

Thermal stability of some aluminium chelate complexes

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Abstract

The paper presents data regarding the synthesis and thermal stability of some aluminium chelates with β -diketones. The thermal degradation of chelates was performed in order to determine the possibility and the conditions for obtaining Al_2O_3 . The oxide obtained by thermal decomposition of aluminium hexafluoroacetyl-acetonate presented a higher catalytic activity for the dehydration reaction of ethanol, than a standard catalyst (γ -alumina activated in air at 500°C). © 1997 Elsevier Science B.V.

Keywords: Aluminium chelate complexes; Catalytic activity; Thermal degradation

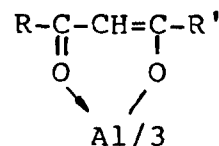
1. Introduction

The Al^{3+} ion is forming, with a series of β -diketones, chelate compounds which are insoluble in aqueous solutions, leading to their quantitative separation [1,2]. The reactions present selectivity and the aluminium could be separated from different mixtures of cations. These chelates could be used, by thermal degradation, to obtain Al_2O_3 as a catalyst support or even as catalyst for varied reactions [3].

2. Experimental

The aluminium chelates with β -diketones were prepared in accordance with the method described by Lodzinka and Rozpoloch [4], the product's purity being determined by chemical analysis [5] and atomic absorption spectroscopy. The general structural for-

mula of the obtained complexes is:



In Table 1 are presented the synthesized chelates as a function of the used β -diketones.

The thermal stability study of the abovementioned complexes was performed using a MOM-Budapest derivatograph with recording of TG, DTG, DTA vs. T curves. In order to obtain comparable data, the same sensitivities for TG (500 mV), DTG (2.5 mV), DTA (1 mV) vs. T (500 mV) were maintained. The samples weight was $\sim 100\text{mg}$, the analyses being performed in air up to 1000°C at three different heating rates – 5, 10 and $20^\circ\text{C min}^{-1}$. All compounds were also degraded in isothermal conditions to determine the reaction rate constants.

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Table 1
The synthesized aluminium β -diketonates

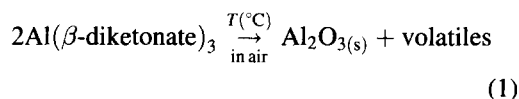
No.	Chelate	Symbol	Radical type		Formula
			<i>R</i>	<i>R'</i>	
1	Aluminium acetylacetonate	Al(AAc) ₃	–CH ₃	–CH ₃	Al(C ₅ H ₇ O ₂) ₃
2	Aluminium benzoylacetonate	Al(BAc) ₃	–C ₆ H ₅	–CH ₃	Al(C ₁₀ H ₉ O ₂) ₃
3	Aluminium hexafluoroacetylacetonate	Al(HFAAc) ₃	–CF ₃	–CF ₃	Al(C ₅ HO ₂ F ₆) ₃
4	Aluminium dibenzoylmethanate	Al(DBM) ₃	–C ₆ H ₅	–C ₆ H ₅	Al(C ₁₅ H ₁₁ O ₂) ₃
5	Aluminium nitrobenzoylmethanate	Al(nDBM) ₃	–C ₆ H ₄ NO ₂	–C ₆ H ₄ NO ₂	Al(C ₁₅ H ₉ O ₆ N ₂) ₃

The aluminium was chemically dosed in the solid residue [5]. The sample obtained after the decomposition of Al(MFAAc)₃ was tested as catalyst for the dehydration reaction of ethanol. The analyses were performed using a CHROM-4 chromatograph, samples of 20 mg γ -Al₂O₃ activated in air at 500°C and synthesized Al₂O₃, nitrogen as gas carrier (20 ml min^{–1}) and an impulse sample of 0.2 μ l.

3. Results and discussion

The thermal stability of aluminium chelates was discussed on the basis of decomposition temperatures and the kinetic parameters. The thermogravimetric data are listed in Table 2.

