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Oligomerization of acetone over titania-doped catalysts (Li, Na, K and Cs): Effect of the alkaline metal in activity and selectivity

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Abstract

The vapor-phase condensation of acetone was studied over TiO_2-doped with 1 wt% of alkaline metals (Li, Na, K and Cs). The reaction was catalyzed by basic sites and the main products were mesityl oxide (MO), isomesityl oxide (ISMO) and mesitylene (M); other compounds as isophorone (IP) and phorone (P) were also obtained. The basic properties of the samples were determined by chemisorption of carbon dioxide. It was found that the number of the basic sites of the TiO_2-doped catalysts increased in the following order: $Li/TiO_2 > Na/TiO_2 \sim K/TiO_2 > Cs/TiO_2$; in contrast, the trend of the basic strength and total activity was $Cs/TiO_2 > K/TiO_2 \sim Na/TiO_2$ Li/TiO_2. On the other hand, the selectivity patterns showed that the higher formation of MO was obtained with the catalyst which showed the lowest basic force (Li/TiO_2). A direct correlation between the activity and the alkaline metal atomic radius was found, while the inverse dependence for the selectivity to mesityl oxide was observed.

Keywords: Alkaline doped titania; Acetone oligomerization; Basic catalysis; Sol–gel titania catalysts

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1. Introduction

The conversion of low price organic compounds like acetone to high value products (fine chemicals) is nowadays an important concern for industrial applications [1,2]. Fine chemicals like isophorone were traditionally prepared in liquid phase in batch reactors, using soluble inorganic bases. However, the increase of the demand of fine chemicals requires a bigger capacity of production, which only can be satisfied increasing the volume of the reactors, by the use of heterogeneous gas-phase reactions. To accomplish this challenge, basic solid catalysts with controlled basicity are required. The heterogeneous catalysts more frequently reported in basic reactions are MgO, BaO, hydrotalcites type catalysts as well as basic zeolites [3–5]; however, most of them are used in liquid-phase reactors. Certainly, the main problem for the application of solid basic catalysts in gas-phase reactions is the low selectivity of the reaction at these conditions. For example, in the particular case of the acetone condensation reaction using catalysts as MgO or alkaline metals supported on MgO, a large number of byproducts, including acetone oligomers, were obtained [6,7]. Tanabe et al. [8,9] have reported important modifications in selectivity in the acetone condensation at 0 °C by the incorporation of Na, Zr and Zn to MgO. The acetone condensation forms diacetone alcohol (Aldol), and the role of the basic sites is the abstraction of the α-proton in order to form the carbanion [10]. The strength of the basic sites of the catalysts plays an important role in the rate of abstraction of the α-proton. Similar concepts are applicable for the isomerization of alkenes, in which the formation of the

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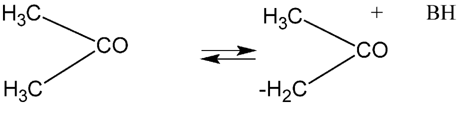
carbanion is postulated over alkaline oxides [11,12].



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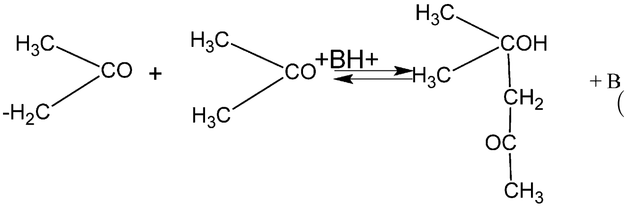

(2)

As mentioned above, the selectivity pattern for the acetone condensation will depend on the strength of the basic sites. The synthesis of catalysts showing a large variety in the number of the basic sites, as well as in the strength of this basic sites, becomes an important and interesting subject. With this in mind, in the present work, we report the synthesis and characterization of TiO_2 doped with alkaline metals. It is known that TiO_2 presents weak acid properties [13–15]; however, TiO_2 with variable acid–basic properties can be obtained by the sol–gel method, co-gelling titanium alkoxide with alkaline metals [16]. It is expected that in function of the atomic radius of the metal (Li, Na, K and Cs), it is possible to improve or diminish the amount of the different alkaline oxides over the surface of the TiO_2 support. For characterization, N_2 adsorption isotherms, X-ray diffraction (XRD), CO_2–TPD, NH_3–TPD and the catalytic test for the gas-phase acetone oligomerization were made.

