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Performance of rGO/V_2O_5 as a heterogeneous catalyst for oxidation of methyl phenyl sulfide

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rGO/V_2O_5 heterogeneous catalyst was prepared by *ex-situ* method and was used for oxidation of methyl phenyl sulfide to produce methyl phenyl sulfoxide and methyl phenyl sulfone. The individual components (rGO and V_2O_5) and the composites (all ratios of rGO:V_2O_5) were analyzed by FTIR, XRD, TGA and SEM. The percent conversion and catalytic effect were studied *via* GC and TLC. The rGO:V_2O_5 in 2:1 ratio was found to give the best result (88.3% conversion); the effect of the amount of oxidizing agent was also determined which shows that with increasing concentration of H_2O_2 the % conversion was also increased.

Keywords: rGO, V_2O_5, catalyst, percent conversion, oxidation

INTRODUCTION

Catalysts were always in demand to enhance the product yield and minimize the requirement for reagents. Apart from the above benefits a catalyst also curtails the issue of excessive use of hazardous reagents. Various catalysts are considered in a particular reaction due to their specific advantages, including selectivity, stability, and reusability. Several effective homogeneous and heterogeneous catalysts have been introduced to meet ecological demands. Out of the numerous catalysts used in various reactions graphene (or reduced graphene, rGO) finds its explicit position. Since its introduction rGO had been employed in numerous applications including catalysis. The properties of rGO such as 2D flat extended surface area, highly reduced band gap, and chemical, mechanical and thermal stability confer specific features to rGO to be employed as a promising catalyst for several reactions [1]. Cuni *et al.* 2021 employed rGO as a carbo-catalyst for the dehydrogenation of N-heterocycles, this catalyst was found to generate an appreciable yield with excellent reusability and stability for the next eight experiments [2]. Ruthenium-supported rGO was used for the generation of hydrogen from ammonia decomposition, The optimal catalytic performance was observed with 2.5:10 of Ru:rGO composition where 96% of ammonia was converted [3]. rGO had not only been used as an individual potent catalyst, but studies also show that rGO, due to its tuneable electrical and physical properties, had been proven a fine catalytic support material for TMOs, thus generating high catalytic surfaces for catalyzing chemical reactions. Askari *et al.* 2022, show the oxidation reaction of methanol by using rGO binary TMO ($MnCo_2O_4$/$NiCo_2O_4$) catalyst [4]. rGO/Co_3O_4 nanocomposites had been introduced as a catalyst for oxygen evolution by Abidat *et al.* 2019 [5]. The current article represents an attempt to use rGO/V_2O_5 in varying compositions to oxidize methyl phenyl sulfide to methyl phenyl sulfone. The compositions were characterized via FTIR, XRD, SEM, and TGA-DSC for their respective chemical and physical properties. The catalytic response of the rGO/V_2O_5 was studied *via* gas chromatography (GC).

EXPERIMENTAL

Material and method

Conc. sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 35.4%), hydrogen peroxide (H_2O_2, 30%), potassium permanganate ($KMnO_4$), graphite, acetonitrile (ACN), methyl phenyl sulfide, and V_2O_5 were purchased from Loba Chemie Pvt. Ltd.

Preparation of GO and rGO

rGO was prepared from GO, produced from graphite *via* Modified Hummer's process. In this method, graphite (5g) was taken in a vessel, to which conc. H_2SO_4 (75 ml) was supplied slowly while maintaining a temperature of 0-5°C. Then $KMnO_4$ (15 g) was slowly added to the reaction mixture. The resulting mixture was continuously stirred for the next 2 h at 5±1°C. After this, the reaction mixture

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was allowed to come to room temperature with continuous stirring for the next ½ h. Further, the reaction temperature was allowed to increase to 98°C by the addition of 200 ml deionized water and keeping the reaction mixture at constant stirring for the next 45 min. Now to the reaction mixture deionized water (140 ml) and H_2O_2 (30 wt. %, 20 ml) were supplied which resulted in the formation of GO (yellow-brown precipitate). The latter was separated by vacuum filtration and washed with 100 ml of aqueous HCl (5%). The obtained solid material was then dried at 60°C in a vacuum oven [6].

