

## **Ru/BEA CATALYSTS FOR SELECTIVE AND STEREO SELECTIVE HYDROGENATION OF PROSTAGLANDIN INTERMEDIATES**

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Ru-BEA catalysts with 5.0wt% Ru were prepared following an "ionic exchange" procedure. These catalysts were investigated using pyridine (Py), 2,6-di-tert-butyl-pyridine (DTBPy), CO-FT-IR spectroscopy and H<sub>2</sub>-chemisorption and were tested in the diastereoselective hydrogenation of a prostaglandin intermediate enone. The relation between the activity, the chemoselectivity to allylic alcohol, the diastereoselectivity, and the metal particle size and the acidity of the support was investigated. The effect of the hydrogen pressure, the substrate/Ru ratio and the reaction time was also studied. It was found that by modification of these properties and of the reaction parameters it is possible to "tune" the activity and selectivity of the catalyst in the investigated hydrogenation reaction.

### **Introduction**

The selective hydrogenation of  $\alpha,\beta$ -unsaturated compounds to produce allylic alcohols has recently attracted much attention because of its importance in the fine chemicals and pharmaceutical industries [1-3]. Studies done up to now in heterogeneous catalysis showed that this reaction may be influenced by modifying the surface properties [4], the presence of the promoters [5], with changes in the metal particle size and morphology [6] or with changes in the nature of the support. Some other authors suggested that the improvement of the chemoselectivity to allylic alcohol was related to the presence of Lewis acidity [7].

BEA zeolite currently received much attention as a potential catalyst in many reactions [8]. In addition to its Brønsted acidic properties, BEA zeolite displays Lewis acidity as well. This Lewis acidity is generated by the extra-framework aluminum species (as is known for USY samples [9]), and also by the framework aluminum atoms in a non-tetrahedral environment. On the other side the replacing of the H or Na compensating cations in zeolites with K cations leads to an increases of the selectivity to unsaturated alcohol [3, 10-11].

In the present paper ruthenium was supported on H-BEA and ion-exchanged K-BEA zeolite supports and were studied in the liquid-phase, batch hydrogenation of a prostaglandin intermediate (PGF<sub>2 $\alpha$</sub> ). Earlier work of our group [12] showed that the

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microporous structure of zeolites imposed molecular constraints on the mobility of the organic, bulk substrate within pores containing metal clusters and favored the so-called “exo-selectivity” in the hydrogenation of large enones. Therefore, the reaction occurred selectively and diastereoselectively on the metal clusters mainly exposed on the external surface of the zeolites.

Zeolite supports induce the possibility of metal-support interactions in addition to shape selectivity or geometric hindrances. H-BEA and K-exchanged H-BEA were chosen in the present study to investigate the effect of the type of neutralizing cation on the selectivity. Cation effects in Ru/Y zeolites have been observed in CO hydrogenation reactions [13]; where increased basicity of the cation resulted in a decrease in the capacity for C=C hydrogenation of primary olefinic products.

## Experimental

HBEA zeolite (PQ,  $\text{SiO}_2/\text{Al}_2\text{O}_3=21.6$ ;  $S_{\text{sp}}=739 \text{ m}^2/\text{g}$ ) was used as received and was modified to produce KBEA support. In this modification, the HBEA was exhaustively ion-exchanged with potassium from an aqueous solution of KCl (0.1 M and 1g solid / 100 ml solution) at room temperature, for 24 h, under stirring. After separation by filtration the solid was washed, dried at 333 K, for 4 h, and calcined at 723 K, for another 4 h, in air flow (1 K/min). Chemical analysis revealed that 92% of the H was exchanged for K in this procedure.

