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Deactivation and regeneration of visible light active brookite titania in photocatalytic degradation of organic dye

Sujaree Kaewgun, Burtrand I. Lee*

School of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA

ABSTRACT

This study was performed to investigate deactivation and regeneration of predominantly brookite titania powders. Visible light active (VLA) polymorphic titania particles were prepared by a water-based ambient condition sol (WACS) process followed by a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. Deactivation of all samples was evaluated by degradation of methyl orange (MO) dye under either UV or VL irradiation for four reaction cycle runs. The photocatalytic activity (PCA) under VL exposure of NMP samples calcined at 200 °C for 2 h in air (NMP-200) was approximately 3.3 times higher than that of a commercial VLA titania (Kronos VLP7000), despite the much lower surface area of the NMP-200. Nonetheless, PCA of all titania samples under VL gradually decreased with an increase in testing time and number of runs. The cause of the deactivation of the titania samples in this study was identified as the deposition of the decomposed MO on the titania nanoparticle surface. Among the possible regeneration or reactivation procedures for the used samples, methanol washing was shown to be the most effective up to ~80% of the PCA recovery. The used NMP-200 samples could not completely be recovered, since a regeneration process would possibly remove some of nitrogen species responsible for the VLA.

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1. Introduction

Titanium dioxide or titania (TiO$_2$) is one of the most well-known and widely used photocatalysts under UV irradiation [1–6]. Nitrogen-doped titania has been widely studied in order to improve the photocatalytic activity (PCA) under visible light (VL) irradiation by narrowing the band gap of titania [7–17].

In our previous articles [18–20], the preparation of VL active (VLA) polymorphic titania samples was reported. It was done by post-treating a water-based ambient condition sol (WACS) polymorphic brookite titania using a solvent-based ambient condition sol (SACS) process with N-methylpyrrolidone (NMP) as the solvent. It was explained in our previous articles [18–21] that SACS calcined sample in air at 200 °C for 2 h showed superior VL photocatalytic performance, evaluated by the degradation of methyl orange (MO) dye, to WACS and commercial titania P25. Despite such frequency and problematic nature of deactivation of catalysts, especially in liquid phase, systematic studies are scarce in the literature. Phillips and Raupp [22] reported that water and organic species adsorbed on TiO$_2$ surfaces possibly cause the reduction of PCA, i.e., the deactivation of photocatalysts. A study of deactivation and regeneration for photocatalytic oxidation of toluene by mixed anatase and rutile TiO$_2$ was reported by Cao et al. [23]. They concluded that severe deactivation of TiO$_2$ is due to the accumulation of partially oxidized intermediates, such as benzaldehyde and benzoic acid, on the active sites. For complete recovery of the deactivated catalysts, the regeneration requires a calcination temperature above 420 °C in air, which may cause the phase transformation of anatase to rutile and reduction in specific surface area of the TiO$_2$ nanoparticles.

TiO$_2$ deactivation of anatase and/or rutile TiO$_2$ has been studied [24–28]. The drop in the PCA during organic oxidation was due to an accumulation of partially oxidized products on TiO$_2$ surface. Nevertheless, the deactivation of unusually high VL active polymorphic brookite titania [18–20], has never been reported.

In this article, we report the deactivation of polymorphic brookite titania in the decomposition of MO dye under both UV and VL irradiation as well as the possible regeneration of the spent catalyst. A commercial VLA TiO$_2$, Kronos VLP7000 [20], was used as the reference.

2. Experimental

A polymorphic brookite titania was prepared by a WACS process, as described in our previous articles [18–21,29–32]. A SACS process, a post-treatment of the WACS sample, is also presented in the references [18–21]. The as-prepared samples were calcined

* Corresponding author. Tel.: +1 202 872 6254; fax: +1 202 972 6319.
E-mail address: Lburtra@yahoo.com (B.I. Lee).

Table 1
The physical properties of fresh and used TiO_2 samples and the reference VLP7000.

