

Effect of Different Mineralizers in the Sonochemical Synthesis of Self-Assembled Nanorods Vanadium Oxide

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The effects of different potassium salts (KNO₃ and KCl) as mineralizer on the synthesis of self-assembled nanorods vanadium pentoxide, V₂O₅ via sonochemical treatment were studied at different duration *i.e.*, 30, 60, 90 and 120 min. All the materials synthesized were further characterized by x-ray diffraction, scanning electron microscopy and transmission electron microscopy. X-ray diffraction patterns revealed that the potassium ion from the mineralizers reacted with the V₂O₅ after prolonged sonochemical treatment duration. The morphology of the V₂O₅ changed from platelet-like structures into nanorods after 90 min of sonochemical treatment. TEM micrographs show the process of formation of the self-assembled V₂O₅ nanorod bundles with increased sonochemical treatment duration.

Key Words: Sonochemical treatment, Mineralizer, Vanadium oxide, Nanorods.

INTRODUCTION

Vanadium pentoxide (V₂O₅) has wide applications as catalyst especially for oxidation catalysis¹⁻³, as a cathode material for solid-state batteries^{4,5} and biochemical sensors⁶. Vanadium oxide nanostructures have attracted a great deal of attention due to their fascinating layered structure, enabling a variety of molecules or cations to be embedded between these layers⁷. Sonochemistry arises from acoustic cavitation *i.e.*, the formation, growth and implosive collapse of bubbles in a liquid. The collapse of bubbles generates localized hot spots through adiabatic compression or shock wave formation within the gas of the collapsing bubble. This local heating produces a wide range of high-energy chemistry⁸. By applying this technique, synthesis of nanostructured inorganic materials has been developed, whereby solutions of mixture compounds are irradiated with high intensity ultrasound and high surface area solids are produced that consist of agglomerates of nanometer clusters with the surface morphology changed as well^{9,10}. This sonochemical treatment technique also has some special advantages: straightforward, surfactant/ template-free, low cost and large-scale production. The presence of the mineralizer is an important factor for influencing the growth of the V₂O₅ nanostructures as they increase the mobility of the components in the system and allows atoms, ions or molecules to adopt appropriate positions in developing crystal lattices⁶.

In this study, the influence of two mineralizers and sonochemical treatment duration on the composition and morphology of the self-assembled nanorods V₂O₅ were investigated with various techniques including X-ray diffraction and electron microscopies.

EXPERIMENTAL

Preparation of nanostructured vanadium pentoxide (V₂O₅): Vanadium pentoxide (1.82 g, 10.0 mmol) and the mineralizer were dissolved in 200 mL of distilled water. Potassium nitrate, KNO₃ (2.02 g, 20.0 mmol) and potassium chloride, KCl (1.49 g, 20.0 mmol) were used as the mineralizers in this study. Then the mixture solution was exposed to high-intensity ultrasound irradiation under ambient air for 30, 60, 90 and 120 min. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (2.6 cm diameter, Ti-horn, 20 kHz, 500 W) immersed directly in the reaction solution. After cooling the sample to room temperature, the precipitate was separated by centrifuging at a rotation rate of 2000 rpm for 5 min, washed with distilled water and absolute ethanol in sequence and dried in air at room temperature. The V₂O₅ samples obtained were denoted as KNO30, KNO60, KNO90, KNO120, KCl30, KCl60, KCl90 and KCl120, respectively.

Characterization of nanostructured V₂O₅: X-Ray diffraction (XRD) analysis was carried out by using a Shimadzu diffractometer model XRD 6000.

The electron microscopy techniques were used to obtain the information on the morphology and size of the samples by LEO 1455 variable pressure scanning electron microscopy (SEM). The morphology was studied at an accelerating voltage of 30 kV. The particles were attached on an aluminium stub by using double-sided tape. The preparation was covered by using a thin layer of gold coating by using BIO-RAD Sputter Coater. The SEM micrographs were recorded by using a digital camera at various magnifications.

The particle size of the samples was examined using LEO 912AB energy filter transmission electron microscope with an acceleration voltage of 120 keV.

