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Can the photo-catalytic reactivity of semiconductor TiO_2 be predicted based on local site information of Ti K-edge X-ray absorption?

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Transition metal cations [1] and hetero anions have been doped to TiO_2 to promote the photo-catalysis for decompositions of volatile organic compounds and industrial dyes under visible light. In this report, TiO_2 and sulfur-doped TiO_2 both with uniform mesopores were synthesized and the Ti local sites were studied using Ti K-edge X-ray absorption.

Mesoporous TiO_2 was synthesized via the hydrolysis of Ti(*i*-PrO)$_4$ in the presence of dodecylamine [2]. Mesoporous S-TiO_2 was synthesized by adding water to the mixture of Ti(*i*-PrO)$_4$, dodecylamine, and thiosulfate with molar ratio 2 : 1 : 2. All the synthetic steps were identical to those for mesoporous TiO_2 except for washing with CS_2 after hydrolysis at 453 K for 10 days (denoted as CU-H). Another mesoporous S-TiO_2 was synthesized similarly except for washing with ether after hydrolysis at 333 K for 4 days (methanol and ether in ref. 2) and washing with CS_2 after hydrolysis for 10 days (denoted as CU-J). Ti K-edge XAFS spectra were measured in transmission mode.

Ti K pre-edge peak patterns for Meso-structured/porous TiO_2/S-TiO_2 (Figure 1a – e) resembled that for Ilmenite $FeTiO_3$ (Figure 1h; d_{Ti-O} = 0.1875 nm, N = 3, d_{Ti-O} = 0.2087 nm, N = 3). Total Ti–O coordination of 3.6 – 4.1 was given at 0.169 – 0.197 nm for mesoporous TiO_2/S-TiO_2 based on Ti K-edge EXAFS analyses. No crystalline peaks were observed in the region $2\theta_{Bragg}$ = 10 – 50 deg in XRD. Thus, octahedral TiO_6 coordination distorted to essentially 4 coordination and constituted amorphous [S-]TiO_2 matrix.

With washing with *p*-toluenesulfonic acid, the shoulder peaks at 4970.5 – 4970.6 eV became relatively greater (Figure 1a, b), suggesting greater distortion of Ti site due to the removal of dedecylamine. After oxidative dehydrogenation of ethanol under visible light [1], no significant change was observed in the Ti pre-edge peak pattern (Figure 1c – e), demonstrating the stability of mesoporous S-TiO_2 samples.

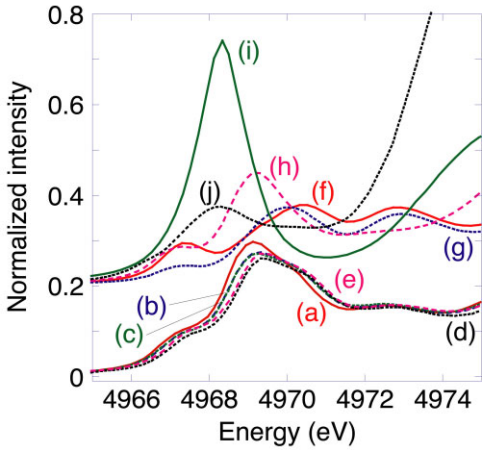

Figure 1. Ti K pre-edge peaks for meso TiO_2 before/after template washing (a, b), meso S-TiO_2 (CU-J) after template washing (c) and after photo-catalysis (d), meso S-TiO_2 (CU-H) after photo-catalysis (e), anatase-type TiO_2 (f), rutile-type TiO_2 (g), $FeTiO_3$ (h), Ti(*i*-PrO)$_4$ (i), and TiS_2 (j).

Uniform mesopores centered at 2.7 nm (mesoporous TiO_2) and 2.9 nm (mesoporous S-TiO_2, CU-H) were detected in XRD in contrast to non-uniform sample CU-J. The presence/absence of uniform mesopores for S-TiO_2 was not detected in XAFS (Figure 1c – e and EXAFS).

References

[1] D. Masih, H. Yoshitake, Y. Izumi, *Appl. Catal. A* **325(2)**, 267 – 282 (2007).
[2] H. Yoshitake, T. Sugihara, T. Tatsumi, *Chem. Mater.* **14(3)**, 1023 – 1029 (2002).

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Table 1: Titanium K pre-edge peak energy positions (eV)

sample	condition	energy position (eV)		
meso TiO_2	before template washing	4967.1(w,sh)	4969.1(s), 4970.4(vw,sh)	4972.6(w)
	after template washing	4967.2(w,sh)	4969.3(s), 4970.5(w,sh)	4972.6(w)
meso S-TiO_2 (CU-J)	after template washing	4967.2(w,sh)	4969.3(s), 4970.5(w,sh)	4972.6(w)
	after visible light catalysis	4967.4(w,sh)	4969.4(s), 4970.6(w,sh)	4972.9(w)
meso S-TiO_2 (CU-H)	after visible light catalysis	4967.3(w,sh)	4969.4(s), 4970.6(w,sh)	4972.9(w)
TiO_2	anatase	4967.4(m)	4970.4(s)	4972.9(m)
	rutile	4967.1(w)	4970.0(s)	4973.0(m)
$FeTiO_3$		4967.1(w)	4969.2(s)	
Ti(*i*-PrO)$_4$			4968.3(s)	
TiS_2			4968.2(s)	