Layered double hydroxides as precursors for catalysts in Claisen-Schmidt condensation

Слоести двойни хидроксиди като предшественици на катализатори за Клайзен-Шмид кондензация

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Abstract. MMgAlO and MAIO mixed oxides (where M = Cu, Co, Zn and Ni) were obtained by thermal decomposition of the corresponding layered double hydroxides (LDH) precursors and used as catalysts for Claisen-Schmidt condensation of 2'-hydroxyacetophenone and benzaldehyde under solvent-free conditions. The catalysts were characterized by X-ray diffraction (XRD), atomic absorption spectrometry and temperature-programmed desorption of CO$_2$ (TPD-CO$_2$). Gas chromatography – mass spectroscopy (GC/MS) methods were used for the identification and quantification of the product mixture. A 2'-hydroxychalcone and 2-phenyl-2,3-dihydro-4H-chromen-4-one (flavanone) were received as main products. 3-Benzyl-2-phenyl-4H-chromen-4-one (3-benzylflavone) was achieved as a new product.

Keywords: Layered double hydroxides, mixed oxides, Claisen-Schmidt condensation.

Introduction

Layered double hydroxides (LDH) are a family of anionic clays with general formula $[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^x[\text{A}^{n-}\cdot\gamma\text{H}_2\text{O}]^{x^+}$, where $\text{M}^{2+}$ and $\text{M}^{3+}$ are divalent and trivalent metal ions, respectively, and $\text{A}^{n-}$ is an $n$-valent anion. When Mg$^{2+}$ is substituted by a trivalent cation, a positive charge appears (Caenave et al., 1991). The electroneutrality is assured by anions $\text{A}^{n-}$ located in the interlayers.

The thermal decomposition of LDH leads to the formation of mixed oxides, which are often found to be more active than their precursors. The acid-basic properties of mixed oxides depend on the nature and ratio of divalent and trivalent cations. Lewis acidity appears as a result of the iconicity of the element – oxygen bond. Surface basicity, associated to the anionic charge of the oxygen species, has the same origin. Therefore, Lewis acidity is generally associated with basicity. The ionic oxides present both basicity and Lewis acidity, but these two opposite properties are balanced differently (Busca et al., 1999). The balance of these two properties depends mainly on the polarizing power (charge/radius) of both cations. Obviously, when both cations are highly polarizing, the Lewis acidity predominates, whereas when both are poorly polarizing (large radius, low charge) the basicity will predominate. Introduction of transition metal cations, such as Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ modify the acid-base equilibrium of the LDH materials. CO$_2$- and NH$_3$-TPD experiments show that transition metal cations in the mixed oxides leads to the pronunciation of their acid character (Pavel et al., 2012). Mixed oxides containing Lewis acidic cations, such as CuAl$_{16}$O$_x$ or Al$_2$O$_3$ present low base site densities compared to oxides, containing less-electronegative cations, such as CuMg$_{10}$O$_x$ or MgO (Di Cosimo et al., 2002). On the other hand, the adsorption of SO$_2$ on a series of Mg/Ni/Al hydroxalites proves that the presence of Mg and Ni cations increases the concentration of basic sites (Casenave et al., 2001). The cited study gives evidence of the
synergistic effect of these two cations favoring the basic properties. The acid-base properties of various MgNiCuAl mixed oxides were investigated through microcalorimetry, by using NH3 and CO2, and conversion of 4-methyl-pentan-2-ol, as a test reaction (Meloni et al., 2008).

Claisen-Schmidt condensation offers a facile preparation of chalcone by reacting of acetonophenone and benzaldehyde. Chalcone is a α, β-unsaturated carbonyl and is also key precursors in the synthesis of many biologically important heterocycles such as flavones. They are a subset of compounds known as flavonoids, exhibiting with great potential applications in medicine (Mahapatra et al., 2015; Leon-Gonzalez et al., 2015). Claisen-Schmidt condensation represents an important base catalyzed carbon-carbon bond formation reaction. In this respect, the base properties of LDH and derived mixed oxides also recommended these materials as suitable catalysts (Climent et al., 2004; Yadav et al., 2020). In the literature have been reported several studies, concerning Claisen-Shmidt condensation between 2'-hydroxyacetophenone and benzaldehyde in the presence of mixed (Mg-Al) oxides as base catalysts (Climent et al., 2004), gold nanoparticles supported on LDH (Yatabe et al., 2015), yttrium-modified LDHs catalysts with molar ratios Mg2+/Al3+ + Y3+ = 3 and Al3+/Y3+ = 1 (Pavel et al., 2020).