RESULTS AND DISCUSSION

X-Ray diffraction (XRD) analysis: XRD patterns for the sonochemical treated V_2O_5 are shown in Figs. 1 and 2. Diffractograms of the samples treated for 0.5 and 1.0 h using both mineralizers show only the presence of the V_2O_5 phase in the material, with the main reflections appeared at $2\theta = 15.4^\circ$, 20.3° , 26.2° , 31.0° and 34.3° , represent the reflection of (200), (001), (110), (400) and (310) planes, respectively¹¹. Interestingly, prolonged sonochemical treatment to 90 and 120 min induced the presence of additional phase *i.e.*, KV_3O_8 with the main reflections appeared at $2\theta = 11.7^\circ$, 15.7° , 25.7° , 27.9° and 45.4° , represent the reflection of (100), (110), (210), (021) and (231) planes, respectively¹².

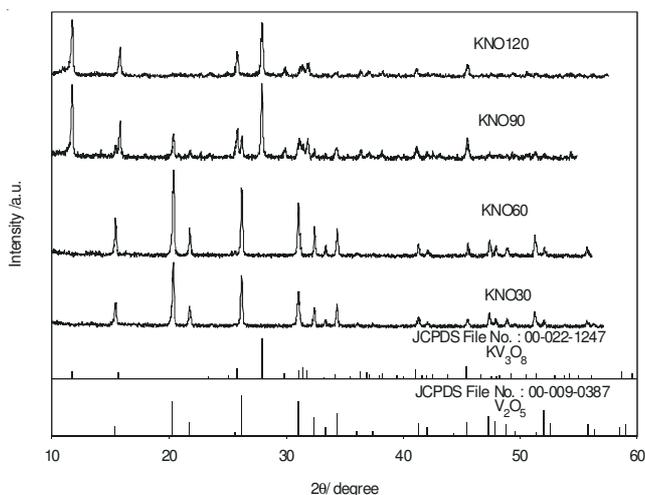


Fig. 1. XRD patterns for sonochemical treated V_2O_5 using KNO_3 as mineralizer

These diffractograms revealed that after sonochemical treatment of 90 min, the K^+ ions from both KNO_3 and KCl mineralizers were found incorporated into the V_2O_5 structures with the formation of a new phase, KV_3O_8 . The prolonged sonochemical treatment provides high energy ultrasound irradiation which is a suitable condition for the K^+ cations to react with the V_2O_5 to form KV_3O_8 . However, this phase was not observed when using sodium fluoride (NaF) mineralizer as reported earlier by Mao and co-workers⁶.

The particle thickness was calculated by applying the Debye-Scherrer equation. The value of the particle thickness, t for the sonochemical treated V_2O_5 were shown in Table-1. The average crystallite thickness of the V_2O_5 samples changes

