



Transformation of 5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-one over Ru-containing BEA zeolites

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Abstract

Ru–BEA catalysts with 1.0–2.5 wt.% Ru were prepared by ion exchange. The acidic properties of these catalysts were investigated using deuterated acetonitrile, pyridine, and 2,6-di-*tert*-butyl-pyridine. The deposited Ru was studied by CO-FTIR spectroscopy. The materials were tested as catalysts in the hydrogenation of a conjugated cyclic keto–enol, namely, 5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-one. Beside hydrogenation, hydrogenolysis products were identified by GC–MS and ¹H NMR techniques. Relations were sought between the selectivity and some physicochemical properties of the catalyst.

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1. Introduction

The selective hydrogenation of unsaturated carbonyl compounds is a very important step in the preparation of fine chemicals [1–3]. In the specific case of hydrogenation of α,β -unsaturated carbonyl compounds to allylic alcohols, most efforts have been focused on the selective hydrogenation of aldehydes, such as cinnamaldehyde, citral, crotonaldehyde [4–13], and benzaldehyde [2,14]. Heterogeneous hydrogenation of unsaturated ketones has also been reported [15,16]. Since many unsaturated carbonyl compounds contain aromatic rings, hydrogenation of the carbonyl group was expected to compete with hydrogenation of the benzenic ring. However, the literature reported no ring hydrogenation of these molecules but indicated the occurrence of hydrogenolysis pathways [3,17]. Most of the

by-products arised from the direct hydrogenolysis of the aryl–carbonyl C–C bond [17]. Thus, toluene and benzene were suggested to result from the hydrogenolysis of benzyl alcohol and benzaldehyde, respectively [18].

The nature of the catalyst controls both the activity and chemoselectivity in such reactions [3]. The observed effects were attributed to changes in the properties of the active metal phase by interaction with the support. However, many authors stressed the differences in hydrogenation of α,β -unsaturated aldehydes and ketones. In the last case, the hydrogen-transfer approach (MPV: Meerwein–Ponndorf–Verley) may provide a better solution to enhance the chemoselectivity to allylic alcohol than the traditional way of using molecular hydrogen [19–21]. Typical reducing reagents are unsaturated hydrocarbons such as cyclohexene or cyclohexadiene, primary or secondary alcohols like methanol, benzyl alcohol or 2-propanol, and formic acid. However, an important disadvantage of MPV reduction is the very long reaction time. Therefore, the chemoselective hydrogenation of α,β -unsaturated ketones

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still is a challenge. Several recent reports illustrate that by an appropriate choice of the metal (Ru, Au, Pt or Ir) and support, it is possible to hydrogenate chemoselectively unsaturated ketones to the corresponding allylic alcohols [16,22–24]. It has also been shown that the acidity of the support is a critical point in obtaining high yields of allylic alcohols. Since, in previous works, most of our attention has been devoted to chemoselective reduction over supported Ru [25–27], we decided to investigate the combination of Ru with H-BEA zeolite as a support.

The aim of this study was to examine the nature of the acidity (Lewis or Brønsted) after deposition of Ru on BEA zeolite, and to use these catalysts for the hydrogenation of a conjugated cyclic keto–enol, namely, 5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a,c*]cyclohepten-6-one. Both the MPV and molecular hydrogen routes have been investigated. Such a reaction is very interesting because of the high number of different possible products which can be obtained via catalytic hydrogenation and hydrogenolysis of this doubly functionalised cyclic compound. Scheme 1 depicts the possible routes of the transformation of this molecule.