Ru-loaded zeolite catalysts were prepared by the impregnation of the HBEA and KBEA supports with  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  ( $3 \times 10^{-2} \text{ M}$ ) as follow: (a) impregnation at room temperature (HBEA or KBEA supports), for 36 h, and then at 353 K, for another 12 h. After that, the catalyst was dried at 333 K for 4 h, and reduced at 623 K, for 4 h, in  $\text{H}_2$  flow (1K/min). The obtained catalyst was named Ru-H and Ru-K; (b) part of the Ru-H catalyst was promoted with potassium in a second impregnation step from an aqueous solution of KCl (0.1 M KCl, 1 g solid / 100 ml solution) to give a molar ratio of  $\text{K}^+:\text{Ru} = 20:1$ . After separation, the catalyst precursor was washed and dried at 333 K, for 4 h, and reduced at 623 K, for another 4 h, in hydrogen flow (1K/min). The catalyst was named RuH-K. After reduction, all catalysts contain 5.0 %wt.Ru.

For the catalysts characterization, the FT-IR measurements were recorded at 4000 to 400  $\text{cm}^{-1}$  region at room temperature on a Magna-IR system 550 FT-IR (Nicolet) spectrometer using a MCT-B liquid nitrogen cooled detector, and equipped with a heatable cell (up to 773 K) with NaCl windows connected to a vacuum system and a gas manifold. Samples in the form of self-supporting pellets (around 5  $\text{mg}/\text{cm}^2$ ) were placed into a carousel sample holder for up to 6 pellets. Usually 200 scans were recorded at a resolution of 2  $\text{cm}^{-1}$  for a single spectrum. IR spectra were normalized to the weight of 10  $\text{mg}/\text{cm}^2$ . Prior to adsorption of the base the samples were dehydrated by evacuation at 673 K, overnight. The molecule of base like Py was adsorbed at room temperature for 30 min on dehydrated samples, while DTBPy molecule was adsorbed at 423 K. Desorption was carried out by evacuation (vacuum better than  $10^{-4}$  Torr) for 30 min, at each temperature step up to 673 K. The adsorption of CO was carried out in two steps, at 35 Torr and 95 Torr, respectively, at room temperature, for 30 min, followed by evacuation to  $10^{-5}$  Torr. Desorption experiments

were performed by heating the adsorbed samples at different temperatures (373, 423, 473, 523 and 623 K) under vacuum. Except the experiments with CO, the maximal desorption temperature was of 673 K. In the case of CO, the maximal desorption temperature was 643 K when the CO is completely eliminated.

H<sub>2</sub>-chemisorption measurements were carried out using a Micromeritics ASAP 2010C apparatus. The reduced samples were evacuated, first at 393 K and then at 723 K. Soon after, a hydrogen flow was passed initially at 308 K for 15 min and then temperature was increased at 723 K at a heating rate of 10 K/min and maintained for 2 h. After reduction, the samples were purged with a helium flow at 690 K for 2 h and then at 308 K for another 30 min. The amounts of chemisorbed hydrogen were measured at 308 K by the desorption method after equilibration for 45 min in 300 Torr of adsorbate. The total hydrogen uptake was determined by extrapolating the linear portion of the adsorption isotherm to zero pressure. Reversible H<sub>2</sub> sorption was measured by out gassing at  $5 \times 10^{-5}$  Torr at the adsorption temperature and running a second isotherm. The difference between the total and reversible uptakes was ascribed to irreversible hydrogen. The particle sizes were determined assuming a H : Ru stoichiometry of 1.

The liquid-phase hydrogenation reactions of the prostaglandin intermediate were carried out in a well-stirred batch autoclave under 2-6 atm of hydrogen at room temperature using 25-50 mg of catalyst (1,25 – 2,5 mg of Ru) and 15-50 mg of prostaglandin intermediate (substrate/Ru molar ratio = 2-30). Methanol (7 ml) was used as a solvent.