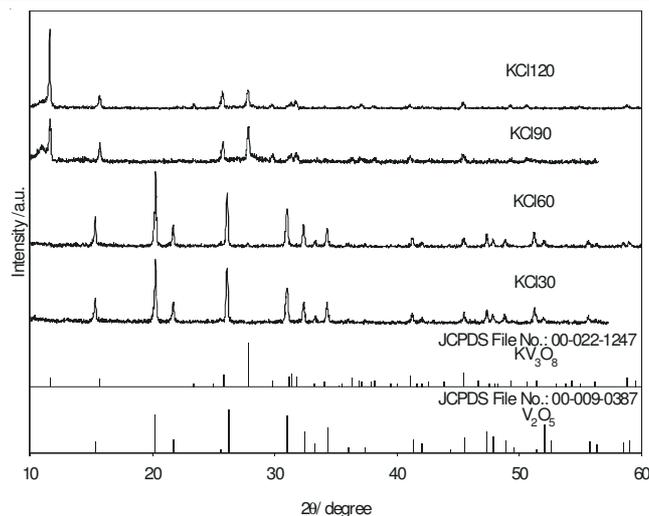


Fig. 2. XRD patterns for sonochemical treated V_2O_5 using KCl as mineralizer

TABLE-1
XRD DATA OF SONOCHEMICAL TREATED V_2O_5

Sample	hkl	Intensity	FWHM ($^\circ$)	t (\AA)	Average t (\AA)
KNO30	200	65	0.1638	8.4436	8.3
	001	179	0.1765	7.8889	
	110	148	0.1710	8.2287	
	400	113	0.1805	7.8804	
	310	64	0.1602	8.9539	
KNO60	200	93	0.1371	10.0882	9.1
	001	238	0.1682	8.2785	
	110	216	0.1450	9.7044	
	400	155	0.1853	7.6766	
KNO90	100	171	0.1831	7.5241	7.6
	110	99	0.1646	8.4054	
	210	73	0.2360	5.9566	
	021	229	0.1953	7.2297	
	231	67	0.1717	8.6513	
KNO120	100	155	0.1909	7.2172	7.0
	110	73	0.1879	7.3639	
	210	67	0.1881	7.4752	
	021	163	0.2000	7.0613	
	231	40	0.2614	5.6852	
KCl30	200	70	0.1600	8.6434	8.5
	001	189	0.1534	9.0759	
	110	175	0.1445	9.7364	
	400	110	0.2167	6.5622	
KCl60	200	99	0.1451	9.5310	8.7
	001	227	0.1677	8.3021	
	110	206	0.1415	9.9429	
	400	136	0.1984	7.1683	
KCl90	100	111	0.1882	7.3200	7.4
	110	47	0.1674	8.2653	
	210	107	0.2078	6.7656	
	021	106	0.1830	7.7165	
KCl120	100	254	0.1800	7.6535	7.7
	110	63	0.1629	8.4927	
	210	91	0.1772	7.9019	
	021	97	0.2096	6.7365	

with sonication treatment duration whereby prolonged sonochemical treatment duration decreased the average crystallite size of the samples as shown in Fig. 3.

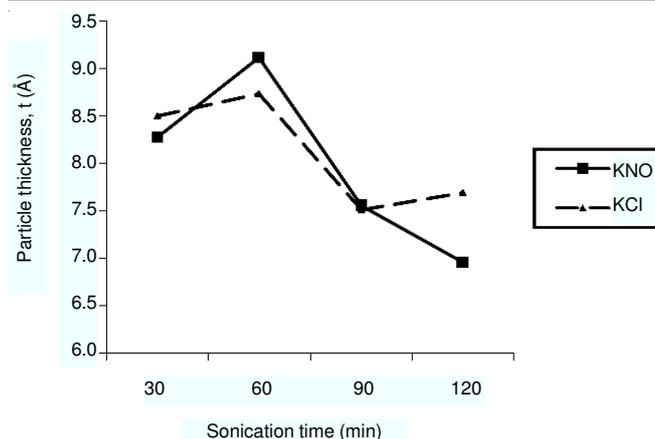


Fig. 3. Plot of the particle thickness (according to the Debye-Scherrer equation) of V_2O_5 samples against sonication time

Scanning electron microscope (SEM): The surface morphologies of the sonochemically treated and untreated V_2O_5 samples were examined by using scanning electron microscopy as shown in Figs. 4-6. For the untreated sample, std. V_2O_5 (Fig. 4), the surface of the bulk phase is almost smooth or level because of the orderly arrangement of the platelets. After 0.5 h of sonication treatment, the plate-like particles of KCl30 (Fig. 5a) and KNO30 (Fig. 6a) started to separate from the bulk phase to become smaller platelets with sizes ranging from 200 nm to 1 μ m causing the surface morphology to be uneven. After 1 h of sonication, the morphology of the particles are still the same for KCl60 (Fig. 5b) and KNO60 (Fig. 6b), but with one difference, the particles tend to agglomerate into stacks of platelets. This could explain the increase in the particle size of the particles measured by TEM. KCl90 (Fig. 5c) and KNO90 (Fig. 6c) show a change of morphology after 90 min of sonication, with the formation of nanorods of V_2O_5 with a diameter of about 100 nm and length of 500 nm. This also agrees with the TEM measurements in Figs. 8 and 9. Bigger plates are also observed to form after 90 min of sonication for KCl90 and KNO90. The appearance of these plates could be due to the presence of the KV_3O_8 phases detected through XRD analysis. These plates continue to appear after 2 h of sonication along with the nanorods of V_2O_5 for KCl120 and KNO120 (Figs. 5d and 6d). This shows the presence of a mixed-phase of V_2O_5 and KV_3O_8 in KCl120 and KNO120 which in agreement with the XRD patterns.