2. Experimental

2.1. Catalysts preparation

Doped-TiO_2 catalysts were prepared by mixing a solution consisting of 3.2 mol of bi-distilled water, the appropriated amount of the corresponding alkaline chloride (Merck, 1.0 wt%) and 1.2 mol ethanol (Baker, 99.9%) with 0.2 ml of nitric acid (Baker, 65 vol.% in water) in a flask, until they reach a pH 3 in the solution. After that, the solution was stirred and put under reflux at 70 °C and then 0.2 mol of titanium *n*-butoxide $Ti(Obut)_4$ (Aldrich, 99.9%) was added dropwise under reflux until the gel was formed. Finally, the samples were dried at 70 °C for 12 h and then annealed at 400 °C during 4 h. The water/alcohol stoichiometric ratio employed was 16.

2.2. X-ray diffraction

Titania crystalline structures were determined by X-ray diffraction with a diffractometer Advanced Bruker D-8, using Cu Kα radiation.

2.3. Specific surface areas

The specific surface areas were calculated from the nitrogen adsorption isotherms obtained with a Quantasorb-3B automatic apparatus.

2.4. CO_2–TPD

The thermal programmed desorption of CO_2 was carried out by using a Micromeritics TPD/TPR 2900 apparatus. The catalysts were re-activated in situ in the glass reactor, in presence of a nitrogen flow (1 ml/min) at 400 °C. Then, the reactor temperature was diminished to room temperature and a gas mixture of Ar–CO_2 (90:10) was passed through the reactor for 30 min and then fluxed with a stream of He (1 ml/min), using a rate program of 10 °C min^{-1}. The amount of CO_2 was calculated by integrating the desorption curve.

2.5. NH_3–TPD

In a similar way to the CO_2–TPD procedure, the ammonia thermodesorption was carried out. A mixture of NH_3 and He (20–80%) was passed through the reactor at 100 °C filled with the reactivated catalyst and then a flux of helium was fed at a rate of 10 °C min^{-1} and a temperature over 400 °C.

2.6. Catalytic activity

The catalytic activity was tested in gas phase using a saturator (0 °C). The acetone mixed with nitrogen gas passed through a glass reactor (3 ml) coupled to a gas chromatograph for the analysis of the reaction products. The temperature used in the experiment was 300 °C and the mass of catalysts was between 25 and 50 mg, keeping the conversion at values lower than 30%. A capillary column PE-1 phenylsilicone was used for the identification of the main products: mesityl oxide (MO), isomesityl oxide (ISMO), mesitylene (M) and small amounts of isophorone (IP) and phorone (P). During the catalytic test (120 min), some deactivation was observed after 60 min in flow. Activity and selectivity were calculated then after 60 min on stream.

3. Results and discussion

The X-ray diffraction spectra for the different samples showed anatase phase for Li, K and Cs/TiO_2 catalyst; only in the Na/TiO_2 sample, the anatase phase as well as the rutile phase were observed. These results can be expected since the samples were annealing at 400 °C and at this temperature, TiO_2 anatase phase is the stable phase [17]. XRD spectra for selected catalysts are shown in Fig. 1. Lithium titanates as $LiTi_2O_4$ or alkaline oxides were not observed in any of the doped-TiO_2 catalysts.

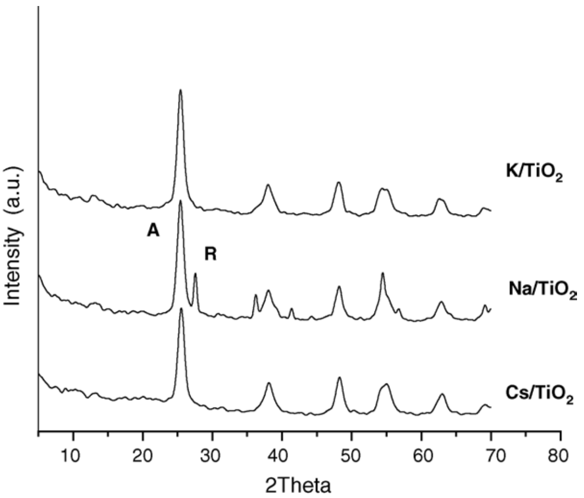

Fig. 1. XRD for Na, K and Cs doped-TiO_2 catalysts.

