Destructive adsorption of chlorinated hydrocarbons over alkaline earth metal oxides: Linking basicity and Lewis acidity to catalyst performances

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Introduction
Chlorinated hydrocarbons are known for their negative environmental effects, with destruction of the ozone layer being one of the most important ones. Although their use in commercial products has greatly diminished in recent years, the problem of their destruction is still of high importance since crucial pharmaceuticals, fungicides, herbicides, etc. still contain chlorine and side-product waste streams have to be treated. The most common method of their destruction is by incineration, which is however costly and may produce toxic byproducts [1]. One of the alternative methods is destructive adsorption on basic oxides. It is well known that basic oxides, such as alkaline earth metal oxides, can convert chlorinated hydrocarbons into products such as CO2. Basic oxides have several advantages like high stability and low price. Also the reaction in their presence takes place at relatively low temperatures. In this work, we have investigated a series of alkaline earth metal oxides (CaO, BaO, SrO and MgO). For environmental reasons we decided to investigate the potential of CaO in more detail as a non-toxic material. Several routes were taken to prepare various CaO materials with different surface areas and acid-base properties. The goal is to link basicity and Lewis acidity to the destruction capacity of the different prepared oxide materials. For this purpose, both spectroscopy and activity measurements have been conducted.

Materials and Methods
The oxides of interest were tested in the destructive adsorption of chlorinated hydrocarbons and the results were correlated with XPS analysis in order to measure the degree of surface chlorination. To examine the physicochemical properties the following analysis techniques were performed: SEM, XRD, BET, IR with probe molecules, such as pyridine. Pyridine adsorption was carried out at room temperature and was followed by evacuation at the same temperature.

Results and Discussion

<table>
<thead>
<tr>
<th>Oxide</th>
<th>v(C=C) ring vibrations band after adsorption of pyridine [cm⁻¹]</th>
<th>BET [m²/g]</th>
<th>Starting reaction temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Evacuation in RT: 1 min</td>
<td>70min</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>*</td>
<td>*</td>
<td>–2.3</td>
</tr>
<tr>
<td>SrO</td>
<td>*</td>
<td>*</td>
<td>–2.3</td>
</tr>
<tr>
<td>CaO-EN</td>
<td>*</td>
<td>*</td>
<td>32</td>
</tr>
<tr>
<td>CaO-SD</td>
<td>*</td>
<td>*</td>
<td>2</td>
</tr>
<tr>
<td>MgO</td>
<td>1602</td>
<td>1602*</td>
<td>–2.3</td>
</tr>
</tbody>
</table>

Table 1. Physicochemical results and starting reaction temperatures of oxides under study.

(*)Broad band difficult to define or no band, only in high temperature evacuation, desorption of pyridine occurs.

The reactivity of alkaline earth metal oxides for the destruction of chlorinated hydrocarbons depends on their acid-base properties. First of all, there is a clear relationship between the reactivity and the basicity. Unlike for lanthanide oxides, their Lewis acidity seems not to be decisive factor.

Significance
The reactivity of alkaline earth metal oxides in chlorinated hydrocarbons destruction was correlated with acid-base properties and a potential reaction mechanism was established.

References