BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (8), 2449—2450 (1979)

The Polymerization of β-Propiolactone by Calcined Synthetic Hydrotalcite

Takuo NAKATSUKA,* Hitoshi KAWASAKI, Shinzo YAMASHITA,** and Shinzo KOHJIYA**
Industrial Technology Center of Okayama Prefecture, Ifuku-cho 4 chome, Okayama 700
***Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto 606*

(Received August 7, 1978)

Synopsis. The calcination of synthetic hydrotalcites of different compositions gave aluminium magnesium double oxides with strong basic sites and a high catalytic activity towards the polymerization of β-propiolactone. The strong basic sites were determined and compared with the apparent polymerization rates, suggesting that the strong basic sites are active sites towards the reaction.

Many catalytic reactions precipitated by either aluminium oxide or magnesium oxide have appeared in the literature; however, only a few works have been found regarding aluminium magnesium double oxide catalyses: the polymerization of formaldehyde,[1] the methylation of 3,5-xylenol,[2] and the depolymerization of paraldehyde.[3] In the last work, the correlation between the reactivity and the acid strength of the catalysts was mentioned. These catalysts were prepared by the calcination of hydroxides, nitrates, or carbonates.

Fukuda *et al.*[4] calcined synthetic hydrotalcites[5] with various molar ratios of the two metals in order to prepare aluminium magnesium double oxides, and studied their catalytic activity towards the decomposition of 4-hydroxy-4-methyl-2-pentanone and the methylation of phenol with methanol. The polymerization of propylene oxide was also found to be catalyzed by the oxide.[6] In this paper, these double oxides will be shown to catalyze the polymerization of β-propiolactone, and the active sites for the reaction will be discussed.

Experimental

Reagents. The hydrotalcites were supplied by the Kyowa Chemical Co., Ltd. The β-propiolactone was obtained commercially, dried over anhydrous sodium sulfate, and distilled under 10 Torr. The toluene was dried over calcium hydride and distilled under nitrogen. The acetone, ethanol, and chloroform used were of a reagent grade.

Calcination of Hydrotalcite. About 0.5 g of air-dried hydrotalcite was placed in a 20 ml test tube, calcined in air at elevated temperatures up to 450 °C, and kept at this temperature for 1 h. Then, the calcined hydrotalcite was cooled to 300 °C in air and subsequently to room temperature over anhydrous calcium chloride. After the determination of the calcination loss of hydrotalcite, the air in the tube was replaced with nitrogen and the tube was sealed with a stop cock.

Polymerization Procedure. To the oxide in the tube, 3 ml of toluene, 3 ml of β-propiolactone, and a magnetic stirring bar were added and the tube was sealed off. The reaction was carried out under stirring at a constant temperature for the necessary period of time. Then the reaction mixture was poured into ethanol, and the resulting precipitate was filtered and dried *in vacuo*. The polymer was extracted from the polymer-oxide composite with hot acetone for 10 h, using a Soxhlet extraction apparatus. The viscosity of the extracted polymer was measured at 30 °C in chloroform (0.5 g/dl).

Results and Discussion

The calcination of synthetic hydrotalcite at 450 °C for 1 h caused an almost complete decomposition, evolving carbon dioxide and water; consequently, aluminium magnesium double oxide was formed. The results of the chemical analysis and the measurement of the surface area are summarized in Table 1. A colour change in the indicator adsorbed on the oxide surface was observed for methyl red ($\mathrm{p}K_a=4.8$), but not for phenylazonaphthylamine ($\mathrm{p}K_a=4.0$). Therefore, the most acidic sites had acid strengths of $4.8 \geqslant H_0 \geqslant 4.0$. In the same manner, the most base strength of the oxides was determined to be $18.0 \geqslant H_- \geqslant 17.2$.

TABLE 1. CHARACTERIZATION OF ALUMINIUM MAGNESIUM DOUBLE OXIDES

Oxide	**1**	**2**	**3**	**4**	**5**
Calcination loss (wt %)	42.5	42.1	41.2	42.9	42.3
Chemical analysis					
MgO (wt %)	47.3	56.7	62.5	72.7	79.4
Al_2O_3 (wt %)	48.0	37.7	30.2	19.7	11.4
MgO/Al_2O_3 (molar ratio)	2.49	3.80	5.23	9.33	17.6
Amount of acid[a] (mmol/g)	0.41	0.32	0.21	0.06	0
Amount of base[b] (mmol/g)	0.63	0.54	0.73	0.85	0.94
Surface area[c] (m^2/g)	216	133	137	187	209

a) This was measured by the titration of butylamine (0.1 mol dm^{-3}) in benzene, using methyl red ($\mathrm{p}K_a=4.8$) as an indicator. b) The value was obtained by the titration of benzoic acid (0.1 mol dm^{-3}) in benzene, using 2,4-dinitroaniline ($\mathrm{p}K_a=15.0$) as an indicator. c) The surface area was measured by the BET method.