Sample ID	Crystallite size (nm)[a]			BET surface area (m^2/g)[b]	Pore volume (cm^3/g)[b]	Pore size average (Å)[b]
	Anatase	Brookite	Rutile			
WACS-200	5	9	11	169	0.1	25
WACS-200-UV#1	7	10	10	177	0.1	27
NMP-200	7	8	13	157	0.1	24
NMP-200-VL#1	7	9	11	220	0.1	25
NMP-200-VL#2	5	8	16	202	0.1	26
NMP-200-VL#3	6	7	12	175	0.1	27
NMP-200-VL#4	7	7	10	185	0.1	27
NMP-200-UV#1	6	7	12	206	0.1	25
VLP7000	7	–	–	290	0.4	56
VLP7000-VL#1	9	–	–	287	0.4	59

[a] Calculated from XRD data using the Scherrer equation. Error of measurement = ±5%.
[b] Using N_2 physisorption at −196 °C. Error of measurement = ±10%.

in air at 200 °C for 2 h, characterized, and named "WACS-200" and "NMP-200".

The deactivation of polymorphic brookite titania was evaluated by observing the photocatalytic degradation of MO under either UV with wavelength of 365 nm, or VL irradiation of 560–612 nm. The experimental MO test and the calculated MO degradation percent value, D, were obtained by the procedure found in the literatures [18,19,21,32]. NMP-200 of 0.1 g, for VLA test, was dispersed in a 100 ml of 20 μM MO solution, and 0.5 g of other TiO_2 samples were used in a 300 ml of 20 μM MO solution. A Spectroline black light lamp (Model BIB-150B operated at 365 nm and 182 W) and a 150W halogen lamp were utilized as the UV and VL sources, respectively. The UV lamp and the VL lamp were positioned above the MO solution 35 and 17 cm, respectively. The MO quantitative spectral results were monitored by a UNICAM UV/vis spectrophotometer (Model: 5625). Titania samples were reused for four reaction cycle runs without any intermittent treatments in a fresh MO solution. After each run, the used titania sample was separated from the MO solution by vacuum filtration, followed by being dried at 150 °C for 4 h in an oven for a next run. Sample IDs of the used TiO_2 samples are composed of the fresh TiO_2 sample ID, UV or VL irradiation or dark, and the number of photocatalytic cycles. For example, the NMP-200 sample after the first run of MO degradation under VL irradiation was called "NMP-200-VL#1".

After the first reaction cycle, the used sample was regenerated by several possible procedures, i.e., solvent washing or recalcination at various temperatures. The regeneration of the catalyst was investigated by reusing 0.1 g of the regenerated titania sample in the second reaction cycle under the same condition as the first one.

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of the titania samples showed the phase compositions of varying proportions: 50–55% brookite, 40–48% anatase, and a small amount of rutile (less than 3%) [18–21]. The reference Kronos samples (VL7000) are 100% anatase having similar crystallite size to our prepared titania. Table 1 gives the crystallite sizes, BET surface areas, pore volume, and average pore diameter of the titania samples. The surface areas of the as-prepared titania samples are approximately 1.8 times smaller than that of Kronos sample.

UV/vis spectra of titania samples are given in Fig. 1(a). The NMP-200 sample exhibited a shift of the absorption shoulders to the VL region, compared to WACS-200 and VLP7000.

3.2. Catalyst recycling and deactivation

The stabilities of WACS-200 and NMP-200, determined by the MO degradation under UV irradiation, are given in Fig. 2(a) and (b), respectively. MO with titania samples stirred in the dark was not degraded. The MO degradation by NMP-200 was 10 min faster than by WACS-200, as expected, because of fewer lattice hydroxyls in NMP-200 sample [18,19]. Both samples were not deactivated after the first reaction cycle. After the second cycle, however, PCA of both samples gradually decreased with the increase in the testing time.
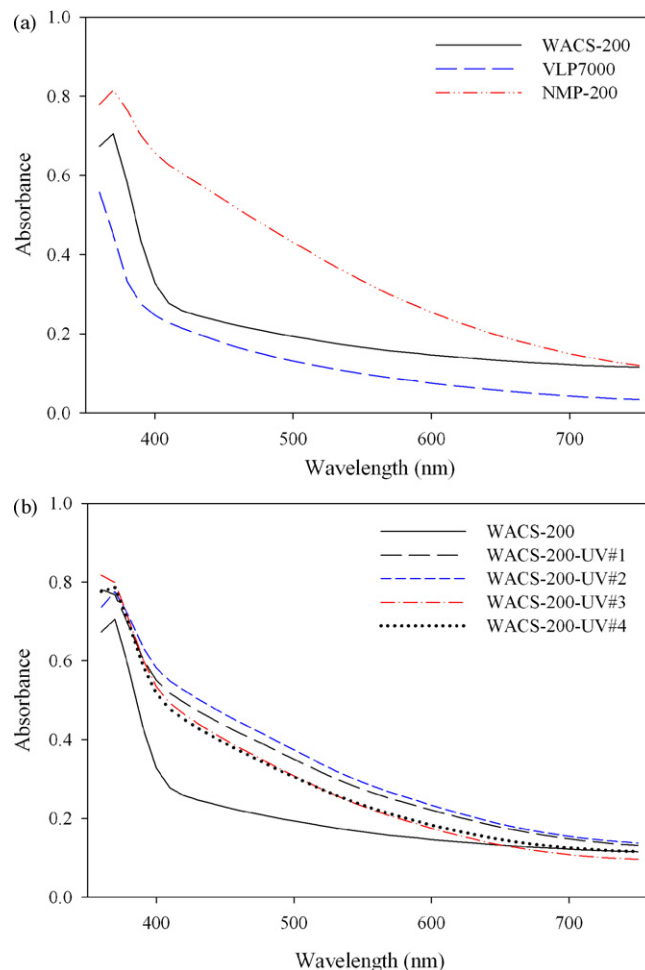

