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Efficient room temperature oxidation of cyclohexane over

highly active hetero-mixed WO₃/V₂O₅ oxide catalyst

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Abstract

An efficient room temperature catalyzed oxidation of cyclohexane to cyclohexanone (K) and cyclohexanol (A) was achieved over hetero-mixed tungsten-vanadia (WO_3/V_2O_5) using H₂O₂ oxidant. WO_3/V_2O_5 exhibited high catalytic activity to initiate the free-radical oxyfunctionalization of cyclohexane to afford up to 90% conversions within 6 h. The KA selectivity was found to depend on reaction time and the amount of catalyst. The WO₃/V₂O₅ catalyst was highly recyclable with consistent catalytic activity.

Keywords: vanadium, tungsten, cyclohexane, oxidation, hetero-mixed, nanostructured

Introduction

Selective liquid-phase oxidation (LPO) of cyclic hydrocarbons inert C-H is of major industrial importance in the production of oxygenates [1]. The challenge in these reactions is to attain improved process efficiency and products selectivity. In general, selectivity is in the trade-off to high conversions in the hydrocarbons LPO thus conversions are restricted to low [2]. An example is the LPO of cyclohexane into cyclohexanone (K) and cyclohexanol (A) that facilitate the production of adipic acid, an intermediate to nylon-6 and nylon-6.6 [3,4]. The industrial-scale LPO of cyclohexane is carried out as non-catalysed process with conversions restricted to 5-10% in order to ensure the KA selectivity in the range of 80-90% [4]. As a result, the development in catalytic LPO of cyclohexane has been one of the most studied hydrocarbons oxidation reactions [5]. In order to address the various shortcomings in the cyclohexane oxidation several heterogeneous catalysts using hydrogen peroxide (H_2O_2) as oxidant have been explored [5]. Shi et al.[6] developed a titanium silicalate with hallow structure (HTS) for cyclohexane oxidation using H_2O_2 to afford up to 60% conversions. In the other study, vanadium phosphorous oxide demonstrated effective catalytic activity with near complete cyclohexane conversions [7]. However, the catalyst displayed poor KA selectivity due to high formation amount of cyclohexyl peroxide. Furthermore, Carabineiro et al.[8] reported excellent activity of gold nanoparticles supported on carbon materials for cyclohexane oxidation although their conversions were relatively poor with KA yields of less than 10% achieved after 6 h. Parida and co-workers [9] developed an intercalated Zn-Al layer double hydroxide Fe(III)-Schiff base complex as effective catalyst to afford up to 45.4% conversions with 100% KA selectivity in 8 h. In line with these reported cyclohexane oxidation process aspects it is apparent that there is

a need for continuing catalyst development in order to improve on reaction times, conversion, KA selectivity and catalyst re-usability for cyclohexane LPO. Apart from these factors critical to obtaining efficient cyclohexane LPO process the design of catalyst that can be active at room temperature would definitely make the process economically competitive.

The uses of vanadium based oxides and metal complexes for LPO of hydrocarbons are well known [10-13]. Furthermore; the activity of supported V_2O_5 has been reported for cyclohexane oxidation although with low conversions of up to 30% [14]. Whilst V₂O₅ proved to possess interesting catalytic properties, explorative studies on catalytic performance of hetero-mixed oxide of V₂O₅ with WO₃ as catalyst for cyclohexane LPO had not been reported. Likewise, WO₃ is a versatile oxidation catalyst in the direct conversion of cyclohexene into adipic acid using H_2O_2 [15]. Thus, the combination of WO_3/V_2O_5 oxide composite and atom-efficient H_2O_2 oxidant would undoubtedly provide a green heterogeneous catalysed LPO process of cyclohexane into KA oil. In this paper, the catalytic performance of WO₃/V₂O₅ for LPO of cyclohexane with the view of improving on poor conversion was investigated. The influences of the different reaction variables on the oxidation rates were evaluated. In order to comprehend the WO₃/V₂O₅ catalytic effect, its resulting structure properties obtained using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), hydrogentemperature reduction (H_2 -TPR), transition electron microscopy (TEM) and N_2 physisorption were correlated to the catalytic results in the cyclohexane oxidation.

