

Structure Sensitivity of Sol-Gel Alkali Tantalates, ATaO₃ (A= Li, Na and K): Acetone Gas Phase Condensation

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Abstract. Perovskite-type compounds such as alkali tantalates, ATaO₃ (A = Li, Na and K), prepared by the sol-gel method are reported as heterogeneous basic catalysts for the acetone aldol condensation. It has been proposed that the activity order and the selectivity patterns (LiTaO₃ > KTaO₃ > NaTaO₃) depend on the octahedral arrangements of the TaO₆ tantalates.

Introduction

The increasing demand of fine chemical intermediates has prompted a renewed interest in the study of novel catalysts for the acetone aldol condensation [1], and the development of alternative basic catalysts still is an interesting research subject. Aldol condensation products such as diacetone alcohol (DAA), mesityl oxide (MO) and isophorone (IP) are widely used as starting materials for the production of a large number of fine chemical compounds. The acetone condensation has usually been performed in liquid phase using ion exchangers [2, 3], hydrotalcites [4-6] and rare earth doped oxides as catalysts [7], however, for the reaction in gas phase the reports are considerably limited. For instance alkali doped magnesium [8, 9] and titanium oxides [10,11] have been used to perform such a reaction. In this work, perovskite-type compounds are proposed as basic catalytic materials for the condensation of acetone in gas phase. Perovskite-type compounds such as alkali niobates and tantalates, AMO₃ (A = Li, Na and K; M = Nb and Ta) have been extensively studied as ferroelectric materials [12], and more recently, as photocatalytic materials to generate hydrogen by water splitting [13] and for the photodegradation of organic compounds [14]. In their structure, basic sites can be developed by the proper distortion of the TaO₆ connections, which depend on the considered alkali metal [15, 16]. Tantalates have usually been prepared by the solid state reaction; however, this method requires high temperatures (~ 1200°C). In the present work, alkali tantalates, ATaO₃ (A = Li, Na and K), were prepared by the sol-gel method, which allows the formation of their crystalline structure at lower temperatures.

Experimental

Lithium acetylacetonate (Aldrich Chemicals, 97.0%), sodium acetylacetonate monohydrate (Aldrich Chemicals, 97.0%), and potassium acetate (Aldrich chemicals 99.0%) were mixed in the appropriate amounts with tantalum (V) ethoxide (Aldrich Chemicals 99.98 %) in an ethanol-water

solution (4:1). Afterwards, the pH of the solution was adjusted to 3 with acetic acid, and the solution was maintained under stirring at 70°C for 5 days. Afterwards, the pH was adjusted to 9 using ammonium hydroxide. Then, the solution was kept under reflux until the gel was formed. The obtained gel was dried at 70°C and annealed at 600°C for 6 h.

The specific surface area of the solids was determined from the nitrogen adsorption isotherms using Quantachrom equipment. The CO₂-TPD was carried out after saturating the solids with an Ar-CO₂ flow, with a Chembet 3000 and a programme rate of 10°C/min. The X-ray patterns were obtained with a diffractometer (Siemens, D-5000) with CuK α radiation. SEM analysis was carried out using a Scanning Electron Microscope LEICA model S440 coupled with an Energy Dispersion Spectroscopy system (EDS). Powder samples were placed in a stainless steel sample holder and then covered with a thin gold layer. Images were recorded using a magnification of 10,000X.

The catalytic activity for the acetone condensation was evaluated by using a fixed bed reactor at comparable conversions (1.9 – 6.0 %) by varying the mass of the catalysts (20-100 mg). Prior to the catalytic test, the catalysts were reactivated at 400 °C for 1 h in nitrogen flow. After, the temperature was lowered to 250 °C, and using nitrogen flow the acetone (66 Torr) was fed into the reactor through a saturator to the reactant system (1.8 L/h). The reaction rate was followed as a function of time by analyzing the products with a FID-gas chromatograph coupled with the reactant system. Diacetone alcohol (DAA), mesityl oxide (MO) and isophorone (IP) were the only detected products (Fig. 1).

