Control of TiO_2-based catalysts. Effect of chromium on TiO_2 phase transition

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Introduction

Titanium dioxide (TiO_2) is a widely investigated material for its chemical and mechanical resistance, photocatalytic and catalytic activities, paint pigment and cosmetic component [1]. Three polymorphs of titania occur in nature: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Submitting TiO_2 to high thermal treatments provokes the transformation of anatase or brookite into the more stable rutile phase. The nature of the phase can affect strongly titania properties, such as catalytic or photocatalytic activity when anatase transforms to rutile [2]. Moreover, the presence of dopants modifies strongly the anatase–rutile transition, changes the photoreactivity of nanosized TiO_2 particles, and enhances catalytic properties of supported metals or oxides [3]. In the present work, we examine the influence of chromium incorporation into the titania lattice as well as the effect on the anatase–rutile transition temperature. Incorporation of chromium to titania was performed by alkoxide-derived sol-gel synthesis and hydrothermal processing as the sol–gel process offers unique advantages for preparing homogeneous multicomponent oxides.

Materials and Methods

The preparation of TiO_2 was carried out by dissolving titanium butoxide in absolute ethanol. A solution of chromium nitrate was added to obtain doped titania. The mixture was stirred for 30 min and then a solution of ethanol and nitric acid was added dropwise in the mixture. White gel was obtained, then dried in a sand bath at 60 °C for 6 h then in an oven at 120 °C for a night. The sample was activated in a muffle furnace at 400 °C for 4 h under air atmosphere. Final chromium oxide content was controlled by ICP-AES: 5, 10 and 20 wt.-%. After preparation and activation, the samples were thermally treated in the range 400 to 800 °C and characterized by X-ray powder diffraction (XRD) and surface area measurements.

Results and Discussion

Figure 1 displays XRD patterns of various samples heated at 800 °C. Quantitative phase composition was obtained from (101) reflection for anatase and (110) reflection for rutile. The rutile fraction in the samples were calculated using the following equation: W_R (% transformation of rutile) = 1/(1+0.8 Ir/Ia), where Ia and Ir are the respective integrated intensities of the anatase and rutile diffraction peaks. The average crystallite size of both phases was evaluated from the same diffraction peaks, using the Scherrer equation. Table 1 presents the evolution of phase composition and crystallite size as a function of treatment temperature and chromium content.

XRD patterns indicated that the dopant is well dispersed in the samples (only a very weak diffraction peak) and had a strong effect on both crystallisation from the gel (cristallite size) and phase evolution on heating. Results indicated that Cr_2O_3 containing samples need to be calcined at 800°C to start the phase transition, whereas this temperature is sufficient for complete transformation of pure anatase. Therefore, the chromium ions incorporated into the TiO_2 structure stabilize the anatase phase with small crystallite size. These results are supplemented by in-situ XRD experiments.

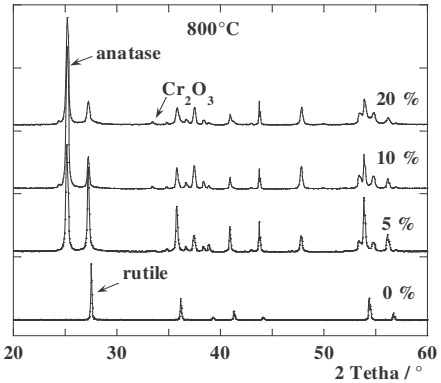

Figure 1. XRD plots of Cr_2O_3 (x %)-TiO_2 samples after treatment at 800 °C.

Table 2 : Phase composition (%) and crystallite size (nm) of anatase (*A*) and rutile (*R*) phases versus calcination temperature.

	TiO_2				5 % Cr_2O_3-TiO_2				20 % Cr_2O_3-TiO_2			
T /°C	% A,	size	% R,	size	% A,	size	% R,	size	% A,	size	% R,	size
400	100	10	0	-	100	7	0	-	100	6	0	-
500	100	16	0	-	100	10	0	-	100	7	0	-
600	85	27	15	41	100	16	0	-	100	9	0	-
700	2	37	98	36	97	22	3	32	100	20	0	-
800	0	-	100	40	53	32	47	37	88	30	12	35

Significance

Chromium ions incorporated in sol-gel prepared TiO_2 anatase phase delay the transformation to rutile and preserve smaller crystallite sizes thus inducing better catalytic activities such as hydrocarbon oxidation [4].

References

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