30.2 (72 h)
AN-511, powder, weak base resin		5.5×10^{-3}	24.5 (72 h)
MP-6204, weak base resin	$-Ph-CH_2-N(CH_3)_2$	5.9×10^{-3}	20.8 (72 h)
MP-500, strong base resin	$-Ph-CH_2-N^+(CH_3)_3Cl^-$	4.2×10^{-3}	25.5 (72 h)
Polyorgs-IV, weak base resin		3.1×10^{-4}	3 (72 h)
K 2641, strong acid resin	$-Ph-CH_2-SO_3^-H^+$	2.9×10^{-4}	0.6 (16 h)

with the formation of stable carbonyl metal complexes [13]. Thus poisoning of the metal complex catalyst by the substrate can occur. However our recent tests have demonstrated that $[Rh_2(O_2CCH_3)_4]$ and $[Ru_2(O_2CCH_3)_4]$ are inert when exposed to CO [14] and thus we have also chosen these compounds as catalytic precursors.

Experimental section

The Ru and Rh complexes presented in table I were obtained by processes given in [15]. The characteristics of the supports are also given in table I. γ-Aminopropyl containing silica gel (γ-AMPS) was obtained by treating the original silica gel with (γ-aminopropyl)ethoxysilane. The modified silica gels (γ-PAS and γ-CAS) were synthesized by treating γ-AMPS with a benzene/aldehyde solution at boiling point for 6–10 h and with a molar ratio amine/aldehyde = 1:10.

$$Si(CH_2)_3\ NH_2 + R\ CHO \longrightarrow Si(CH_2)_3\ N{=}CH{-}R$$

(where R = Cl or ).

The corresponding modifications of the supports were studied with IR analysis.

The ion-exchange resins Amberlyst-31-wet, K2641, MP 500, MP 6204 were supplied by Bayer. The anion-exchange resins AN-5ll and Polyorgs-IV were obtained from the Institute of Polymers, Moscow. A treatment by ethanol or by a mixture of ethanol and benzene was applied to eliminate low molecular weight impurities from these resins. Obtention of the OH^- form of some of these materials was achieved using a solution of 4% KOH in ethanol. The original complexes were fixed on the supports from stirred solutions at 20 °C and the resulting solids were washed in boiling ethanol. All these operations were carried out under argon.

The catalytic hydrogenation was carried out in a static reactor with a continuous flow of hydrogen at 120–180 °C using 0.1 mol cinnamaldehyde, 0.1 g catalyst, and 20 mL propylene carbonate as solvent. The catalyst was activated in situ at 180 °C prior to the aldehyde introduction. The values of the activity and the selectivity were obtained from gas-phase chromatographic analysis of the liquid mixture on a CPSIL8 capillary column. The activities presented in the following tables are the initial rates of reaction Wo (in mol of substrate converted/mol of metal · min or h).

Results

$[Ru_2(O_2CCH_3)_4]$ fixed on modified silica gels

As shown in table II the activity of the heterogenized systems was affected considerably by the support, especially by the functional groups fixed at the surface. The activity of the Ru complex immobilized on the silica gel containing γ-aminopropyl groups (γ-AMPS) was 15–80 times higher than that obtained by the fixation of the same complex on the -NHCHO (γ-PAS) silica gel or on γ-CAS silica gel substituted by a pyridine Schiff base. In contrast, the selectivity of the $[Ru_2(O_2CCH_3)_4]/\gamma$-AMPS system was significantly less than that of the Ru complex fixed on the weak base γ-CAS (table III). In the presence of the Ru complex immobilized on the weak acid γ-PAS, only the C=C bond was hydrogenated (table III).

Table III. Hydrogenation of cinnamaldehyde in the presence of $[Ru_2(O_2CCH_3)_4]$ fixed on modified silica gels. Influence of functional groups fixed on the support on the selectivity. S:Ru = 200 (400):1, T_r = 130 °C, T_a = 130 °C, [Ru] = 4.9–9.8 × 10^{-6} mol, [aldehyde] = 19.6 × 10^{-4} mol.

Support	*Conversion (%)*	*Ss ald (%)*	*Ss alc (%)*	*S uns alc (%)*
γ-AMPS	10	92.7	3.1	4.2
	25	91.0	4.0	5.0
	50	89.0	8.5	2.5
	90	81.5	15.5	3.0
γ-PAS	10	100	0.0	0.0
γ-CAS	10	73	0.0	27

s ald = saturated aldehyde (φ–CH_2CH_2CHO); s alc = saturated alcohol (φ–$CH_2CH_2CH_2OH$); uns alc = unsaturated alcohol (φ-$CH{=}CHCH_2OH$).