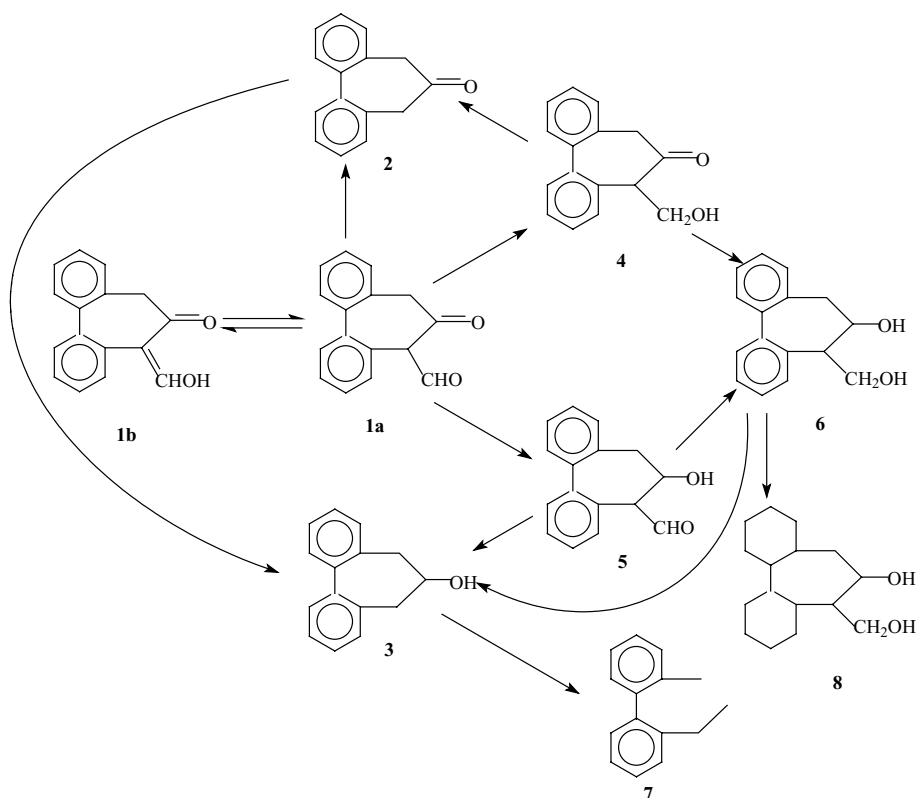
2. Experimental

The catalysts were prepared by exchange at room temperature for 72 h of a BEA zeolite (PQ, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 21.6$; S_{sp}

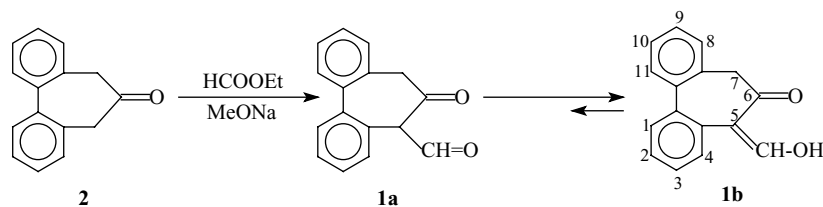
$= 739 \text{ m}^2/\text{g}$; H^+ -form) with $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ solutions with concentrations between 1.0×10^{-3} and 5.2×10^{-3} M. The solid was then separated by filtration and dried at 383 K for 2 h. A part of the samples was calcined at 623 K for 4 h in flowing air (30 mL min^{-1}), and then reduced at 723 K for 6 h in flowing H_2 (30 mL min^{-1}). Another part was directly reduced (723 K for 6 h in a 30 mL min^{-1} H_2 flow). Following these procedures, catalysts with 1.0, 1.2, 1.5, 1.8, 2.0, 2.2, and 2.5 wt.% Ru were prepared. The solids are designated as HBRu x and HBRuCR x , where “R” denotes activation via reduction, “CR” for activation via calcination and reduction, and x is the Ru wt.%.

For the characterization of the HBRu x catalysts, FTIR measurements were performed at room temperature with a Magna-IR 550 FTIR 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 wafers (around 5 mg/cm^2) were placed in a carousel sample holder for up to six pellets. Usually 200 scans were recorded with a resolution of 2 cm^{-1} for a single spectrum. IR spectra were normalized to the weight of 10 mg/cm^2 . Prior to the adsorption of the base, the samples were dehydrated by outgassing at 673 K overnight.

The bases, CD_3CN and pyridine (Py), were adsorbed at room temperature for 30 min on dehydrated samples, while 2,6-di-*tert*-butylpyridine (DTBPy) was adsorbed at 423 K. Desorption was performed by evacuation under a residual



Scheme 1. Possible reaction pathways in the transformation of cyclic keto–enol **1b**.



Scheme 2.

pressure below 10^{-4} Torr for 30 min at 373, 423, 473, 523, 623, and 673 K. In the case of CO, desorption at room temperature was performed in several steps, at 95 Torr, 35 Torr, and finally at 10^{-4} Torr. Thereafter, the sample was heated under vacuum at 373, 423, 473, 523, and 623 K. At 623 K, all CO was eliminated from the sample.

The starting conjugated keto–enol, namely, 5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a,c*] cyclohepten-6-one (**1b**) in Scheme 2 was prepared following the procedure previously described [28], using the condensation of dibenzocycloheptanone (**2**) [29] with ethyl formate in the presence of sodium methoxide. The formyl derivative (**1a**) is totally tautomerized to the keto–enol (**1b**) as shown by the spectral data [28].