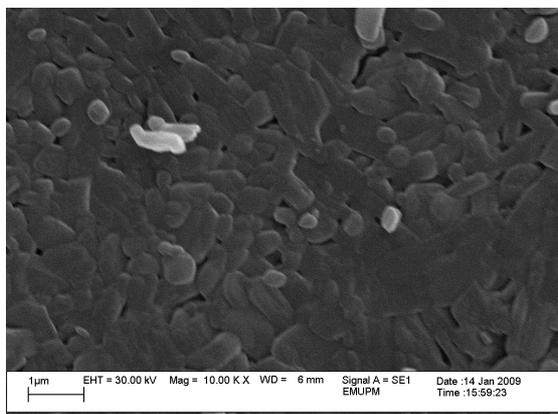


Fig. 4. SEM micrograph of V_2O_5 std

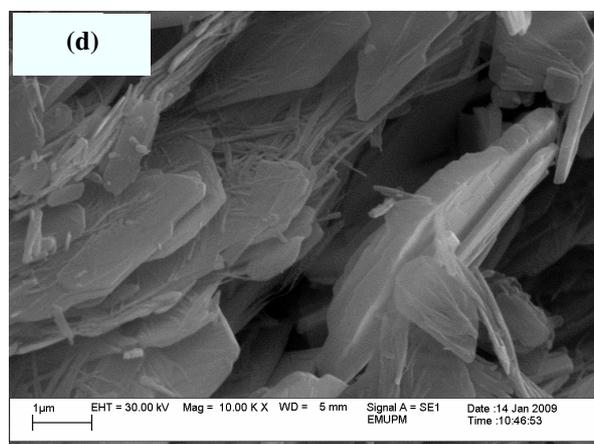
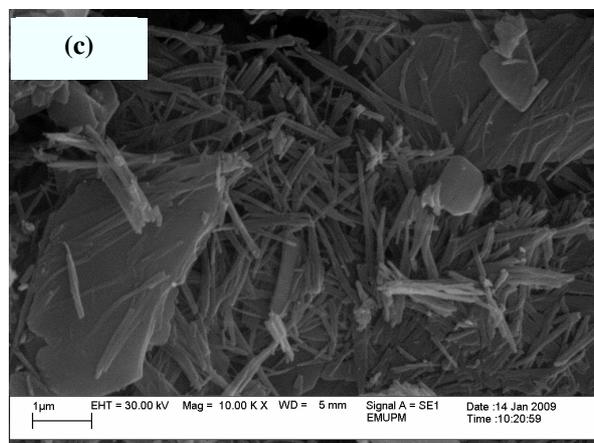
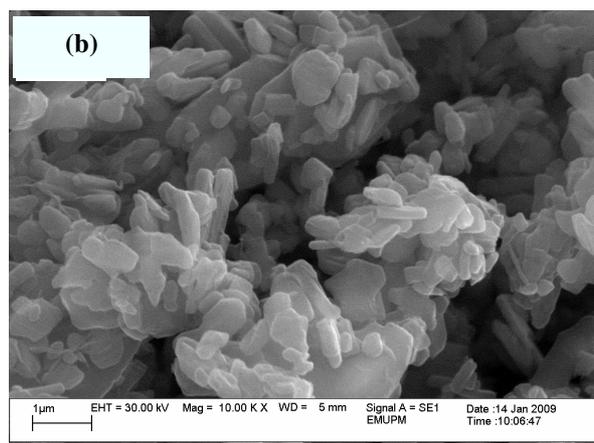
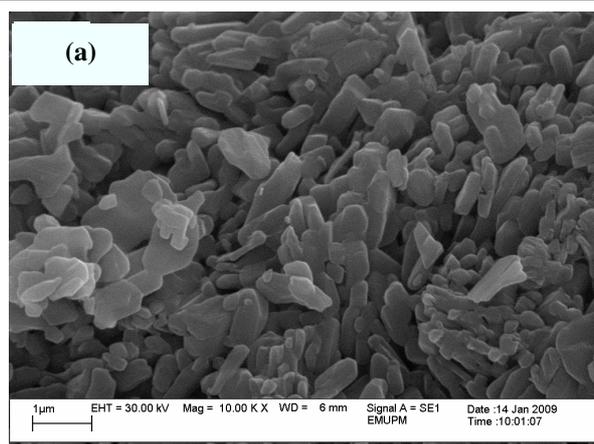