$[Ru_2(O_2CCH_3)_4]$ immobilized on the functionalized resins

The activities of the catalysts obtained by the fixation of diruthenium tetraacetate on the resins containing aliphatic amine groups were similar (table II). $[Ru_2(O_2CCH_3)_4]$ immobilized on modified Polyorgs-IV (a weak base resin containing methylpyrazole groups), as well as on K 2641 (a strong acid cation-exchanger with sulfonic acid groups), exhibited extremely low activity in the hydrogenation reaction (table II). The Ru complex fixed on MP-6204 (a weak base anion-exchanger containing tertiary amine groups) and on MP-500 (a strong base anion-exchanger with quaternary ammonium groups) had a significant selectivity for forming unsaturated alcohol (table IV). Using AN-511, a weak base anion-exchanger modified with chelating ethylenetriamine groups as a support, led to a greater selectivity to unsaturated alcohol (table IV). [It should be noted that, although the activity of $[Ru_2(O_2CCH_3)_4]$ fixed on AN-511 did not change when powdered, the selectivity improved considerably (table IV)]. The selectivity of $[Ru_2(O_2CCH_3)_4]$ immobilized on Polyorgs-IV was almost the same as when AN-511 was used as support (table IV).

Generally the activity of the catalysts obtained from the fixation of $|Ru_2(O_2CCH_3)_4|$ on the modified resins was less (about 16 times) than that obtained with the same complex immobilized on silica gel modified by γ-aminopropyl groups (γ-AMPS). This could be due to the formation of stable chelate complexes on the surface of the support as was demonstrated for the case of $|Na_2PdCl_4|$ supported on an anion exchanger modified with ethylene diamine [5]. On the other hand the selectivity for forming unsaturated alcohol when the anion exchanger was used as the support was three to ten times higher than that obtained with $|Ru_2(O_2CCH_3)_4|$ on γ-AMPS.

Table IV. Hydrogenation of cinnamaldehyde in the presence of $[Ru_2(O_2CCH_3)_4]$ fixed on modified supports on the selectivity. S:Ru = 200 (400):1, T_r = 130 °C, T_a = 130 °C, [Ru] = 4.9–9.8 × 10^{-6} mol, [aldehyde] = 19.6 × 10^{-4} mol.

Support	*Conversion (%)*	*Ss ald (%)*	*Ss alc (%)*	*S uns alc (%)*
AN-511, gran weak base	8.0	52.5	0.0	47.5
	25	80.0	5.0	15.0
AN-511, powder, weak base	8.0	53.5	0.0	46.5
	25	51.0	13.0	36.0
MP-6204, weak base	8.0	86.5	0.0	13.5
	25	74.0	9.4	16.6
MP-500, strong base	8.0	83.0	0.0	17.0
	25	86.7	4.3	9.0
Polyorgs-IV, weak base	2.5	56.0	0.0	44.0
K 6241, strong base	0.6	100	0.0	0.0

Fixed $|Rh_2(O_2CCH_3)_4|$

The activity of a Rh complex fixed on a γ-AMPS support was similar to that of a Ru complex (table V). However the Rh catalyst exhibited a 100% selectivity for saturated aldehyde. On an AN-511 support, Rh had a considerably higher activity than that of Ru (tables II, V). However the selectivity of Rh for unsaturated alcohol was in contrast about seven times less than that of a system containing Ru (tables IV, V). The results observed with the same Rh complex fixed on polyorgs-IV were quite the opposite of those observed with Ru tetraacetate (tables IV, V). This catalytic system has a relatively high activity similar to that of $|Rh_2(O_2CCH_3)_4|/\gamma$-AMPS catalysts and led to a 100% selectivity for saturated aldehyde (table V).

Table V. Activity and selectivity of $[Rh_2(O_2CCH_3)_4]$ immobilized on the modified supports in the hydrogenation of cinnamaldehyde. S:Rh = 200:1, T_r = 130 °C, T_a = 130 °C, [Rh] = 9.8 × 10^{-6} mol, [aldehyde] = 19.6 × 10^{-4} mol.

Support	*Conversion (%) (Wo mol/ mol·h* $\times 10^2$*)*	*Ss ald (%)*	*Ss alc (%)*	*S uns alc (%)*
γ-AMPS	90 (6.6)	100	0.0	0.0
AN-511	25 (5.5)	97.0	0.0	3.0
	50	92.0	1.0	7.0
Polyorgs-IV	90 (9.3)	99.5	0.5	0.0

Immobilized $|Pd(NH_3)_4Cl_2|$ and $PdCl_2$

The heterogenization of $PdCl_2$ on γ-AMPS produced a catalyst approximately 100 times less active than that obtained by the immobilization of $|Pd(NH_3)_4Cl_2|$ on the same support (table VI). Nevertheless the selectivity was the same in both cases. Table VI also shows that

Table VI. Hydrogenation of cinnamaldehyde in the presence of immobilized Pd complexes: influence of the support on the activity and the selectivity. S:Pd = 200:1, T_a = 130 °C, T_r = 130 °C.