Fig. 1. UV/vis spectra of (a) fresh titania samples, and (b) fresh and used WACS samples.
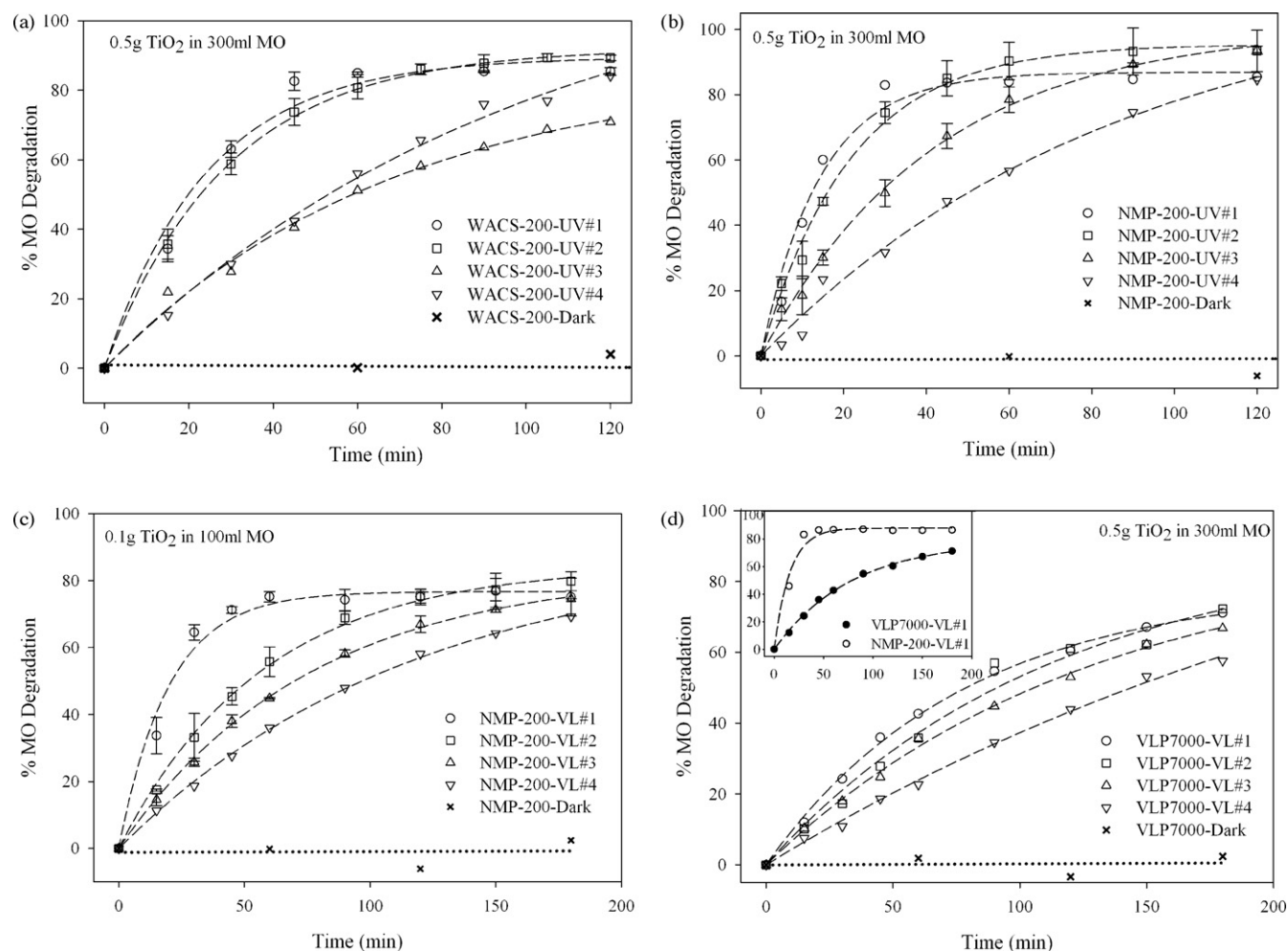
Fig. 2. The stabilities, determined by the MO degradation, of (a) WACS-200 under UV irradiation, (b) NMP-200 under UV irradiation, (c) NMP-200 under VL irradiation, (d) VLP7000 under VL irradiation, and inset of (d) showing the first reaction cycle of MO degradation under VL exposure of NMP-200 and VLP7000.

