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Hydrogenation of aromatics under mild conditions on transition metal complexes in zeolites. A cooperative effect of molecular sieves

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The hydrogenation of aromatics, i.e. benzene, toluene, α-methylstyrene, anisole, and ethyl benzoate, can be carried out under a very low (1/12000) catalyst to substrate ratio, and mild reaction conditions (80°C, 6 atm of H_2O), on Rh and Ni organometallic complexes anchored on USY zeolites. A strong cooperative effect between the faujasite surface and the transition metal surface complex is thought to be responsible for the simultaneous enhancement of concentrations of arene and H_2 in the neighborhood of the catalytic centers, and for the observed electronic effects.

Keywords: metal transition complexes on zeolites; catalytic hydrogenation of aromatics; heterogeneization of homogeneous catalysts on zeolites

1. Introduction

Catalytic hydrogenation of aromatic hydrocarbons has long been dominated by heterogeneous systems containing group VIII metals as Ni, Pt, Ru and Rh [1]. When hydrogenation is attempted with homogeneous organometallic catalysts, the results are generally poor unless high pressure ($P \approx 20$ atm) and/or high catalyst/substrate ratios (~ 1 : 500 metal atom-g/mol reactant) are used [2]. Moreover, most of these catalysts should, in practice, be handled under carefully controlled conditions. Indeed, in many cases the complex may decompose and metal particles are formed in the very initial stages of the hydrogenation of arenes. These metal particles then act as catalyst. We report here that by anchoring transition metal complexes in micropores of modified faujasites, the complexes become stabilized, and their activity is greatly enhanced owing to a cooperative effect between the zeolite and the transition metal complex. With these catalysts it is possible to perform the hydrogenation of arenes under mild conditions, at catalyst/substrate ratios as low as 1/12000 (metal atom-g/mol reactant) and with high turnovers.

2. Experimental

The cationic Rh(I) complexes (**1a**, **1b**) with NN-bidentate ligands (2-(tert-butyl- and 2-(3-triethoxysilylpropyl-aminocarbonyl)pyrrolidine) were prepared by cleaving the Cl-bridge of the dimeric $[RhCl(COD)]_2$ (COD = cycloocta-1,5-diene) via the reaction with the corresponding NN-ligands in presence of a non-coordinative anion (PF_6^-). The Ni-complexes (**2a**, **2b**) were synthesized by ligand displacement in $Ni(acac)_2$ by the same NN-ligands [3]. The metal content of the different catalysts is given in table 1. The preparation of the nitrogen ligands has been reported previously [3]. A NH_4-Y zeolite (Si/Al = 2.4) was steam-calcined at 1023 K, followed by treatment with a 0.33 mol ℓ^{-1} citric acid solution at 403 K in order to generate pores of ~20 Å diameter [4]. The resulting sample was converted in the H^+, Na^+, or Cs^+ form by calcination of the NH_4^+ form, or by ion-exchange with a solution of Na^+ or Cs^+. To carry out the anchoring, the complexes (0.15 mmol in 10 ml of dry CH_2Cl_2) were added to 1.0 g of zeolite in dry toluene (50 ml), and the mixture was stirred at room temperature for 24–48 h. The solid was then separated and dried. The metal loading was determined by atomic absorption analysis of Rh and Ni, together with elemental analysis of C, H, N. The results are given in table 1. The immobilized catalysts are stable in air, and no special storage conditions are required.

The turnover numbers presented in table 2 were calculated for the maximum

Table 1
Organometallics on metal content of the zeolite catalysts

Sample	Type of metal	Amount of metal (wt%)
Zeol–**1b**	Rh	0.83
NaZeol–**1b**	Rh	0.72
CsZeol–**1b**	Rh	1.07
Zeol–**2b**	Ni	0.89
NaZeol–**2b**	Ni	0.60
CsZeol–**2b**	Ni	0.92

Table 2
Turnover number[a] for hydrogenation of arenes catalyzed by Rh- and Ni-complexes (catalyst/substrate = 1/12000)

Compounds	**1a**	**2a**	Zeol–**1b**	Zeol–**2b**	NaZeol–**1b**	CsZeol–**1b**
benzene	721 (5)[b]	177	1587	1200	2282	2894
toluene	189 (4)[b]	106	344	347	451 (368)[c]	647 (532)[c]
α-Me-styrene	122[d]		225	106	515	994
anisole	54 (>30)[e]	0	160	74	779	945
ethyl benzoate	54 (>30)[e]	2 h-15%	302	186	492	560

[a] Based on corresponding cyclohexane monitored by GLC.