Fig. 5. SEM micrographs of (a) KCl30; (b) KCl60; (c) KCl90; (d) KCl120

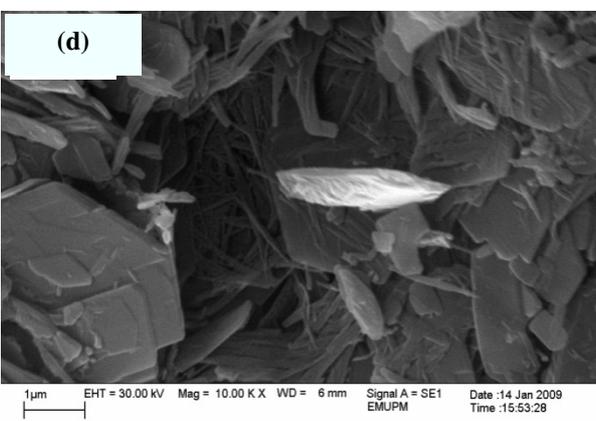
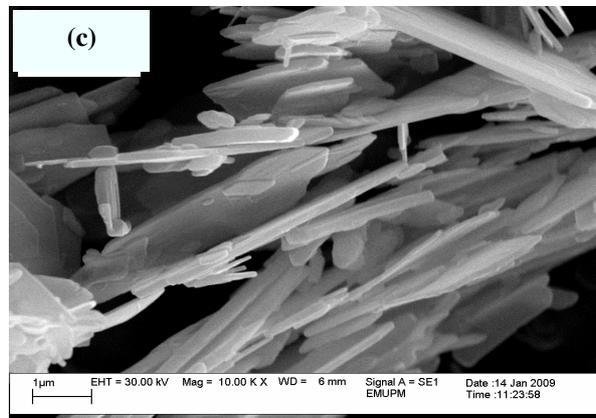
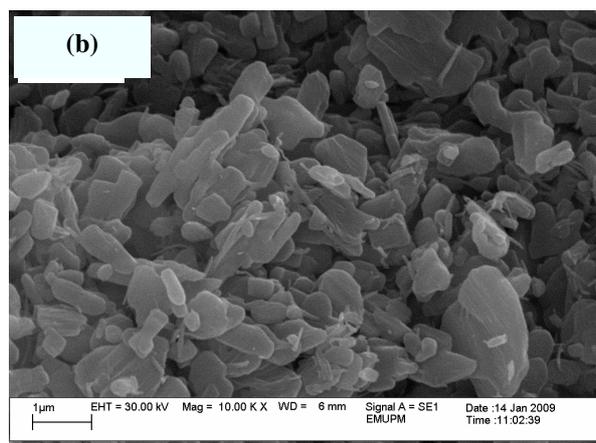
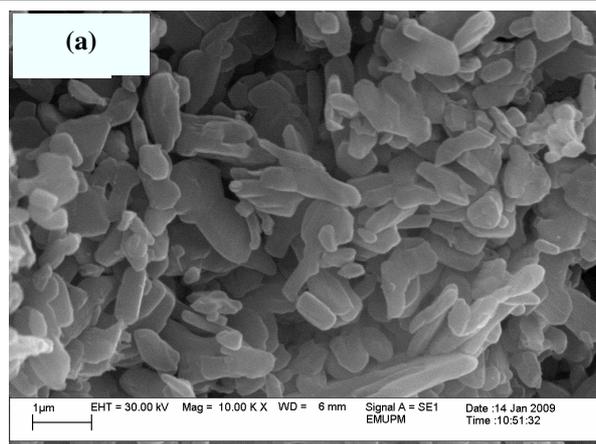


Fig. 6. SEM micrographs of (a) KNO30; (b) KNO60; (c) KNO90; (d) KNO120

Transmission electron microscope (TEM): Fig. 7 shows large particles observed for bulk V_2O_5 (std. V_2O_5). As the sonication duration increased, the amount of the large bulk particles decreased and smaller particles were observed for KCl30 and KNO30 (Figs. 8a and 9a). These small particles could serve as seeds for the growth of V_2O_5 nanorods. When the reaction time reached 60 min, the particles began to grow up and V_2O_5 nanorods were observed for KCl60 and KNO60 (Figs. 8b and 9b). At 90 min, the V_2O_5 nanorods were the main morphology for KCl90 and KNO90 (Figs. 8c and 9c) and reached a stable state after 120 min for KCl120 and KNO120 as shown in Figs. 8d and 9d which in agreement with the mechanism of formation of self-assembled nanorods V_2O_5 bundles proposed by Mao and co-workers⁶.