The deactivation of NMP-200 and VLP7000, evaluated by MO degradation under VL irradiation, is reported in Fig. 2(c) and (d), respectively. The MO degradation rate by NMP-200 exhibited approximately 3.3 times higher than that of VLP7000, as shown in the inset of Fig. 2(d), despite the much lower surface area of NMP-200 than that of VLP7000. This VLA superiority of NMP-200 must be due to the presence of brookite phase with the significant proportion of anatase [20], compared to 100% anatase for VLP7000. It is also supported by UV/vis spectra in Fig. 1(a) that NMP-200 can absorb more VL than VLP7000. Nonetheless, both NMP-200 and VLP7000 were gradually deactivated with the increasing number of reaction cycles. The initial rate of MO degradation of NMP-200-VL#2 was approximately 47% less than that of NMP-200-VL#1. MO degradation by VLP7000 in the second cycle was 30% slower than the first cycle. However, the same amount of NMP-200-VL#4 (i.e., the 4th cycle) presented significantly higher VLA than VLP7000-VL#1 (the 1st cycle). The catalyst deactivation is possibly attributed to the deposition of the decomposed MO species. The carbonaceous deposit [23,27,33] was examined by FT-IR (Fig. 3(a) and (b)), TGA (Fig. 4), and XPS (Fig. 5(a) and (b)). FT-IR spectra of MO are given in the inset of Fig. 3(a). The two FT-IR peaks at wave numbers of 1150 and 1210 cm^{-1}, which can be assigned for C–O stretch in –C–O–C– and –C–OH [34], were found in all of the used samples, and their relative intensities increased with the increasing number of reaction cycles. It can be concluded from the FT-IR spectra that the deposition of decomposed MO products was observed in all used TiO$_2$ samples. Weight loss percentage, calculated from TGA

in Fig. 4 at temperatures between 425 and 800 °C, shows that the carbonaceous deposit can be removed from titania samples at a temperature of about 420 °C in air atmosphere as reported by Cao et al. [23]. The % weight loss, which was attributed to the amount of carbonaceous deposits, of all samples increased with increasing number of cycle runs. The results agree well with FT-IR results. Moreover, the observed color of used WACS-200 samples changed from off-white to light brown resulting from the deposition of the decomposed MO. UV/vis absorption of used WACS-200 samples, given in Fig. 1(b) also shifted to VL region.

The chemical state of carbon in NMP-200 samples was examined using XPS as shown in Fig. 5(a) and (b). The XPS spectrum of fresh NMP-200 in Fig. 5(a) reveals three C 1s peaks at 282.7, 283.4, and 284.6 eV. Fig. 5(b) is the C 1s XPS peak of NMP-200-VL#1 revealing two peaks at binding energies of 282.8, and 286.7 eV. The C peak at ~283–284 eV was assigned to a carbonaceous species remained in the precursor organic compound, while the peak of 286.7 eV at higher binding energy was attributed to C–O bond (either C–OH or C–O–C) [35,36]. The XPS results suggested that there was carbonaceous species remained in the precursor organic compound in both samples, but only the used NMP-200 sample was found to have oxidized carbonaceous deposits.

