

The effect of phosphorus on nano-sized TiO_2 particles dispersed on Al_2O_3

Wei Li*, Shengxiang Li, Minghui Zhang, Keyi Tao

Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071, China

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Abstract

The influence of phosphates on the surface characterization of TiO_2 – Al_2O_3 mixed oxides was investigated using a variety of techniques, such as nitrogen adsorption, TEM, XRD, XPS, and FT-IR. The XRD and XPS results indicate that the addition of phosphates can increase the dispersion of titanium component on the surface of alumina. And smaller TiO_2 clusters can be observed by TEM. The FT-IR patterns show that the samples modified by the presence of phosphates possess more adsorption-active sites, and a larger monolayer dispersion capacity for TiO_2 , which accounts for the increased dispersion of TiO_2 on the surface of the Al_2O_3 .

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1. Introduction

In recent years, the problem of the deep removal of sulfur has become more serious due to the increasingly lower limits imposed on the sulfur content of finished fuel products. The heavier feeds often contain a greater proportion of substituted dibenzothiophenes, such as 4-methyl dibenzothiophene (4-MDBT) or 4,6-dimethyldibenzothiophene (4,6-DMDBT). These substituted dibenzothiophenes are very difficult to hydrodesulfurize due to the steric hindrance of the methyl groups, which hinder an adequate interaction between the sulfur atom and the catalytic active site. traditional HDS catalysts supported on alumina are becoming difficult to meet the requirements of deep HDS of heavy feeds. Several approaches are being used to develop new more active HDS catalysts. New active phases such as carbides, nitrides, and phosphides, have been proposed, and the performance of these phases continues to be explored for practical applications. Other approach which appears promising and has been widely investigated is the use of new supports [1,2].

Recent reports in the literature suggest that catalysts based on titania (anatase) have higher intrinsic activities in hydro treatment processes than conventional alumina-based catalysts [3–6].

However, the inconvenience of a low surface area and a poor thermal stability restricts the widespread use of bulk titania as a catalyst support. To overcome these handicaps, mixed oxides containing TiO_2 , such as TiO_2 – SiO_2 , TiO_2 – ZrO_2 , TiO_2 – Al_2O_3 mixtures have been proposed as catalyst supports. In particular, the TiO_2 – Al_2O_3 system has received the greatest attention [7]. TiO_2 – Al_2O_3 supports can be prepared using various methods, such as sol–gel, coprecipitation, chemical vapor deposition, grafting, and impregnation [8–13]. In recent years, sol–gel technology has been used to prepare TiO_2 – Al_2O_3 supports by many researchers, because it can provide uniform particle size and a high surface area. However, in an alumina rich TiO_2 – Al_2O_3 system, the TiO_2 is probably dissolved in the Al_2O_3 [12], which may hinder TiO_2 exhibiting its advantages during catalytic activity. Therefore, in the case of TiO_2 – Al_2O_3 , a key issue is how to better disperse the TiO_2 component on the surface of the Al_2O_3 while maintaining the pore structure of the Al_2O_3 intact. Some researchers have reported that alumina-coated titania mixtures can be prepared using a grafting technique [8,10,13]. For low Ti contents (<10 wt.%), TiO_2 can disperse well on the surface of the alumina, but on increasing the Ti component, aggregation of the TiO_2 particles becomes increasingly marked.

On the other hand, it is well known that for the dispersion of oxides, much depends on the surface properties of the support, and phosphorus ions can play an important role in modifying alumina. Therefore, we attempted to prepare an alumina support with highly dispersed TiO_2 clusters on the surface of the

* Corresponding author. Tel.: +86 22 23508662; fax: +86 22 23508662.
E-mail address: weili@nankai.edu.cn (W. Li).

alumina with the addition of phosphorus ions. To impregnate the phosphorus in the form of phosphates, an $\text{NH}_4\text{H}_2\text{PO}_4$ solution was used instead of an H_3PO_4 solution, as it has been shown that upon impregnation by phosphoric acid, a partial solubilization of Al^{3+} ions occurs, and AlPO_4 is precipitated during the drying procedure [14]. In addition, $\text{NH}_4\text{H}_2\text{PO}_4$ solutions are less acidic, and its interaction with the surface atoms of the Al_2O_3 is, therefore, weaker.

