Lactic acid and ethyl lactate dehydratation over alkaline earth phosphates: origin of the catalytic efficiency

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Introduction

Acrylic acid (AA) is a platform molecule produced at 4 Mt/year by selective oxidation of propene, whose price is growing quickly because of increasing demand and rarefaction of petroleum. An alternative green route consists in dehydration of lactic acid (LA) that can be produced by dehydrogenation of glycerol [1]. High yields to acrylic acid were obtained using modified zeolites [2] or calcium phosphates [3-4]. In the present work, alkaline-earth pyrophosphates (MPP) and orthophosphates (MOP) were prepared, evaluated both for gas phase dehydration of LA and ethyl lactate (EL) and the origin of the catalytic efficiency was investigated crossing various techniques.

Materials and methods

All the catalysts were prepared by co-precipitation method. Catalytic testing was carried out in gas phase at different temperatures (300-390°C) and contact times (0.1-10 s). Catalysts were characterized by XRD, BET measurements and ICP analysis and the active phases were determined crossing XPS, ^{1}H-^{31}P CP-MAS NMR, TEM and *in situ* DRIFT. Acidity and basicity were measured by NH_3/CO_2 TPD respectively and pyridine adsorption.

Results and discussion

Catalytic performances of the prepared catalysts are presented in Table 1. Good performances were obtained at 380°C for LA dehydration using alkaline-earth OP and PP as catalysts with selectivity to AA reaching 50% near complete conversion [5].

Table 1. Catalytic performances at 380°C, GHSV 1750 h^{-1}, gas feed composition LA(EL)/H_2O/N_2= 3(9)/66(0)/31(91). S_{mol} (%) = 100 x number of moles of product/moles of moles of LA (EL) reacted.

Catalyst	LA conversion			EL conversion		
	Conv. (%)	S_{mol}(A) (%)	S_{mol}(AA) (%)	Conv. (%)	S_{mol}(A) (%)	S_{mol}(AA+EA) (%)
CaPP	70	46	46	15	9	88
SrOP	90	43	45	4	13	65
BaPP	67	52	42	6	11	65
BaOP	93	45	50	25	18	74

NH_3 and CO_2-TPD curves revealed efficient catalysts contained mainly weak acid and base sites. Additionally, correlation between acid-base balance and AA selectivity has been established for LA conversion [5].

Surface characterization of the catalysts revealed the presence at the surface of P-rich hydroxylated phase (XPS, CPMAS NMR). An amorphous overlayer of few nanometers was clearly evidenced by TEM (Fig. 1a). Formation of alkaline-earth hydrogenophosphates should allow the presence at the surface of acid-base pairs. Additionally, one OH stretching vibration of $(HPO_4)^{2-}$ species was observed by DRIFT for catalysts treated at 380°C under He flow (Fig. 1b). Such species were stabilized by high water partial pressure whereas they reacted with AL and EL at 380°C (Fig1.c) revealing they are active on both cases.

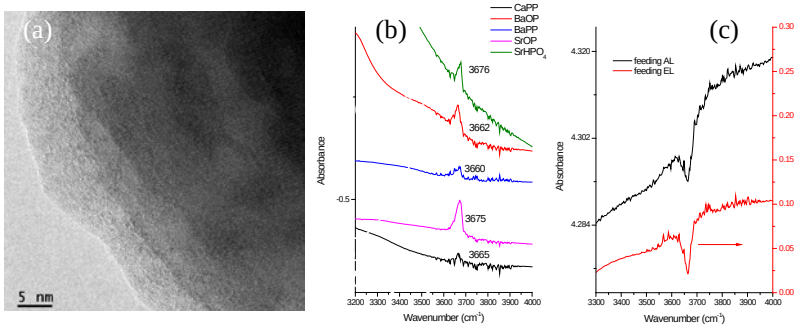

Figure 1. (a) TEM image of BaOP catalyst, (b) DRIFT spectra of catalysts treated at 380°C under He and (c) *in situ* DRIFT spectra of BaOP catalyst feeding AL and EL at 380°C (the background corresponds to the spectrum of the catalyst pre-treated at 380°C under He).

Significance

The characterization of the most efficient catalysts showed that a thin amorphous layer of alkaline-earth phosphates was present over crystalline orthophosphates and pyrophosphates. Hydroxylated phosphorous species present in such layer were shown to be active for LA and EL conversion. This leads to the conclusion that the same reaction mechanism might be involved although different catalytic performances were obtained. These differences could arise from water vapor effect.

References

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