2 Experimental

2.1. Preparation of the catalysts

The preparation of WO₃, V₂O₅ and WO₃/V₂O₅ oxides was achieved by using ethylene glycol solvent and polyvinylpolypyrrole (PVP) as structure templating agent. Typically, ammonium metavandate (NH₄VO₃) in oxalic acid solution was mixed with sodium tungstate dehydrate (Na₂WO₄·2H₂O, Aldrich) in 1:1 metal ratio into ethylene glycol followed by addition of 5 wt% PVP based on the total metals content. The solution mixture's pH was adjusted to 11 using ammonium hydroxide and stirred vigorously for 48 h under reflux. The solids were recovered by vacuum filtration, washed with ethanol and followed by drying at 100 °C for 12 h. Similarly, the individual oxides were prepared following the same procedure. The dried samples were calcined under air condition heated from room temperature to 500 °C at a heating rate of 10 °C/min and held for 4 h at 500 °C.

2.2. Catalyst characterisation

The Brunauer–Emmett–Teller (BET) surface area and micropores volume were measured by nitrogen (N₂) physisorption at 77 K, using a Micromeritics TriStar II surface area and porosity analyzer (USA). Before analysis, samples were degassed at 120 °C for 6 h under N₂ flow. XRD experiments were recorded on a PAnalytical XPERT-PRO diffractometer using Ni filtered CuK α radiation ($\lambda = 1.5406$ Å) at 40 kV/50 mA. The diffraction measurements were collected at room temperature in a Bragg-Brentano geometry with scan range, $2\theta = 10-90^{\circ}$ using continuous scanning at a rate of 0.02° /s. H₂-TPR studies were performed on a Micromeritics Autochem AC2920

apparatus (USA) gaseous mixture of 10%H₂/Ar at a heating rate of 10 °C/min from 50 to 1000 °C and total gases flow rate of 50 ml/min. The H₂ consumption was monitored by a calibrated thermal conductivity detector (TCD). The morphology and structure of the catalysts were characterised JEOL-JSM 7500 high resolution FESEM operated at an accelerating voltage of 2 keV coupled to EDX for elemental mapping analysis. Before the analysis samples were sputter coated with gold in order to minimize their possible charging. TEM measurements were performed by JEOL JEM 2100 operated at an accelerating voltage of 200 kV. Powder samples were sonicated for 5 min dissolved in ethanol and dispersed on copper grid for TEM analysis.

2.3. Catalytic activity testing

Catalytic testing was performed in a 50 ml two-necked flask equipped with magnetic stirrer, reflux condenser and thermometer. To a reactor were added cyclohexane (10 mmol, 0.84 g), acetonitrile solvent (5 ml), catalyst (0.05 g) and 50% H₂O₂ oxidant (30 mmol). The oxidation products samples were treated with triphenylphosphine before gas chromatograph (GC) coupled to flame ionization detector (FID) analysis using a Supelco SPB-20 column (30 m × 0.25 mm i.d. × 0.25 μ m). No differences in products quantitative amounts were observed for the samples analysed directly without the triphenylphosphine to those treated indicating that the catalyst was effective to decompose readily the formed cyclohexyl peroxide into carbonyls.

3 Results and discussion

3.1 Catalyst characterisation

Figure 1a illustrates the XRD patterns of calcined WO₃, V₂O₅ and WO₃/V₂O₅ catalysts at 500 °C. The patterns of WO₃ exhibited those of previously reported monoclinic phase [16], while typical reflections belonging to V_2O_5 phase were confirmed by the XRD. Both XRD of WO₃ and V₂O₅ showed the formation of well-defined crystalline peaks. The redox H₂-TPR profiles of the catalysts are illustrated in Figure 1b. The V₂O₅ exhibited three-stage reduction peaks at 496 °C, 576 °C and 710 °C, respectively. This reduction pattern has been associated to the sequential reducibility of vanadia surface oxygen removal which corresponds to the $V^{+5}/V^{+4}/V^{+3}$ oxidation states, respectively. In comparison to the previous reported reduction temperature regions, our catalyst showed signification low shift reduction temperatures [17]. This could perhaps be attributed to the observed nanostructure particles morphology that can results into easily reducible exposed surface vanadia species as opposed to usual bulk V₂O₅. For WO₃, only one high temperature reduction peak was observed which corresponded to tungsten carbide WC formation from WO₃. For the WO₃/V₂O₅ composite, the reduction peaks indicating both oxides were observed but with slightly temperature shifts to high that could be the indication of possible internal structure properties alterations and strong solids interactions. Such interactions in the mixed oxides of V and W metals have been elaborated previously for solid solution formation with V₂O₅ dissolving in the WO₃ structural framework or WO3 dissolving in V2O5 depending on the composition ratios [18].

