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ARTICLE

# Liquid Phase Oxidation of Acetophenone over Rice Husk Silica Vanadium Catalyst

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**Abstract:** Rice husk silica catalyst loaded with 10 wt% vanadium was synthesized from agricultural biomass via a sol-gel synthetic route at pH = 9. The catalyst was characterized by different physico-chemical methods. The FTIR spectra showed the formation of Si–O–V and V=O stretching bands. The presence of vanadium was confirmed by EDX elemental analysis. RH-10V possessed a high specific surface area of 276 m<sup>2</sup>/g and pore volume of 0.83 ml/g. The prepared catalyst possessed a narrow pore size distribution centered around 7.9 nm. The catalytic performance of RH-10V was tested in the oxidation of acetophenone at 70 °C. RH-10V was found to be an active catalyst in the oxidation of acetophenone, producing 36.28% conversion efficiency. The products identified were benzoic acid, 2-hydroxyacetophenone, phenol, acetic acid, and 3-hydroxyacetophenone.

Key words: vanadium; rice husk silica; oxidation; acetophenone; sol-gel technique

Acetophenone is an asymmetric ketone and its oxidation results in the formation of a mixture of products such as benzoic acid, benzoylformic acid, dibenzoylfunzan 2-oxide, benzyl alcohol, and phenol which have well-established industrial applications [1–5]. For example, benzoic acid is used as plasticizer, as a food preservative, in flavoring, in the synthesis of perfumes and antifungal agents [6]. Phenol is widely used to produce phenolic resin, solvents, dyes, and pharmaceuticals [7]. Nevertheless, only few researchers [1–5] have studied the oxidation of acetophenone. This is presumably due to acetophenone being a terminal ketone which has no hydrogen atoms on the carbinol carbon. Thus, oxidation of acetophenone can only be possible by breaking the  $\alpha$  carbon-carbon bond [8].

Perkin [1] has reported the conversion of acetophenone to benzoic acid using sodium hypochlorite, which is the haloform reaction. However, from an environmental point of view, this method is not suitable for industrial use due to the formation of chloroform as a side product. Homogeneous catalysts such as 1,3-dinitrobenzene [2] and nitric acid [3] have been used to oxidize acetophenone. These homogeneous systems create problems in the separation process and catalyst recovery. Hence, Chumbahale and co-workers [4] have reported the vapor phase oxidation of acetophenone by  $V_2O_5$ -MoO<sub>3</sub> catalyst resulting in the formation of maleic anhydride, benzyl alcohol, benzaldehyde, benzoic acid, and phthalic anhydride. They have also observed trace amounts of toluene, xylene, and phenol as by-products. Although this method manages to achieve high selectivity toward benzoic acid, it needs high temperature and long contact times which are limitations.

Vanadium shows a wide range of oxidation states (+2 to +5) in aqueous solution. Moreover, heterogeneous vanadium catalysts have been used in various oxidation reactions [9–11]. To the best of our knowledge, the oxidation of acetophenone has not been carried out using catalyst synthesized from biomass rice husk (RH) silica. Since RH silica exhibits high surface area and high porosity [12], it is thought to be advantageous to prepare vanadium incorporated RH silica and evaluate the synthesized catalyst in the oxidation of acetophenone with aqueous hydrogen peroxide under mild conditions. This work describes the simplest, cost-effective, and green preparation of RH-vanadium catalyst for the liquid-phase oxidation of acetophenone.

# 1 Experimental

# 1.1 Preparation of sodium silicate

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Preparation of sodium silicate was carried out by a modification of the technique reported by Adam and Chew [13]. The dried RH (30.0 g) was stirred in 600 ml of 1.0 mol/L HNO<sub>3</sub> for 24 h to remove unwanted metal. The acid treated RH was filtered and washed with copious amount of distilled water until it reached a constant pH. It was oven dried at 383 K overnight. On cooling, the rice husk (RH-HNO<sub>3</sub>) was weighed. The RH-HNO<sub>3</sub> was stirred in 500 ml of 1.0 mol/L NaOH for 24 h. The mixture was suction filtered to obtain sodium silicate to be used as the silica source. The recovered residue (RH-NaOH) was washed with distilled water and dried in an oven at 383 K and the mass of RH-NaOH weighed. The difference in the mass between RH-HNO<sub>3</sub> and RH-NaOH was assumed to be equivalent to the mass of silica extracted.