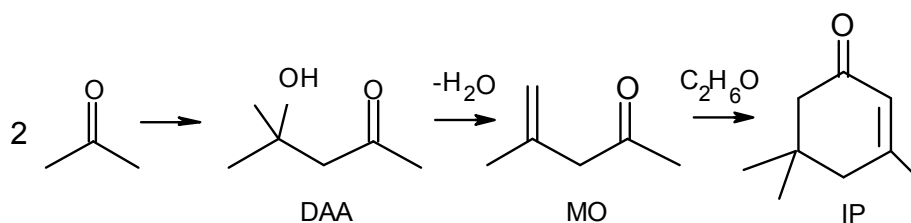


Fig. 1. Acetone aldol condensation pathway.

Results and Discussion

The crystalline structure of the powders as a function of the annealing temperature was analyzed by XRD, and it is illustrated for the NaTaO₃ sample in Fig. 2. Below 400°C, the sample was almost amorphous; as for the sample annealed at 600°C, the corresponding NaTaO₃ orthorhombic crystalline structure (01-089-8061 ICDD) can be seen. For the KTaO₃ and LiTaO₃ samples, the XRD patterns show the same behaviour, i.e. well defined orthorhombic crystalline structures were obtained at 800 °C (Fig 3). As expected, the crystalline size of the solids increased with increasing the calcinations temperature. According to the XRD peak sharpness, at the same annealing temperature 800 °C, the crystalline size of the different solids showed the following order: KTaO₃ > NaTaO₃ > LiTaO₃.

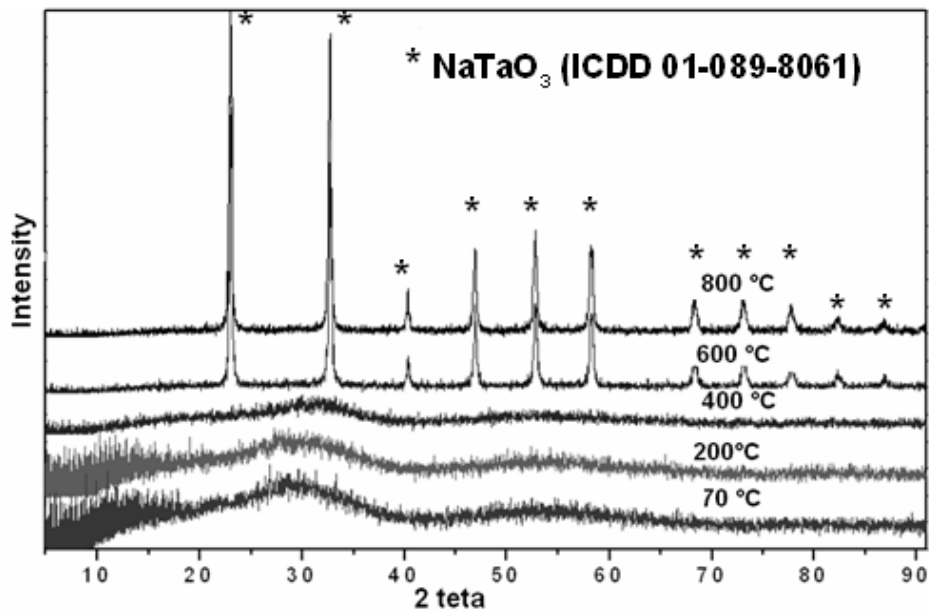


Fig. 2. XRD patterns for NaTaO₃ as function of the annealing temperature.