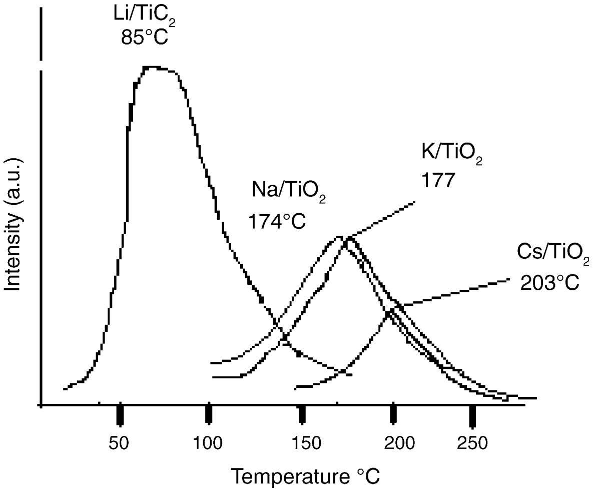

Fig. 2. CO_2–TPD for Li, Na, K and Cs doped-TiO_2 catalysts.

Table 1

CO_2–TPD desorption values obtained for the various alkaline doped-TiO_2 catalysts

Catalyst	BET area (m^2/g)	CO_2 (mmol/g)	CO_2 ($\times 10^3$ mmol/m^2)
Li/TiO_2	90	0.677	7.5
Na/TiO2	151	0.114	0.7
K/TiO_2	139	0.139	1.0
Cs/TiO_2	102	0.054	0.5

The specific surface areas obtained for the different catalysts are reported in Table 1. They are comprised between 90 and 151 m^2/g. At this point, it could be assumed that alkaline doping does not show a systematic effect either in the specific surface area or the formation of the crystalline TiO_2 anatase phase.

3.1. CO_2–TPD results

Thermal program CO_2 desorption curves are shown in Fig. 2. It can be seen that the temperature desorption peaks are shifted depending on the alkaline metal considered. Moreover, also important differences in the area of the curves can be noted. Assuming, as it is generally accepted, that the strength of the basic sites can be correlated with the temperature desorption peak [15], the order of basicity strength was the following: Cs/TiO_2 >Na/TiO_2 ~ K/TiO_2 > Li/TiO_2. The quantity of basic sites was obtained by integrating the respective desorption curves. The values calculated in this form are reported in Table 1. It can be seen that the number of basic sites depends on the alkaline metal added; this result was expected since we prepare catalysts with 1 wt% of alkaline metals.

Activity and selectivity for the several doped-TiO_2 catalysts are reported in Table 2. The trend for the activity showed that this was increasing at higher atomic radius of the alkaline metal highest. For Li/TiO_2, Na/TiO_2, K/TiO_2 and Cs/TiO_2 catalysts, specific rates were 1.8, 2.4, 3.3 and 5.4×10^{-7} mol/(m^2 s), respectively. When we compare the results of the activity with those reported in Table 1 concerning the number of basic sites (CO_2 ads), we can note that the higher activity corresponds to the catalyst having the lower number of basic sites. A better agreement is obtained when the strongest of the basic sites, classified by means of the maximum of the CO_2 desorption peak (Fig. 2), was analyzed. In fact, it was clearly showed that as higher is the temperature of desorption, higher is the activity in the acetone oligomerization. From these results, we can say that the number of acetone molecules converted mainly depends on the strongest of the basic sites.

On the other hand, in Table 2, the selectivity pattern for the different products in the acetone oligomerization is shown. For Li/TiO_2, the selectivity to MO was the higher since it was of 72% while for Na/TiO_2, K/TiO_2 and Cs/TiO_2, the selectivity to MO was 43, 43 and 34%, respectively. It is

Table 2

Activity and selectivity for the acetone oligomerization on doped titania

Catalyst	Selectivity (%, ISMO)	Selectivity (%, MO)	Selectivity (%, M)	Selectivity (%, P)	Selectivity (%, IP)	Rate ($\times 10^5$ mol/(g s))	Rate ($\times 10^7$ mol/(m^2 s))	C (%)
Li/TiO_2	21.5	72.5	4.7	0.3	1.0	1.67	1.8	18.7
Na/TiO_2	18.2	43.9	33.5	0.2	4.2	3.6	2.4	19.5
K/TiO_2	19.4	43.4	32.5	1.0	3.7	4.6	3.3	25.2
Cs/TiO_2	11.3	34.3	47.9	1.0	4.0	5.4	5.4	28.3

ISMO: isomesityl oxide; MO: mesityl oxide; M: mesitylene; P: phorone; IP: isophorone.