Complex	*Support*	*Conversion (%) (Wo mol/mol·h)*	*Ss ald (%)*	*Ss alc (%)*	*S uns alc (%)*
$PdCl_2$	γ-AMPS	90 (3.0×10^{-2})	88.2	11.8	0.0
$[Pd(NH_3)_4Cl_2]$	γ-AMPS	90 (0.36)	96.0	4.0	0.0
$[Pd(NH_3)_4Cl_2]$	AN-511, weak base	10 (1.85×10^{-2})	77.5	5	17.5
		25	68.4	24.3	7.3
		50	62.0	33.0	5.0
		90	51.9	44.7	3.4
$[Pd(NH_3)_4Cl_2]$	MP-6204, weak base	10 (2.72×10^{-2})	94.0	0.0	6.0
		25	83.3	1.7	15.0
		50	76.0	13.0	11.0
		90	71.0	27.0	2.0
$[Pd(NH_3)_4Cl_2]$	MP-500, strong base	50 (4.5×10^{-2})	78.2	21.8	0.0
$[Pd(NH_3)_4Cl_2]$	Amberlyst 31 Wet, CN 4% strong acid	90 (0.23)	80.0	20.0	0.0
$[Pd(NH_3)_4Cl_2]$	K 2641, CN 20%, strong acid	90 (1.7)	70.0	30.0	0.0

the activity of the $[Pd(NH_3)_4Cl_2]$ complex was about 100 times greater when linked to the γ-AMPS support than to modified base resins. In contrast, in the presence of a strong acid cation exchanger the activity of Pd was the same (Amberlyst 31) or higher (K 2641) than that on γ-AMPS.

As regards the selectivity, it can be seen from table VI that the unsaturated alcohol was formed in an appreciable amount when the Pd complex was fixed on the weak base resins (AN 511 and MP 6204).

Discussion

Effect of the support

Unsaturated alcohol was formed with an appreciable selectivity when weak base supports contained aliphatic (AM-511) or heterocyclic (γ-CAS and Polyorgs-IV) amino groups with the capacity of chelating the metal complexes. This effect could be explained in relation to the characteristics of homogeneous systems, for which the mechanism of the carbonyl group hydrogenation includes the nucleophile attack of hydride (coordinated to the metal) on the carbon atom of the carbonyl group [17, 18]. The formation of such a hydride form of a metal complex with a hybrid catalyst might occur during the hydrogen pretreatment (depending on the hydrogen partial pressure). The activation process of $[Ru_2(O_2CCH_3)_4]$ and $[Rh_2(O_2CCH_3)_4]$ involves the splitting of one or two acetate ligands and the heterolytic addition of hydrogen [19, 20]:

$$[M_2(O_2CCH_3)_4] + H_2 \longrightarrow [HM_2(O_2CCH_3)_3] + CH_3COOH$$

where M = Rh, Ru.

Since the $[Ru_2(O_2CCH_3)_4]$ and $[Rh_2(O_2CCH_3)_4]$ complexes may coordinate without degradation with amino groups of the support (as was shown for γ-AMPS and Polyorgs-IV [10, 11]), an analogous activation process can be suggested when these complexes are immobilized on base supports. The hydrogen pretreatment of immobilized $Pd(NH_3)_4Cl_2$ leads to the complete splitting of the labile NH_3 groups and the formation of a hydride complex stabilized by the support ligands. It has been shown that the Pd(II) species are preserved by the polymer matrix via the electron-donor ligands [21]. The reactivity of the catalyst therefore depends on the electron-donor ability of the ligands of the metal complex. Most likely, the coordination with groups such as ethylenetriamine, methylpyrazole or substituted pyridines (Schiff bases) increases the nucleophilic properties of the metal in the immobilized complex. However, due to the formation of these highly coordinated stable metal complexes, the activity of the corresponding catalysts is rather low.

There is an alternative explanation for the increased selectivity when using supports containing amines. It is well known that one of the reduction paths for the carbonyl group over the immobilized transition metal complexes is a hydrogen transfer from donor to acceptor [22]. Such a reduction is promoted by basic compounds (organic or mineral) and proceeds via a Meerwein–Pondorf–Verley intermediate complex [23]. Thus, the carbonyl group of the unsaturated aldehyde could interact with the surface ligands facilitating the (>C=O) hydrogenation.