Hydrogenation of the keto–enol (**1b**) was carried out at 273 and 333 K under 2 bar of hydrogen in a stirred stainless steel autoclave, using the following conditions: catalyst: 50 mg; substrate: 50 mg; solvent: 9 mL of ethanol. The MPV reductions were carried out in glass vials at 333 K, under vigorous stirring, using 4 mL of 2-propanol as solvent and hydrogen donor. The amount of catalyst was 50 mg and 50 mg of substrate were used. For comparison, BEA zeolite and BEA calcined at 773 K were also tested in MPV reduction. These samples were denoted as HB and HB773, respectively. In all the cases, the reaction products were regularly withdrawn from the reaction vessels. Analysis of reactant and products was done by GC–MS and ^1H NMR. The ^1H NMR spectra were recorded with a Varian Gemini 300BB instrument operated at 300 MHz. The variation of the concentration of the components in the reaction mixture (in both reactions) was followed with a Carlo Erba instrument (HRGC 5300 Mega Series) equipped with flame ionization detector (FID) and 50 m long capillary column with internal diameter of 0.32 mm and film thickness of 1.20 μm . Identification of reaction products was performed with a MD 800 mass spectrometer from Fisons Instruments (EI^+ – ionization at 70 eV – mass max. 500–600) coupled to a GC with a Chrompack CP-SIL 5CB column.

3. Results

3.1. Catalyst characterization

The CD_3CN -FTIR measurements in the spectral region between 2250 and 2350 cm^{-1} show the interaction of the

–CN group with electron acceptor or proton donor sites (Fig. 1) [30,31]. The intense band at 2323 cm^{-1} corresponds to CD_3CN coordinated on Lewis acid sites (L.A.). Since this band is also observed for the starting H–BEA material, it must be due to Al-related Lewis acid sites. The intensity of this band does not markedly increase with a change of the Ru content, indicating that after reduction, the metal does not appreciably contribute to the Lewis acidity. Evidence for CD_3CN interaction with Brønsted acid sites is provided by the absorption between 2250 and 2300 cm^{-1} . Decomposition of the spectra, as performed in Fig. 1, shows that two ν_{CN} bands can be distinguished at 2298 (B1.A.) and 2284 cm^{-1} (B2.A.). It is, however, uncertain whether this pair of bands should be ascribed to two different acid sites.

Pyridine adsorption reveals the presence of strong Lewis acid sites, as characterized by a band at 1620 cm^{-1} , and Brønsted acid sites with a band at 1638 cm^{-1} . The band at 1595 cm^{-1} suggests that an important amount of pyridine remains physically adsorbed. A comparison of the intensity of the bands at 1445 and 1545 cm^{-1} , characteristic for Lewis and Brønsted acid sites, suggests that in all these catalysts, the Lewis sites are dominant. Both the Lewis and Brønsted sites are sufficiently strong as to retain the pyridine adsorbed even after outgassing at high temperatures.

DTBPy-FTIR spectra showed, after adsorption of the probe molecule, bands at 1530, 1616, and 3370 cm^{-1} ,

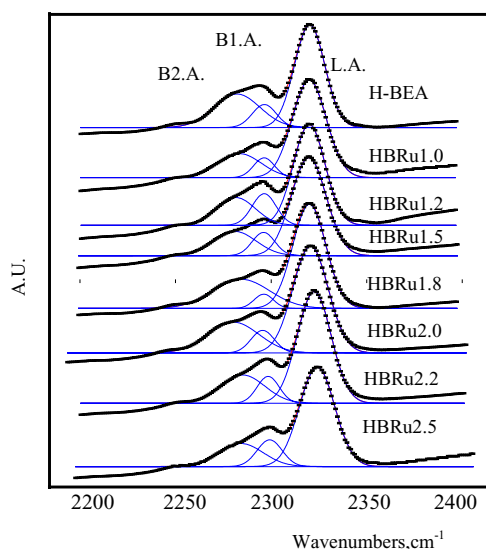
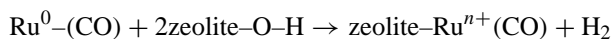


Fig. 1. CD_3CN -FTIR spectra of HBRuRx catalysts after desorption at RT for 1 h.

which can be assigned to the DTBPyH⁺ ion. In principle, these bands are diagnostic for Brønsted acid sites [32,33]. Irrespective of the ruthenium loading, the OH band at 3610 cm⁻¹ completely disappeared, proving the easy penetration of DTBPy into the BEA pore network. This suggests that the framework remains well accessible even to large molecules; Ru metal clusters don't seem to obstruct the access to the micropores.

Finally, CO-FTIR spectra of the reduced samples are shown in Fig. 2. For a low amount of ruthenium (1.0 wt.%), the CO-FTIR spectrum exhibits bands at 2163 cm⁻¹ (not shown in the figure), 2110, 2104, and 2088 cm⁻¹. For a higher content of ruthenium bands are observed at 2163, 2110, 2102, 2095, and 2088 cm⁻¹. Except for the band centred at 2088 cm⁻¹, the intensity of the bands increases with increasing ruthenium content (Fig. 2). It is striking that only a very weak absorbance is observed in the domain between 2000 and 2070 cm⁻¹; bands in this region are generally ascribed to CO chemisorbed on Ru particles, with larger particles giving rise to bands at lower wavenumbers [34].

