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## Lanthanum-Containing Catalysts for Hydrogenation: New Possibilities for the Provision of Raw Material to Industry

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### Abstract

Fluorination of lanthanum oxide with ammonium fluoride is studied. Among all the known rare earth elements, lanthanum oxide is most commonly used as a stabilizing catalyst component, in particular in the hydrogenation of heteroatomic compounds of biofuel. Previous thermodynamic and thermogravimetric studies point to the multistage fluorination of  $\text{La}_2\text{O}_3$  with ammonium fluoride. The reaction kinetics is correctly described by the kinetic equation of a contracting sphere with the activation energy equal to 33.65 kJ/mol. The X-ray phase analysis of the formed crystal phase showed that complex fluorides like  $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{LaF}_6 \cdot 0.5\text{H}_2\text{O}$  are formed as impurities during the interaction of  $\text{La}_2\text{O}_3$  with  $\text{NH}_4\text{F}$  in addition to the major product ( $\text{LaF}_3$ ).

**Keywords:** fluoride, lanthanum oxide, cracking catalyst

### INTRODUCTION

Rare earth elements (REE) are an essential and integral part of many modern technologies. Their application in alloys and compounds may determine the productivity of complicated engineering systems: automobile catalytic converters, catalysts of oil processing, production and polish of glass, ceramics, permanent magnets, metallurgical additives and alloys, as well as luminophores, monitor panels, radiolocation and X-ray intensifying films [1–4].

REE are extensively studied both in the free and oxidized state as structural and electronic promoters to improve activity, selectivity and thermal stability of catalysts [5–8].

As described in review [9], lanthanum oxide  $\text{La}_2\text{O}_3$  may act as an efficient stabilizer for nickel or copper active component of hydrodeoxygenation catalyst. La–Ni–Mo–B systems were also studied as the catalysts of hydrodeoxygenation [10].

The use of catalysts containing precious and rare elements is complicated by their deactiva-

tion during operation: carryover of the active component, carbonization. Some deactivation processes develop so that they do not allow catalyst regeneration, so it is necessary to choose and study various methods of REE processing in order to isolate them from worked out catalysts.

The search for the sources of raw material basis for obtaining REE is urgent too. The world market of REE compounds is monopolized by China, which forces other countries to create and develop their own sources of mining and production of these rare elements. Ore from the Chuktukon-skoe deposit [11] with REE content up to 6 mass % and worked out catalyst of cracking (WCC) [12] may be considered as promising sources.

Various methods of the treatment of raw materials with high REE content ( $\geq 3$  mass %) are known, in particular, treatment with sulphuric acid at 155–230 °C [13], alkaline treatment with sodium hydroxide at 140 °C [14], roasting with sodium carbonate at 900 °C and with sodium fluoride at 800–825 °C [15]. To search for an optimal processing technology, it is necessary to under-

stand the chemical nature of the interaction of separate components and the mixture in general with the material to be processed. REE compounds are present in the ore mainly in the form of their oxides. It is promising to use ammonium fluoride as one of the materials for REE (in particular lanthanum) isolation [12].  $\text{NH}_4\text{F}$  is commercially available and does not bring special danger to the environment. The formed lanthanum fluoride may be easily separated and transformed into oxide with a high degree of purity, which is important for its subsequent use as a component of a hydrogenation catalyst.

The basis of WCC processing is in the consecutive separation of the main components of the catalyst:  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  [12]. Silicon dioxide heated for a long time with ammonium fluoride sublimes in the form of  $(\text{NH}_4)_2\text{SiF}_6$ . For more detailed investigation of the possibility of WCC processing, it is necessary to understand and study intermediate processes that take place in the reaction system at the moment of fluorination.

The goal of the present work was to study the kinetics of the interaction of lanthanum oxide with ammonium fluoride ( $\text{NH}_4\text{F}$ ) for the purpose of obtaining the pure component for subsequent use as a stabilizing component of hydrogenation catalyst for heteroatomic compounds of bio oil.

## EXPERIMENTAL

The object of investigation of lanthanum oxide (Kh. Ch. reagent grade), the most frequently used REE oxide for the development of catalytic systems. Kinetic studies were carried out within temperature range 100–130 °C at a step of 10 °C in a reactor made of aluminium. The amount of evolved ammonia was estimated using chromatography. The reaction system composed of  $\text{La}_2\text{O}_3$  and a two-fold excess of  $\text{NH}_4\text{F}$  (Kh. Ch. grade)

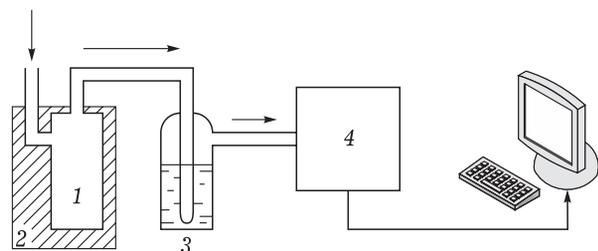


Fig. 1. Scheme of the set-up for catalytic studies of lanthanum oxide fluorination with ammonium fluoride: aluminium reactor (1), furnace (2), Drexel bottle (3), chromatograph (4).

was thoroughly mixed and placed in the reactor (Fig. 1). The reactor was blown with argon for 10 min at a flow rate of 40 ml/min to remove excess air, so the reaction was carried out in the atmosphere of argon. The gas mixture running out of the reactor was passed through a Drexel bottle filled with powdered NaOH (Kh. Ch. grade) to bind excess water and hydrogen fluoride. Then the gas mixture under analysis entered the chromatograph to determine the amount of evolved ammonia.

