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Alkaline doped TiO_2 sol–gel catalysts: Effect of sintering on catalyst activity and selectivity for acetone condensation

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Abstract

In this paper, we prepared by the sol–gel method alkaline titania catalysts, doped by gelling titanium alkoxide with aqueous solutions containing potassium, rubidium or cesium chlorides. XRD patterns showed that samples annealed at 400 and 600 °C contained a single crystalline phase, anastase. Specific surface areas were higher in samples annealed at 400 °C (>100 m^2/g) than in those annealed at 600 °C (25 m^2/g). The weight density of basic sites determined by CO_2–TPD drastically diminished in samples treated at 600 °C. Catalysts were tested for the self-condensation of acetone at 300 °C; main reaction products were isomesityl oxide, mesityl oxide and mesitylene. Samples annealed at 600 °C showed lower acetone conversion rate and low formation of mesitylene than that obtained on samples annealed at 400 °C. It is proposed that the formation of mesitylene occurs via the Michael reaction over the titania support.

Keywords: Acetone condensation; Titania alkaline doped catalysts; Sol–gel titania; Catalysts deactivation; Titania sol–gel synthesis; Basic catalysts

1. Introduction

There is a renewed interest in the study of the acetone aldol condensation because several reactions products like diacetone alcohol (DAA), isomesityl oxide (ISMO), mesytil oxide (MO), phorone (P), isophorone (IP) or mesytilene (M), are widely used in fine chemistry, cellulose, and plastic industries. Traditionally, the acetone aldol condensation reactions are carried out over catalyst based on basic oxides like CaO, BaO and more frequently over MgO [1–5]. However, it has been reported that the acetone conversion rate may be improved by using alkaline doped MgO or MgO–Al_2O_3 hydrotalcite type catalysts [6,7]. Diacetone alcohol is usually the main product when the self-condensation of acetone is carried out in liquid phase at low temperature [8]. However, the addition of a third molecule of acetone takes place when the reaction is carried out in gas-phase at high temperature [3]. The formation of isomesityl oxide, mesityl oxide, mesitylene and isophorone was reported by Di Cosimo and coworkers [9] in the gas-phase acetone condensation at 300 °C over MgO-based catalysts. Formation of highly unsaturated trimeric compounds during the gas-phase acetone condensation often leads to the consecutive formation of coke that causes the deactivation of the catalyst on stream [10,11].

On the other hand, TiO_2 is also active for the aldol condensation of acetone or acetaldehyde, producing mainly dimeric, trimeric and cyclic trimeric compounds [12–14]. Similarly to MgO catalysts, TiO_2 may suffer rapid deactivation on stream during aldol condensation reactions [15–17]. Other important applications of TiO_2 are their use as photocatalyst for the toxic organic compounds mineralization [18–21], which make of it a very interesting material with multiple catalytic usages.

The aim of this work was to investigate the use of alkaline doped titania for the gas-phase aldol condensation of acetone. In particular, we studied the effect of thermal treatments on catalyst activity, selectivity and stability.

2. Experimental

2.1. Catalysts preparation

Alkaline-titania doped catalysts were prepared as follows: in a flask were mixed, 3.2 mol of deionized water containing the corresponding amount to obtain 1.0 wt.% of the alkaline

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Table 1
Specific surface area, CO_2 chemisorption, activity and TOF for the acetone condensation at 300 °C on doped titania sol–gel catalysts

Catalyst	Annealed (°C)	BET area (m^2/g)	Pore diameter (nm)	Basicity CO_2 (mmol/g)	Activity (mol/g s) $\times 10^5$	TOF (s^{-1})
$K–TiO_2$	200	190	6.6	0.239	4.4	0.18
	400	139	7.9	0.139	4.6	0.33
	600	44	9.8	0.078	1.6	0.21
	800	7	13.0	0.030	0.8	0.25
$Rb–TiO_2$	400	125	7.8	0.056	4.2	0.74
	600	22	10.3	0.010	0.5	0.50
$Cs–TiO_2$	400	102	7.9	0.054	5.5	1.0
	600	25	9.5	0.006	0.4	0.6

chloride (Baker 99%), 1.2 mol of ethanol (Baker 99.9%) and 0.2 ml of nitric oxide (Baker 65% volume in water) to adjust the pH of the solution at 3.0. The solution was refluxed at 70 °C and then 0.2 mol of titanium tetra *n*-butoxide was added dropwise to the solution and maintaining the reflux until gelling. After the samples were dried at 70 °C over night and then annealed in air for 4 h at 400 and 600 °C using a heating program rate of 20 °C/min. A reference TiO_2 support with out doping was prepared under at the same conditions described above.