The GO synthesized was reduced to rGO using ascorbic acid as a reducing agent, for the process GO (1 g) was dispersed in deionized water (400 ml) to which ascorbic acid (10 g) was slowly added and was stirred for the next 2 h at 60±1 °C. A black slurry was obtained after the above-mentioned time, which was centrifuged and was further supplied with H_2O_2 (30 wt. %, 10-20 ml) and stirred for ½ h at 60±1 °C to remove excess reducing agent. The final product was then repeatedly washed with ethanol and water and then dried in a vacuum oven [6].

Preparation of rGO/V_2O_5 composite

Solvothermal method was employed for the preparation of rGO/V_2O_5 composites in varying ratios of 1:1, 1:2, and 2:1. In this *ex-situ* method rGO was added with the requisite amount of V_2O_5 and was further stirred for 1 h at room temperature. These various compositions were further sonicated for ½ h for better insertion of the V_2O_5 into the layers of rGO. The final product was separated by centrifugation and was dried.

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of all samples were recorded on a Diamond ATR detector Perkin Elmer spectrometer in the range of 400 to 4000 cm^{-1}. The FTIR spectrum of GO shows a peak at 1063 cm^{-1} due to C-O stretching. A C-O-C bending peak was detected at 1224.85 cm^{-1}, a C=C stretching peak at 1623 cm^{-1}and an intense C=O peak at 1700 cm^{-1}. A broad peak at ~3342.37 cm^{-1} was observed related to OH stretching vibrations and absorbed moisture. Peaks observed in GO were found to get less intense or removed in the FTIR spectra of rGO. The broad peak of -OH was nearly lost signifying the reduction of GO to rGO (Fig. 1). A peak near 1600 cm^{-1} demonstrates the presence of a C=C stretching peak of benzene while a peak at 1066 cm^{-1}shows C-O stretching [7]. For V_2O_5, peaks at 513.35 and 464 cm^{-1} were attributed to the presence of symmetric and asymmetric stretching of coordinated oxygens. Peaks at 830.23 cm^{-1}denote the vibrations of bridged oxygen (V-O-V), while a peak related to V=O was observed near 1003 cm^{-1} (Fig. 1) [8]. In the FTIR of rGO/V_2O_5 (2:1) peaks related to O-H and CO stretching were observed at 3318 and 1211 cm^{-1}, respectively. A peak for rGO representing C=C stretching was observed at 1560 cm^{-1}. The peak observed near 1003 cm^{-1} shows stretching vibrations for terminal bonds of oxygen (V=O) (Fig. 1).

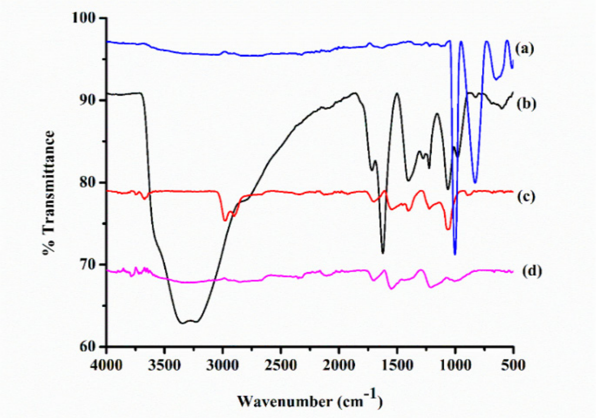


Fig. 1. FTIR spectra of (a)V_2O_5; (b) GO; (c) rGO; (d) rGO:V_2O_5 (2:1)