In the present samples, the bands observed at wavenumbers between 2163 and 2088 cm⁻¹ can be ascribed to CO coordinated to oxidized Ru species, or to Ru carbonyl species [35–37]. The oxidized Ruⁿ⁺ species might be formed, in the presence of CO, by electron transfer from metallic Ru⁰ to acid protons on the support, as for instance:



Clearly, such an oxidative disruption of the Ru clusters will be favored when the dispersion is high. Summarizing, the CO spectra give no evidence for large Ru assemblies; rather they indicate that after the reductive pre-treatment, the Ru has a high dispersion in the BEA zeolite.

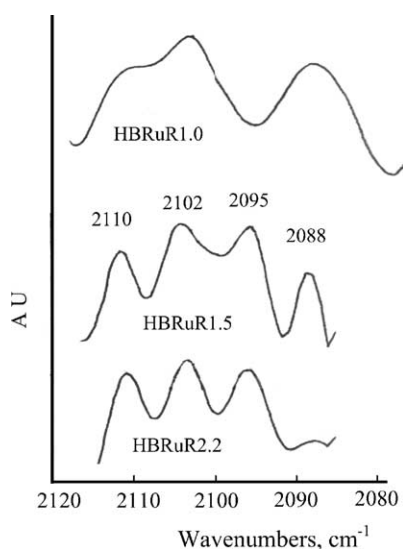


Fig. 2. FTIR spectra of CO adsorption on reduced catalysts in the 2120–2080 cm⁻¹ domain. Spectra were recorded at 298 K and 35 Torr CO.

3.2. Catalytic behaviour

3.2.1. Hydrogenation reaction

The liquid phase hydrogenation of keto–enol (**1b**) in ethanol over Ru-based catalysts using molecular hydrogen led to **2** and **3** as main products, and to compounds **6** and **7** as secondary products. Compounds **2** and **3** result from the direct hydrogenolysis of the starting molecule leaving the CHO group followed by a subsequent hydrogenation of C=O. The ¹H NMR spectral characterisations (δ (ppm), CDCl₃, only aliphatic region) for the compounds **1a**, **2** and **3** in Scheme 1: (**1a**): 3.50 (d, *J* = 12.0 Hz, –CH_AH_B–), 3.61 (d, *J* = 12.0 Hz, –CH_AH_B–); (**2**): 3.53 (d, *J* = 15.0 Hz, –CH_AH_B–), 3.61 (d, *J* = 15.0 Hz, –CH_AH_B–); (**3**): 2.45 (dd, *J* = 13.3; 5.9 Hz, –CH_AH_B–), 2.70 (dd, *J* = 13.3; 5.9 Hz, –CH_AH_B–), 4.47 (cv, *J* = 5.9 Hz, –CH–OH).

Compound **7** results from the hydrogenolysis of the seven-membered cycle of compound **3**, while compound **6** might result from the hydrogenation of **4** and **5**. Compound **6** may also undergo partial hydrogenolysis to **3**. However, the compounds **4** and **5** were not identified, neither in the MS nor in the NMR analysis. The amounts of **6** and **7** were rather small (not shown in Table 1) indicating that both the hydrogenolysis and hydrogenation to the diol **6** were limited. In addition, as mentioned above, part of **6** was transformed in **3**. This sequence of reactions was suggested by the variation of the reaction with time (Fig. 3). In all the experiments, the aromatic ring remained intact. The conversion of the substrate was 100%, regardless of the ruthenium loading, activation procedure or reaction conditions. For each series of catalysts, the yield of alcohol decreased as a function of the ruthenium loading, regardless of the catalysts pre-treatment (Table 1). However, the pre-treatment influenced the distribution of the reaction products. The samples activated by reduction led to an advanced hydrogenation, namely, to a higher concentration of alcohol (**3**). It is well known that a previous calcination may result in a decrease of the dispersion of the metallic phase.

3.2.2. MPV reduction

As in the case of using molecular hydrogen, the catalysts were very active, leading to a complete conversion of the

Table 1
Yields of ketone **2** and alcohol **3** in the presence of molecular hydrogen, at RT after 3 h

Entry	Catalyst	Yield of ketone (%)	Yield of alcohol (%)
1	HBRuCR1.0	61.5	14.0
2	HBRuCR2.0	66.5	10.7
3	HBRuCR2.2	76.6	5.0
4	HBRuR1.0	63.0	21.0
5	HBRuR2.5	79.0	8.3
6	HBRuR1.0 ^a	28.4	60.0
7	HBRuCR2.2 ^a	56.5	15.7
8	HBRuR2.5 ^a	58.0	14.0

^a The reaction temperature was 60 °C.