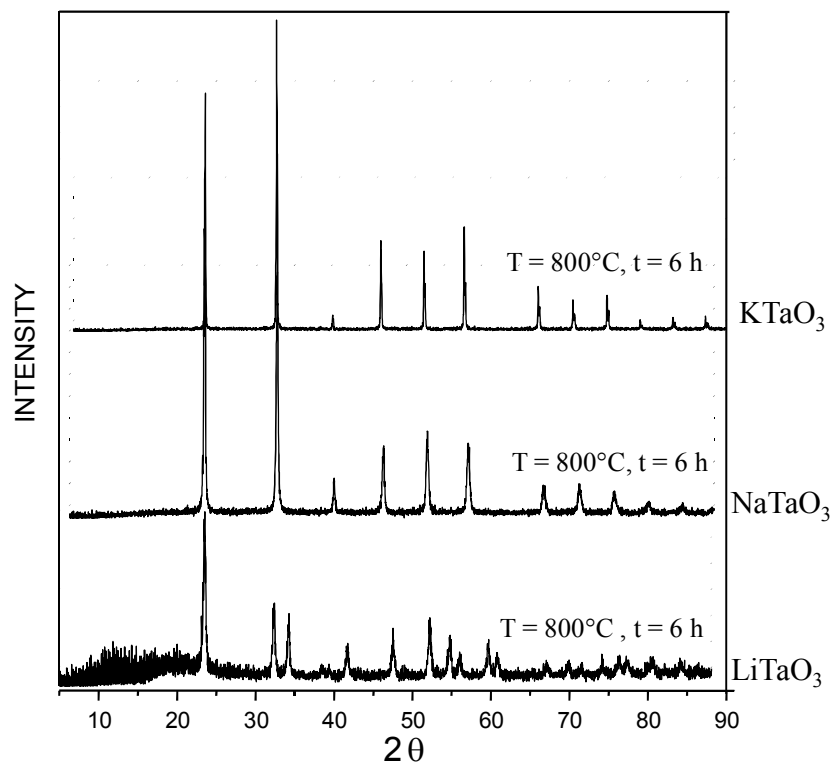


Fig. 3. XRD patterns for the alkali tantalates annealed at 800 °C.

SEM micrographs of the alkali tantalates annealed at 400 °C show solids with a particle size lower than 1 micron in (Fig. 4). The particles observed by SEM are joined together forming clusters with a type-sponge microstructure as it is observed in Fig.4. However the size of the clusters is different for each one of the alkali tantalates. According to the SEM micrographs, the clusters size of the samples annealed at 400 °C increases in the following order: KTaO₃ > LiTaO₃ > NaTaO₃.

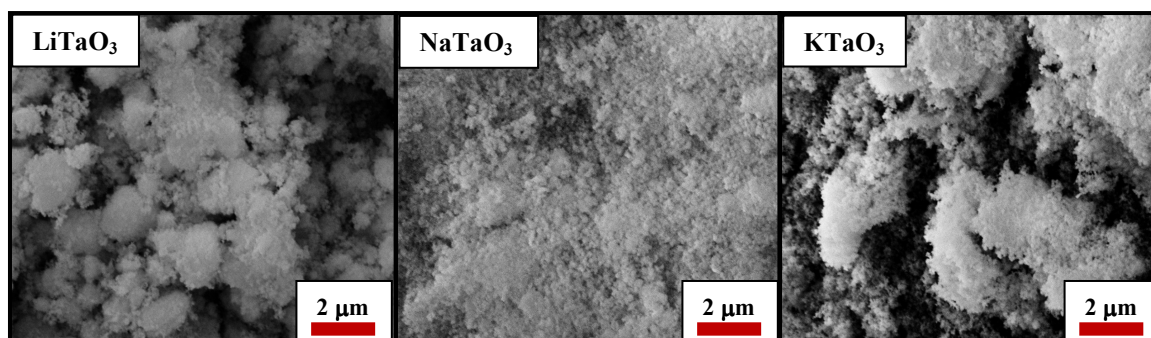


Fig. 4. SEM micrographs for the alkali tantalates annealed at 400°C.