2. Experimental

2.1. Sample preparation

2.1.1. $\text{TiO}_2\text{-Al}_2\text{O}_3$

Agent-grade titanium butoxide was used as the precursor, Analar-grade anhydrous ethanol was used as the dilutant, distilled water was used as the promoter, and nitric acid was used as the inhibitor in mole ratios of 1:9:3:0.3. The total volume of distilled water and nitric acid, and half the volume of ethanol required, were initially mixed together, and slowly dripped in the magnetically stirred titanium butoxide dissolved in the residual ethanol. The as-prepared titanium solution (sol) was stirred for half an hour, and then added drop wise into a suspension, which is prepared by stirring the commercial pseudo-boehmite power in distilled water for 10 min. The resulting solid mixture was exposed to air for 24 h and then dried at $T = 333$ K for 6 h, at $T = 393$ K for 4 h, and then calcined at $T = 473$, 573, 673, and 823 K for 2 h per temperature. The volume of sol added could be controlled to yield different TiO_2 content in the resulting samples. The samples were denoted as TA_x (where x = the weight percentage of TiO_2 in the final sample).

2.1.2. $\text{P-TiO}_2\text{-Al}_2\text{O}_3$

The same procedure as above was adopted in the preparation of the $\text{P-TiO}_2\text{-Al}_2\text{O}_3$ samples, with the exception that Analar-grade $\text{NH}_4\text{H}_2\text{PO}_4$ was added to the suspension of pseudo-boehmite in volumes that were calculated to yield a nominal concentration of 1 wt.% P in the solid resulting from the thermal

decomposition of the precursors. The samples were similarly denoted as PTA_x .

2.2. Characterization

The XRD patterns of the samples were recorded in range $5^\circ \leq 2\theta \leq 80^\circ$ in a D/max-2500 diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The specific surface areas, the pore volumes, and the pore diameter distributions were determined from the N_2 desorption isotherms at 77 K using a Micromeritics ASAP 2010 analyzer. The specific surface areas were calculated using the five-point BET method. The BJH method was used to determine the pore diameter distributions. XPS measurements on the ceramic supports were performed at room temperature in a Perkin-Elmer Phi (4) 5300 ESCA analyzer. The particle size was determined using a Philips EM 400ST TEM. The samples for the TEM observations were dispersed by ultrasound in ethanol, and dripped onto a micro-grid mesh, and the TEM observations were carried out after drying the mesh. The FT-IR spectra of the samples were recorded at a resolution of 4 cm^{-1} in absorbance mode using a Bruker Vector 22 FT-IR spectrometer. Self-supporting wafers were prepared by pressing about 20 mg of powdered sample under a load of 2000 MPa, and the compact loaded into the sample holder of the IR cell. All the samples were activated at $T = 673$ K in vacuo (residual pressure $\leq 10^{-3}$ Pa) for a period of 2 h. All the IR spectra were recorded at room temperature and normalized to a sample mass of 20 mg.

3. Results and discussion

3.1. XRD and XPS

The XRD measurement data from the PTA_x and TA_x samples is shown in Fig. 1a and b, respectively, showing that the TiO_2 (anatase) peak intensity increases with the enhancement of the TiO_2 content in both series of samples. However, the anatase diffraction peaks in the PTA_x series are broader and weaker for the same experimental conditions, indicating that TiO_2 particles