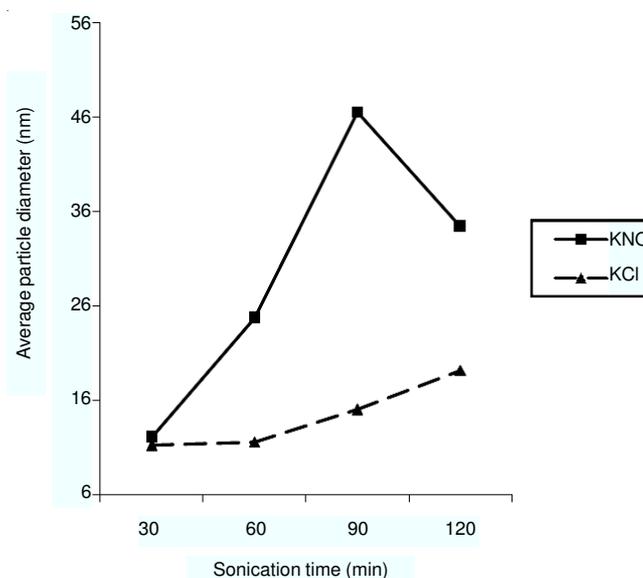


Fig. 7. Effect of sonication duration on the particle diameter

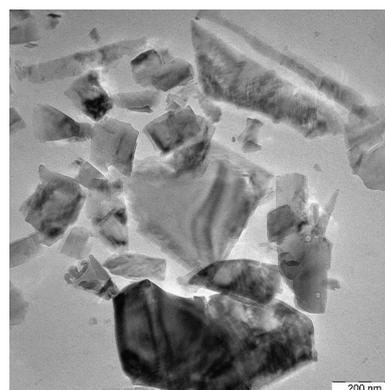


Fig. 8. TEM image of V_2O_5 std

The particle sizes of the V_2O_5 samples treated sonochemically was also measured using TEM with the data collected and a plot of average particle diameter against sonication time was drawn as shown in Fig. 10. It is observed that KCl30, KCl60 and KNO30 have smaller average particle sizes if compared to the other V_2O_5 samples, with KCl30 having the smallest average particle size. This increase of the particle diameter with prolonged sonochemical treatment duration correlates with the proposed growth mechanism of the V_2O_5

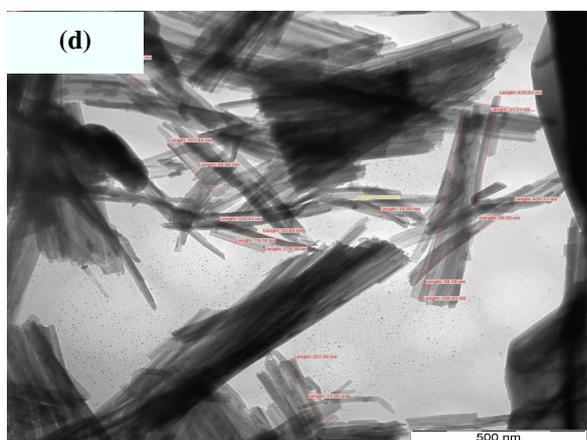
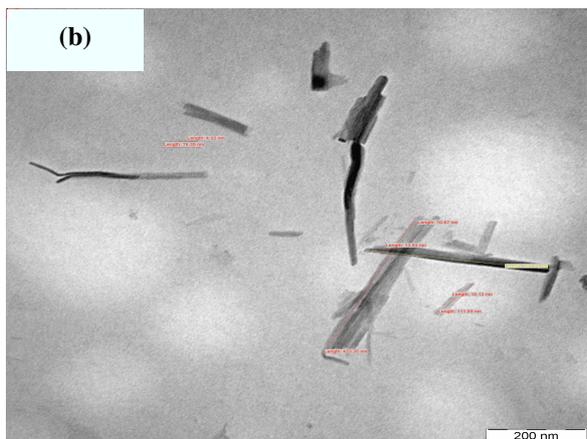
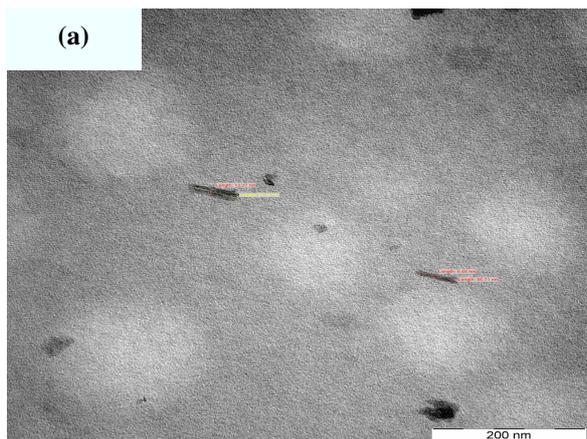