2.2. Catalysts characterization

The crystalline phases of doped titania were identified by X-ray diffraction with an advanced Brucker D-8 Diffractometer using Cu Kα radiation. Specific surface areas were calculated from the nitrogen adsorption isotherms by the BET method using a Quantasorb automatic apparatus. Basicity was determined from the CO_2–TPD desorption curves using a Micromerictis TPD/TPR 2900 equipment. Before TPD study the samples were reactivated in situ in N_2 flow at 400 °C in the quartz cell. Then the sample was cooled at room temperature and a flow Ar/CO_2 (90:10) was passed through the cell for 30 min. After that, the CO_2 adsorbed was fluxed with He, at 100 °C for 1 h and then the CO_2–TPD was recorder, from 100 to 500 °C, using a temperature program rate of 10 °C/min.

2.3. Catalytic activity

The evaluation of the activity in the acetone condensation was carried out in gas-phase at 300 °C and atmospheric pressure in a flow reactor (3 mL) coupled to a gas chromatograph (Varian CP-3800) equipped with a capillary column (30 m, PE-1 100% phenylsilicone) and FID detector. Typically, 50 mg of the catalysts was used, and the acetone was passed through a saturator (0 °C partial pressure 66 Torr) in flowing nitrogen 3.6 L/h (WHSV 20 h^{-1}). Because samples often deactivate on stream, catalytic data were compared at initial conditions. Thus, the activity and selectivity values reported in Tables 1 and 2 were obtained at 15 min on stream.

3. Results and discussion

3.1. Catalysts characterization

X-ray diffraction patterns of the various doped titania catalysts calcined at 400 and 600 °C are reported in Fig. 1. It can be seen in all the samples that the predominant crystalline phase was anatase (>97 wt.%). Titania generally transforms to rutile phase at temperatures higher than 600 °C, and for the K/TiO_2 selected sample annealed at 800 °C the predominant phase was rutile (95%) with a small amount of anatase (5 wt.%). The identification of the corresponding crystalline titania phase and their proportions in each sample was made using Rietveld refinement, as it was reported elsewhere for titania sol–gel samples [22]. For example, the crystallite size of the Rb/TiO_2 catalyst annealed at 400 °C increases from 14 to 38 nm when it is thermally treated at 600 °C. It has been reported that, in TiO_2 catalysts, the crystalline structure of TiO_2 plays an important role in the acetone aldol condensation [23]. In pure anatase, only the formation of dimeric compounds was

Table 2
Selectivity patterns for the acetone oligomerization at 300 °C on doped titania

Catalyst	Annealed (°C)	Sel % ISMO	Sel % MO	Sel % M	Sel % P	Sel % IP	Conversion (%)
$K–TiO_2$	200	23	50	24	1	2	42
	400	19	43	33	1	4	49
	400	20	48	29	1	2	9
	600	28	64	5	1	2	2
	800	31	65	2	0	2	2
$Rb–TiO_2$	400	11	44	40	1	4	45
	600	18	75	0	0	7	2
$Cs–TiO_2$	400	13	34	48	1	4	59
	600	16	62	13	5	4	4

