Study of the Meerwein–Ponndorf–Verley Reduction over Sn(Fe)-Mg(Zn)/Al Mixed Oxides

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Highlights

- Hydrotalcite-derived mixed oxides were evaluated as MPV catalysts
- Fe-modified Mg_2Al showed enhanced activity in cinnamaldehyde reduction
- Catalytic activity depended on the surface acid–base properties
- Zn-containing mixed oxides were unsuitable due to low basicity.

1. Introduction

The Meerwein–Ponndorf–Verley (MPV) reaction is a well-established hydrogen transfer process between an alcohol and a carbonyl compound and represents an important transformation in organic synthesis[1]. Originally carried out in the homogeneous phase using metal alkoxides, it has later attracted considerable interest in heterogeneous catalysis, where solid catalysts offer advantages in terms of stability, recovery, and process safety.

The reaction proceeds via hydride transfer through a six-membered cyclic transition state formed on paired acid–base sites of the catalyst surface. Although extensively studied, the precise roles and optimal balance of Lewis acidic and basic sites remain not fully clarified. The MPV reaction is particularly attractive for the selective reduction of *α,β*-unsaturated aldehydes, as it enables preferential reduction of the C=O bond under mild conditions without the need for pressurized hydrogen.

Hydrotalcite-derived Mg–Al mixed oxides are among the most promising heterogeneous MPV catalysts[2-5] due to their tunable acid–base properties by varying the Mg/Al ratio, synthesis method, calcination temperature, or by incorporating additional metal oxides. Their catalytic activity and selectivity strongly depend on surface alkalinity, which can be tailored by catalyst composition and preparation conditions. However, the relationship between catalyst structure, surface properties, and catalytic performance is not yet fully understood. Therefore, systematic investigation of Sn(Fe)-Mg(Zn)/Al mixed oxides with tailored acid–base properties remains essential for a deeper understanding of structure–activity relationships in MPV catalysis.

2. Methods

Preparation of catalysts

(Sn/Fe)MgAl, (Sn)ZnAl and (Sn)MgZnAl hydrotalcites were synthesized by co-precipitation of a basic solution and a metal salts solution at pH 9.5 and 60 °C. The basic solution consisted of KOH (2 mol dm^{-3}) and K_2CO_3 (0.2 mol dm^{-3}) in demineralized water, while the metal precursor solution contained Mg, Zn, Al, Fe, and Sn salts in the required ratios with a total metal concentration of 1 mol dm^{-3}. Both solutions were simultaneously added to the reactor under stirring and aged for 1 h. The precipitate was filtered, washed to neutral pH, dried overnight at 110 °C, and calcined at 450 °C for 6 h to obtain the mixed oxides.

Catalytic tests

Freshly calcined catalyst in an amount of 0.5 g was weighed into a 25 ml flask and isopropyl alcohol was added. The molar ratio of carbonyl compound:IPOL was 1:12. The mixture was heated under reflux. Carbonyl compound was added to initiate the reaction. The weight ratio of carbonyl compound:catalyst was 1:1. Samples were taken at specified time intervals and analyzed on a gas chromatograph.

Characterization of prepared catalysts

XRF was used to determine the catalysts' composition. The specific surface area of all prepared catalysts was measured by nitrogen physisorption. The acid-base properties of the mixed oxides were determined using temperature programmed desorption (TPD) of pyridine and CO_2.

3. Results and discussion

In this work, hydrotalcite-derived mixed oxides based on (Sn/Fe)MgAl, (Sn)ZnAl, and (Sn)MgZnAl with varying metal ratios were prepared, calcined, and characterized. Their catalytic performance was evaluated in the MPV reduction of cinnamaldehyde, using conversion after 24 h as the measure of catalytic activity. A Mg_2Al mixed oxide (Mg/Al = 2:1) served as the reference catalyst.

Iron-modified Mg_2Al catalysts generally exhibited higher cinnamaldehyde conversion than the reference sample; however, increasing Fe content led to a slight decrease in activity. While basicity remained comparable, Fe incorporation increased surface acidity and specific surface area, and a positive correlation between acidity and conversion was observed, indicating the importance of a balanced acid–base character.

In contrast, tin modification did not significantly enhance activity, in disagreement with literature reports[6], likely due to differences in catalyst composition or surface properties. Within the $SnFeMg_2Al$ series, catalysts with similar acidity and surface area showed markedly different activities, suggesting a synergistic effect of Fe content. Catalysts from the (Sn)MgZnAl series exhibited poor performance, attributed to their low basicity and limited surface area, highlighting the importance of accessible basic sites for effective hydride transfer in MPV catalysis.

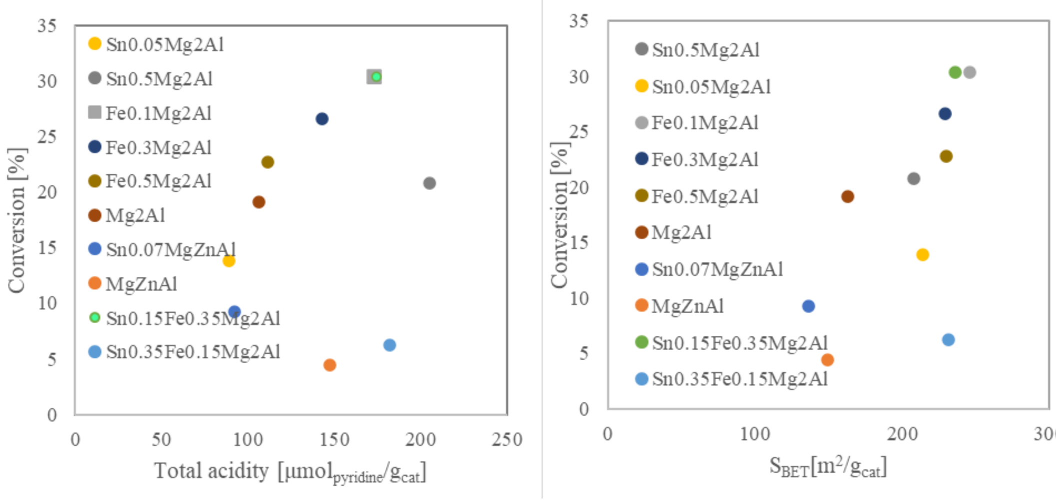

Figure 1. Conversion dependence after 24 hours Response to total acidity and specific surface area of prepared catalysts.

4. Conclusions

Hydrotalcite-derived Mg–Al mixed oxides proved to be effective catalysts for MPV reduction of cinnamaldehyde, with activity strongly influenced by surface acid–base properties. Iron incorporation enhanced catalytic performance, whereas Zn-containing systems showed limited catalytic activity. The results highlight the necessity of an optimal balance between basic and acidic sites for efficient MPV catalysis.

References

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Keywords
MPV reduction; mixed oxides; hydrotalcites; acid-base properties.