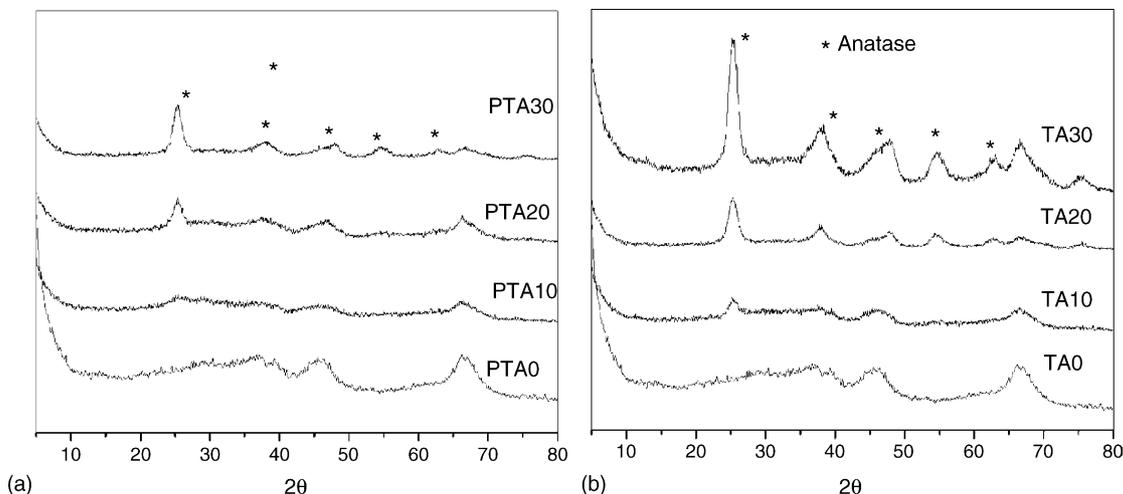


Fig. 1. XRD patterns of PTA_x (a) and TA_x (b).

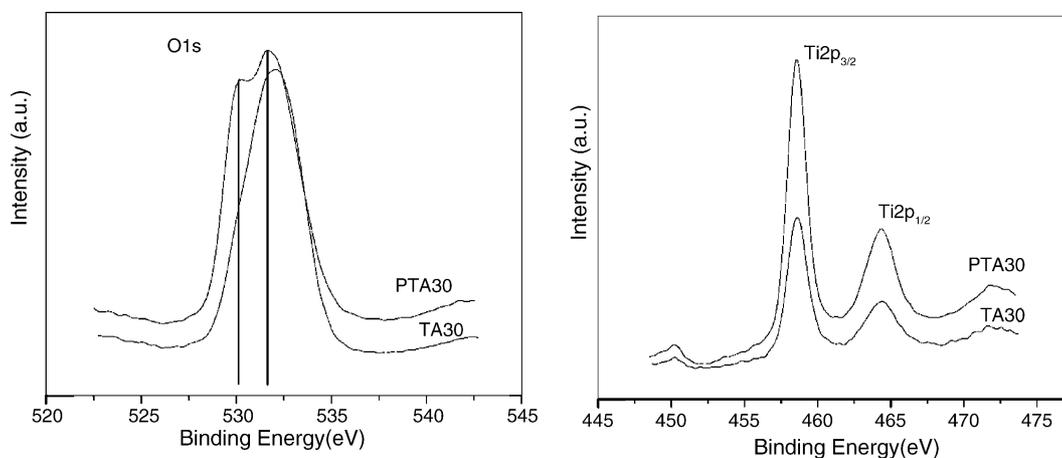


Fig. 2. O 1s and Ti 2p XPS spectra of PTA30 and TA30.

dispersed on the surface of the PTA_x samples are smaller than those dispersed on the surface of the TA_x samples.

Because of its high surface sensitivity (probing depth ca. 2 nm), XPS has been considered as one of the best techniques for studying the dispersion of metal oxides on various supports and to gain knowledge on the type of interaction involved. By combining the data on surface and bulk properties, more structural information can be attained.

To compare the dispersion of TiO₂ in mixed oxides with high Ti content, TA30 and PTA30 samples were investigated using XPS. The O 1s and Ti 2p XPS spectra of Samples PTA30 and TA30 are shown together in Fig. 2. The Al 2p spectra are not shown in our work, as there was only a small difference between the Al 2p spectra between these two samples. The O 1s line with $E_b = 530.0\text{--}530.4$ eV was assigned to the TiO₂ lattice oxygen atoms, and the higher binding energy ($E_b = 531.1\text{--}531.7$ eV) was due to the lattice oxygen of the Al₂O₃. One can see that there was a sharp peak at $E_b = 530.2$ eV in Sample PTA30 compared to Sample TA30, though the TiO₂ content of the two samples was the same. In addition, the Ti 2p patterns of the two samples show that the intensity of the Ti 2p peak was much stronger in Sample PTA30 versus Sample TA30. The Ti:Al atomic ratios, as determined by XPS for Samples PTA30 and TA30, were 0.22