The evolution of the acetone condensation as a function of time with the alkali tantalates is illustrated in Fig. 5. As for the gas phase, acetone aldol condensation deactivation phenomena have been frequently observed as an effect of oligomerization reactions [8, 9].

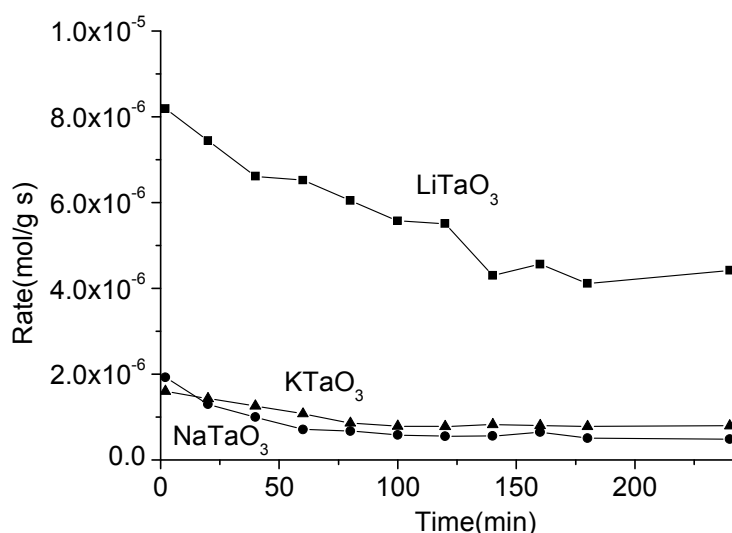


Fig. 5. Catalytic evolution as a function of time for the acetone aldol condensation on alkali tantalates.

In some cases, the efficiency of the catalysts strongly depends on a moderate deactivation. In our case, the loss of activity for the Li, Na and K tantalates was around 30 %, and after 150 min in stream, the steady state was reached. Then, they showed a moderate evolution as a function of time.

By taking into account the deactivation of the catalysts, the conversion, rate and selectivities reported in Tables 1 and 2 were calculated from the values obtained after 180 min in stream (Fig. 5). The activity and selectivity order to mesityl oxide was the following: $\text{LiTaO}_3 \gg \text{KTaO}_3 > \text{NaTaO}_3$.

Table 1. Characterization and activity in the acetone aldol condensation for the alkali tantalates.

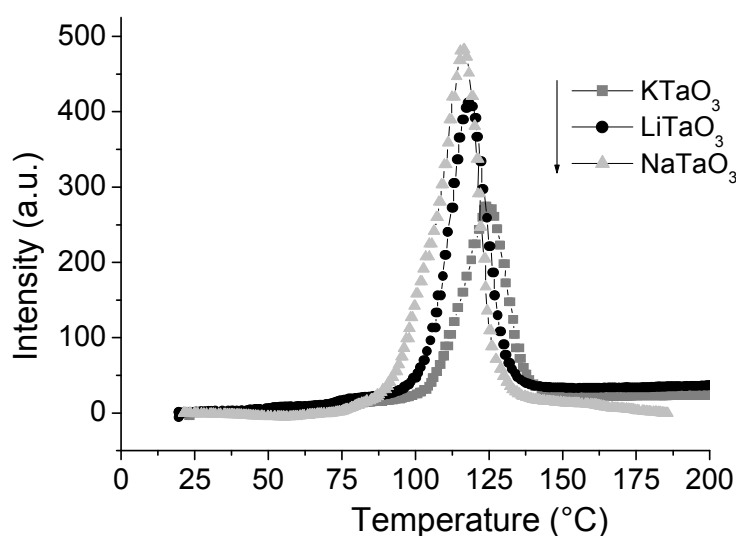
Perovskite-type	BET Area ^a	CO ₂ ^b	C (%) ^c	Rate ^d	Rate/CO ₂ ^e
LiTaO ₃	16	26	6.0	7.3	280
NaTaO ₃	16	15	1.9	0.67	44
KTaO ₃	5	41	2.4	0.80	19

^a m²/g; ^b μmol/g; ^c conversion; ^d mol/g s × 10⁻⁶ (180 min); ^e s⁻¹ × 10⁻³

Table 2. Selectivity (% mol) in the acetone aldol condensation.