After any reaction cycles, the percent of titania phases, the crystallite size, and the crystallinity of the used samples did not change as expected, since the MO degradation was operated at room temperature. The average particle size of fresh and used titania samples, obtained from TEM micrographs (data not given), did
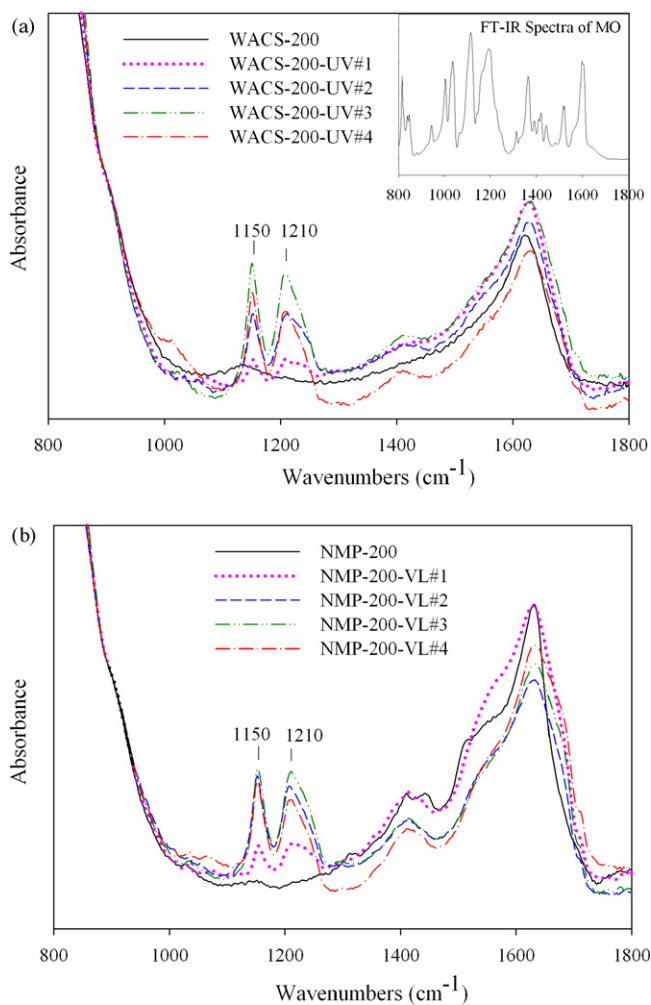
Fig. 3. FT-IR spectra of (a) fresh and used WACS-200 samples, inset of (a) showing that of MO, and (b) fresh and used NMP-200 samples.

not significantly differ. Thus, the used titania nanoparticles did not agglomerate.

BET surface areas of the used WACS-200 and VLP7000 were similar to those of fresh WACS-200 and VLP7000, respectively. On the other hand, the used NMP-200 samples, after the MO degradation
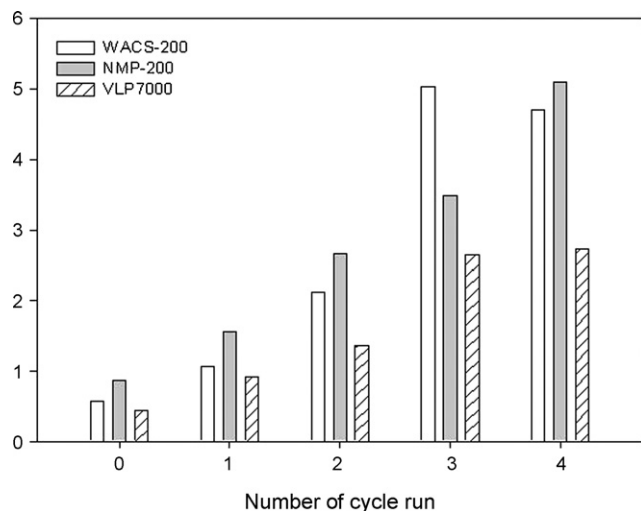