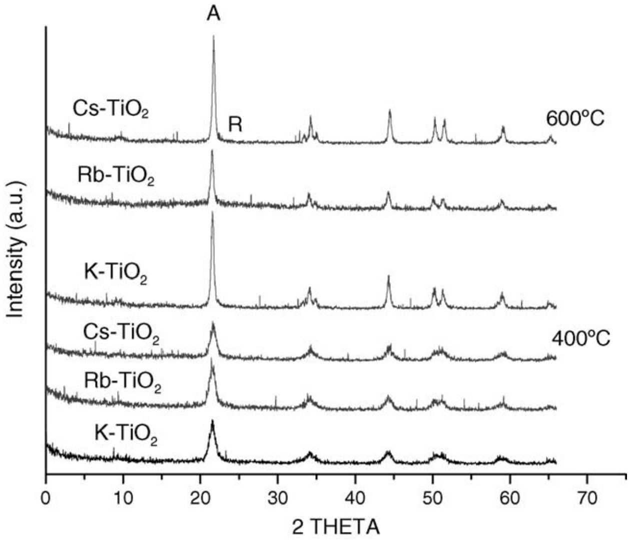

Fig. 1. X-ray diffraction patterns of alkaline doped titania sol–gel catalysts.

observed; however, when TiO_2 is an anatase/rutile mixture (70:30 wt.%, Degussa P-25), the formation of trimeric and higher molecular weight compounds was observed [23]. In our case, anatasa is the predominant crystalline phase in the alkaline doped catalysts, annealed at 400 or 600 °C. Therefore, the effect of crystalline titania phases in the acetone aldol condensation can be ruled out and the discussion will be focused in the important decrease on the specific surface area of the samples annealed at 600 °C.

In Table 1, the specific surface areas for the doped catalysts annealed at different temperatures are reported. Specific surface areas for the samples annealed at 400 °C were 139, 125 and 102 m^2/g for K/TiO_2, Rb/TiO_2 and Cs/TiO_2, respectively. When the samples were annealed at 600 °C lower specific surfaces areas were obtained. The sintering of TiO_2 catalysts is illustrated in Table 1, where it can be seen that for the K/TiO_2 sample annealed at 800 °C the specific surface area was 7 m^2/g. The mean pore size diameter was also modified by effect of the thermal treatments (Table 1).

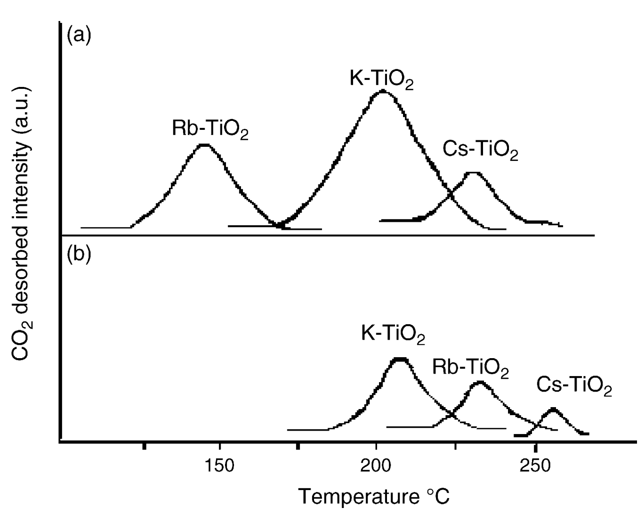

Fig. 2. CO_2–TPD on alkaline doped titania sol–gel catalysts: (a) annealed at 400 °C; (b) annealed at 600 °C.

The number of basic sites obtained from the CO_2–TPD curves is reported in Table 1 for the various catalysts. In samples annealed at 400 °C the number of basic sites was 0.139, 0.056 and 0.054 mmol CO_2/g for K, Rb and Cs doped titania catalysts, respectively. When the samples were annealed at 600 °C the number of active sites notably diminishes to 0.078, 0.010 and 0.006 mmol CO_2/g, respectively.

