

# Ethanol-coupling reactions over MgO, MgO-SiO<sub>2</sub>, and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts: The effect of promotion by transition metal oxide

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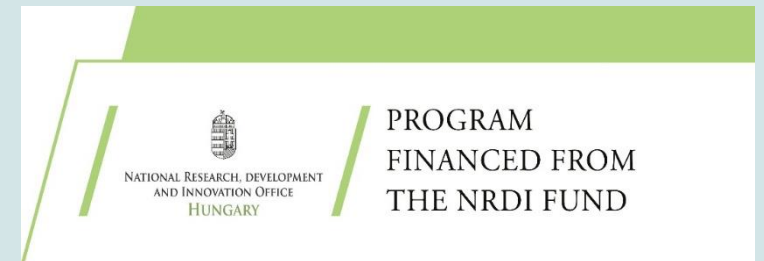
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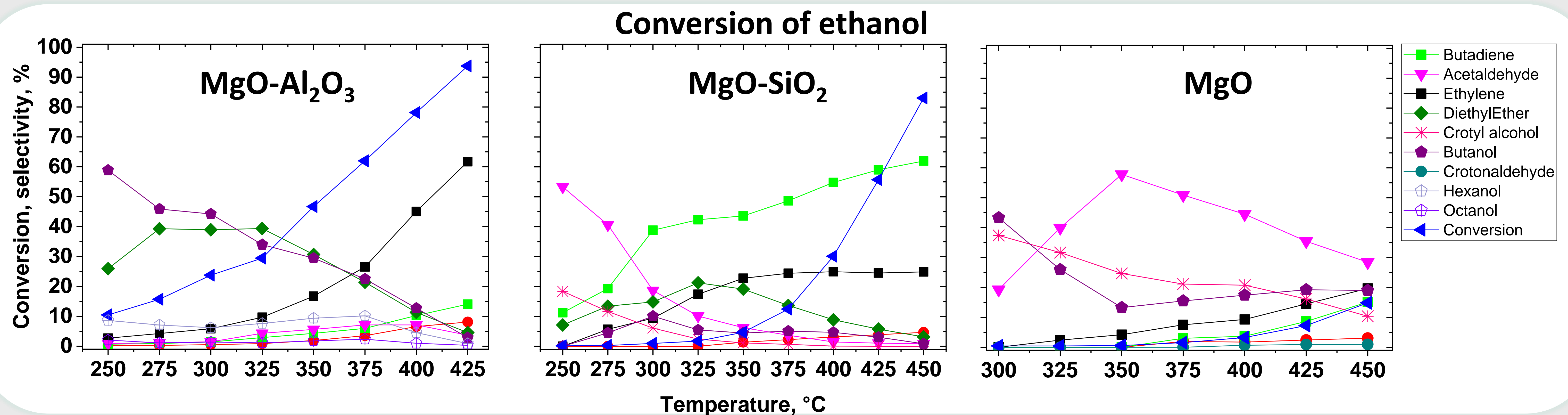