The aim of this study is to investigate the catalytic activity of MMgAlO and MAIO mixed oxides as catalysts for the synthesis of chalcone and flavanone by condensation of 2'-hydroxyphenone and benzaldehyde.

Materials and methods

LDH precursors of the used catalysts were prepared by a co-precipitation method at room temperature (Cavani et al., 1991). The MMgAl-LDH were synthesized by the following procedure: aqueous solutions as Mg(NO3)2.6H2O and Al(NO3)3.9H2O (Mg/Al = 3) were added dropwise into a well-stirred beaker, containing transition metal nitrate solution such of Cu(NO3)2.3H2O, Co(NO3)2.6H2O, Ni(NO3)2.6H2O and Zn(NO3)2.6H2O. The pH was kept at 10±0.2. The M2+/M3+ (Mg + Al) atomic ratio was 0.05 and the transition metal content was 5% with respect to cations. The resultant precipitates were aged in their mother liquor at 90 °C for 24 h, filtered and washed. The corresponding mixed oxides (MMgAlO) were obtained by calcination at 600 °C for 7 h. The MAI-LDH precursors were prepared by dropwise mixing of two solutions: the first solution containing transition metal (M) nitrate such as Cu(NO3)2.3H2O; Ni(NO3)2.6H2O; Zn(NO3)2.6H2O; Co(NO3)2.6H2O and Al(NO3)3.9H2O (M/Al = 2), and 1M NaOH, the second solution. The pH values of the obtained solutions were maintained at about 8. The resulting slurries were hydrothermally treated in their mother liquor at 90 °C for 24 h, filtered and washed repeatedly. The corresponding mixed oxides (MAIO) were obtained by calcination of dried samples for 4 h at different temperatures. CoAlO was obtained at 400 °C, whereas CuAlO, NiAlO and ZnAlO were obtained at 600 °C, respectively.

Powder X-ray diffraction measurements with filtered Cu-Kα radiation were used. It was operated with 0.02° (20) steps in the interval of 4–80 2θ angular range with 1.5 s counting time per step. Chemical composition tests of the catalyst samples were performed by using atomic absorption spectrometry (Perkin-Elmer 3030) after disintegration in HNO3.

TPD-CO2 measurements were carried out on an apparatus coupled with an online residual gas infrared analyzer ABB-AO2040 to detect CO2. The sample was heated in a flow of dry argon (24 ml/ min) up to 680 °C (heating rate: 5 °C/min) and it was held at this temperature for 1 h. The physically adsorbed CO2 was removed with argon flow (24 ml/min) for 30 min.

The catalyst (192 mg) was activated at 500 °C for 1 h, then transferred into a three-necked-round bottom flask equipped with a reflux condenser and 67 mg (35 wt% on the catalyst) of distilled water was added directly dropwise just before reaction (Climent et al., 2004). After this, benzaldehyde (35.5 mmol) and 2'-hydroxyacetophenone (29.6 mmol) were added. The resultant mixture was rapidly heated to 150 °C under vigorous stirring in an oil bath. The reaction time for all experiments was 1 h.

GC/MS analyses were performed on an HP 6890 chromatograph with an HP 5973 MS. The column used was HP-5/MS, 30 m x 0.250 mm x 0.25 µm. The mass balances were always higher than 95%.

Results and discussion

The XRD patterns of mixed oxides are shown in Fig. 1 A. The MMgAlO samples exhibited, in all cases, the same peaks at 29.6 mmol) were added. The resultant mixture was rapidly heated to 150 °C under vigorous stirring in an oil bath. The reaction time for all experiments was 1 h.

The chemical composition of the MMgAlO mixed oxides showed that the Mg/Al atomic ratio varied between 2.5 and 3.2 (theoretical 3). The transition metal content of the MMgAlO catalysts was slightly higher than the theoretical (theoretical 0.05, experimental 0.06), while in the case of MAIO sam-
samples it was lower than the nominal value (theoretical 2, experimental 1.5–1.9).

TPD-CO$_2$ was performed to determine the basicity of the tested mixed oxides and the rate of CO$_2$ evolution as a function of sample temperature are shown in Fig. 1 B. On the basis of our TPD results the surface basicity of used mixed oxides may be described as “weak” basic sites for CO$_2$ desorption occurring at about 100 °C, “medium” basic sites for CO$_2$ desorption occurring in the range between 150 °C and 250 °C, and “strong” basic sites above 300 °C.