The microstructure morphology and particles shape of the catalysts was further characterised by FE-SEM (Figure 2a-g). Some particles with nano-needle shape morphology of 150–200 nm size in length were observed by FE-SEM for V₂O₅ (Figure 2a-b). These particles were grouped together to form irregular round shape with the nano-needle growing outwards as illustrated by the high magnification image (Figure 2b). For WO₃, the formations of platelets morphology-like particles were observed which showed the shape of nanorods for high magnification image (Figure 2c-d). The composite WO₃/V₂O₅ exhibited distinctive particles morphology to those of the pure WO₃ and V₂O₅ oxides that were clustered nanoparticles with size diameter of less 100 nm (Figure 2f-g). The elemental mapping of the composite WO₃/V₂O₅ (Figure 2h) confirmed uniform metals distribution interface. This was further illustrated by EDX (Figure 2g) of the mapped area, which indicated the presence of both elements at composition closer to the theoretical 1:1 ratio. The formation of well-dispersed WO₃ nanoparticles diameter size in a range of 40-100 nm were observed (Figure 3).

The BET surface areas and micropores volume of the catalysts are summarised in Table 1. The V₂O₅ exhibited the highest surface area of 37 m²/g while WO₃ had the low of 14 m²/g and the WO₃/V₂O₅ catalyst exhibited the in-between surface area of 23 m²/g. The micropores volume and size corresponded relatively with the catalysts surface area and their respective porosity morphology as observed in the FE-SEM results especially for the WO₃/V₂O₅ composite catalyst (Figure 2).

3.2 Catalytic activity

Figure 4a-d list the catalytic results of the tungsten-vanadia catalysts tested in the cyclohexane oxidation using H₂O₂ at room temperature. All the catalysts improved the cyclohexane oxidation rates with up to 65% conversions achieved after 3 h when compared to less than 1% for non-catalysed reaction (Figure 4a). In terms of conversion efficiency, the catalysts followed the increasing order of $WO_3/V_2O_5 > WO_3 > V_2O_5$. The V₂O₅ exhibited both poor KA selectivity and conversion when compared to all other catalysts. On the other hand, both WO₃ and WO₃/V₂O₅ displayed closely related KA selectivity, however with WO₃/V₂O₅ exhibiting the highest cyclohexane conversion. The observed KA selectivity and cyclohexane conversion rates somehow did not follow the obvious trend of the catalysts surface areas, thus indicated that there were other factors of the materials structural properties which were critical to obtaining the catalyst with highly active sites. By considering the redox recycle results (Figure 4a), it was clear that the combination of the two metals had an effect on their modified redox that could also suggest possible alteration of electron charge transfer of the individual metals the composite catalyst, thus enhancing on their mobility during in the oxidation/reduction cycle to improve the oxidation rates. Another intriguing aspect worth mentioning was the possible contribution of the oxides acidity which was however not investigated that could have influenced the composite catalyst performance significantly. Continuous studies are underway to elaborate further on this catalyst aspect. Such structure-property effect would require the studies on the influence of oxides composition on the overall performance of the catalyst activity. This was however, demonstrated by the poor KA selectivity and activity of V₂O₅ when used alone in relation to WO₃, of which when combined both enhanced relatively the

conversion and KA selectivity. The main role of the catalyst in H_2O_2 catalysed LPO is to improve on the controlled decomposition rates of H_2O_2 into reactive OH/HOO species to initiate the H-abstraction of hydrocarbons C-H into free-radicals that in turn traps them to form stable oxygenates. In order to determine the effect of the catalyst amount on the cyclohexane oxidation rates and products selectivity the mass of the catalyst was varied over a range of 25-100 mg (Figure 4b). It can be seen that conversion increased from 30% at 25 mg of catalyst to 71% at 100 mg (Figure 3b). However, the high catalyst amount proved to be detrimental to KA selectivity, thus 50 mg appeared to give satisfying process performance.

Next, we evaluated the time-course evolution of cyclohexane conversion and KA selectivity up to 5 h reaction time including the formation of other over oxidation products (Figure 4c). It can be seen that after 5 h the reaction showed near completion substrate conversion forming plateau at around 90%. At 24% conversion (1 h), the KA selectivity was still about 98% of which thereafter began to drop gradually with both increasing reaction time and conversion. After 6 h reaction time at about 90% cyclohexane conversion the KA selectivity had dropped significantly to 63% and the other by-products accumulated to the total amount of 37%. Based on the observed results it could be suggested that the gradual drop of KA selectivity was the factor of both high conversion and prolonged reaction time that facilitated further overoxidation of the formed KA possibly accelerated by the catalyst itself. Some of the identified over-oxidation products due to high substrate conversion and prolonged reaction time that facilitated further overoxidation time included ϵ -caprolactone, 6-hydroxyhexanoic acid and adipic acid (Scheme 1 and Figure 4c). As a result, to obtain satisfying KA selectivity of above 90% in the present study