and 0.48, respectively. However, the stoichiometric value is 0.27. This observation provides further evidence for the presence of a highly dispersed TiO₂ component on the surface of the alumina. Furthermore, there was a slight shift in the O 1s peak at $E_b = 531.7$ eV, towards lower energy in Sample PTA30, which indicates a change in the electronic environment around the O atom. It is possible that the presence of phosphorous results in more Al–O–Al bonds being substituted by Ti–O–Al linkages.

3.2. TEM

TEM was also employed to observe the shape and the size of the TiO₂ particles dispersed on the alumina in PTA30 and TA30. The TiO₂ particles were identifiable as black spots with different sizes, and could be clearly distinguished from the alumina. The average TiO₂ particle size in Sample TA30 was around 5 nm (see Fig. 3b). In contrast, Sample PTA30 had even smaller TiO₂ particles, most of which showed a particle size in the 1–3 nm range (see Fig. 3a). Only a few particles agglomerates could be identified in the micrographs. Combining the XRD and XPS results, we can affirm that the presence of phosphorus leads to a better dispersion of TiO₂ on the surface of alumina in the TiO₂–Al₂O₃ system.

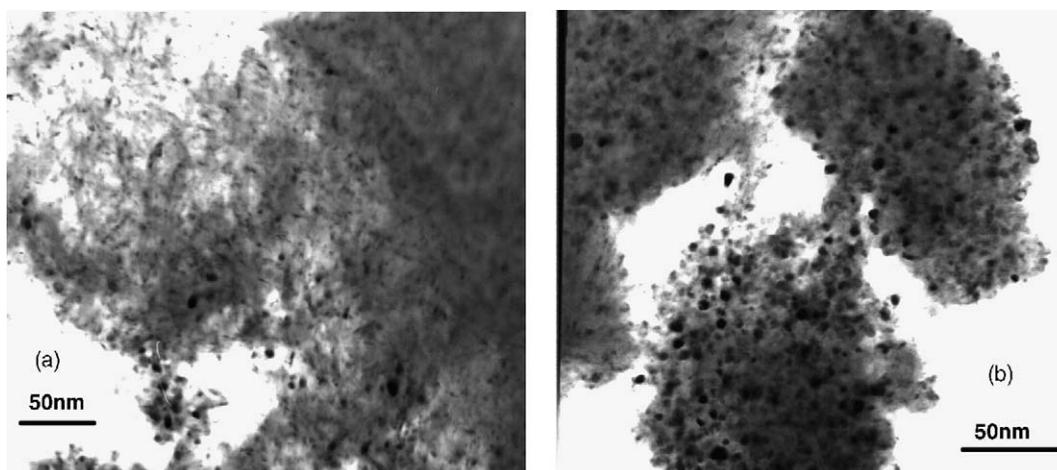


Fig. 3. TEM images of PTA30 (a) and TA30 (b).