As shown in Table 2, the thermal decompositions occurred in only one stage and the weight losses were calculated for the general reaction:



As can be observed, Al(HFAAc)₃ presented the lowest thermal stability both from the of decomposition starting temperature as well as the *T*_{0.5} (temperature corresponding to 50% weight loss) points of view. On the other hand, the higher the heating rate, the higher the thermal stability. Among the five studied chelates, only Al(AAc)₃ had a much higher experimental weight loss as compared to the calculated one.

Table 2
Thermogravimetric data for the decomposition of some aluminium β -diketonates

Chelate	Heating rate (°C min ^{–1})	Decomposition field in (°C)	<i>T</i> _{0.5} (°C)	Overall weight losses (%)	
				found	calculated
Al(AAc) ₃	5	155–417	255	94	—
	10	170–488	263	91	84.3
	20	170–458	292	92	—
Al(BAc) ₃	5	200–560	360	87	—
	10	185–635	370	87	90
	20	185–742	375	87	—
Al(HFAAc) ₃	5	91–353	180	95	—
	10	150–430	270	92.2	92.2
	20	150–500	295	94.5	—
Al(DBM) ₃	5	145–390	304	89	—
	10	183–675	443	88	92.6
	20	241–800	480	88	—
Al(nDBM) ₃	5	130–564	430	91.5	—
	10	145–595	410	88	94.7
	20	150–740	455	89.5	—

Table 3

Values of the activation energy (kJ mol^{-1}), reaction order for nonisothermal decomposition and rate constant for isothermal decomposition of aluminium β -diketonates

Chelate	Heating rate						Rate constant at 210°C (min ⁻¹)
	5°C min ⁻¹		10°C min ⁻¹		20°C min ⁻¹		
	<i>E</i> _a	n	<i>E</i> _a	n	<i>E</i> _a	n	
Al(AAc) ₃	79.18	0.2	86.93	0.4	80.29	0	0.3818
Al(BAAc) ₃	57.24	0	91.28	0	81.25	0	0.0315
Al(HFAAc) ₃	45.2	0	60.35	0	56.63	0	0.2883
Al(DBM) ₃	51.77	0	65.27	0	62.19	0	0.1869
Al(nDBM) ₃	49.42	0	62.04	0	59.22	0.3	0.0489

Table 4

Comparative data regarding the reaction products for the dehydration of ethanol when standard and synthesized Al_2O_3 was used

Temperature (°C)	Obtained Al_2O_3			γ -Alumina reaction products (%mol)		
	ethanol	ethene	ether	ethanol	ethene	ether
175	41.5	29.8	28.7	48.9	24.3	26.8
200	38.5	36.2	25.3	38.0	39.8	22.2
225	30.4	53.6	16.0	26.5	55.1	18.4
250	16.8	78.7	4.5	18.2	72.7	9.1
275	4.0	95.1	0.9	7.0	89.9	3.1
300	—	100	—	1.7	97.3	1.0
325	—	100	—	—	100	—

This fact could be explained by the volatilization of the complex as indicated by Moshier and Sievers [2], the process being influenced by the heating rate.

The activation energy and the reaction orders were estimated by means of Coats–Redfern method [6].

In order to calculate the rate constants for the decomposition of all samples, an isothermal treatment at 210°C was performed.

Studying the data from Table 3 it was observed that the complex compound Al(HFAAc)₃ had the lowest activation energy at any used heating rate. From the isothermal data it was observed the Al(AAc) had the highest decomposition rate being followed up by the Al(HFAAc)₃ complex.

Analysing the obtained results, we can conclude that the complex compound Al(HFAAc)₃ is a potential precursor for the synthesis of Al_2O_3 . The data regarding the catalytic activity of the obtained oxide on the dehydration of ethanol are listed in Table 4.

Comparing the molar composition of the reaction products when γ -alumina (supplied by Merck) acti-

vated in air at 500°C and Al_2O_3 , obtained from decomposition of Al(HFAAc)₃, were used, the following observation can be made:

- The obtained oxide led to a higher yield than the standard catalyst.
- For temperatures that are higher than 250°C, the obtained Al_2O_3 had a higher selectivity; at 300°C the only one reaction product being ethene.

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