## Results and discussion

FT-IR measurements shows that following the described preparation procedure Ru did not occupied any cationic position in the zeolite framework. No band in the spectral region 800 – 1000 cm<sup>-1</sup> was detected indicating any perturbation of the zeolite framework by these cations. The deposition of ruthenium by ion exchange implies that some Ru ions should act as charge compensating ions that is not the case here. As we previously shown [14] hydrolysis of ruthenium cations is also very probable. The reduction of these cations with hydrogen may result in a generation of protons, whereas reduction of oxo-ions, such as [Ru-O]<sup>+</sup>, will lead to the formation of water molecule and a proton. Py adsorption reveals the presence of strong Lewis acid sites, as characterized by the  $\nu_{8a}$  band at 1620 cm<sup>-1</sup> and of Brönsted acid sites, as characterized by the  $\nu_{8a}$  band at 1638 cm<sup>-1</sup>. A simple comparison of the intensity of the  $\nu_{19b}$  bands at 1445 and 1545 cm<sup>-1</sup>, characteristic to Lewis and Brönsted acid sites, suggests that in all catalysts Lewis sites are dominant. However, both the Lewis and Brönsted sites are enough strong to be determined even after the samples were out gassed at 623 K. In the case of Ru-K and RuH-K samples the intensity of the band characteristic to Lewis acid sites is even higher. This is a consequence of the fact that an important amount of Brönsted acid sites disappear as a result of the ion-exchange process with potassium chloride.

DTBPy-FT-IR spectra shows bands at 3370, 1616, and 1530 cm<sup>-1</sup> which can be assigned to DTBPyH<sup>+</sup> ion and which can, in principal, be used to survey Brönsted acid sites [15]. The intensity of these bands strongly decreased in the case of Ru-K and RuH-K samples. Even so, in all catalysts, irrespective of the support nature, an easy penetration of DTBPy into the

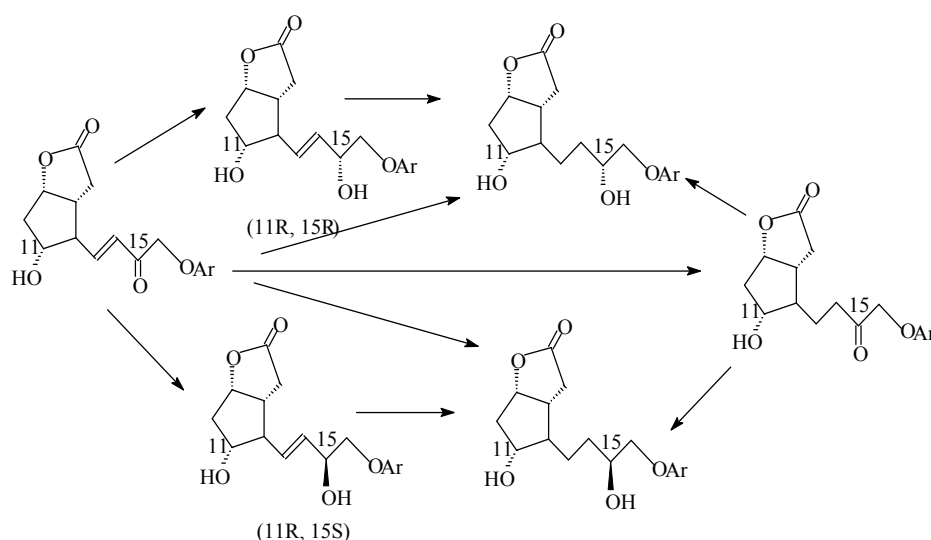
BEA pore network and a complete disappearance of the OH acidic band at  $3610\text{ cm}^{-1}$  was observed which suggested a large accessibility and the formation of large bidimensional patches.