## Introduction

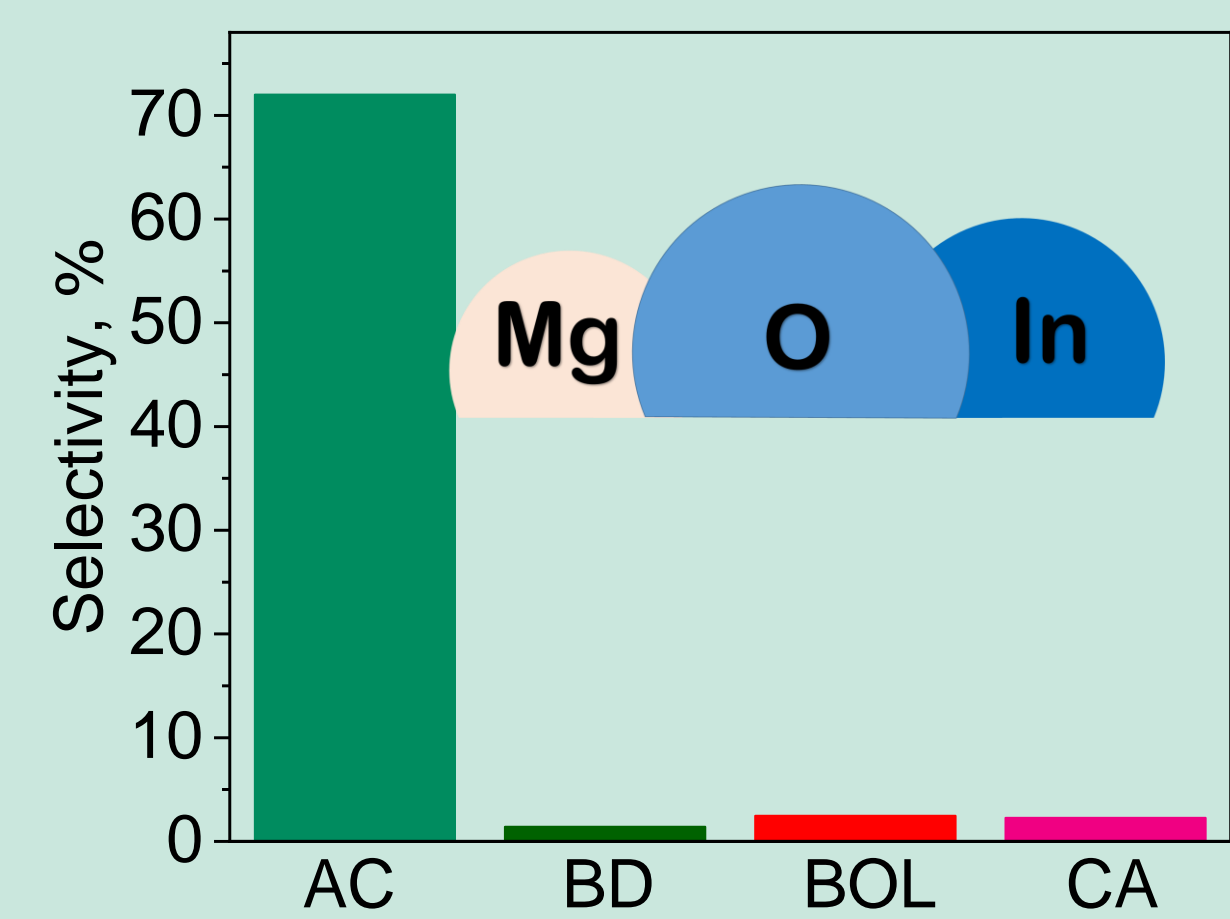
Bioethanol, as a renewable source, can serve as raw material of important chemical products. Recently, the heterogeneous catalytic ethanol-coupling reactions, giving 1,3-butadiene or n-butanol were receiving special attention. It was proposed that the successive reactions of ethanol take place on a single multifunctional catalyst that either contains spatially separated active sites with hydrogenation/dehydrogenation, C-C coupling and optionally dehydrating activity, or on a catalyst in which ensembles of active sites are able to induce all the mentioned transformations of a 4-carbon activated surface complex. The 1,3-butadiene is formed by dehydration, whereas butanol is obtained by hydrogenation of this intermediate. It is well known that over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxide catalysts butadiene and butanol is formed, respectively, with high selectivity. Neat MgO is also known to have a high catalytic efficiency in ethanol coupling, mainly producing butanol and crotyl alcohol. Our present study concerns the role of transition metal oxide additives on the ethanol coupling reactions.

