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HYDROTALCITE AS A BASE CATALYST IN ALDOL CONDENSATION

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The study provide the description of the catalytic behaviour of hydrotalcite as a base catalyst in aldol condensation. The testing reactions were carried out in a vapor-phase, a flow reactor at atmospheric pressure. The main products of aldol condensation were phorone, isophorone, mesityl oxide, isoxylitones and tetramethyltetralone. A relation between experimental temperature, conversion of acetone and main products was found.

Key words: aldol condensation, acetone, hydrotalcite.

INTRODUCTION

Anionic clays are natural and synthetic layered mixed hydroxides, containing exchangeable anions. Hydrotalcite belongs to this large class of anionic clays and have found many practical applications mostly as catalysts and adsorbents. The most interesting properties of the oxides obtained by calcinations are the following:

- high surface area;
- basic properties;
- formation of homogeneous mixtures of oxides with very small crystal size, stable to thermal treatments ;

- property for reconstruction, under mild conditions, of the original hydrotalcite structure.

The first two properties have found application in the field of heterogeneous catalysis as a base catalysts and supports. In the literature are depicted some base-catalyzed reactions: polymerization of β -propiolactone (Nakatsuka et al., 1979) and propene oxide (Kohjiga et al., 1981), and aldol condensation of acetone (Reichle, 1980; Reichle, 1985) or acetone and formaldehyde (Suzuki et al., 1988).

The present work is concerned with testing a heat-treated hydrotalcite as catalyst for vapor-phase aldol condensation of acetone.

EXPERIMENTAL

CATALYST PREPARATION

Initial hydrotalcite samples were prepared by coprecipitation of 1 M $\text{Mg}(\text{NO}_3)_2$ and 1 M $\text{Al}(\text{NO}_3)_3$ solutions with 1 M NaOH and 0.5 M Na_2CO_3 . The reaction was carried out in polypropylene vessels at 50 °C and pH of 10.5.

The precipitates were aged at 90 °C for 48 h and then filtered, washed until the pH of the washing water reached 8–8.5 and air-dried (Miyata, 1980; Pausch et al., 1986). The hydrotalcite sample was heated at 350 °C. X-ray diffraction (XRD) patterns indicate three diffraction line (at $d = 2.48$, $d = 2.021$ and $d = 1.448$) which is characteristic feature of the mixed (Mg-Al) oxide (MO).

The grain size of prepared mixed oxide was estimated using Scherrer's equation and the value is about 3–4 nm. The small-angle scattering at $2^\circ \theta$ XRD pattern also demonstrate nano-size of MO-grains (Petrova et al., 2005). The Mg and Al contents were determined by atomic absorption spectroscopy (AAS) and the Mg/Al ratio of MO was 2:1.

CATALYTIC INVESTIGATIONS

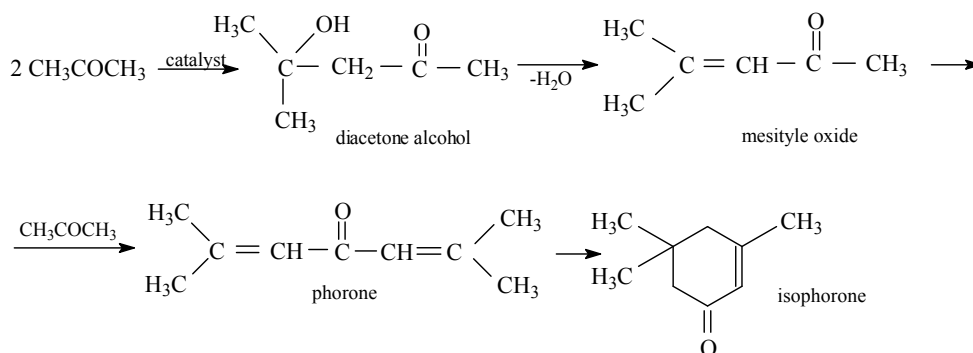
Base catalytic properties of the so-obtained mixed oxide are investigated in a continuous-flow reactor, operating at atmospheric pressure. The aldol condensation of acetone is used as a test reaction. Starting acetone is a fresh-distilled chromatographically clean product.

Aldol condensation result in numerous, large-volume chemicals, such as mesityl oxide, diacetone alcohol, isophorone and 2-ethylhexanal, which are frequently hydrogenated to yield valuable solvents, lubricants and plasticizers. Catalytic conversions of acetone are conducted at reaction conditions as follows: temperature interval of 120–370 °C, space velocity of 0.96 h^{-1} and catalyst content of 4 cm^3 (particle size is about of 18–20 mesh). Preliminary the hydrotalcite is calcined for 10 h at 350 °C in gas flow of dry N_2 . Duration of the reaction is 30 min. The liquid reaction products are analyzed by GC/MS.

Analytical conditions for the GC/MS analysis were as follows: column – HP 5/MS whit $30 \text{ m} \times 0.200 \text{ mm} \times 0.25 \mu\text{m}$ ft. Temperature program – from 50 to 280 °C, whit $8 \text{ }^\circ\text{C}/\text{min}$. Split injectionq with split ratio 1 : 25. MS ionization method was EI at 70 eV.

RESULTS AND DISCUSSION

The reaction scheme for the aldol condensation is shown in the figure:



Other by-products are mesitylene, isoxylitones, tetramethyltetralone.

The conversion of acetone increases with rise in temperature – from 87.4 wt% at 120° to 97.5 wt% at 370 °C.

It makes a great impression, that primary products phorone and isophorone are in different correlation by variety of temperature. The quantity of isophorone (11.5%) predominate at lower temperatures, while at temperature of 370 °C the quantity of isophorone is 7.7%. Phorone is obtained about 3.9% at 120 °C and with increasing of temperature to 370 °C this quantity rise to 5.3%, i. e. correlation phorone/isophorone increase twice with rise of temperature (from 0.34 to 0.69 respectively). It is supposed that the quantity of cyclic product decreases with rise of temperature because of opening of the ring. This conclusion is of a great importance according to the assumption of Reichle (Reichle, 1980) that the isophorone is opening the ring and after a number of transformations is converted to mesitylene.

These facts in our investigations are in good confirmation with the decrease of a tetramethyltetralone quantity at higher temperature – from 11.7% at 120 °C to 3.7% at 370 °C. The higher temperature favore the ring opening and leads to other organic compounds.

Quantities of isoxylitones are in a similar correlation. More of these products are obtained at a lower temperature.

The quantity of the obtained mesityl oxide practically do not changes with varying of the temperature. This product is in the range of 14.4–14.8%.

Thus, by changes of the temperature can be regulated the correlation between open chain products and cyclic products, which are obtained as result of aldol condensation and other concomitant reactions.

In order to check the catalytic stability of the MO are conducted some consistent catalytic experiments. The sample is calcined for 3 h at 300° in flow of dry N₂ after every experimental run. Results of these investigations shows that the MO has a long

lifetime and high stability and it can be used repeatedly without regeneration. The stability of MO is confirmed by X-ray measurements on repeatedly-work catalyst. There can not be seen considerable structure changes.

CONCLUSIONS

These catalytic investigations demonstrate high catalytic activity and selectivity for the testing reaction and the possibility to use hydrotalcite as a base catalyst in aldol condensation of acetone instead of conventional heterogeneous catalysts. The mixed oxide shows good stability during the experiments, which allows repeated use.

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