CO-FT-IR spectra of the reduced samples shown for all samples four bands at  $2110$ ,  $2102$ ,  $2095$  and  $2088\text{ cm}^{-1}$ . The intensity of the band centered at  $2088\text{ cm}^{-1}$  slowly increased in the case of Ru-H and RuH-K samples. According to literature [16], the CO vibrational bands at  $2163$  and  $2110\text{ cm}^{-1}$  correspond to CO bonded to an irreducible  $\text{Ru}^{n+}$  in strong interaction with the support; the one at  $2088\text{ cm}^{-1}$  is due to the Ru carbonyl, and the bands at  $2102$  and  $2095\text{ cm}^{-1}$  to the multiple adsorption of CO on reduced Ru particles. The position of the CO bands in these spectra may account to the size of the supported species. For alumina-supported ruthenium catalysts, Dalla Betta [17] indicated that the band at  $2028\text{ cm}^{-1}$  might be attributed to particles of  $90\text{ \AA}$  while smaller bands near  $2140$ ,  $2080$  and  $2040\text{ cm}^{-1}$  corresponded to particles of  $60\text{ \AA}$ . The same behaviour was observed by other authors [16, 18]. The first band may correspond to highly dispersed Ru, the second to clusterized Ru, which by adsorption of CO yields a carbonyl cluster, and the third to Ru metal particles with a diameter equally or greater than  $1.0\text{ nm}$ .

In correlation with CO adsorption results, the hydrogen chemisorption on Ru-H and Ru-K gave metal particle sizes of  $1.3$  and  $1.8\text{ nm}$  respectively, based on the irreversible hydrogen chemisorption and on the assumption of a five-sided cube for particle morphology.

The deposition of Ru on the zeolite surface could occur in several ways both on Al sites and framework silanols, following an ion-exchange and grafting mechanism [14]. Py-FT-IR analysis indicated the consumption of the zeolite Brønsted sites but in this process occurred Ru did not occupied any cationic position in the zeolite framework. CO-FT-IR analysis indicated that irrespective of the support nature, at least four species could be formed. Anyway, it seems that the main species are the irreducible  $\text{Ru}^{n+}$  species.

The possible paths of prostaglandin intermediate hydrogenation are given in Scheme 1.



*Scheme 1. Possible pathways in the hydrogenation of prostaglandin intermediate*

Catalytic results obtained in the presence of Ru-H, Ru-K and RuH-K samples are listed in Table 1:

**Table 1. Influence of the acido-base properties upon the catalytic performances (6 atm of hydrogen, substrate/Ru ratio = 7; reaction time 15 min).**

Catalyst	Ru-K	Ru-H	RuH-K
Conversion, %	77.98	93.94	81.22
Selectivity to allylic alcohol, %	11.04	0.31	0.95
D.e. (configuration), %	80 (R)	racemic	10.50 (S)

As is shown in Table 1, a high acidity of the support favors the hydrogenation of C=C double bond. On Ru-K catalyst, the selectivity to allylic alcohol increases, in agreement with the literature reports [3, 10-11]. The acid strength of the protons in BEA zeolite decreases if protons are changed with potassium. This decrease in acidity results in greater electron density on the small metal particles onto the zeolite support. An increase in charge density of the metal may cause a suppression in the C=C hydrogenation rate by enhancing the delocalization of electrons in the adsorbed conjugated substrate. Selectivity to allylic alcohol would thus be enhanced.

Other suggestions have been made to describe the apparent electronic effects of alkali species on adsorption and reaction on metal catalysts. Therefore, the higher selectivity to allylic alcohol may be due to the combination of an increase in the C=O hydrogenation rate due to direct C=O-K interactions and a decrease in the C=C hydrogenation rate due to suppression of C=C-Ru interaction because of increased electron density of the metal particles.

The diastereoselection is also influenced by the acidic-base properties of the catalyst. Therefore, for a more basic catalyst (Ru-K sample) the formation of the *epi-configuration* of allylic alcohol (80%) is favored whereas for an acidic one (Ru-H sample) the allylic alcohol obtained is in *racemic form* (Table 1). The addition of alkali promoter to Ru-H catalyst (the RuH-K sample) results in a significant change in the diastereoselection from the *epi-configuration* to the *natural* one. The selectivity in allylic alcohol is not much increased in this case.