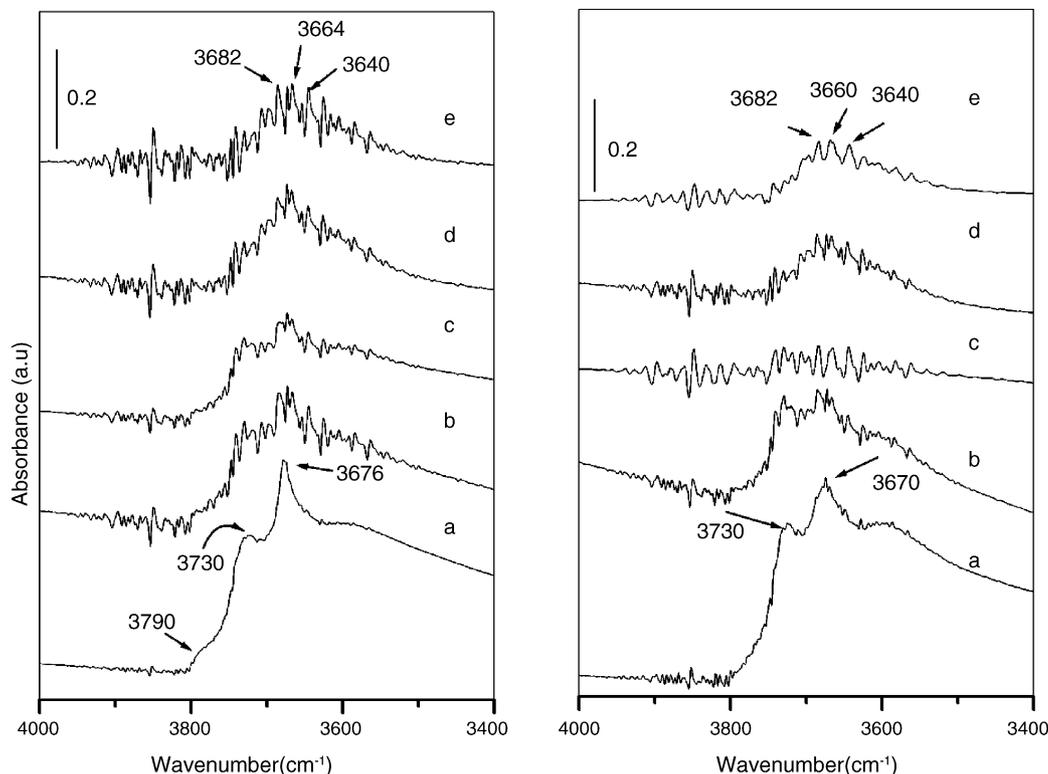


Fig. 4. IR spectra in the OH stretching region of TA x (right) and PTA x (left) samples with x value is 0 (a), 5 (b) 10 (c), 20 (d), and 30 (e).

3.3. Nitrogen adsorption

The texture and porosity of the TA30 and PTA30 determined from the nitrogen adsorption and desorption isotherms are shown in Table 1. In regards to the samples with a high TiO₂ content, although the presence of phosphates did not change the surface area, it did enlarge the pore volume and increased the average pore diameter.

3.4. FT-IR

To clarify the reasons for the effect of P on the TiO₂–Al₂O₃ system, FT-IR was used to probe the changes in surface properties of our samples. As shown in Fig. 4, IR peaks were observed at 3790, 3730, and 3670 cm⁻¹, which were attributed to isolated –OH groups. According to the description of surface –OH groups and the relevant band assignment proposed by Knözinger and Ratnasamy [15], the peaks at 3790, 3730, and 3670 cm⁻¹ are assigned to terminal –OH (I_b and I_a), doubly bridging –OH (II_b

and II_a), and triply bridging –OH groups, respectively. For the TA x samples ($x \leq 10$), the intensity of the different –OH groups site on Al ions decline sharply with increasing TiO₂ content, and become negligible in Sample TA10 (Fig. 4c, left-hand side). In the samples with even higher TiO₂ content (e.g., TA20), the bands in the 3630–3680 cm⁻¹ region of the spectrum begin to dominate. These have been attributed to –OH groups on different sites and to various interactions between the –OH groups and TiO₂ [16,17]. The shape and intensity of bands do not change with further increases in TiO₂ content. The spectral patterns in Fig. 4a (left-hand side), show that the presence of P leads to a marked increase in peak intensity in the 3770–3800 cm⁻¹ region due to the terminal –OH groups on the surface of the alumina, with a strong band centered at 3676 cm⁻¹ arising from the surface P–OH groups [14]. In contrast to the TA x samples, the small concentration of TiO₂ introduced into the PTA x samples does not lead to a sharp decrease in the number of –OH sites on alumina surface, but rather, leads to the disappearance of the P–OH peaks. (There was no observable difference between the spectra from Samples TA05 and PTA05 in the range 3670–3680 cm⁻¹.) This indicates that the Ti component may prefer to interact with the P–OH groups on the surface of the solid during the mixed oxide preparation process, presumably because of the strong acidity of the P–OH groups. On increasing the TiO₂ content in the samples, the observed spectra (Fig. 4d and e, left-hand side) become similar to those of the TA x samples (Fig. 4d and e, right-hand side). These data, along with those from the XRD and XPS results, indicate that the PTA x system should possess