X-ray diffraction (XRD) analysis

XRD was used for the determination of the morphology of all samples by Bruker AXS D8 Advance A25-X1-1A2Z2C4B0. All spectra were recorded in a 2θ range of 10 to 70°, with λ=1.54 Å at 25°C. For GO at 2θ =10.5° a sharp peak is observed which is considered to be characteristic of GO (Fig. 2a). In the XRD pattern of rGO, the peak at 2θ =10.5° disappeared due to GO reduction. Peaks at 23° and 43° clearly signify the reduction of GO to rGO. Fig. 2b demonstrates the XRD of V_2O_5, the orthorhombic phase of V_2O_5 is mentioned by the peaks present at 16°, 20°, 22°, and 31°, the sharp peaks represent the crystalline nature of the metal oxide [9]. In Fig. 2c, all peaks related to rGO were intensified due to the presence of V_2O_5 in the matrix [10].

Thermogravimetric analysis (TGA)

TGA analysis was carried out a Perkin Elmer thermal analyzer. The temperature ranged from 50 to 550°C in inert conditions (N_2 flow) with a heating rate of 10ºC/min. The TGA curves of rGO, V_2O_5, and the composite are represented in Fig. 3. TGA curve of rGO was found to be stable due to less oxygenated functional groups. Up to 200°C, there is around 20% weight loss attributed to loss of moisture and volatile components, from 200 to 400°C a 41% weight loss is attributed to the loss of CO_2 and CO. In the case of V_2O_5 slight loss (15.4%)

is reduced up to 200°C, which increased to 37% from 200 to 400°C and increases to 44.37% reaching 550°C. For the composite (rGO/V_2O_5), up to 200°C the weight loss was 7%, which increased to 24% when reaching 400°C, and maximum mass loss (33.7%) was recorded till 550°C [8, 10].

Scanning electron microscopy (SEM)

The morphological study of the gold-coated composite (rGO/V_2O_5) was carried out by FESEM: JSM-7610F-Plus (Figs. 4a and 4b). rGO was found to show a flaky structure, and V_2O_5 particles were found to show bead-like shapes due to agglomeration on the surface of rGO [11].