[b] Estimated induction period (h) in brackets.

[c] Corresponding turnover number of Ni-catalysts in brackets.

[d] Turnovers for aromatic ring reduction obtained after total hydrogenation of double bond.

[e] Decomposition of catalyst before total reduction takes place.

rate (usually 0–40% conversion) and are expressed in converted molecules of substrate per metal atom per hour.

The aromatic compounds were hydrogenated in a batch reactor (Autoclave Engineers) of 100 ml capacity at 353 K and 6 atm of hydrogen. The substrates were added to a solution, or suspension, of the catalyst in freshly distilled ethanol (50 ml). The reaction was monitored by GLC on a S30 column, using nitrogen as carrier gas. After hydrogenation, the heterogeneized catalyst was separated by filtration and recycled.

3. Results and discussion

In preliminary experiments, it was checked that no hydrogenation occurred in the absence of the catalyst. To determine if some leaching of metal occurred, the possible presence of Rh in the reaction solution was analyzed after the reaction occurred and the catalyst was filtered. No Rh was detected. The Rh content of the filtered catalyst was also analyzed and the differences observed with respect to the original were within the error limits. In any case, and in order to check if traces of Rh which could be leached and not detected by our analysis were responsible for the hydrogenation, an experiment was carried out in which the liquid left after catalyst filtration, still containing 50% benzene, was further reacted. However, no additional benzene hydrogenation occurred. A similar experiment was then performed in which the more easily hydrogenated cyclohexene, was added to the solution left after catalyst filtration. After 3 h under reaction conditions, no hydrogenation of cyclohexene was observed. Therefore, we can conclude that no leaching of the complex occurred during reaction, and the catalytic activity is only due to the complex–zeolite catalyst.

When the unsupported Rh complex (**1a**) was used as catalyst for the hydrogenation of aromatics, an induction period (sigmoid reaction profiles) was observed. Benzene hydrogenation is presented as an example in fig. 1. However, when the above complex was included in an ultrastable HY zeolite (Zeol–**1a**) no induction period was present (fig. 1) indicating that the catalytic active species were in this case very rapidly produced from their precursor.

Under the reaction conditions indicated in table 2, and using the zeolite containing the Rh complex, complete hydrogenation of benzene, toluene, α-methylstyrene, anisole and ethyl benzoate was achieved after reaction times of 6, 18, 24, 100 and 70 h, respectively. The complex **1a**, when supported by the zeolite, remained stable and was recycled four times preserving the catalytic activity. Moreover, table 2 shows that when the Rh-complex was anchored in the ultrastable HY zeolite, the turnover numbers increased at least twice for the hydrogenation of benzene, toluene and α-methylstyrene, while no hydrogenolysis was observed. The Ni organometallic complex **2a** was less active than the corresponding Rh-complex (**1a**), and its activity and stability also increased after anchoring in the zeolite.

When anisole and ethyl benzoate were hydrogenated using the unsupported organometallic catalysts (**1a**, **2a**) the complexes decomposed with time, so that 100% conversion could not be achieved. However, they remained stable when anchored through the silyl group in the zeolite and the reaction could be completed.