### 1.2 Preparation of RH-10V catalyst

The resulting sodium silicate was titrated slowly (ca. 1.0 ml/min) to pH = 9 with 150 ml of 3.0 mol/L HNO<sub>3</sub> containing 2.03 g of NaVO<sub>3</sub>·H<sub>2</sub>O to get 10 wt% of vanadium in the catalyst. A brown gel was obtained and aged for 48 h. The gel was suction filtered, washed thoroughly with distilled water, and followed by hot water several times in order to remove Na<sup>+</sup>, and oven dried at 383 K for 24 h. The powder was allowed to cool in a desiccator and ground into fine powder and the sample denoted as RH-10V was kept for further use.

#### 1.3 Catalyst characterization

RH-10V was characterized by FTIR spectroscopy (Perkin Elmer System 2000),  $N_2$  adsorption-desorption analysis (Micromeritics Instrument Corporation model ASAP 2000, Norcross), transmission electron microscopy (TEM, Phillips CM12), energy dispersion spectroscopy (EDS, Edax Falcon System) and DR/UV-Vis analysis (Lambda 35, Perkin Elmer).

#### 1.4 Catalytic activity

As a common practice, prior to the reaction, RH-10V (50 mg) was activated for 24 h in an oven at 383 K. The catalyst was removed from the oven and cooled in a desiccator prior to use in the catalysis. The round-bottom flask equipped with a condenser was set up in a temperature control oil bath at 343 K. Acetophenone (2.40 g) in 10 ml of acetonitrile was placed into the flask. H<sub>2</sub>O<sub>2</sub> (4.53 g, 30%) was added drop wise into the reaction vessel within 5 min. The reaction was allowed to run for 3 h. During the reaction, 0.5 ml of the sample was withdrawn and filtered, then 10  $\mu$ l of cyclohexane was added as internal standard and analyzed by gas chromatography (Perkin Elmer Clarus 500) equipped with Elite Wax (30 m × 0.2 mm ID) and further confirmed by GCMS (Perkin Elmer, Clarus 600) analysis. The following are the GC and GCMS condition

used: initial oven temperature = 383 K, final oven temperature = 503 K, ramp 1 = 20 K/min to 403 K, ramp 2 = 10 K/min to 503 K, total run time = 11 min.

# 2 Results and discussion

#### 2.1 Characterization of catalyst

The infrared spectra of RH-10V before and after reaction are illustrated in Fig. 1. As shown in Fig. 1(1), the band at 3462 cm<sup>-1</sup> was either due to the O-H stretching vibration of the silanol or adsorbed water molecules on the silica surface. The band at 1639 cm<sup>-1</sup> was due to the bending vibration of the water molecules. The strong band at 1096 cm<sup>-1</sup> corresponded to the asymmetric vibration of the siloxane bond Si-O-Si, and the band at 805 cm<sup>-1</sup> was assigned to the bending vibration of Si–O–Si bond. The transmission band observed at 472 cm<sup>-1</sup> was due to the stretching vibration of the Si-O-Si bond. The presence of a band at 974 cm<sup>-1</sup> indicated the Si-OH stretching vibration in the parent silica reported in our previous study [15]. When H was exchanged with metal, in this case vanadium, an obvious shift of this band could be observed. Therefore, in RH-10V, the observed Si-OV vibration was shifted to 974 cm<sup>-1</sup> due to the exchange of the H with V. Thus, it was possible to conclude that the band at 974  $\text{cm}^{-1}$  in the vanadium containing catalyst was due to the presence of Si-OV bonds [14]. Moreover, the shoulder at  $\sim 1024$  cm<sup>-1</sup> was assigned to the V=O stretching vibration as reported by Gomez et al. [16] for vanadia- zirconia catalyst.

The N<sub>2</sub> adsorption-desorption isotherms of RH-10V (Fig. 2) shows type IV isotherms and H1 hysteresis loops. H1 hysteresis loop is a characteristic of mesoporous material consisting of agglomerates or spherical particles having a relatively uniform pore size [16]. The specific surface area of RH-10V was found to be 276 m<sup>2</sup>/g, and the pore volume was 0.83 ml/g. The catalyst showed a narrow pore size distribution in the range of 5–8 nm which is in accordance with the characteristics of H1



Fig. 1. FT-IR spectra of RH-10V before (1) and after (2) the reaction.



Fig. 2. The  $N_2$  adsorption-desorption isotherms and narrow pore size distribution (inset) of RH-10V.



Fig. 3. TEM image of RH-10V catalyst showing the distribution of particle sizes.

hysteresis loop.

The TEM image of RH-10V is shown in Fig. 3. The incorporation of V resulted in smaller particles. The elemental composition of RH-10V was determined by EDX analysis as represented in Table 1 which confirmed the presence of carbon, oxygen, silicon, and vanadium. Si and O were detected due to the formation of siloxane bond (Si–O–Si) and silanol group (Si–OH). These Si and O could form a Si–O–V bond, whereas the presence of small amount of carbon might arise from rice husk.