Fig. 4. Percent of weight loss, calculated from TGA at temperatures between 425 and 800 °C.
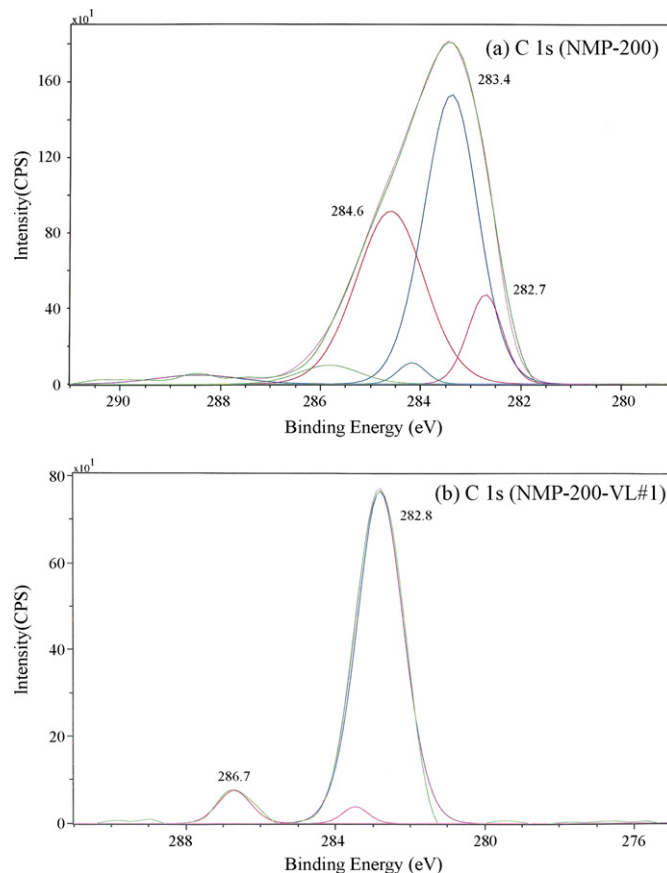

Fig. 5. C 1s XPS spectrum of (a) NMP-200 and (b) NMP-200-VL#1.

under either UV or VL exposure, exhibited approximately 30–40% larger BET surface area than the fresh one. In order to explain the increasing in surface area, NMP-200 was tested under a controlled experimental setup: 0.5 g of NMP-200 was added to 300 ml of water and the suspension was kept in the dark with or without stirring for 3.5 h. After 3.5 h, the NMP-200 particles were separated from water and dried at 150 °C for 4 h. The BET surface areas of those NMP-200 samples were similar to NMP-200-VL#1. This means that water itself affected the BET surface area and pore size of NMP-200 sample. However, water did not have an effect on the surface area of WACS-200. Therefore, an increase in the surface area can be explained by water possibly opening up the pores in NMP-200 by removing or leaching some NMP or any species which blocked the pores of NMP-200. The increase of surface area can explain why the PCA under UV irradiation of NMP-200-UV#1 and WACS-200-UV#1 were similar to those in the second cycle. Nevertheless, the VL-PCA of NMP-200-VL#2 was lower than NMP-200-VL#1 due to the leaching of VLA nitrogen species on the TiO_2 surface during the first reaction cycle. This nitrogen loss of the used NMP-200 sample is supported by the N 1s peak result from XPS (data not shown). There was 0.7 wt% of N on the fresh NMP-200 surface, while the N 1s could not be observed in the used NMP-200 sample, which means that the N content of the used sample was less than the instrument detection limit (<0.5 wt%).