Fig. 9. TEM images of (a) KCl30; (b) KCl60; (c) KCl90; (d) KCl120

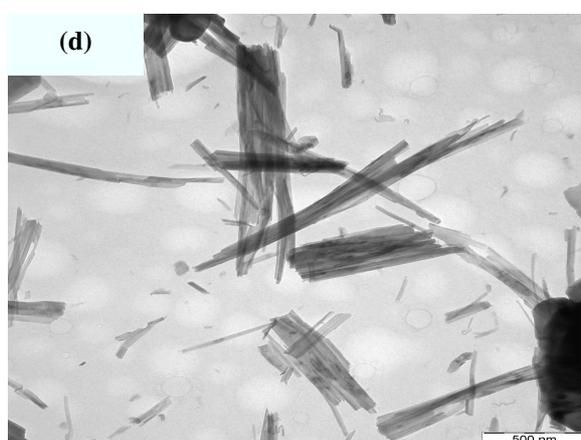
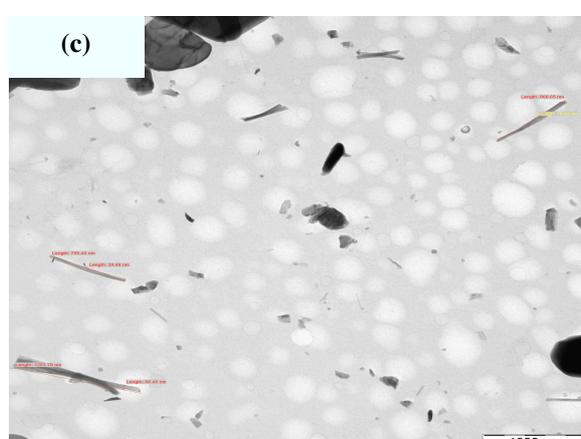
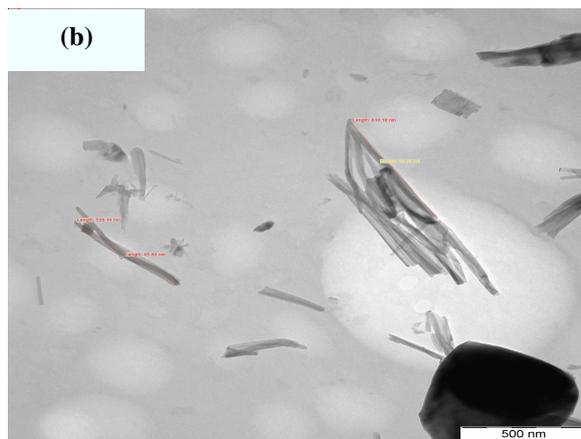
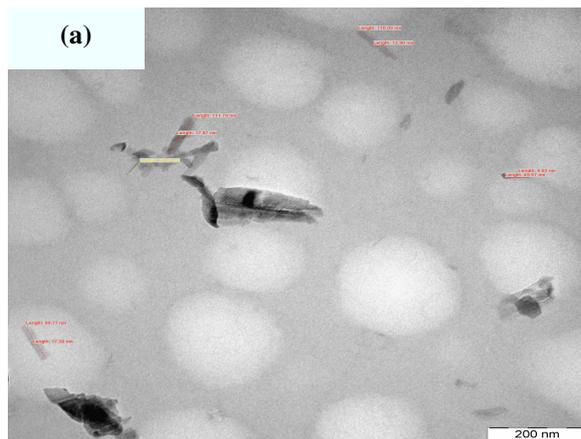


Fig. 10. TEM images of (a) KNO30; (b) KNO60; (c) KNO90; (d) KNO120

bundles, as the primary nanoparticles of V_2O_5 fused together to form nanorods of V_2O_5 , followed by the side-by-side attachment of these nanorods to form nanorod bundles.

Conclusion

The mineralizer salts used affected the morphology and composition of nanostructured V_2O_5 formed. The potassium ions from KNO_3 and KCl , reacted with the bulk V_2O_5 to produce a new phase, KV_3O_8 through the high-energy activation after 90 min of sonochemical treatment. This KV_3O_8 phase was seen to have a shape of big plates while the bulk V_2O_5 that had undergo ultrasound irradiation changed from a platelet-like morphology to V_2O_5 nanorods which were self-assembled into nanorod bundles after prolonged sonochemical treatment duration.

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