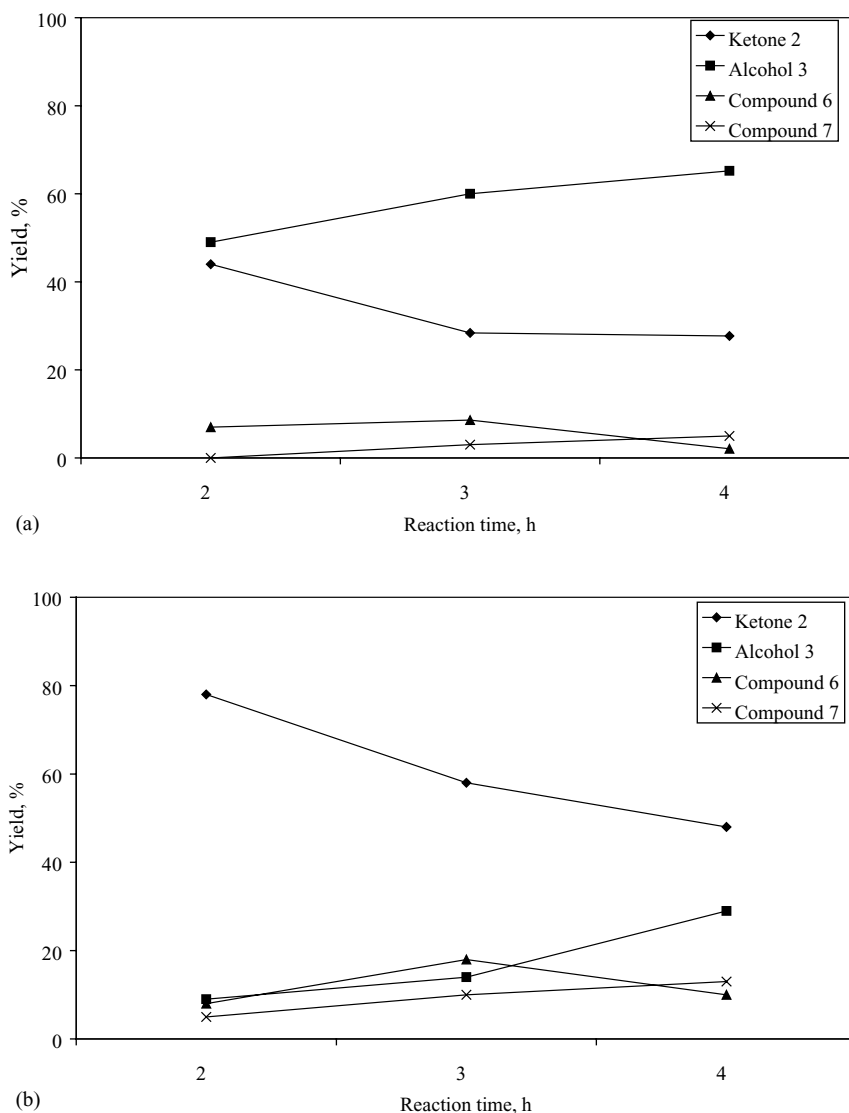


Fig. 3. Variation in time of the reaction over HBRuR1 (a) and HBRuR2.5 (b) (60 °C).

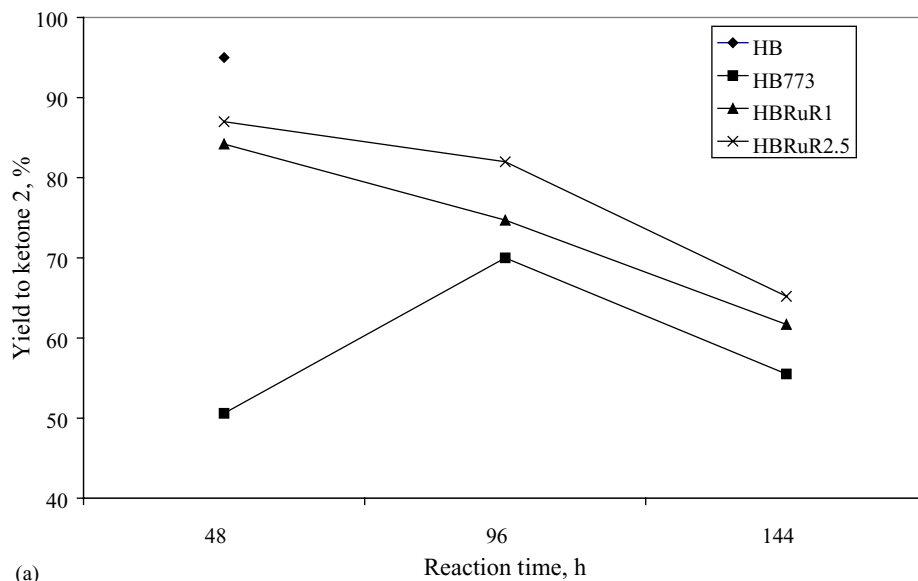
reactant molecule. But in terms of yield of alcohol, the use of the 2-propanol as hydrogen source was less effective relative to molecular hydrogen, as inferred from the rather poor hydrogenation activity under MPV conditions. Pure zeolites exhibited a different behavior as a function of the thermal pre-treatment. On HB, the yield of ketone was very high. Re-calcination of the zeolite (sample HB773) led to an increased amount of alcohol (Fig. 4). The increase in the yield of alcohol at 144 h results from the hydrogenolysis of **6** to **3**.