It is very well known that under homogeneous conditions, the stereoselectivity may be predicted and controlled considering the Cram rules [19] and the properties of the ligands exhibit a crucial contribution in such processes. To generate and control the diastereoselectivity is more complicated in heterogeneous catalysis conditions. The catalysts used in these reactions generally involve supported metal species with relatively low dispersions. Such catalysts are obtained by deposition of a relatively high amount of metal, usually higher than 5 wt.%, which determines a quite large reduction in metal surface area [20]. In addition, many of the molecules subjected to diastereoselective reactions are quite large. Very recently we have shown that when using mesoporous molecular sieves as support, the porous structure can also exhibit an influence on the stereoselective reactions [21]. Therefore, experiments carried out using MCM materials showed that the pore diameter is large enough to be penetrated by molecules as large as prostaglandin intermediates and could, furthermore, allow better stereoselectivities in hydrogenation reactions. But on almost all porous catalysts the reactions occur on the external surface, the pores being inaccessible for these molecules [22]. This is also the case of employing BEA zeolite as carrier for ruthenium species. Therefore, the hydrogenation

reaction takes place in fact on the active sites located on the external surface of the support. In this case we can not talk about a possible sterically hindered due to of the support pores.

The variation of the conversion, the chemoselectivity to allylic alcohol and the d.e. to epi-configuration, as a function of the hydrogen pressure, on Ru-K catalyst, is shown in Figure 1. The conversion increases with the hydrogen pressure whereas the chemoselectivity to allylic alcohol and the d.e. in epi-configuration decreases with the same parameter.

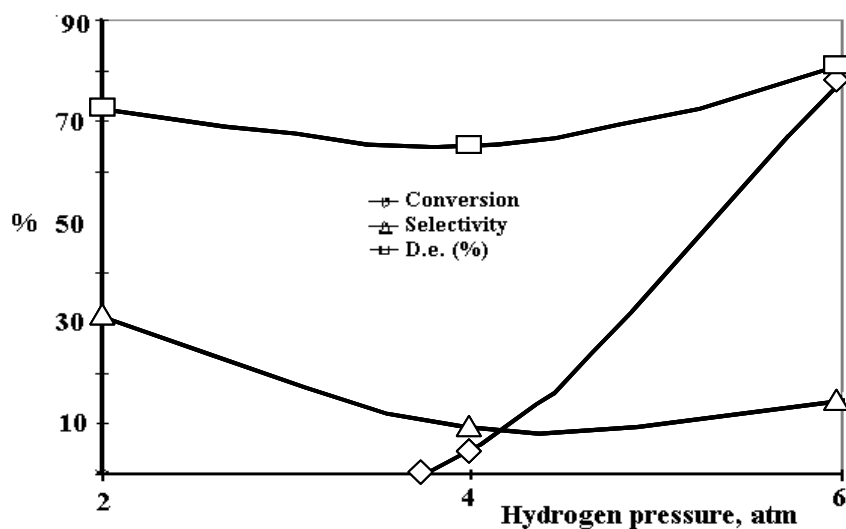


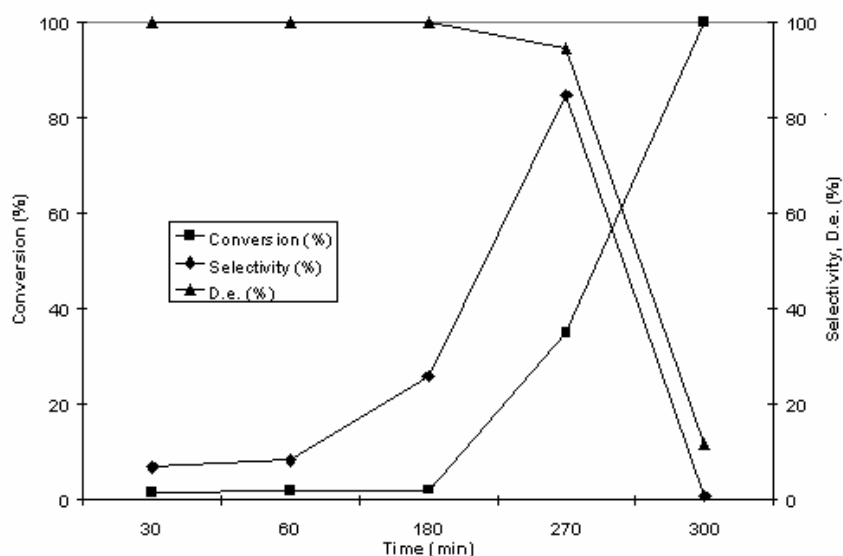
Fig. 1. The variation of the conversion, the chemoselectivity to allylic alcohol and the diastereoselectivity as a function of the hydrogen pressure (RT, 25 mg Ru-K catalyst, substrate/Ru=7, 15 min)