The dynamic curves were linearized to determine the degree of transformation with the help of basic kinetic dependences for solid-phase reactions [16]. Subsequent calculation of activation energy was carried out according to the Arrhenius equation.

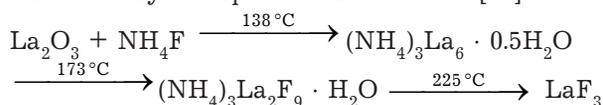
X-ray phase analysis (XPA) was carried out using a Shimadzu XRD-7000 diffractometer ( $\text{CuK}_\alpha$  radiation, Ni filter, angle range  $2\theta$  5–70°, step 0.05°) at room temperature and atmospheric pressure. Results of experiments were treated with the help of PowderCell 2.4 and WINFIT 1.2.1 software packages. The phase composition of initial and resulting compounds was established by indexing powder diffraction patterns of the samples by analogy with theoretical diffraction patterns. The fluorinated sample for XPA was prepared by annealing the mixture of lanthanum oxide with ammonium fluoride at 250 °C for 3 h.

## RESULTS AND DISCUSSION

Initial lanthanum oxide was analyzed by means of XPA to identify the crystalline phase.

One can see (Fig. 2) that lanthanum oxide used in the work is single-phase: all peaks in the diffraction patterns correspond to the phase of lanthanum oxide (III) (Card No. 000-22-0369).

To establish the probabilistic sequence of the reactions of ammonium fluoride with lanthanum (III) oxide, at the initial stage of the investigation we carried out thermodynamic analysis within temperature range 300–1000 K and proved the principal possibility of chemical interaction to proceed [17]. We also carried out thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as described in [17]. The sequence of reactions involved in the fluorination of  $\text{La}_2\text{O}_3$  with ammonium fluoride may be represented as follows [17]:



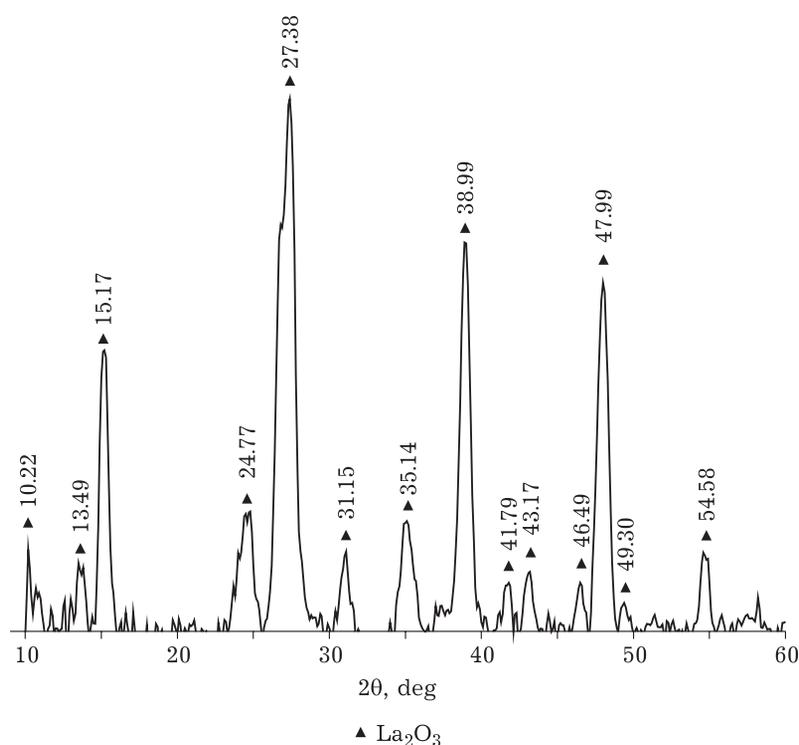


Fig. 2. Diffraction patterns of initial lanthanum oxide sample.