It is conventionally accepted that the CO_2 maximum desorption peak can be related to the strength of basic sites; as higher is the temperature of desorption higher will be the strength of the adsorbed molecule over the active sites [24]. To analyze the strength of the basic sites in our sol–gel doped titania catalysts the CO_2–TPD curves are shown in Fig. 2. For samples annealed at 400 °C, the temperature of the maximum of the CO_2 desorption peaks show the following order: $Cs/TiO_2 > K/TiO_2 > Rb/TiO_2$. In samples annealed at 600 °C a shift to higher temperatures of the CO_2 desorption peaks can be observed and the order of the temperature desorption peak is different: $Cs/TiO_2 > Rb/TiO_2 > K/TiO_2$. The CO_2–TPD curves for both series of catalysts show that the stronger basic sites are those formed on Cs/TiO_2 catalysts.

3.2. *Catalytic properties*

The rate for the acetone condensation in the synthesized catalysts is reported in Table 1. In the samples annealed at 400 °C were 4.6, 4.2 and 5.5 mol × 10^{-5}/g s, for K/TiO_2, Rb/TiO_2 and Cs/TiO_2 catalysts, respectively. Thus, in spite that K/TiO_2 catalyst shows the highest number of basic sites its was of the same order of the samples showing a lower number of basic sites. These results are not surprising, since both the number and the strength distribution of the basic sites are the factors that determine the rate for acetone condensation as it has been reported in recent paper over Li/TiO_2 catalysts [14]. For catalysts annealed at 600 °C, a dramatic decrease in activity is observed; the low activity showed by these catalysts can be due to the important diminution of the total weak and strong basic sites. Undoped TiO_2 reference catalyst (400 °C) was also tested in the reaction and it shows a fast deactivation as compared with doped TiO_2 (Fig. 3); the TiO_2 activity was negligible after 90 min on stream.

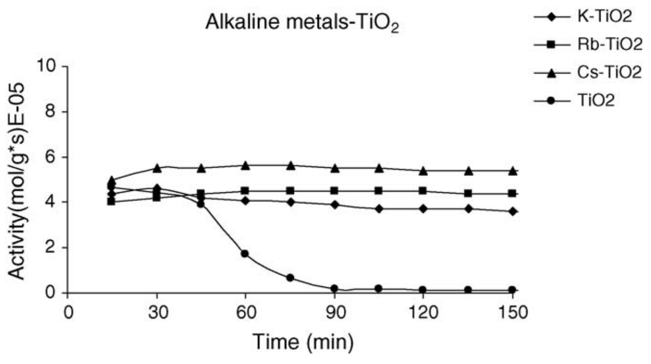

Fig. 3. Activity as a function of time on doped titania annealed at 400 °C for the acetone condensation at 300 °C; acetone partial pressure 66 Torr and WHSV 20 h^{-1}.

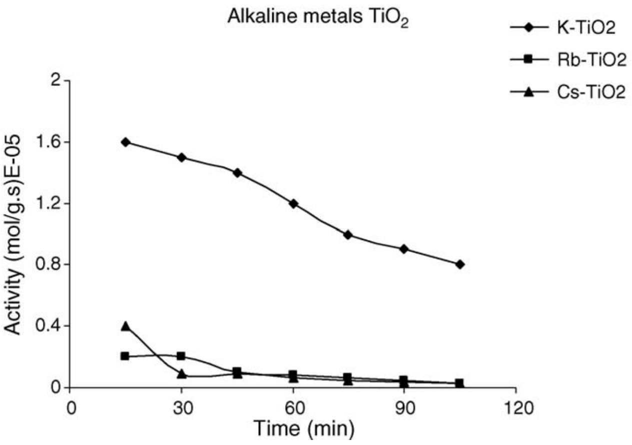

Fig. 4. Activity as a function of time on doped titania annealed at 600 °C for the acetone condensation at 300 °C; acetone partial pressure 66 Torr and WHSV 20 h^{-1}.

Since we prepared the catalysts considering a content of alkaline metal of 1.0 wt.%, the turnover frequency (mol acetone/g s converted by mol CO_2/g adsorbed) was calculated and the results are reported in Table 1. The TOF values were 0.33 and 0.21 s^{-1} for the K/TiO_2, 0.74 and 0.5 s^{-1} for Rb/TiO_2 and 1.0 and 0.6 s^{-1} for Cs/TiO_2 catalysts annealed at 400 and 600 °C, respectively. Thermal treatment diminishes the reaction rate and the total number of active basic sites, but the intrinsic catalytic properties of the catalysts are practically unmodified (Table 1).