3.3. Catalyst regeneration

Possible regeneration procedures of used NMP-200 samples, i.e., solvent washing or recalcination at various temperatures, were investigated. To study the catalyst regeneration by solvent washing, NMP-200-VL#1 was washed with various solvents, i.e., methanol
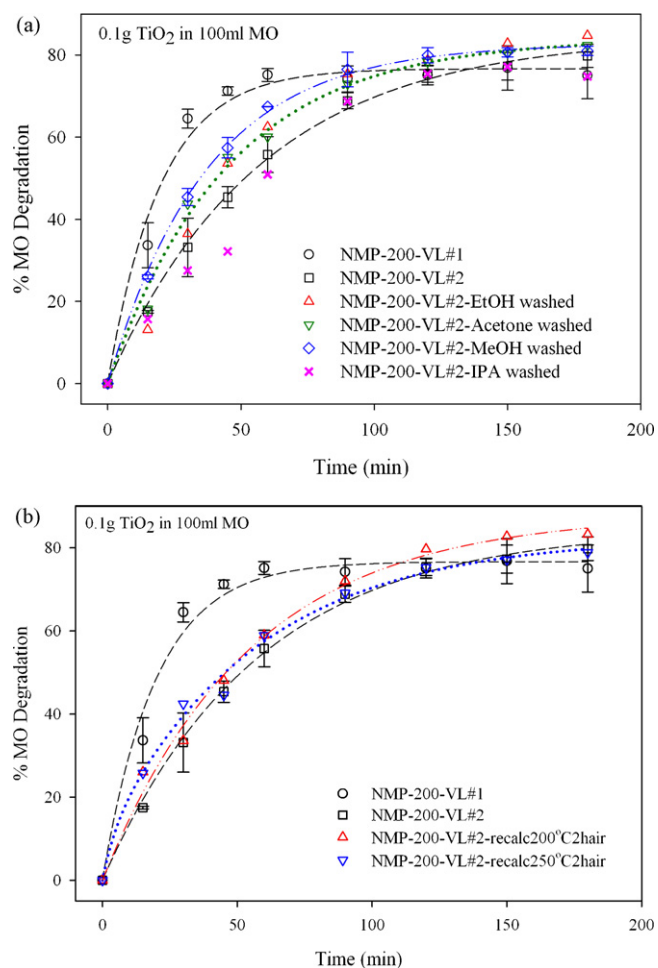
Fig. 6. The regeneration of NMP-200-VL#1, evaluated by the MO degradation under VL irradiation, by (a) washing and (b) recalcination.

(MeOH), ethanol (EtOH), isopropanol (IPA), or acetone. After washing, the titania particles were filtered and dried at 100 °C for 4 h. For regeneration by recalcination, the used NMP-200 samples were heated at either 200 °C or 250 °C in air. From our previous studies [18,19], both NMP and nitrogen, responsible for VLA properties, in NMP-200 samples can likely be released by calcination at temperatures above 250 °C for 2 h in air. Moreover, the surface area of NMP samples, calcined at temperatures above 350 °C, rapidly decreased and their average particle size would increase proportional to the increased temperature due to sintering [18,19]. Fig. 6(a) and (b) present the regeneration of NMP-200-VL#1 by washing and recalcination, respectively, evaluated by the MO degradation under VL irradiation. Among the washing procedures of the used samples, given in Fig. 6(a), MeOH washing was shown to be the most effective up to ~80% recovery of the fresh sample. The initial rate of MO degradation of recalcined NMP-200 samples, as shown in Fig. 6(b), was about 75% of that of NMP-200-VL#1. Therefore, NMP-200-VL#1 could not completely be recovered by the recalcination at both 200 °C and 250 °C, as expected. This can be explained by TGA analysis that the carbonaceous deposit on the used NMP-200 sample could only be removed by combustion at the temperature above 420 °C [23]. The complete recovery of deactivated catalysts was limited by the sintering and nitrogen removal by high temperature heat treatment, and/or nitrogen leaching by solvent washing. Hence, further regeneration procedures by the combination of solvent washing and recalcination in vacuum at low temperatures may be needed.

4. Conclusions

NMP-200 was found to be much more VL active than VLP7000, although NMP-200 has smaller BET surface area than VLP7000. This VLA superiority of NMP-200 is due to the mixed brookite and anatase titania phases, compared to pure anatase phase of VLP7000. However, PCA under VL of both NMP-200 and VLP7000 gradually decreased with increasing the number of reaction cycles. The cause of the deactivation of the titania samples in this study was identified as the deposition of the decomposed MO or the carbonaceous deposit. Nevertheless, WACS-200 and NMP-200 did not show the deactivation after the first reaction cycle, because of an increase in surface area. In the regeneration of the used NMP-200 samples, NMP-200-VL#1 could not fully be recovered by recalcination at both 200 °C and 250 °C since the carbonaceous deposit would not be removed at temperatures below 420 °C. Among the solvent washing procedures for used NMP-200, MeOH washing was shown to be the most effective with up to ~80% of the PCA recovery. The NMP-200 sample could not be completely recovered since the regeneration process would possibly remove some of the nitrogen species responsible for the VLA and decrease its surface area with a high regeneration temperature. Further studies on alternative regeneration procedures by compromising solvent washing and recalcination in vacuum at low temperatures should be the next step.

Acknowledgments

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