## Experimental/methodology

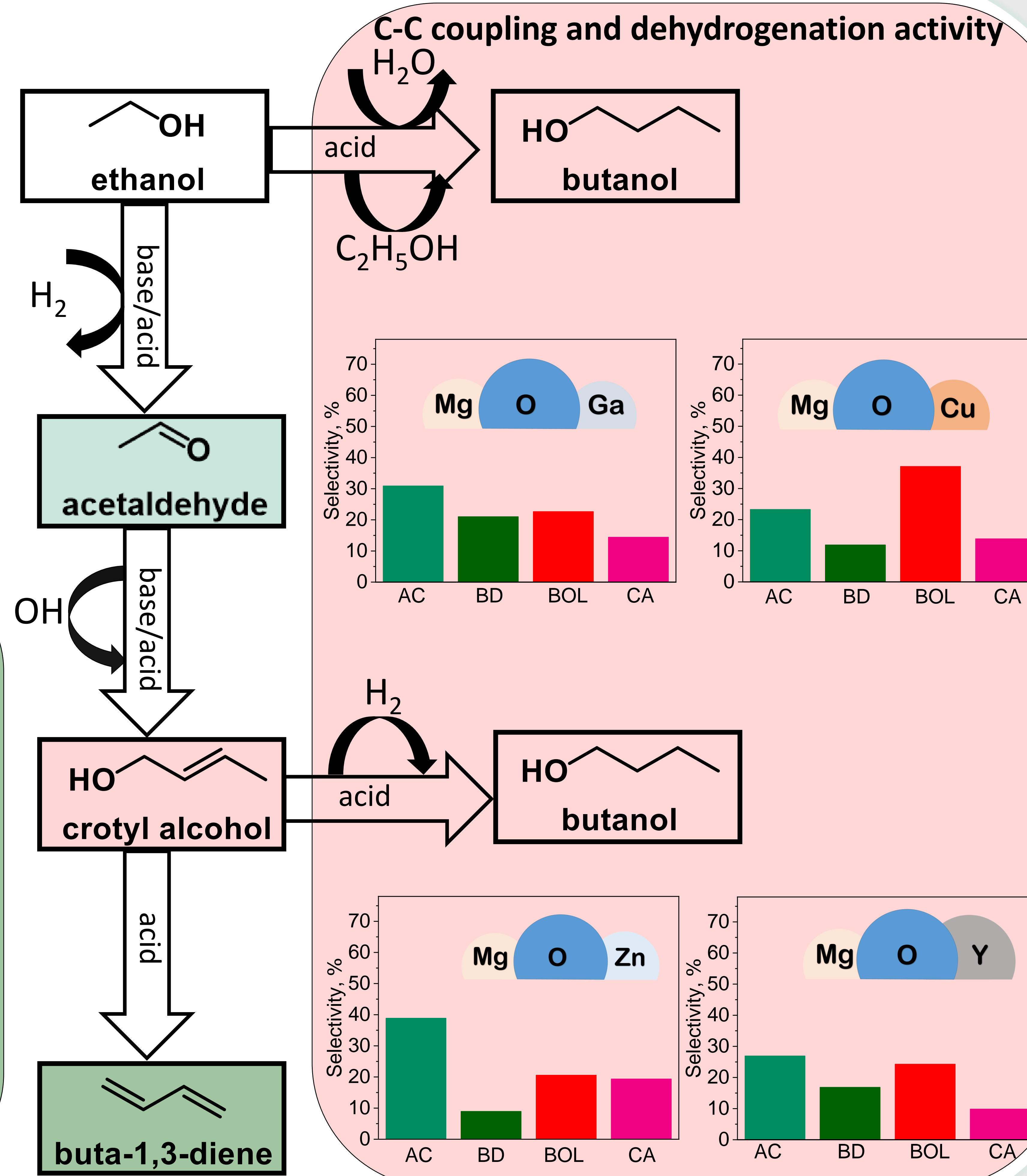
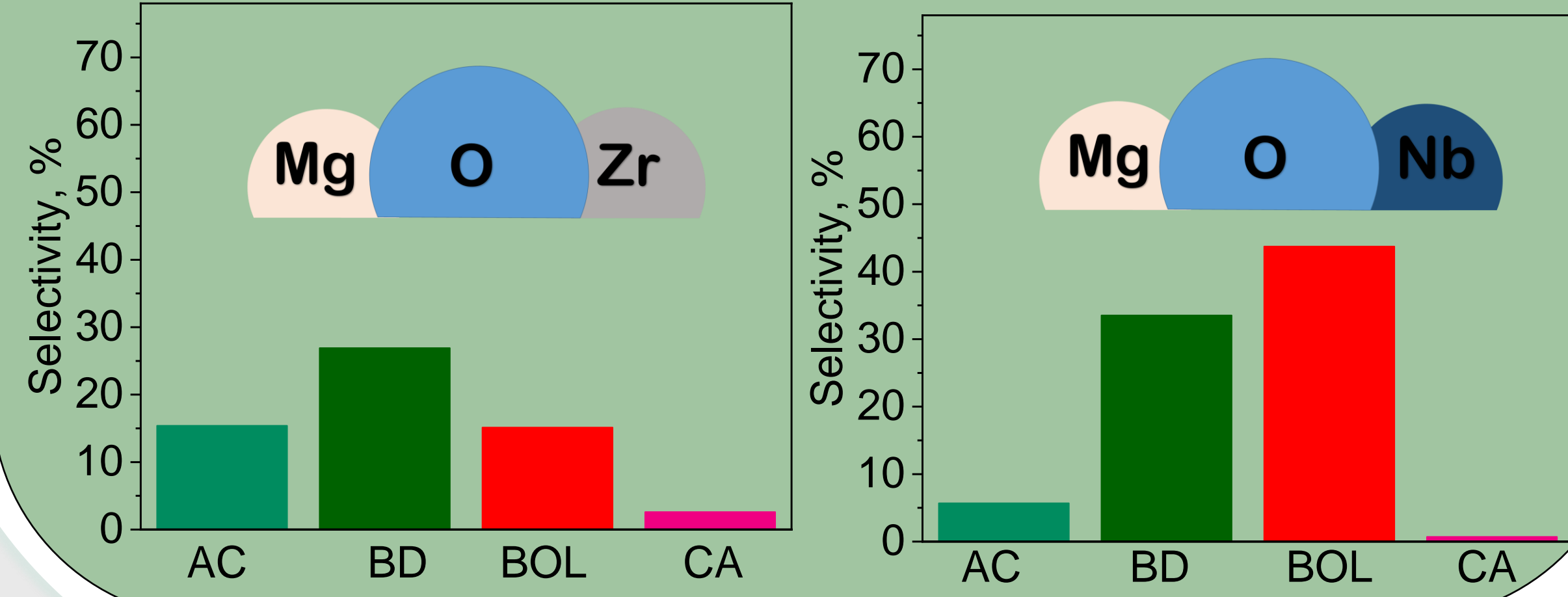
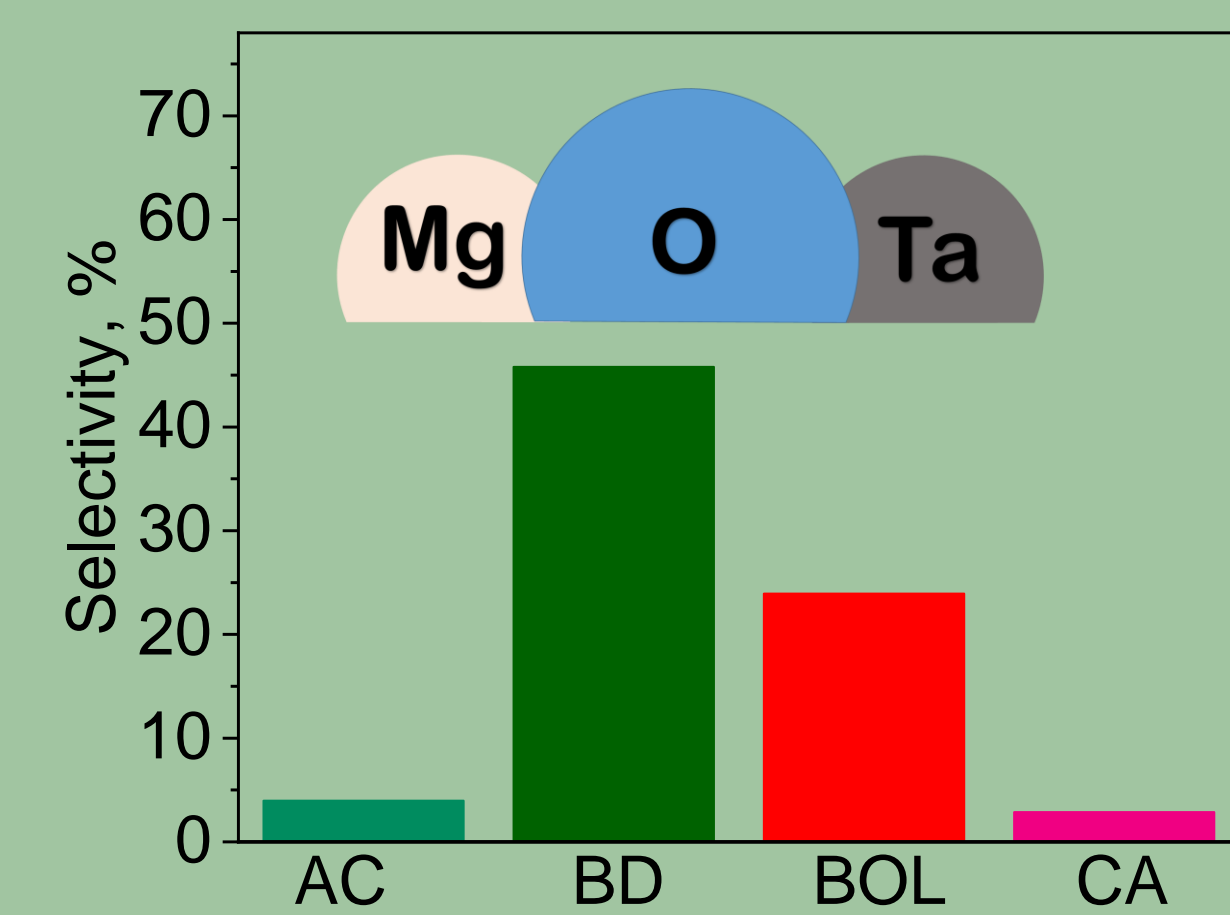
Catalytic reactions were carried out using a fixed bed, continuous flow microreactor at atmospheric pressure. The adsorbed intermediate species formed in the reaction were identified by operando FT-IR measurements. Structure and properties of catalyst preparations was characterized by XRD, STEM, EDS, N<sub>2</sub> physisorption. The binding of acidic and basic adsorbates, such as CO<sub>2</sub>, CDCl<sub>3</sub>, and NH<sub>3</sub>, pyridine, respectively, to the catalyst surface was studied by TPD, and FT-IR measurements



## Dehydrogenation activity



## Dehydration activity



## Results and discussion

Butadiene and butanol were the main ethanol conversion products formed over MgO-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub> catalysts, respectively, whereas butanol and crotyl alcohol were obtained over pure MgO catalyst. The effect of transitional metal oxide promoters was investigated on the activity of pure MgO. Over Y<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, ZnO, and CuO promoted catalysts the product distribution was similar to that obtained by pure MgO catalyst under identical reaction conditions. However, the conversion was slightly higher due to the Lewis acidic character of the additives and butadiene also appeared among the products. Relative to above mentioned catalysts, promotion of MgO by Nb<sub>2</sub>O<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub> resulted in higher dehydrogenating activity, and high butadiene selectivity, while the formation of butanol and crotonaldehyde was suppressed. High acetaldehyde selectivity showed that In<sub>2</sub>O<sub>3</sub> promoter increased dehydrogenation activity. The modification ZrO<sub>2</sub> strongly enhanced dehydration, bringing about high butadiene and ethylene selectivities. Catalytic test reactions using promoted mixed oxides are in progress, as well as, reactions of possible intermediates, and their mixtures.