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Modifications of the citral hydrogenation selectivities over Ru/KL-zeolite catalysts induced by the metal precursors

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Abstract

Three Ru/KL-zeolite catalysts containing 2 wt% of Ru were prepared from $Ru_3(CO)_{12}$, $RuNO(NO_3)_3$ and $Ru(C_5H_7O_2)_3$ precursors. The samples named Ru(c)/KL, Ru(n)/KL and Ru(a)/KL were studied by temperature-programmed reduction (TPR), by microcalorimetry of CO adsorption, by volumetric hydrogen chemisorption, by X-ray diffraction (XRD) and also by infrared spectroscopy of the CO adsorbed species (CO-FTIR). The catalytic activities and selectivities were evaluated in the hydrogenation of citral at 323 K and 5 MPa, in a stirred batch reactor. Metal dispersion follows the order Ru(c)/KL > Ru(n)/KL > Ru(a)/KL. The CO-FTIR spectra show a set of different ruthenium species on the support, suggesting the presence of large metal particle outside the zeolite and small crystallites inside the channels, the latter being majority in the Ru(c)/KL sample. Hydrogenation activity per surface metal atom (TOF) was found to be independent on the metal dispersion and, consequently, on the precursor used. The selectivity towards unsaturated alcohols (geraniol + nerol) is in the order Ru(c)/KL < Ru(a)/KL = Ru(n)/KL, while the citronellal selectivity is maximum over the Ru(c)/KL catalyst. This latter effect can be correlated to the special catalytic properties of the smaller Ru particles located inside the zeolite cavities.

Keywords: Ruthenium catalysts; Selective hydrogenation; Citral; Geraniol; Nerol; Citronellal; KL-Zeolite; CO-FTIR; Adsorption microcalorimetry

1. Introduction

The selective catalytic hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols has attracted much interest in the recent years, because of the relevance of these compounds in the fine chemical and pharmaceutical industries. A lot of attempts have been made to develop heterogeneous catalysts suitable for these reactions. Moreover, different approaches have been used to improve the generally low selectivity of the catalysts to the desired alcohols or to other important products. It is known that the final selectivity of an active metal can be modified by employing an adequate support, which interacts with the metal, or by adding a second component, which acts as a promoter. Electronic and geometric effects have been suggested as the explanation for the improvement in selectivity towards the unsaturated alcohols.

Earlier studies carried out on hydrogenation of α,β-unsaturated aldehydes proved that unpromoted metallic catalysts have specific selectivities towards unsaturated alcohols. Iridium and osmium are rather selective; palladium, rhodium and nickel are unselective or little selective; platinum, ruthenium and cobalt are moderately selective [1]. The intrinsic selectivities of the metals have been explained in terms of the different radial expansion of their d bands [2]. Singh and Vannice [3] investigated the citral hydrogenation over SiO_2-supported groups VIII metals in the liquid-phase and found that Os, Ru and Co exhibit high selectivity towards unsaturated alcohol isomers, while Ni, Pd and Rh are highly selective to citronellal and isopulegol.

On other hand, the environment of the metal particles can produce steric constraints, which orientate the adsorption of the reactant molecules and direct the selectivity of the

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reaction. Thus, metal clusters (Pt, Rh, Ru) located in the cages of Y and beta zeolites have been reported to be very selective catalytic systems for the production of unsaturated alcohols [4–6]. This high selectivity was attributed to molecular constraints in the zeolite microporous cages, which force the reactant molecule to adsorb on the encaged metal particles via the C═O group and hamper the adsorption of the C═C bond.

In addition, the mode of adsorption of the α,β-unsaturated aldehyde molecules can be governed by the electronic structure of the metal surface. Thus, enrichment of the metal surface with electrons by interactions with a support or ligand could, on the one hand, decrease the binding energy of the C═C bond via an increase of the repulsive four-electron interaction and, on the other hand, favor the backbonding interaction with the π^*_{CO}-orbital and the hydrogenation of the C═O bond with respect to that of C═C. Finally, when the reaction is conducted in liquid phase the nature of the solvent may have an important effect on the selectivity of the reaction. Mäki-Arvela et al. [7] studied the hydrogenation of citral in liquid phase with different solvents and they found that side reactions, acetalization and cyclization, can be diminished by using longer chained alcohols, like 2-pentanol or 2-methyl-2-propanol, as solvents.