Addition of ruthenium decreased even more the yield of alcohol. Such a behavior is associated to the increased amount of **6**. Fig. 4 shows that, irrespective of the reaction time, the amount of **6** increased with the amount of Ru. However, these compounds in MPV conditions were formed indeed in very small amounts. As a direct consequence, in comparison with the reactions carried out with molecular hydrogen, the reaction performed in MPV conditions stopped mainly at the level of compound **2**.

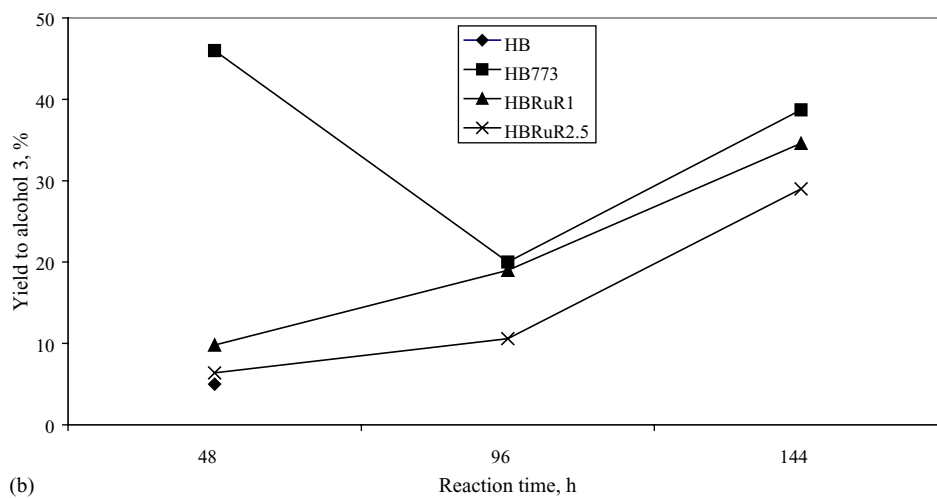
4. Discussion

The FTIR study of the catalysts with various Ru contents gives some insight in both the acidity and structure of the metal phase on BEA zeolite. Adsorption of CD₃CN and pyridine showed convincingly that both Al-related Lewis and Brønsted acid sites are present in the zeolite before loading with Ru. Deposition of various amounts of Ru affects only to a minor extent the contents of the Lewis and Brønsted sites. The number of Lewis acid sites appears to be higher than that of the Brønsted acid sites, as established by integration of the spectra of adsorbed pyridine.

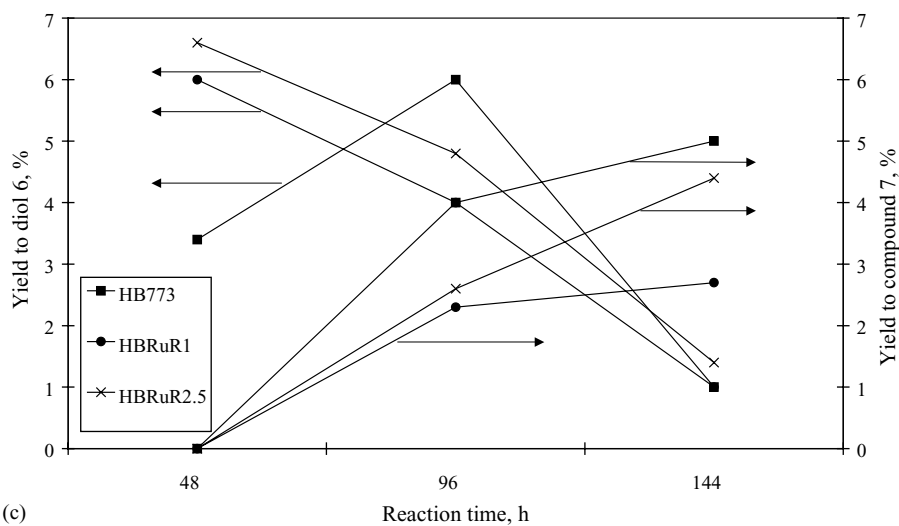
The easy penetration of DTBPy and its complete reaction with the zeolite acid sites allows one to infer that the access to the zeolite micropores is not blocked by the Ru deposition and the various pretreatments. The CO adsorption data for the reduced catalysts give no evidence for CO chemisorbed on large metal particles. Rather, it seems that Ru is highly



(a)