the conversion of cyclohexane would need to be limited to approximately 40% as is usually practiced in hydrocarbons LPO. This conversion of 40% was found achieved within reasonable reaction time of 2 h in the present study at room temperature, thus making the catalyst productivity space-time-yield efficient (Figure 4c). Whilst the catalysed LPO of cyclohexane using H_2O_2 as oxidant present green protocol, on the other hand the effectiveness of the catalyst for this process would depend on its ability to control the efficiency of H₂O₂ conversion into the desired cyclohexane products rather than to H_2O by-products. As a result, we controlled this issue by adding H_2O_2 drop-wise in order to minimize its waste decomposition into water. Such method of adding H₂O₂ slowly has been found to be beneficial in maximizing its usage efficiency for cyclohexane oxidation [19]. Finally, we investigated the recyclability performance of WO₃/V₂O₅ in number of reaction cycles. The catalyst was highly recyclable maintaining its initial activity even after re-used for four consecutive reaction cycles (Figure 4d). The ICP analysis of the hot filtrate solution for leaching after the reaction was stopped at the desired time showed trace amount of only vanadium metal (≈ 54 ppb) and further oxidation of this solution without the catalyst proved to be slow reaction rates with negligible increase in conversion. Thus, this showed that the presence of any possible leached WO₃/V₂O₅ catalyst into the solution was not adequate to catalyze effectively the cyclohexane LPO at room temperature.

Conclusion

In summary, an efficient room temperature oxidation process of cyclohexane to cyclohexanone (K) cyclohexanol (A) by highly active nanostructured WO_3/V_2O_5 composite has been demonstrated that afforded up to 90% conversions. The catalytic

results appeared to suggest a possible existence of strong interaction effect of the two combined metal oxides that enhanced their performance when compared to individual oxides. The enhanced performance of WO_3/V_2O_5 was partly attributed to the redox and possible structural modifications due to the metals strong interaction. We believe that these achieved initial catalytic results provide the basis for further studies on WO_3/V_2O_5 material development as a promising catalyst for liquid-phase oxidation of typical hydrocarbons inert C-H such as cyclohexane.

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Caption to Figures, Tables and Schemes

Table 1. N₂ physisorption characterisation data of the tungsten-vanadia based catalysts

Figure 1. (a) XRD and (b) H₂-TPR analysis of tungsten-vanadia based catalysts.

Figure 2. FESEM images of (a, b) low and high magnification V_2O_5 , (c,d) low and high magnification of WO₃, (e,f) low- and high-magnification of WO₃/V₂O₅, (g) elemental mapping of WO₃/V₂O₅, (h) EDX of WO₃/V₂O₅.

Figure 3. TEM image of WO₃-V₂O₅ nanostructured catalyst.

Figure 4. (a) Comparison performance of the tungsten-vanadia based catalysts activity in cyclohexane oxidation. (b) Effect of WO_3/V_2O_5 catalyst amount, (c) Effect of reaction time on WO_3/V_2O_5 performance, and (d) Recyclability performance of WO_3/V_2O_5 . Other conditions used otherwise described: Cyclohexane (10 mmol), catalyst (50 mg), 50% H₂O₂ (30 mmol), acetonitrile solvent (5 ml), time (3 h) and all reactions were performed at room temperature.

Scheme 1. Plausible mechanism route to cyclohexane liquid-phase oxidation products formation.

Table 1.

| Entry | Catalyst | BET surface areas | Pores volume | Pores diameter size | |
|-------------|--|-------------------|--------------|---------------------|--|
| | | (m^2/g) | (cm^3/g) | (nm) | |
| 1 | WO ₃ | 14 | 0.12 | 24.53 | |
| 2 | V ₂ O ₅ | 37 | 0.26 | 16.28 | |
| 3 | WO ₃ /V ₂ O ₅ | 23 | 0.19 | 21.14 | |
| SCHER MANNE | | | | | |







Figure 2



Figure 3

Fig.



Graphical abstract



Research Highlights

- Nanosized structured WO₃/V₂O₅ mixed oxide was synthesized.
- WO_3/V_2O_5 was active for oxidation of cyclohexane with high substrate conversion.
- Mixing of WO₃ and V₂O₅ enhanced both conversion and selectivity.
- WO_3/V_2O_5 was highly recyclable with consistent catalytic activity.

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