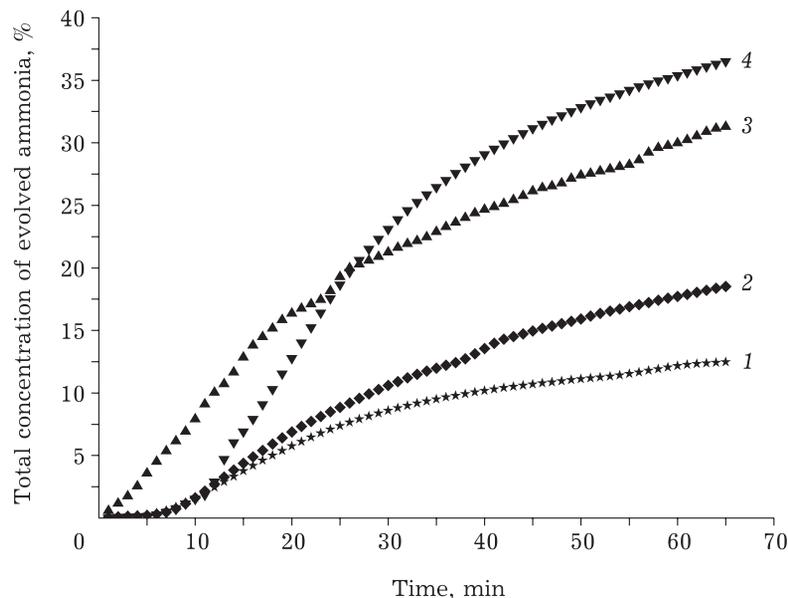


Fig. 3. Overall dynamics of ammonium evolution at reaction temperature, °C: 100 (1), 110 (2), 120 (3), 130 (4).

Analysis of the kinetic curves was carried out according to the proposed procedure to establish the kinetic model of solid-phase interaction of  $\text{La}_2\text{O}_3$  with  $\text{NH}_4\text{F}$ .

The kinetic curves of the overall dynamics of ammonia evolution with time are presented in Fig. 3. Mathematical treatment of the experimen-

tal data on the interaction of lanthanum oxide with ammonium fluoride was carried out over six equations: contracting sphere, Jander, Krack-Ginstling-Brounstein, Valency-Carter, anti-Jander and anti-Valency-Carter. The applicability of these equations was determined from the maximal correlation coefficient for  $k = f(\alpha, \tau)$  de-

pendences [16, 18–20]. On the basis of the obtained dependences, the percentage of the highest linearization (correlation coefficients 0.95–0.98) of the dependence of transformation degree on time at different temperatures for the fluorination of lanthanum (III) oxide with ammonium fluoride corresponded to the model of contracting sphere. Then the dependence of lanthanum oxide transformation degree ( $\alpha$ ) on time ( $\tau$ , s) and temperature ( $T$ , K) was deduced:

$$\alpha = 1 - \left( 1 - 65.4e^{-\frac{33650}{8.314T}\tau} \right)^3 \quad (1)$$

The use of the model of contracting sphere allowed us to make the following conclusions: the activation energy of the process is equal to 33.65 kJ/mol, the limiting stage of the process is the rate of the chemical reaction.

Lanthanum oxide in mixture with  $\text{NH}_4\text{F}$  was annealed at 250 °C for 3 h and then subjected to X-ray phase analysis for the purpose of identifying the formed components.

According to the results of XPA (Fig. 4), the synthesized sample contains three components: intense peaks in the region of small angles  $2\theta$  and peaks in the region of large angles  $2\theta$  in the diffraction patterns correspond to  $\text{LaF}_3$  phase (card No. 000-08-0461), other peaks correspond to  $(\text{NH}_4)_3\text{LaF}_6 \cdot 0.5\text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$  (card Nos. 000-46-0079 and 000-28-0071, respectively). The three-component composition of the system

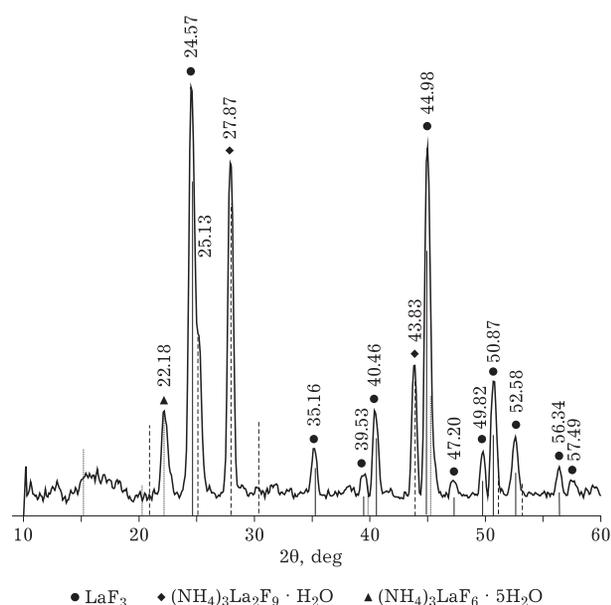


Fig. 4. Diffraction patterns of the sample obtained as a result of the interaction of lanthanum oxide with ammonium fluoride at 250 °C.

explains non-coincidence between theoretical and practical data on mass decrease observed during TGA [17].

## CONCLUSION

Fluorination of lanthanum oxide with ammonium fluoride was studied for the purpose of determining the kinetic features of their interaction. It was shown that reaction kinetics is described by the equation of the contracting sphere with the activation energy of the process equal to 33.65 kJ/mol. The dependence of the degree of lanthanum oxide transformation on time within temperature range 100–130 °C was determined. X-ray analysis of the final mixture points to the presence of complex fluorides having the composition  $(\text{NH}_4)_3\text{LaF}_6 \cdot 0.5\text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{La}_2\text{F}_9 \cdot \text{H}_2\text{O}$ , in addition to  $\text{LaF}_3$ .

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