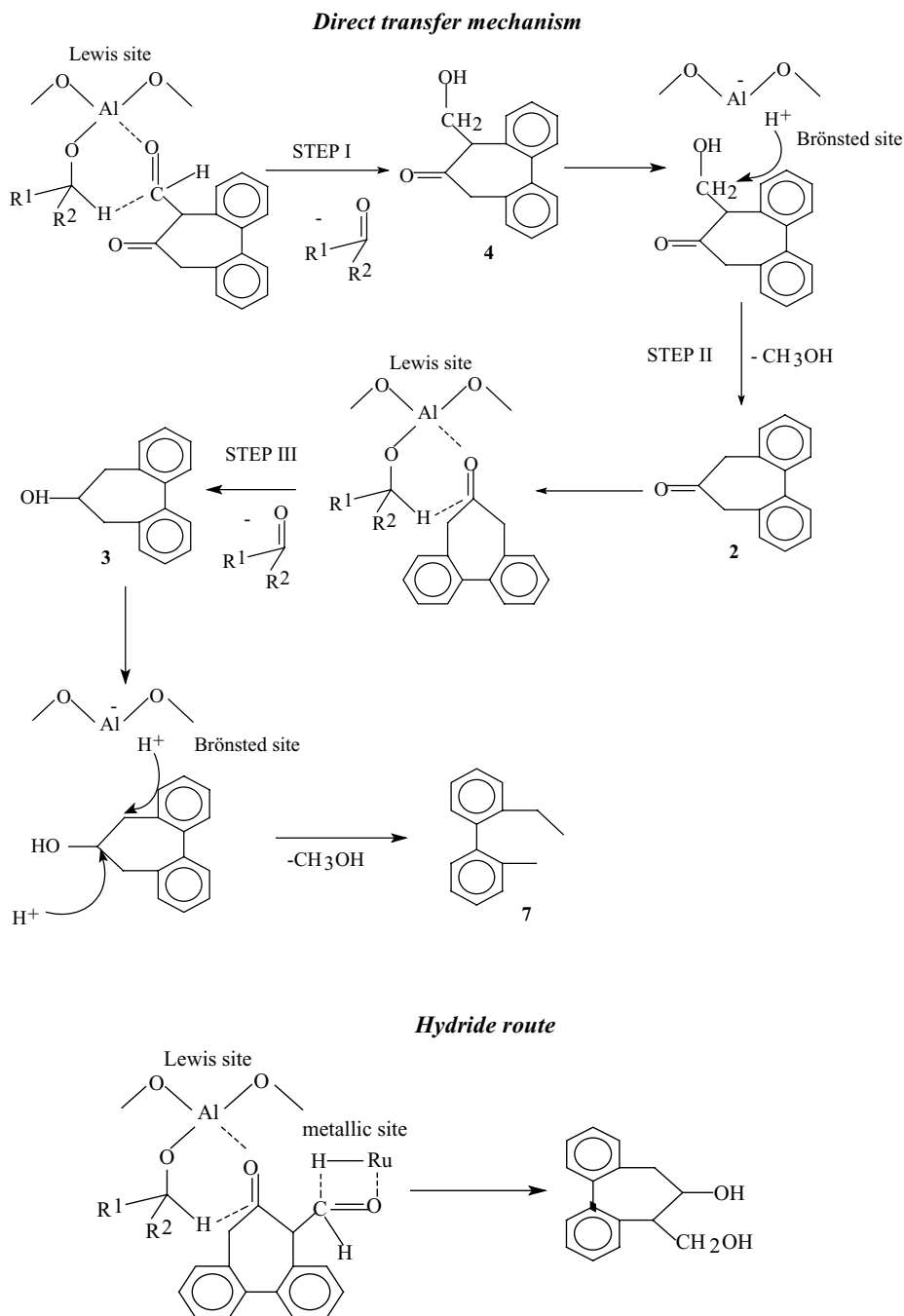


(b)



(c)

Fig. 4. Variation with time of the yields to ketone (a), alcohol (b), and diol 6 and compound 7 (c) on HB773 and Ru-BEA zeolites in MPV conditions.

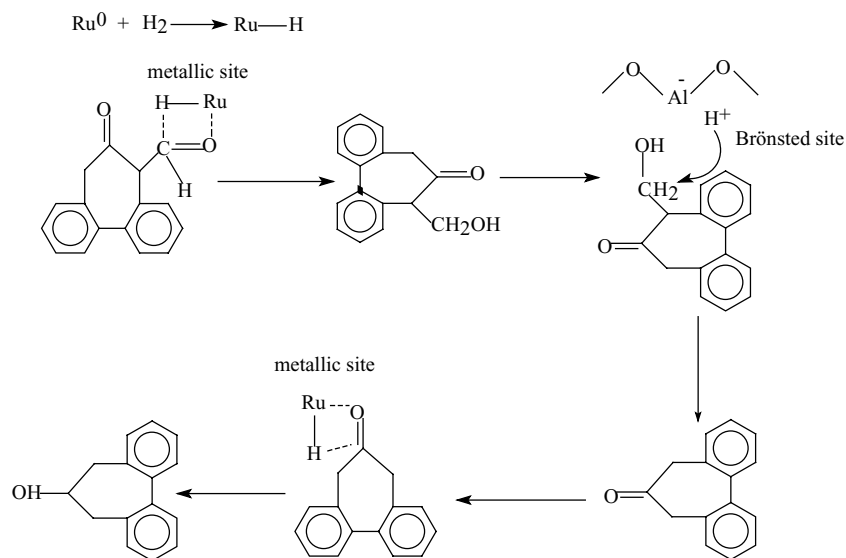


Scheme 3. Reaction pathways in MPV reaction on the investigated catalysts.