KL is a non-acidic synthetic zeolite whose structure consists of a tri-dimensional system with a channel constituted by cages of 0.48 nm × 1.24 nm × 1.07 nm, connected by windows of 12-membered rings with a diameter of 0.71 nm [8]. Catalysts of platinum supported on KL zeolite have been reported to be highly active and selective in the dehydrocyclization of light alkanes due, in part, to the singular property of the zeolite to stabilize electron rich metallic particles inside the channels [9–11]. In order to evaluate the KL-zeolite as a support and obtain catalysts with different physicochemical properties for the selective hydrogenation of α,β-unsaturated aldehydes, we have prepared several Ru/KL samples using different ruthenium precursors. Since KL is a non-acidic zeolite [8], it is expected that reactions involving acid sites are minimized. For the same reason, we have used chloride free ruthenium precursors and 2-propanol as solvent. The catalysts were characterized by X-ray diffraction (XRD), hydrogen chemisorption, temperature-programmed reduction (TPR), infrared spectroscopy of CO chemisorbed (CO-FTIR) and microcalorimetry of CO adsorption. The catalytic behavior was studied in the hydrogenation reaction of citral to unsaturated alcohols and citronellal and the results were associated with the size of the ruthenium particles and their interaction with the support.

2. Experimental

2.1. Catalyst preparation

Three catalysts containing 2 wt% of ruthenium were prepared using a commercial KL-zeolite as support (Union Carbide, SK-45, $K_9Al_9Si_{27}O_{72}$ in atoms per unit cell and average particle grain, 53 μm) previously calcined at 873 K for 3 h. Two portions of this support were impregnated with ruthenium (III) 2,4-pentanedionate (Alpha Aesar) and tri-ruthenium dodecacarbonile (Aldrich) acetone solutions, respectively. Another catalyst was prepared from an aqueous solution of ruthenium (III) nitrosylnitrate (Alpha Aesar). After drying at 393 K overnight, all the samples were reduced at atmospheric pressure under hydrogen flow at 673 K for 2 h and then cooled down to room temperature under inert flow.

2.2. Catalysts characterization

The number of exposed metal atoms was measured by hydrogen chemisorption at 373 K using a conventional volumetric system. A catalyst sample (300 mg) previously reduced at 673 K under hydrogen atmosphere, was outgassed at the same temperature for 2 h. After cooling down at 373 K successive hydrogen pulses were introduced between 66 and 13.100 Pa and the loss of pressure due to the adsorption was measured. Measurements were conducted at 373 K, due to the characteristic activated hydrogen chemisorption on ruthenium catalysts [12]. The hydrogen uptake was determined extrapolating to zero pressure the linear portion of the adsorption isotherm. Metal dispersions of the catalysts (D_H) is defined as $D_H = 100\ Ru_S/Ru_L$ where Ru_S is the number of exposed Ru atoms per gram of catalyst and Ru_L is the total number of Ru atoms per gram of catalyst, as determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The number of exposed metal atoms was calculated assuming an atomic stoichiometry Ru/H = 1/1 [13].

Heats CO adsorption measurements were performed in a Tian Calvet heat-flow microcalorimeter (Setaram C-80 II) operated isothermally at 330 K and connected to a glass vacuum-dosing apparatus. The apparatus has been described in detail elsewhere [14]. The catalysts samples were first reduced in situ under hydrogen flow at 673 K for 2 h, outgassed overnight at the same temperature and cooled to 330 K. Pulses of the probe gas (12 ml) were introduced into the system to titrate the metal surface of the sample. Both calorimetric and volumetric data were stored and evaluated by microcomputer processing. In this case, metal dispersion (D_{CO}) was calculated from the total CO uptake at the monolayer (N_{CO}), considered to be attained when the evolved heat falls to the physisorption field (40 kJ/mol), and assuming a molar stoichiometry Ru/CO = 1/1 [15]. The average particle sizes were calculated from the dispersion values, assuming spherical metal particles, d (nm) = $1.32/D_{CO}$ [16].

Temperature-programmed reduction (TPR) experiments were carried out in dynamic, employing a U-shape quartz reactor. The TPR profiles were registered heating the samples from room temperature to 973 K at 2.5 K min^{-1} under a flow of 10% H_2/He mixture (20 ml min^{-1}). The gas effluents of the reactor were analyzed in a gas chromato-