A high hydrogen pressure will ensure not only a high amount of hydrogen present in the gas phase but also will increase the gas/liquid transport and the solubility of the gas in the liquid phase. These factors increase the availability of the hydrogen to the catalyst. For 2 bars of hydrogen, the selectivity to allylic alcohol may reach almost 31% with a d.e. in epi-configuration higher than 70%, but the conversion is only few percent. An increase of hydrogen pressure will lead to an advanced hydrogenation of the allylic alcohol to saturated alcohol decreasing in this way the chemoselectivity to allylic alcohol.

The catalytic activity, the chemoselectivity to allylic alcohol and the diastereoselectivity to epi-configuration was also influenced by the substrate/Ru ratio. For a substrate/Ru ratio higher than 12, the d.e. to this configuration started to decrease (till almost 20%). The fact that the d.e. decreased parallel with the chemoselectivity to allylic alcohol may be an indication that the epi-configuration of allylic alcohol was faster transformed in saturated alcohol than the natural one. The best chemoselectivities to allylic alcohol and d.e. to epi-configuration were obtained at low hydrogen pressure (2 atm) and at low substrate/Ru ratio (Ent/Ru=7) but in these conditions the conversion was very low. Varying the quantity of the catalyst in the reaction medium is also a way of modifying the hydrogen availability to the catalyst. A larger quantity of catalyst represents, in fact, a

larger liquid/solid interfacial area. A given concentration of dissolved hydrogen is spread over this area so the concentration per unit area is smaller. Therefore, an increase of the catalyst amount (substrate/Ru=2) will have the same effect as the hydrogen pressure.

The variation of the conversion, the selectivity to allylic alcohol and the d.e. as a function of the reaction time shown that the chemoselectivity to allylic alcohol has a maximum at 84.6% with a d.e. of 94.3% to epi-configuration, for a conversion of 34.8%, after 270 min (Figure 2).



**Fig. 2.** The variation of the conversion, the chemoselectivity to allylic alcohol and the d.e., on 5%Ru/K-BEA catalyst (50 mg catalyst, 2 atm, substrate/Ru=2)

## Conclusion

The deposition of Ru on the zeolite surface could occur in several ways both on Al sites and framework silanols, following an ion-exchange and grafting mechanism. Therefore, the process implies that some Ru ions should act as charge compensating ions. The FT-IR analysis of the catalysts showed that the acidity is especially due to the ruthenium species deposited on the support surface. Remaining Brønsted acidity makes an important contribution in controlling the catalysts activity. Replacing of the H<sup>+</sup> compensating cations in the BEA zeolite with K<sup>+</sup> cations and an optimisation of the parameters of the reaction can lead to very good results. For instance, on Ru-K catalyst, for a conversion of 34.8%, the chemoselectivity to allylic alcohol may reach 84.6% with a d.e. to epi-configuration of 94.3%. The addition of alkali promoter (K<sup>+</sup>) to the Ru-H catalyst result in a significant change in the diastereoselection from epi to natural-configuration but the chemoselectivity to allylic alcohol is not much improved in this case. These results can be explained if we take into account the effect of the alkali cations and of the ruthenium particle size.

Therefore, to be an active and selective catalyst there is an ideal combination between the nature of the ruthenium particles (as chemical nature and particles size) and the catalyst acidity. These results show that the catalyst can be “tuned” to give enhanced activities and chemoselectivities to allylic alcohol.

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