dispersed, and the spectra show that some of the surface Ru must exist as a cationic species. It is possible that Ru is oxidized during CO chemisorption, e.g., via the so-called oxidative disruption of the clusters, which occurs by reaction of zerovalent Ru with H^+ . CO-FTIR also differentiated $HBRuR_x$ and $HBRuCR_x$ catalysts. The spectra recorded for the two series of catalysts suggest that Ru is more dispersed in the $HBRuCR_x$ catalysts than in the $HBRuR_x$ ones.

The reaction of the keto–aldehyde occurred with total conversion both with molecular hydrogen and in MPV condi-

tions. Such a behavior should be related to the participation of the acid sites in the first hydrogenolysis step, namely, the elimination of the CHO group, an assumption supported by the fact that, in MPV experiments, the substrate was more easily hydrogenolyzed in **2**, with subsequent hydrogenation to the alcohol **3**. By comparison with the re-calcined zeolite, and for reactions carried out with molecular hydrogen, the presence of metal sites blocks the reaction mainly at the level of compound **2**. Such a behavior could be associated with the physical blockage of the surface, which finally



Scheme 4. Reaction pathways in the presence of molecular hydrogen.

leads to the blockage of the Lewis acid sites which are active in the MPV reactions. The differences between HB773 and Ru-BEA zeolites account for this behavior.

Scheme 3 describes the reaction mechanism under MPV conditions. The calcination of HB at 773 K (HB733) provides an increased concentration of Lewis sites, which allow a subsequent hydrogenation of **2** to **3**. Non-calcined zeolite contained a large population of Brønsted acid sites (Fig. 1), which actually stops the reaction at the ketone **2**. Scheme 3 also distinguishes between the “direct transfer” mechanism occurring on the pure zeolites (HB and HB773) and the hydride route, occurring on Ru.

In the procedure with molecular hydrogen, the reaction pathway is different, involving a bifunctional mechanism (Scheme 4). Both the metal dispersion and the acid sites of the zeolite participate in the reaction. The sample containing the lowest amount of Ru and activated by direct reduction (HBRuR1.0) gives an appreciable yield of alcohol. This actually corresponds to the highest dispersion of Ru. According to previous hydrogenation studies of ketones, an optimal ratio between the size of the metal particles and the acid sites in close proximity is required. The results may thus also suggest that, for this particular catalyst, such a ratio has been achieved for this metal loading. Such a promotion of the chemoselectivity by Brønsted or Lewis acidity is illustrated by several examples from the literature. Indeed, von Arx et al. [16] indicated that the hydrogenation of keto-isophorone over Pd/Al₂O₃ in CH₃COOH/MeOH leads, as a majoritary product, to allylic alcohol (although Pd is well known to prefer C=C over C=O bonds), ascribing an important role to the acid solvent. Also, De Bruyn et al. [24] demonstrated that Ir could reduce a variety of unsaturated ketones to allylic alcohols when it is supported on H-BEA. Less acidic or non-acidic supports, e.g., Al₂O₃ or C, are much less effective.

The results in MPV reduction of this substrate are accounted for by the same characteristics of the catalysts. This reaction occurs on the acid sites of the support. Although the deposition of Ru was found, from the FTIR characterization, to have no marked influence on the acidity of the support, the decrease of the yield of compound **3** might reflect a decrease of the acidity.

In all the experiments, the yield of alcohol increased with time. This may be related to in situ ‘carbonyl activation’ of some active sites during the hydrogenation. This phenomenon, also known as ‘reaction-induced selectivity improvement’, has previously been described in the literature [9,38].

5. Conclusions

The acid properties and metal dispersion of Ru-containing BEA zeolites have been studied by FTIR spectroscopy. The reaction of 5-hydroxymethylene-5H-6,7-dihydrodibenzo[*a*, *c*]cyclohepten-6-one both in MPV and with molecular hydrogen was found to result in the ketone **2**, which is actually a hydrogenolysis product. Further reaction, namely, the reduction of this compound to the corresponding alcohol was controlled by the acidic properties and metal dispersion of the catalysts. Low Ru loadings favoured the hydrogenation of this compound with molecular hydrogen while the acidic sites were effective in MPV conditions.

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