Perovskite-type	DAA	Mesityl Oxide	Isophorone
LiTaO ₃	17	80	3
NaTaO ₃	31	61	8
KTaO ₃	26	70	4

It has been reported that both the activity and selectivity in the acetone aldol condensation depend on the strength of the basic sites [1]. In Fig. 6, the CO₂-TPD desorption peaks appear around 115-125 °C for the three studied tantalates, and then, we can consider similar basic site strengths of these samples. However, the activity per adsorbed CO₂ molecule, reported in Table 1, shows that LiTaO₃ is 6 or 14 times more active than both NaTaO₃ and KTaO₃, respectively.

Fig. 6. CO₂-TPD for the perovskite-type tantalates.

The marked differences in activity per basic site determined by the number of desorbed CO₂ molecules by the TPD-CO₂ of catalysts cannot be justified by the differences in either the specific surface area or CO₂ desorption temperature; then, both the activity and selectivity of the basic sites could reside in the structure of the tantalates. The basic sites in the tantalates can be developed upon the proper distortion of the TaO₆ angles. The LiTaO₃ structure shows the presence of TaO₆ octahedral arrangements forming angles of 143°, whereas in the Na and K tantalates, the octahedral arrangements form angles of 163 and 180°, respectively [15, 16], (Fig. 7).

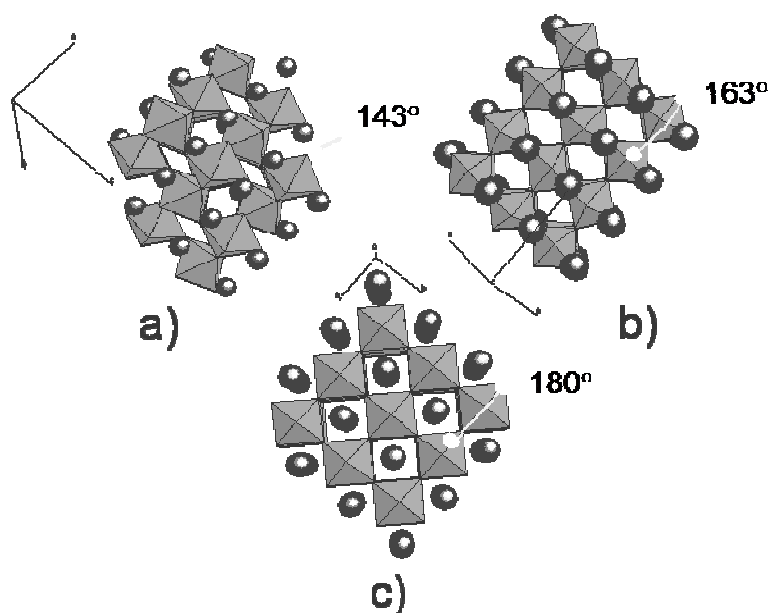


Fig. 7. Perovskite-type structures for: a) LiTaO_3 ; b) NaTaO_3 and c) KTaO_3 with octahedral arrangement angles of 143° , 163° and 180° , respectively

The most distorted structure corresponds to LiTaO_3 , which is the tantalate with the highest activity and selectivity. As the structure becomes less distorted, as it can be seen in the Na and K tantalates, the activity in the acetone aldol condensation strongly diminishes.

Conclusions

According to the aforementioned results, it can be proposed that the acetone condensation, when performed on sol-gel prepared perovskite-type alkali tantalates, is a reaction depending on the TaO_6 tantalate octahedral arrangements. As far as we are concerned, it is the first time that perovskite-type tantalates were reported as structure sensitivity basic catalysts. These results open important future applications for the tantalates when used as basic catalysts.

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