Influence of V_2O_5 and Nb_2O_5 on thermal stability of TiO₂-anatase

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Titania has numerous industrial applications in the production of plastics, enamels, artificial fibers, electronic materials and rubber [1]. Polycrystalline TiO₂, mainly in the anatase phase, has been widely employed for several photocatalytic reactions for the elimination of many organic pollutants from waste waters [2]. The influence of several transition-metal species on the photo-activity of pure TiO_2 for such reactions has also been the subject of some recent investigations for improving the efficiency of these processes. TiO₂-based catalysts are also widely used for the HCN (Hydrogen Cyanide) and COS (Carbon Oxysulphide) hydrolysis and silica-supported titania for the olefin epoxidation. Among the vanadium oxide-based catalysts, V2O5/TiO2 (anatase) is the most important one, because this catalyst is commonly used for the $DeNO_x$ process and for the selective oxidation of hydrocarbons [3-5]. Many theories have been proposed to explain the unique effect of anatase as a support in V₂O₅/TiO₂ catalysts. Vejux and Courtine [6] have shown the crystallographic similarity between faces 001, 100 and 010 of anatase and face 010 of vanadium pentoxide, and they proposed the opinion that, during deposition, epitaxial growth of vanadium oxide crystals with exposure of face 010 occurs. This face contains V = O groups that are responsible for good catalytic properties. Thus, titania in the form of anatase has been widely employed as a support as well as a catalyst for a variety of applications [4, 5, 7]. Heating of anatase at and above 1073 K results in the formation of rutile phase. Impurities and additives decrease the transition temperature [8, 9], which is often a reason for deactivation of anatase-supported catalysts [5, 7]. Although Nb falls in the same group of vanadium in the periodic table, the catalytic properties of Nb₂O₅ and its influence on the phase transformation of TiO₂ has not been studied. Niobium is an element in which interest in catalysis, materials science and other areas remain limited at present [5, 10].

The primary objective of this study was to determine the influence of V_2O_5 and Nb_2O_5 on the thermal stability of TiO_2 anatase with samples of identical composition and on the same support material.

A pure TiO₂ anatase (AR grade, May & Baker, England) sample was used in this investigation to deposit V₂O₅ and Nb₂O₅. The titania was impregnated with vanadia or niobia (0.02 mol%) to result in a single monolayer [4, 11] of oxides on the TiO₂ surface (BET surface area = 7 m² g⁻¹) from ammo-

nium metavanadate (AR grade, Fluka) and niobium ethoxide (AR grade, Aldrich), respectively, by the standard impregnation method. The impregnated samples were calcined in a flow of oxygen at 773 K for 6 h. Some portions of these samples were once again heated at various temperatures from 773 to 1273 K for 6 h in a closed electrical furnace in an open-air atmosphere. The X-ray powder diffraction (XRD) patterns were recorded on a Siemens D-500 diffractometer using CuK_{α} radiation source and a scintillation counter detector. The XRD phases present in the samples were identified with the help of ASTM Powder Data Files. Fourier-transformation (FTIR) spectra were infrared recorded on a Nicolet 740 spectrometer at ambient conditions by using KBr discs.

The XRD patterns of the pure TiO_2 support calcined at 773 and 1073 K are shown in Fig. 1. As can be noted from this figure, the TiO₂ sample used in the present investigation is in the crystalline state and in the form of anatase phase. With an increase in the calcination temperature from 773 to 1073 K, an increase in the intensity of lines due to further improvement in the crystallinity of anatase phase can be observed. Most importantly, no change in the anatase to rutile phase can be seen, even up to the 1073 K calcination temperature. The XRD patterns of V₂O₅/TiO₂ and Nb₂O₅/TiO₂ samples calcined at various temperatures are shown in Figs 2 and 3, respectively. No indication of crystalline V2O5 or Nb2O5 are noted from XRD or from FTIR measurements when the V_2O_5/TiO_2 and Nb_2O_5/TiO_2



Figure 1 XRD patterns of TiO₂ support calcined at 773 and 1073 K: (\odot) characteristics lines due to anatase phase.