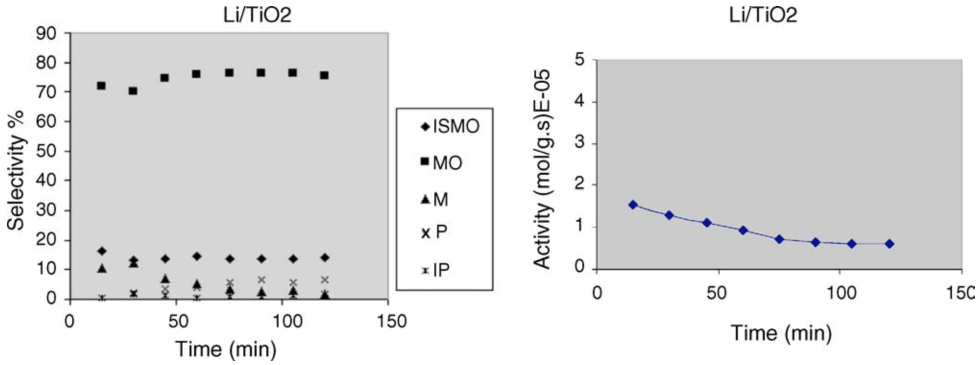

Fig. 3. Selectivity and activity behavior in function of the time for the Li/TiO_2 catalyst in the acetone condensation at 300 °C.

noticeable that the formation of MO depends on the number of basic sites but not on its strength.

The selectivity in function of time varies only slightly. As an example of the catalysts studied, the pattern of the selectivity in function of time for the Li/TiO_2 catalyst is shown in Fig. 3. It can be seen that selectivity is constant after 2 h on stream, while activity diminishes slightly in the same period of time.

To explain the behavior of the catalysts, we must consider the probable mechanism for acetone oligomerization (Fig. 4). In the acetone condensation, the initial step implies the abstraction of a proton from the α position of the carbonyl group, forming the corresponding carbanion; the addition of a second acetone molecule to the enolate gives the formation of the diacetone alcohol, which by dehydration forms mesityl oxide and isomesityl oxide. The formation of a great number of products occurs via complex reactions including cross-condensation between the diacetone alcohol and another molecule of acetone. When a third acetone molecule is added to mesityl oxide the product is isophorone, while if the oligomerization is carried out via the isomesityl oxide the product formed is mesitylene.

Assuming that the reaction pathway is over the surface of the catalysts without re-adsorption of products, the first stable products are MO and ISMO. If the basicity of the site is strong, the MO or the ISMO remain on the surface without desorption, and a third acetone molecule will react with the dimer and then the selectivity to isophorone or mesitylene