The DR/UV-Vis spectrum of the vanadium containing catalyst (Fig. 4) showed a strong band centered at 278 nm. This band could be assigned as  $V^{5+}$  in tetrahedral coordination [17].

Table 1	The elemental	composition	of RH-10V
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Elemental	Average weight (%)	
С	2.1	
0	69.1	
Si	23.4	
V	5.4	
Total	100.0	



Fig. 4. The DR/UV-Vis spectrum of RH-10V.

The band around 330–500 nm region was due to the octahedral coordinated  $V^{5+}$  [18]. In this case, the *d*–*d* transitions were also observed between 650 and 700 nm [17]. Thus, it could be concluded that vanadium was present solely as  $V^{5+}$  in the framework of silica.

#### 2.2 Catalyst evaluation

The prepared catalyst was tested in the liquid phase oxidation of acetophenone. Table 2 shows the acetophenone conversion with respect to the mass of the catalyst at 343 K. The acetophenone conversion was found to increase sharply from 11.4% to 36.3% when the catalyst mass used was increased from 30 to 50 mg. However, further increase in the catalyst mass to 100 mg resulted in a decrease in acetophenone conversion to 12.6%. This was due to the rapid decomposition of H<sub>2</sub>O<sub>2</sub> over the large surface area available with a higher amount of catalyst [19]. At a higher dose of catalyst, the availability of more active sites resulted in rapid decomposition of H<sub>2</sub>O<sub>2</sub>, leading to lower yields. As a result, 2-hydroxyacetophenone was observed as a by-product and decreased the selectivity of benzoic acid.

The reaction temperature was found to have a great influ-

 Table 2
 Oxidation of acetophenone using different amounts of catalyst

Catalyst mass	Acetophenone conversion	Selectivity (%)			
(mg)	(%)	Acetic acid	2-Hydroxyacetophenone	Benzoic acid	3-Hydroxyacetophenone
30	11.4	21.1	50.4	28.5	
50	36.3	20.4	49.1	19.9	10.6
70	16.4	25.8	50.0	24.2	_
100	12.6	17.3	62.9	19.8	—

Reaction conditions: catalyst = RH-10V, 343 K, molar ratio of substrate:H2O2 = 1:2, 10 ml CH3CN, 3 h.

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Temperature	Conversion	Selectivity (%)				
(K)	(%)	Acetic acid	2-Hydroxyacetophenone	Benzoic acid	3-Hydroxyacetophenone	Ph
303	24.3	26.5	48.2	25.3	_	_
323	30.4	22.8	44.6	20.2	12.4	_
343	36.3	20.4	49.2	19.8	10.6	_
353	39.2	14.5	58.2	16.3	_	11.0

 Table 3
 The oxidation of acetophenone as a function of temperature

Reaction conditions: 50 mg RH-10V, molar ratio of substrate:  $H_2O_2 = 1:2$ , 10 ml CH<sub>3</sub>CN Solvent, 3 h.

ence on the conversion of the reaction. Thus, in the oxidation of acetophenone, the effect of temperature on the reaction was studied in the range of 303-353 K (Table 3). With an increase in the reaction temperature from 303 to 343 K, there was a significant increase in the conversion from 24.3% to 36.3%. Raising the reaction temperature higher to 353 K resulted in a slight increase of the conversion to 39.2%. This was due to the rapid decomposition of H<sub>2</sub>O<sub>2</sub> at 353 K [12]. Moreover, the selectivity toward 2-acetophenone increased with increasing temperature, this might be due to the formation of water from  $H_2O_2$  to hydrolyze acetophenone. However, decomposition of H<sub>2</sub>O<sub>2</sub> caused lack of oxidant to convert acetophenone into benzoic acid and acetic acid. Even though there was increase in conversion with temperature, the optimum reaction temperature was set at 343 K, because at high temperatures, there are moderate conversion and rapid decomposition of H<sub>2</sub>O<sub>2</sub>.

The effect of  $H_2O_2$  was studied by varying acetophenone:  $H_2O_2$  molar ratio from 1:1 to 1:3 (Table 4). The conversions were 4.1% and 36.3% for 1:1 and 1:2 molar ratios, respectively. However, at a molar ratio of 1:3, the acetophenone conversion decreased. Generally, the decomposition of  $H_2O_2$  produced water as the by-product. The water might poison the catalyst by adsorbing strongly to the vanadium centre and thus inhibiting the reaction [18]. Furthermore, decomposition of  $H_2O_2$  (oxidant) reduced the formation of acetic acid and benzoic acid, while the hydroxylation product, 2-acetophenone was easily formed in the presence of water. It was thus concluded that the optimum molar ratio was 1:2.