With respect to the selectivity patterns, they were strongly modified in depending of the annealing temperature of the catalysts. The principal products obtained for the evaluation at 300 °C were isomesityl oxide (ISMO), mesityl oxide (MO) and mesitylene (M) with small quantities of phorone (P) and isophorone (IP). In samples annealed at 400 °C the selectivity for K, Rb and CS doped titania the formation of mesitylene was comprised between 33% and 48% (Table 2). However, in samples annealed at 600 °C, the selectivity to mesitylene strongly diminishes after 15 min on stream (0–13%), increasing on the other hand the formation of mesityl oxide.

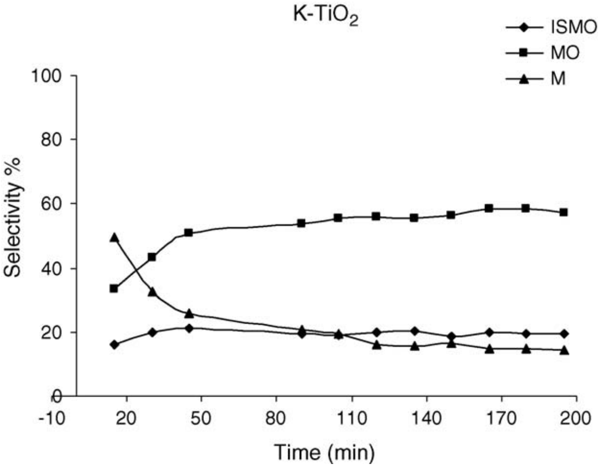

Fig. 5. Selectivity as a function of time on K–TiO_2 annealed at 400 °C for the acetone condensation at 300 °C acetone partial pressure 66 Torr and WHSV 20 h^{-1}.

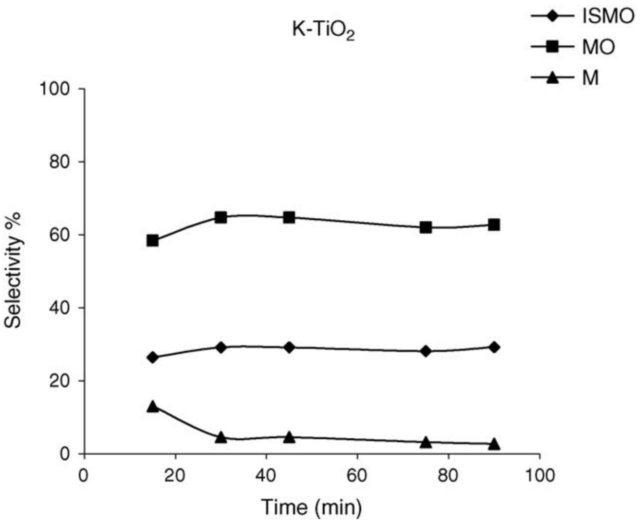

Fig. 6. Selectivity as a function of time on K–TiO_2 annealed at 600 °C for the acetone condensation at 300 °C; acetone partial pressure 66 Torr and WHSV 20 h^{-1}.

The activity as a function of the time for the doped TiO_2 catalysts annealed at 400 °C is shown in Fig. 3. It can be seen that the activity was maintained in all the interval of time studied, while for the catalysts annealed at 600 °C a strong deactivation is observed (Fig. 4). When the catalytic activity was carried out at different conversions important effects in deactivation rate can be induced [25]. In our catalysts such effects are minimized since the conversions for the samples annealed at 400 °C are of the same order (45–59%) and the same is observed for the catalysts treated at 600° (2–4%). It is generally accepted that at higher conversion higher will be the deactivation rate and such phenomenon is not observed in the catalysts tested. The catalysts which present the higher conversion (400 °C) are those showing the highest stability.