It would also be interesting to compare the tendencies observed for the supported metal and hybrid systems of the present study. Blackmond et al have established that in the case of Ru, Pt and Rh deposited on zeolites, the replacement of Na^+ compensating cations in the zeolite with K^+ cations results in an increase in the unsaturated alcohol selectivity [3].

This was explained by the increased electron density on the metal particles. The results presented in this paper also showed a correlation between the acid–base properties of the support and the selectivity trend in the hydrogenation reaction. In the case of immobilized metal complexes, the flexibility/rigidity of the support and the chelating ability of the grafted ligands may be involved such that there is a correlation between the basicity of the anchored amines and the selectivity for cinnamyl alcohol of Rh-containing systems. The unsaturated alcohol is formed only by using AN-511 as a support for the Rh complex, this being more basic than γ-AMPS or Polyorgs-IV. As for the Ru and Pd systems, the combination of the above-mentioned factors also influenced the hydrogenation. The deviation from the trend (ie, an increase in selectivity for forming unsaturated alcohol with an increase in support basicity) in the case of Rh and Pd complexes on the weak base AN-511 and strong base Amberlyst 31 Wet might be explained by the formation of chelating complexes between ethylamine ligands (AN-511) and the carbonyl compounds.

The supports containing heterocyclic amino groups (3(5)-methylpyrazole and pyridine, Polyorgs-IV and γ-CAS respectively) are of particular interest due to their well-developed π-electron systems, which can interact with a conjugated substrate. This interaction may provide an additional delocalization of the electrons in the carbonyl group and can therefore decrease the ability of the catalyst to hydrogenate the C=C bond. The influence of an increase in electron delocalization in the absorbed substrate on the selectivity towards a saturated aldehyde has been pointed out for the heterogeneous catalytic system [3]. Thus, although the basicity of the heterocyclic amines is lower than that of aliphatic ones, the selectivities towards cinnamyl alcohol achieved over $[Ru_2(O_2CCH_3)_4]$/Polyorgs-IV and $[Ru_2(O_2CCH_3)_4]$/AN-511 are almost equal. Flexible resins, in contrast to mineral supports, have the additional capacity to form chelate complexes on the surface. The selectivity for forming unsaturated alcohol using $[Ru_2(O_2CCH_3)_4]$/Polyorgs-IV is clearly greater than that obtained with the $[Ru_2(O_2CCH_3)_4]/\gamma$-CAS system.

Effect of the metal

The results obtained show that the activity of heterogenized catalysts containing Pd is significantly higher than that of Ru complexes immobilized on the same supports. The high activity of $[Pd(NH_3)_4Cl_2]$ fixed on strong acid anion exchangers (Amberlyst 31 Wet and K 2641) could be due to the Pd(0) particles or to the largely dispersed zerovalent Pd formed on the surface of the support during pretreatment and the reaction. It is known that acidic medium aids olefinic bond hydrogenation over heterogeneous Pd catalytic systems [24]. In contrast, the Ru complex $[Ru_2(O_2CCH_3)_4]$ has an extremely low activity on the same supports. The formation of metal particles probably does not occur here, which could be explained by the stabilizing effect of the bridge acetate ligands. Unlike the heterogenized Ru systems, the formation of unsaturated alcohol does not occur in the presence of $[Pd(NH_3)_4Cl_2]$ immobilized on γ-AMPS or a strong-base anion-exchanger MP-500.

Thus, the best results concerning the selectivity to form the unsaturated alcohol were obtained with an immobilized Ru complex $[Ru_2(O_2CCH_3)_4]$. The heterogenized Rh and Pd systems are more active in comparison with samples containing Ru but their selectivity to form unsaturated alcohol is less than that of the catalysts derived from a Ru complex.

Conclusion

The present work is an attempt to find new trends for the preparation of hybrid catalysts for the selective hydrogenation of α,β-unsaturated aldehydes. The catalytic systems were synthesized from the immobilization of Ru, Rh and Pd complexes on various modified mineral or polymer supports. Their activity and selectivity were tested in the hydrogenation of cinnamaldehyde, chosen as a model compound. The selectivity for forming unsaturated alcohol increases when using base supports containing electron-donor aliphatic or heterocyclic aminogroups and which form chelate complexes with metals. The metal also affects the catalytic properties: the best results regarding the selectivity to form unsaturated alcohol were obtained with an immobilized $[Ru_2(O_2CCH_3)_4]$ complex, while $[Rh_2(O_2CCH_3)_4]$ on the same supports catalyzes C=C bond hydrogenation. With Pd-containing solids the activity, rather than the selectivity, is more significant and this is partially due to the partial transformation of the metal precursor into Pd particles.

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