The positive influence of the zeolite microenvironment can be explained, to a first approximation, in terms of a cooperative effect of the molecular sieve owing to an increase in the concentration of reactants inside the pores. Concentration effects in zeolites result from the high adsorption capacity of these materials, especially at low temperatures. This leads to increased concentrations of the reactants inside the cavities and strongly enhances the rate of bimolecular reactions. Indeed, it has been shown that H_2 is adsorbed and polarized in zeolites even at temperatures as

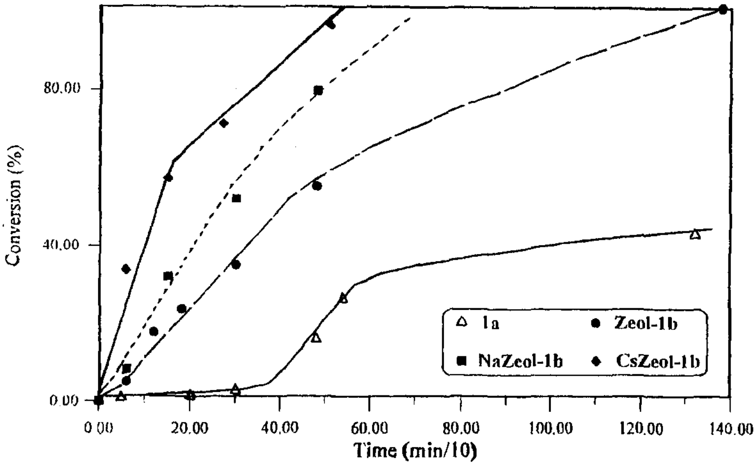

Fig. 1. Hydrogenation of benzene with different Rh-catalysts. Catalyst/substrate ratios are 1/22500 and 1/5900 units for supported and unsupported catalysts, respectively.

low as 77 K [5]. In our case when the adsorption of H_2 was carried out on the H-ns Y zeolite, at the temperature of reaction (353 K) and 100 Torr of constant pressure, 2×10^{-15} mol of H_2 per gram of zeolite were adsorbed. This indicates that in the case of the zeolite based catalyst there is a higher concentration of H_2 in the vicinity of the active sites compared to that in the liquid phase. Also, arenes can generally be adsorbed on the cations, and on the 12-ring oxygens of the zeolite framework [6]. By such adsorption effects, the concentrations of benzene and hydrogen are expected to increase simultaneously in the neighborhood of the metal active sites, and the reaction rate therefore is enhanced (table 1). Furthermore, when benzene is adsorbed on the faujasite zeolites, an increase in benzene–oxygen interaction with framework basicity occurs [6,7]. Meanwhile, it has been shown [6] that when going from a Na^+ to a Cs^+ faujasite the amount of benzene adsorbed on 12-ring windows increases, whereas it decreases on the cations. If adsorption occurs on the oxygens of the 12-ring windows, benzene can be considered as a slightly acidic molecule interacting with the framework oxygen of the zeolite and electron transfer from the zeolite framework to the aromatic ring may take place to some extent, allowing the molecule to be activated for hydrogenation. In order to theoretically check this assumption, the mean oxygen charge (i.e., the basicity of the framework) was calculated for HY, NaY and CsY zeolite, and the calculated Sanderson's electronegativity [8] of the three zeolites is 4.2, 3.7 and 3.4, being the average oxygen charge of −0.23, −0.32, and −0.37, respectively. From the above hypothesis and taking into account the basicity of the framework oxygens one should expect an increase in catalytic activity, when going from HY to NaY and CsY zeolite supported catalysts. This is consistent with our experimental results (table 2). It appears then, that besides concentration effects, electronic effects can also have an influence on the activity.

4. Conclusions

It has been shown here that when Rh- and Ni-complexes are covalently anchored via a silyl group on a faujasite type zeolite containing supermicropores their stability is greatly enhanced. In this situation they are able to hydrogenate aromatics with high efficiency under very mild conditions and with very low catalyst/substrate ratios. The catalysts can be recycled several times without losing activity. The turnover numbers for the complexes increase when these are anchored on the zeolite, probably as a consequence of both concentration and electronic effects.

Thus, the high activity of Rh- and Ni-complexes in zeolites, together with their easy handling, high stability to air and moisture, easy separation from the reaction mixture and the stable catalytic activity (recycling), make these catalysts a real alternative for the heterogeneous hydrogenation of aromatics under mild conditions.

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