Figure 2 XRD patterns of V_2O_5/TiO_2 sample calcined at various temperatures: (\odot) characteristic lines due to anatase phase; (\bullet) lines due to rutile phase.

catalysts are calcined at 773 K. This clearly indicates that V₂O₅ and Nb₂O₅ are in a highly dispersed and amorphous state on the support. Oxygen chemisorption measurements obtained as per the procedure described elsewhere [9] also supported this observation. With an increase in calcination temperature from 773 to 1073 K, a gradual transformation of anatase into rutile can be noted from Fig. 2. At 773 K, the TiO_2 is in the form of anatase phase, while at 1073 K it is in rutile phase. However, the same is not true with Nb_2O_5/TiO_2 samples (Fig. 3), which show a different behavior. This sample contains predominately anatase phase even after calcination at 1073 K. A total anatase-into-rutile phase transformation is seen only at 1273 K. Another important point to mention from this figure is that after high-temperature treatments at 1173 and 1273 K, the formation of crystalline Nb₂O₅ is clearly noted. A closer look at the XRD patterns of V_2O_5/TiO_2 and Nb_2O_5/TiO_2 samples (Figs 2 and 3) calcined at different temperatures reveals at least two principle differences in their spectra. The first one is that the transformation of anatase to rutile, in this case V_2O_5/TiO_2 , occurs at lower temperatures than that of pure TiO₂. However, in the case of Nb₂O₅/TiO₂ this transformation is noted only at much higher temperatures. The second observation is that the crystalline Nb_2O_5 , in the case of



Figure 3 XRD patterns of Nb₂O₅/TiO₂ sample calcined at various temperatures: (\odot) characteristic lines due to anatase phase; (\bullet) lines due to rutile phase; (\blacktriangle) lines due to Nb₂O₅.

 Nb_2O_5/TiO_2 , is noted in addition to the anatase and rutile phases after high-temperature calcination. No such crystalline V_2O_5 phase is seen in the case of V_2O_5/TiO_2 samples.

It is an established fact in the literature that the dispersed vanadia on the TiO₂ support surface lowers the activation temperature of the anatase-to-rutile phase transformation, which is normally expected to be 1073 K and above in the impurity-free TiO₂ samples [7, 12-14]. It is also well known that at elevated temperatures the dispersed vanadia on titania initiates the anatase-into-rutile phase transformation, and during this transformation some of the V₂O₅ is normally reduced and is incorporated into the rutile structure as $V_x Ti_{(1-x)}O_2$ (rutile solid solution) [15, 16]. In the present study, however, the reactivity of Nb₂O₅ toward the TiO₂ appears to be different. The Nb₂O₅ does not seem to be as effective as V₂O₅ in inducing the so-called phase transformation of anatase into rutile. The Nb₂O₅ also induces the anatase-into-rutile phase transformation, however, at higher temperatures and without being incorporated into the rutile structure. Therefore, the Nb_2O_5/TiO_2 catalyst can be employed for various purposes where high temperatures are required. Although niobia belongs to the same VA-group metal oxides as vanadia, it seems that niobia exhibits different characteristics than vanadia.

The following conclusions can be drawn from this study: vanadia and niobia behave differently when deposited on the surface of TiO_2 ; vanadia is more reactive than niobia in transforming anatase into rutile; crystalline vanadium oxide on TiO_2 does not exist when this catalyst is calcined at and above 1073 K; on the contrary, the crystalline Nb₂O₅ is seen when the Nb₂O₅/TiO₂ catalyst is calcined at and above 1173 K and the TiO₂ anatase is quite thermally stable up to 1073 K in the presence of Nb₂O₅. Finally, further studies are needed to understand fully the microscopic mechanism of the transformation of anatase to rutile phase under the influence of vanadia and niobia.

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