

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

The group of Klabunde [2] examined the destructive adsorption of CCl₄ on CaO and postulated a mechanism involving the nucleophilic attack of CaO basic oxygen on the carbon atom, with the subsequent adsorption of the leaving chloride on a Lewis site (coordinatively unsaturated Ca atom). On the other hand, in case of lanthanide oxides their activity in this reaction was recently found to be increasing with the strength of their Lewis acidity [3]. A mechanism was proposed that involved the initial abstraction of Cl by the Lewis site, followed by the formation

of the C-O bond. We have attempted to find the relationship between acid-base properties and reactivity for the oxides under study. The general observed trend was that the reactivity of the alkaline earth metal oxides increased with their basicity, i.e. BaO > SrO > CaO > MgO. In order to examine Lewis acidity, IR tests with pyridine as a probe molecule were performed. Careful studies of the $\nu(\text{C}=\text{C})$ ring vibrations, especially in the region 1400-1700 cm⁻¹, allowed us to examine the strength of Lewis sites of tested samples. All materials exhibited the presence of weak Lewis acid sites, but it was possible to distinguish the differences in their strength (Table 1). The weakest Lewis acidity was shown by the most basic materials and the strongest Lewis acid sites were found on CaO prepared in critical conditions by the autoclave method. Different morphologies of the examined materials were observed by SEM. We noticed that conventionally prepared CaO, which has a similar morphology as its parent calcium hydroxide also, retains a higher number of surface OH groups. Therefore, its basicity is higher and Lewis acidity lower than of the 'critical' CaO which has a different, platelet-like morphology.

Oxide	$\nu(\text{C}=\text{C})$ ring vibrations band after adsorption of pyridine [cm ⁻¹]		BET [m ² /g]	Starting reaction temperature [°C]
	Evacuation in RT			
	1 min	70min		
BaO	*	*	~2-3	300
SrO	*		~2-3	310
CaO-CR	1595	1599	54	-
CaO-CP	1593	1596	76	340
CaO-EN	*	*	32	370
CaO-SD	1593	1594	2	375
MgO	1602	1602*	~2-3	380

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

- [1] Blakenship, A., Chang, D. P. Y., Jones, D. A., Kelly, P. B., Kennedy, I. M., Matsamura, F., Pasek, R., Yang, G. *Chemosphere* 28, 183 (1994).
- [2] Koper, O., Lagadic I., Klabunde, K.J. *Chem. Mater.* 9, 838 (1997).
- [3] van der Heijden, A. W. A. M., Belliere, V., Espinosa Alonso, L., Daturi, M., Manoilova, O. V., Weckhuysen, B. M., *J. Phys. Chem. B* 109, 23993 (2005).