In order to examine the effects of these strong basic sites on the polymerization, the basic sites which have the base strength of $H_- \geqslant 15.0$ were determined (Table 1). The amount of the base was shown to increase with an increase in the molar ratio of magnesium oxide to aluminium oxide, except for the oxides **1** and **2**. This might be due to the increase in the surface area. The amount of the acid ($H_0 \leqslant 4.8$) correlates reversely with the magnesium oxide content. By X-ray analysis, the oxides showed only magnesium oxide diffraction patterns and no hydrotalcite patterns. The aluminium oxide moiety was likely to make a non-crystalline structure.

The results of the polymerization of β-propiolactone

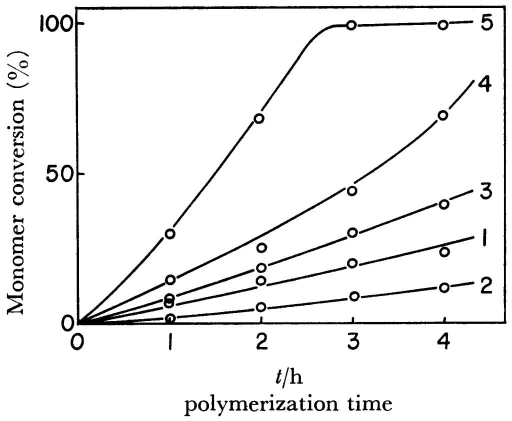

Fig. 1. Time-conversion curves for the polymerization of β-propiolactone catalyzed by the oxides listed in Table 1. β-propiolactone 3 ml, toluene 50 vol % solution, at 50 °C. Oxides **1** to **5** were prepared by the calcination of 0.5 g of corresponding hydrotalcites.

using the oxides in Table 1 as catalysts are summarized in Fig. 1. Since the reproducibility of the reaction was poor, *e.g.*, the variation coefficient of the monomer conversion (oxide **3**; 50 °C; 3 h) over 10 runs was 13%, the calcination and polymerization for hydrotalcites in a experiment were carried out at the same time. From the reaction products (reaction time 3 h; *cf.* Fig. 1), polymers were extracted with acetone. The polymers exhibited ester bands at 1730 and 1170 cm^{-1} in the ir spectra. The values of the weight per centage of the extracted polymer to the polymer-oxide compositions were 31, 36, 34, 25, and 8 for oxides **1** to **5** respectively. The values of the intrinsic viscosity were found to be 0.21, 0.11, 0.25, 0.36, and 0.26, showing that the polymers obtained did not have large molecular weights.[7)]

A comparison of the amounts of the bases ($H_{-} \geqslant 15.0$) of the oxides in Table 1 with the overall initial polymerization rates in Fig. 1 implies that the reaction was initiated by a strong base. On the addition of a small amount of water, the oxides lost their polymerization activity. A carbon dioxide atmosphere also deactivated them. Such variations in the reaction conditions were found to diminish the amount of the strong base. Therefore, the active sites seem to correlate with the basic sites. However, the calcination of hydrotalcites at a reduced pressure (*ca.* 3 Torr) was also found to give oxides with a poor catalytic activity. This finding will be discussed elsewhere.

According to Malinowski's report,[8)] magnesium oxide may have two kinds of basic sites on the surface: a strong basic site, O^{2-}, and a weak basic site, OH^-. The probable active site might be attributed to the strong basic surface oxygen. The role of aluminium oxide in the reaction is not yet clear; however, it contributed to the appearance of the strong basic sites ($H_{-} \geqslant 15.0$) on the double oxide. Magnesium oxide alone, prepared by the calcination of magnesium carbonate, did not exhibit such a strong basicity nor any polymerization activity.

The authors wish to thank Mr. Teruhiko Kumura for the generous gift of hydrotalcites and for the measurement of the surface area.

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