From the data in Tables 3 and 4, phenol was only detected at 353 K when the acetophenone: $H_2O_2$  molar ratio was 1:3. The formation of phenol must originate from the breaking of the bond as shown in Scheme 1. While acetic acid was detected under all the experimental conditions studied, it was not clear why phenol was only detected under certain conditions as noted above. It was concluded that this anomaly required further investigation.



Scheme 1. The formation of phenol.

After optimization of the reaction conditions it resulted in 36.28% conversion of acetophenone yielding 20.4% acetic acid, 19.8% benzoic acid, 49.2% 2-hydroxyacetophenone, and 10.6% 3-hydroxyacetophenone. In previous studies, 1,3-dinitrobenzene [2] had been used as the solvent for this reaction and by adding t-BuOK, a conversion of 91.7% acetophenone and 58.2% yield of benzoic acid were achieved. However, the utilization of t-BuOK as an additive is expensive for the industrial production of benzoic acid and secondly, the homogeneous system creates problem for separation. Some researchers [3,5] used acid catalyst in a two-step oxidation of acetophenone by forming  $\alpha$ -nitroso-acetophenone as the intermediate. However, the intermediate formed is unstable in acidic condition and isomerizes to form benzoylformaldehyde oxime as a by-product. Hence, the two-step oxidation of acetophenone is not practical in the industry due to the difficulty in isolating the products and the lengthy time involved. Chumbahale et al. [4] used vapor phase oxidation of acetophenone over a long contact time (58.5 h) to obtain a high conversion (74.8%) and high selectivity (96.9%) towards benzoic acid. However, this method yielded side-products such as maleic anhydride, benzyl alcohol, benzaldehyde, phthalic anhydride, and other unidentified products. It is quite clear that RH-10V is by far a better catalyst for the oxidation of acetophenone and to break the C–C single bond  $\alpha$  to the carbonyl group.

To test the catalyst reusability, RH-10V was used consecutively for 3 cycles as shown in Table 5. The used catalyst was filtered and regenerated by heating at 383 K for 24 h. After 3 runs, there was a decrease in conversion (17.7%). The re-used

Table 4 The oxidation of acetophenone using different acetophenone:H<sub>2</sub>O<sub>2</sub> molar ratios

Acetophenone:H <sub>2</sub> O <sub>2</sub>	Conversion			Selectivity (%)		
molar ratio	(%)	Acetic acid	2-Hydroxyacetophenone	Benzoic acid	3-Hydroxyacetophenone	Ph
1:1	4.1	56.3	43.7	_	_	_
1:2	36.3	20.4	49.2	19.8	10.6	_
1:3	17.2	14.4	54.3	21.1	_	10.2

Reaction conditions: 50 mg RH-10V, 343 K, CH<sub>3</sub>CN solvent, 3 h.

Table 5The reusability of RH-10V

Cycle	Conversion (%)	
1	36.3	
2	21.5	
3	17.7	

Reaction conditions: 50 mg RH-10V, 343 K, molar ratio of substrate:  $H_2O_2 = 1:2$ , 10 ml CH<sub>3</sub>CN solvent, 3 h.

catalyst was subjected to FT-IR analysis as depicted in Fig. 1(2). The appearance of the vibration at 2979 cm<sup>-1</sup> in the FT-IR spectrum of the used catalyst might be due to adsorption of the organic compounds on the catalyst surface. This showed that the temperature for regeneration is not enough for removing the adsorbed organic compounds which resulted in catalyst poisoning. Hence some active sites of the catalyst had been blocked by the organic products and thereby lowering the catalytic activity. The objective of the present study did not involve any attempt to remove the organics, however, further work is in progress to remove organics adsorbed on the catalyst so that its efficiency can be improved.

# 3 Conclusions

In summary, a template-free vanadium-silica catalyst was successfully synthesized from RH via a simple sol-gel and solvent extraction techniques. The catalyst was developed in a simple, cost-effective, and green procedure to investigate the liquid phase oxidation of acetophenone. RH-10V was found to be more active to break the C–C single bond  $\alpha$  to the carbonyl group compared with the catalysts published in the literature. The preparation of the catalyst does not involve calcination which reduces the demand on the energy necessary in the synthesis. This study have benefits to both academic and industry for alternative methods to break the C–C bond linking

the  $\alpha$ -carbon connected to the carbonyl carbon in ketones. Further studies are in progress in our group to improve the reusability of RH-10V by removing the organics adsorbed on the catalyst.

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