Table 1
Surface areas and pore properties of TA30 and PTA30

Sample	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
TA30	274	0.50	4.93
PTA30	272	0.65	6.45
Al ₂ O ₃	350	1.00	10.2

a larger dispersion capacity for TiO₂ than the TA_x system does. And the enlarged dispersion capacity of PTA_x possibly accounts for the better dispersion of TiO₂ on the alumina in high Ti content samples.

4. Conclusions

The addition of phosphorus during the preparation of TiO₂–Al₂O₃ samples can lead to a large increase in the dispersion of the titanium component on the surface of the alumina from the generation of smaller TiO₂ particles. The investigation of surface –OH groups using FT-IR reveals that the presence of phosphates can enlarge the TiO₂ monolayer dispersion capacity on Al₂O₃, which results in the better dispersion of TiO₂ on the alumina in high Ti content samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.colsurfa.2005.07.035](https://doi.org/10.1016/j.colsurfa.2005.07.035).

References

- [1] J. Ramírez, G. Macías, L. Cedeño, A. Gutiérrez-Alejandre, R. Cuevas, P. Castillo, *Catal. Today* 98 (2004) 19.
- [2] Víctor Santes, Javier Herbert, Maria Teresa Cortez, René Zárate, Leonardo Díaz, Prakash Narayana Swamy, Mimoun Aouine, Michel Vrinat, *Appl. Catal. A* 281 (2005) 121.
- [3] J. Ramírez, S. Fuentes, G. Díaz, M. Vrinat, M. Breyse, M. Lacroix, *Appl. Catal.* 52 (1989) 211.
- [4] S. Srinivasan, A.K. Datye, C.H.F. Peden, *J. Catal.* 137 (1992) 513.
- [5] Z.B. Wei, Q. Xin, X.X. Guo, P. Grange, B. Delmon, *Appl. Catal.* 75 (1991) 179.
- [6] S.K. Maity, J. Ancheyta, L. Soberanis, F. Alonso, M.E. Llanos, *Appl. Catal. A* 244 (2003) 141.
- [7] G. Murali Dhar, B.N. Srinivas, M.S. Rana, M. Kumar, S.K. Maity, *Catal. Today* 86 (2003) 45.
- [8] N. Solange de Resende, J.G. Eon, M. Schmal, *J. Catal.* 183 (1999) 6.
- [9] C. Pophal, F. Kameda, K. Hoshino, S. Yoshinaka, K. Segawa, *Catal. Today* 39 (1997) 21.
- [10] Z.B. Wei, Q. Xin, X.X. Guo, E.L. Sham, P. Grange, B. Delmon, *Appl. Catal.* 63 (1990) 305.
- [11] E.Y. Kaneko, S.H. Pulcinelli, V. Teixeira da Silva, C.V. Santilli, *Appl. Catal. A* 235 (2002) 71.
- [12] A. Gutiérrez-Alejandre, M. González-Cruz, M. Trombetta, G. Busca, J. Ramírez, *Micropor. Mesopor. Mater.* 23 (1998) 265.
- [13] N. Macleod, R. Cropley, J.M. Keel, R.M. Lambert, *J. Catal.* 221 (2004) 20.
- [14] E.C. Decanio, J.C. Edwards, T.R. Scalzo, D.A. Storm, J.W. Bruno, *J. Catal.* 132 (1991) 498.
- [15] H. Knözinger, P. Ratnasamy, *Catal. Rev. Sci. Eng.* 17 (1978) 31.
- [16] H. Knözinger, *Adv. Catal.* 25 (1976) 184.
- [17] B. Erdem, R.A. Hunsicker, G.W. Simmons, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *Langmuir* 17 (2001) 2664.