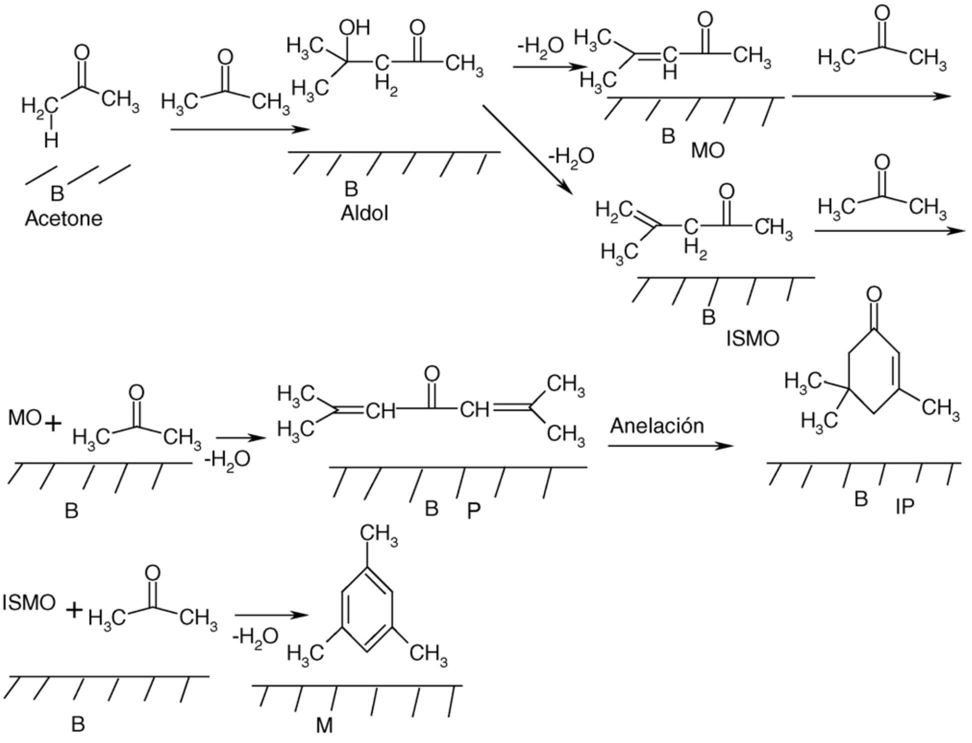

Fig. 4. Proposed mechanism for the acetone oligomerization in gas phase at 300 °C.

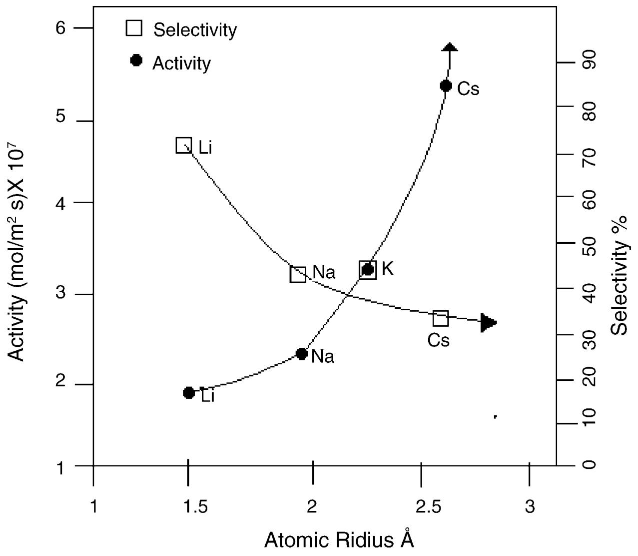

Fig. 5. Activity and selectivity for the acetone oligomerization in function of the alkaline metal atomic radius.

will increase (Cs/TiO_2). However, if the strength of the basic site is weak (Li/TiO_2), the MO and ISMO formed will be desorbed giving high selectivity to these products (Table 2).

The basic strength, catalytic properties and selectivity certainly are an effect of the preparation method. These catalysts were prepared by adding the corresponding alkaline chlorides to the gelling titanium butoxide in nitric acid medium and some acidity can be developed in the catalysts. A transformation of phorone in mesitylene can be then produced by the acid sites developed during the catalysts preparation. NH_3–TPD in two selected showed the acidity of 0.35 and 0.35 NH_3 mmol/g for Na/TiO_2 and Cs/TiO_2, respectively, which are of the same order of that frequently observed for commercial γ-alumina (0.28 NH_3 mmol/g).

In titania doped catalysts prepared by the sol–gel method, it is quite possible that alkaline ions will be present in the titania network, as well as on its surface, the latter as an effect due to the segregation of them during the thermal treatments. The catalyst showing the big number of basic sites was Li/TiO_2 as a consequence of the big number of lithium atoms added during its preparation since the catalysts were prepared in weight content (1 wt%) of metal. However, the most important effects observed are not related to the total number of basic sites. Activity and selectivity in acetone condensation depend almost on the basic strength, as higher is the basic strength higher is the activity and this property seems to be related to the atomic ratio of alkaline metal. As shown in Fig. 5, as the atomic ratio of the alkaline metal increases, the activities of the catalyst do it. Then, a good correlation between the atomic properties of the alkaline metals in doped titania and its activity for gas-phase acetone condensation was found.

4. Conclusions

In the synthesis of titania doped with alkaline metals and prepared by adding the alkaline compound to gelling titanium alkoxide (sol–gel method), catalysts showed the anatase crystalline phase as the main phase, as well as high specific surface areas. The basic strength of the catalysts determined by means of CO_2 adsorption showed that the weakness basicity corresponds to the Li/TiO_2 catalyst, while the strongest basicity corresponds to the Cs/TiO_2. Activity in acetone condensation is related to the strength of the basic sites, while selectivity depends on the weakness of the basic sites. A direct relation between the atomic radius of the alkaline metal and activity was found: the higher activity corresponds to the catalyst with the alkaline metal having the largest atomic radius (Cs/TiO_2), while the better selectivity to mesityl oxide is obtained with the catalyst having the lowest atomic radius (Li/TiO_2). For Na/TiO_2 and K/TiO_2 catalysts, an intermediate behavior was observed.

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