

Chemicals from Ethanol-The Ethyl Acetate One-Pot Synthesis

Alexandre B. Gaspar, Flavia G. Barbosa, Sonia Letichevsky, Lucia G. Appel*

DCAP, Instituto Nacional de Tecnologia, Rio de Janeiro (Brazil),

*luciagor@int.gov.br

Introduction

Ethyl acetate has been largely used as a solvent in paints, coatings, inks and adhesives and sometimes replacing aromatic compounds. The direct production of ethyl acetate from ethanol, has been proposed by two different routes: the dehydrogenative process, which uses copper or palladium based catalysts [1,2] and the oxidative one, which employs PdO supported catalysts [3]. The former one produces, besides ethyl acetate, hydrogen and also, other byproducts which make the acetate purification expensive. In the case of the oxidation process, the purification is straightforward and the catalysts are very stable. However, due to the explosive limits, the ethanol/air ratio should be very low, increasing the reactor size or very high, increasing the recycle ratio. The main byproduct in this case is the acetic acid.

The formation of acetaldehyde by dehydrogenation or oxidative dehydrogenation of ethanol is the first step of the above mentioned processes. The second step is a nucleophilic addition of either ethanol or surface ethoxide to acetaldehyde in order to form a hemiacetal, which is dehydrogenated producing the ethyl acetate [1,3]. During the reaction, acetaldehyde is adsorbed on Lewis acid sites. In fact, there are very few pieces of information related to this condensation step. Taking into account that both this aldehyde and ethanol can be adsorbed on many different surfaces, it is not clear yet if this reaction occurs on the metal or oxide active sites, on the interface of these phases with the support or only on the support. Therefore, the aim of this work is to improve the description of the second step of the ethyl acetate synthesis from ethanol considering both the dehydrogenative and oxidative routes.

Materials and Methods

The PdO/ZrO₂ (1wt. %) catalyst (oxidation) was prepared using the ionic exchange method, whereas Cu/ZnO/Al₂O₃ (dehydrogenation) and ZrO₂ (tetragonal (*t*), monoclinic (*m*) and amorphous (*a*)) are commercial samples. The ZrO₂ samples and the catalysts were characterized by XRD, N₂ physisorption, DLS, UV-VIS, pyridine and CO₂ adsorption. Both catalytic tests were performed in conventional fixed bed reactors using PdO/ZrO₂ (25mg) and Cu/ZnO/Al₂O₃ (100 mg) and also physical mixtures of these catalysts with ZrO₂. The compositions of the gaseous mixtures (20 mL.min⁻¹) were N₂:O₂:ethanol = 76.6:20.4:3.1 for the oxidation reactions and N₂:ethanol = 68.2: 7.8 vol% for dehydrogenation reactions.

Results and Discussion

Table 1 shows that Cu/ZnO/Al₂O₃ catalyst is not able to synthesize ethyl acetate. However, after adding the ZrO₂ samples to it (physical mixture), ethanol conversion increases and ethyl acetate is formed. These results suggest that the condensation reaction occurs on ZrO₂. It was also observed that in the case of a dual bed reactor where this catalyst is placed at the bottom and ZrO₂ at the top with glass wool separating the layers, ethyl acetate is not synthesized. This result shows that acetaldehyde generated at the bottom of the reactor does not

readsorb on the support. Table 1 also displays that when ZrO₂ content is increased in the physical mixtures the catalytic performance does not modify, showing that the contact between the catalyst particles and ZrO₂ is relevant. It was also observed that the conversion and the selectivities to acetaldehyde and ethyl acetate were not significantly affected by the ZrO₂ crystalline phase.

Table 1 displays that PdO/*m*-ZrO₂ catalyst is able to synthesize acetic acid, acetaldehyde and ethyl acetate in these experimental conditions. When ZrO₂ is added, it can be observed that the acetic acid selectivity drops whereas the other ones increase. It can also be inferred that the effect of the ZrO₂ crystalline phase is more relevant for the oxidation process than for the dehydrogenation route. It is worth stressing that adding *m*-ZrO₂ to the PdO/*m*-ZrO₂ catalyst, there is a 300% increase of Lewis acid sites, which are related to acetaldehyde adsorption sites.

Taking all these pieces of information into account, it can be suggested that the spillover of acetaldehyde occurs from the active sites to ZrO₂ and that the condensation reaction occurs on this oxide, which can be used either as a support or in the physical mixture. In other words, once acetaldehyde is formed on Cu⁰ or PdO, it can be desorbed or oxidized to acetic acid or it can spill over on the ZrO₂ surface and react with ethanol generating ethyl acetate.

Table 1. Ethanol conversion (X), selectivities to acetaldehyde (S_{acetal}), ethyl acetate (S_{acetate}) and acetic acid (S_{acid}), temperature (T) and ratio between the catalyst and the ZrO₂ (R).

Catalysts or Physical mixtures	T (°C)	R (wt.)	X (%)	S _{acetal} (%)	S _{acetate} (%)	S _{acid} (%)
Cu/ZnO/Al ₂ O ₃	150	-	8.2	80.1	-	-
Cu/ZnO/Al ₂ O ₃ + <i>m</i> -ZrO ₂		1.00	16.2	44.8	43.6	-
Cu/ZnO/Al ₂ O ₃ + <i>m</i> -ZrO ₂		0.50	15.4	41.0	42.1	-
Cu/ZnO/Al ₂ O ₃ + <i>t</i> -ZrO ₂		1.00	15.8	44.3	41.6	-
Cu/ZnO/Al ₂ O ₃ + <i>t</i> -ZrO ₂		0.50	16.3	44.1	40.3	-
PdO/ <i>m</i> -ZrO ₂	175	-	32.4	29.2	34.6	37.2
PdO/ <i>m</i> -ZrO ₂ + <i>m</i> -ZrO ₂		0.25	39.3	49.2	47.1	-
PdO/ <i>m</i> -ZrO ₂ + <i>t</i> -ZrO ₂		0.25	44.9	34.3	67.5	-
PdO/ <i>m</i> -ZrO ₂ + <i>a</i> -ZrO ₂		0.25	33.0	52.5	43.8	3.7

Significance

The American and Brazilian huge production of ethanol offers a good opportunity for the development of new chemical processes or products using this alcohol as a raw material. Ethyl acetate is one interesting example of this new industry. This work shows that the oxidative and the dehydrogenative routes are similar and also that the support has a major role in the one-pot ethyl acetate synthesis.

References

1. Inui, K., Kurabayashi, T., Sato, S.; Ichikawa, N. *J. Mol. Catal. A* 216, 147 (2004).
2. Colley, S.W., Tabatabaei, J., Waugh, K.C., Wood, M.A. *J. Catal.* 236, 21 (2005).
3. Ramos, R.M.S., Libergott, E.K., Appel, L.G., Pereira, S.E., Almeida, V.C. BR9104562 (1992).