The evolution of the selectivity in function of the time is illustrated in Figs. 5 and 6 for the K/TiO_2 catalyst annealed at 400 and 600 °C, respectively. It can be seen that after 30 min on stream the selectivity patterns did not show appreciable modification. However, the relative amounts of mesityl oxide and mesitylene are totally different in both samples. For the sample annealed at 600 °C the formation of mesitylene practically disappears, while the mesityl oxide increases (Fig. 6).

Di Cosimo et al. [13] report that important deactivation occurs during the acetone aldolisation in gas-phase at 300 °C, over alkaline magnesia doped catalysts. The authors propose that, the formation of trimeric compounds like phorone, is the intermediate step for the formation of coke, inhibiting the formation of cyclic trimers like mesitylene or isophorone. We strongly agree with this assumption, since for the catalysts treated at 400 °C, in which the highest selectivity to mesitylene was obtained (Table 2) and only a very low deactivation was observed (Fig. 3).

The scheme showed in Fig. 7 illustrates the acetone condensation reactions. The formation of mesitylene is presented via the addition of a third acetone molecule, to mesityl oxide, forming trimeric highly unsaturated compounds, which after

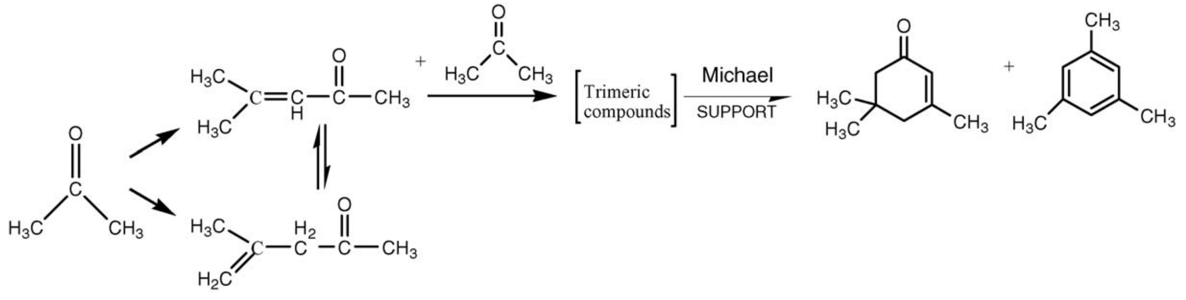

Fig. 7. Scheme of the gas-phase acetone oligomerization.

Michael reaction form mesytilene as a stable product. If we assume that Michael reaction occurs over the TiO_2 support, this reaction should be more important in samples showing higher specific surface areas, producing high amounts of mesitylene. This assumption is supported by the results of Table 2, where it is showed that the highest selectivity to cyclic compounds is obtained in catalysts annealed at 400 °C. The mechanism suggests that trimeric compounds can be spread over the TiO_2 support and then transformed in cyclic trimeric compounds, like mesitylene or isophorone.

Acetone condensation reactions are successive reactions and the selectivity can be strongly affected by the conversion degree. Additional test was carried out on the K/TiO_2 catalyst varying the conversion from 49% to 9% and the selectivity patterns showed the same behavior, i.e. a high amount of mesitylene was obtained in both cases (Table 2). These results support the hypothesis that in our work conditions the formation of mesitylene strongly depends of the high specific surface area showed by this catalyst.

Additionally, the K/TiO_2 catalyst was treated at different temperatures and tested for the self-condensation of acetone; the results are reported in Tables 1 and 2. For annealing temperatures of 200 and 400 °C (190 and 139 m^2/g, respectively) a high selectivity to mesitylene was obtained. In contrast, the selectivity to mesitylene was strongly inhibited (Table 2) on samples annealed at 600 and 800 °C with low specific surface areas (44 and 7 m^2/g).

4. Conclusions

The main conclusions of the present work are: (i) thermal treatments have strong influence in the activity and selectivity of alkaline doped titania sol–gel catalysts; (ii) fast deactivation is mainly observed on catalysts annealed at 600 °C which exhibit low specific surface area; (iii) titania sintering diminishes the surface basic site density of the samples; (iv) it is proposed that in catalysts showing high specific surface areas the formation of trimeric cyclic compounds via the Michael reaction is favored.

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