The synthesis of (2E)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (2’-hydroxychalcone) and its isomer – 2-phenyl-2,3-dihydro-4H-chromen-4-one (flavanone) are the main products in the Claisen-Schmidt condensation between 2’-hydroxyacetophenone and benzaldehyde. As a new product was received 3-benzyl-2-phenyl-4H-chromen-4-one (3-benzylflavone) and it was identified by its mass spectrum (MS /EI): [M]$^-$ m/z = 312(34), 191(100), 283(9), 207(20), 188(89), 165(57), 121(33), 115(29), 92(68), 63(24)).

The reactions were carried out in the absence of a solvent. The conversion and yields of the reaction products are given in Table 1.

Comparing the activity of the MMgAlO and MAIO catalysts, the first ones were more active, as indicated by the conversion rate. Among the MAIO, the most active were CuAlO and ZnAlO catalysts, while the CoAlO realized only 10.65% conversion. The catalytic behavior of MMgAlO and MAIO catalysts can be correlated to the differences in their surface acid-base properties. According to our TPD-CO$_2$ results, the MAIO catalysts are more acidic and contain weaker surface basic sites compared to MMgAlO samples. We assume the route of reaction is base-catalyzed, which involves the formation of the 2’-hydroxyacetophenone anion, followed by its attack on the carbonyl group of benzaldehyde.

Table 1. Conversion of benzaldehyde and reaction products (%) at 150 °C, catalyst-192 mg and reaction time 1h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion %</th>
<th>Flavanone %</th>
<th>Chalcone %</th>
<th>3-Benzylflavone %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMgAlO</td>
<td>100</td>
<td>50.73</td>
<td>25.8</td>
<td>23.49</td>
</tr>
<tr>
<td>CoMgAlO</td>
<td>100</td>
<td>47.35</td>
<td>35.74</td>
<td>19.35</td>
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<tr>
<td>ZnMgAlO</td>
<td>97.64</td>
<td>58.01</td>
<td>27.02</td>
<td>14.96</td>
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<tr>
<td>NiMgAlO</td>
<td>93.47</td>
<td>48.98</td>
<td>44.97</td>
<td>6.05</td>
</tr>
<tr>
<td>CuAlO</td>
<td>92.48</td>
<td>59.79</td>
<td>32.89</td>
<td>7.32</td>
</tr>
<tr>
<td>CoAlO</td>
<td>10.65</td>
<td>54.02</td>
<td>44.83</td>
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<tr>
<td>ZnAlO</td>
<td>82.14</td>
<td>48.66</td>
<td>38.22</td>
<td>13.12</td>
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<tr>
<td>NiAlO</td>
<td>26.40</td>
<td>55.76</td>
<td>41.98</td>
<td>2.27</td>
</tr>
</tbody>
</table>
resultant 2'-hydroxychalcone undergoes an intramolecular cyclization to form flavanone.

The new product could be obtained by condensation between flavanone and benzaldehyde. It might be concluded that the reaction is rather specific to OH\(^-\) and works worse on oxygens O\(^2-\) species even if the base strength is higher. Obviously, the 3-benzylflavone formation is possible only with participation of Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\) which provide acid and base species with a suitable strength. The highest yield of 3-benzylflavone was obtained in the presence of CuMgAlO, although according to the CO\(_2\)-TPD results ZnMgAlO is a more basic catalyst. Among the MAIO catalysts the most active were CuAlO and ZnAlO, which realized highest yields of 3-benzylflavone (Tabl. 1).

Conclusions

The results presented here show that MMgAlO and MAIO mixed oxides are active catalysts for solvent free Claisen-Schmidt condensation of 2-hydroxyacetophenone and benzaldehyde. 100% conversion is achieved in the presence of CuMgAlO, although according to the CO\(_2\)-TPD results ZnMgAlO is a more basic catalyst. The new product could be obtained by condensation between flavanone and benzaldehyde. It might be concluded that the reaction is rather specific to OH\(^-\) and works worse on oxygens O\(^2-\) species even if the base strength is higher. Obviously, the 3-benzylflavone formation is possible only with participation of Cu\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\) which provide acid and base species with a suitable strength. The highest yield of 3-benzylflavone was obtained in the presence of CuMgAlO, although according to the CO\(_2\)-TPD results ZnMgAlO is a more basic catalyst. Among the MAIO catalysts the most active were CuAlO and ZnAlO, which realized highest yields of 3-benzylflavone (Tabl. 1).

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