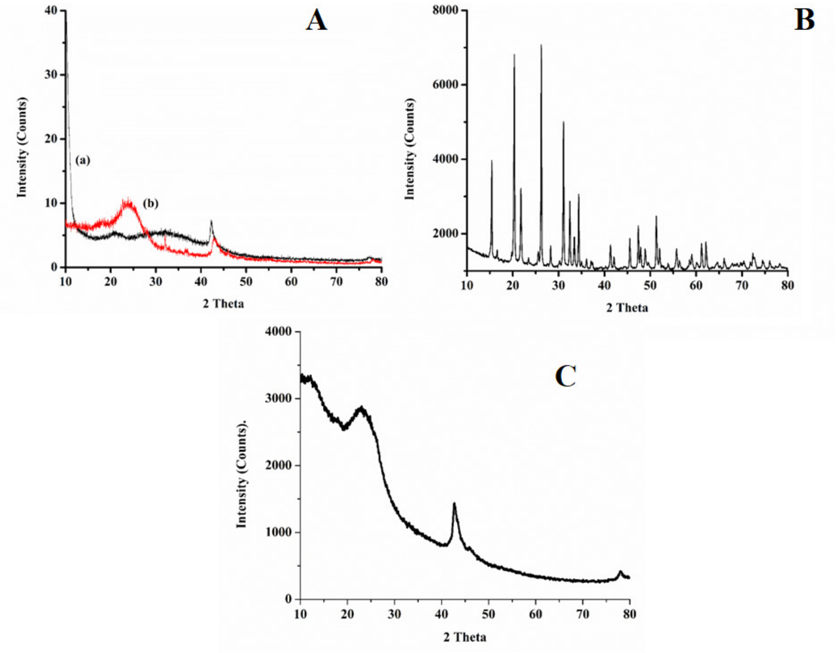


Fig. 2. XRD pattern of (A) GO and rGO: (B) V_2O_5; (C) rGO/V_2O_5

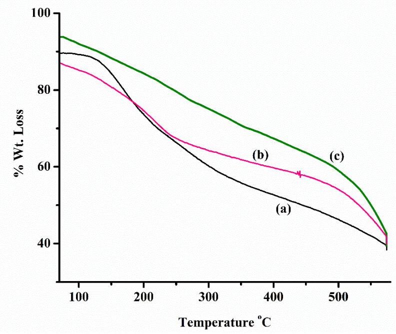


Fig. 3. TGA curves of (a) rGO; (b) V_2O_5: and (c) rGO/V_2O_5

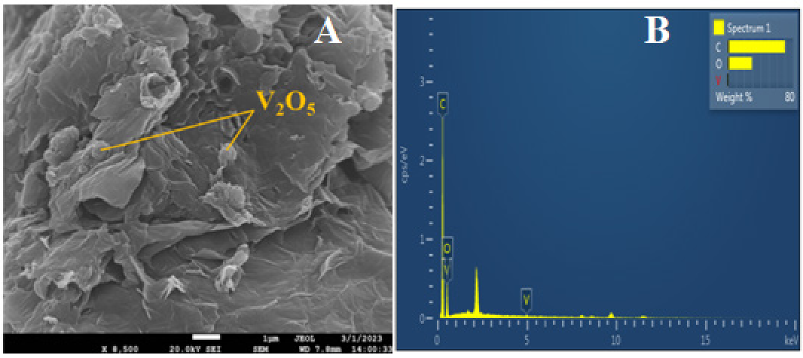
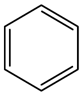


Fig. 4(a) SEM of rGO/V_2O_5; **(b)**EDX spectra of rGO/V_2O_5



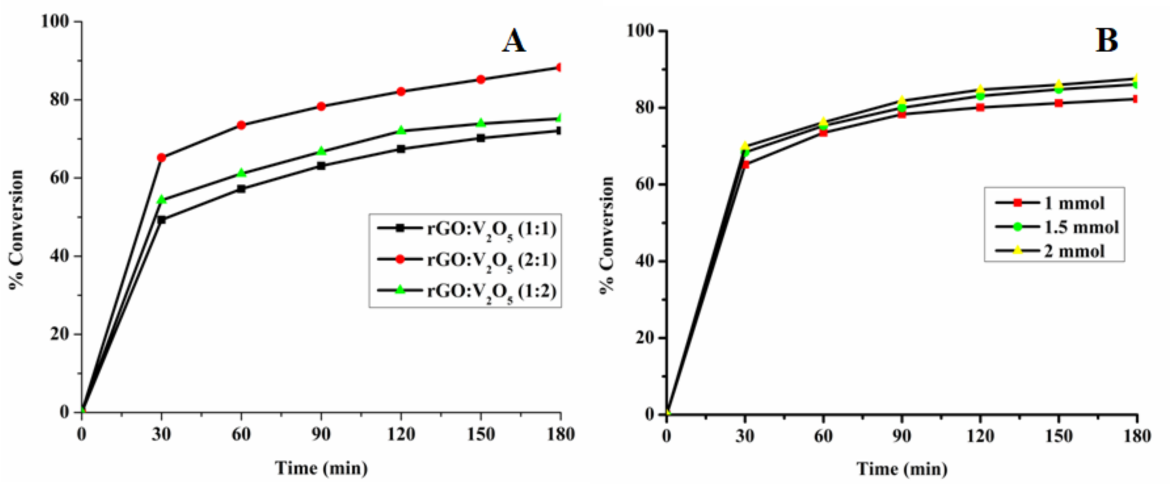


Figure 5. Role of (A) catalyst ratio and (B) catalyst (rGO:V_2O_5 in 2:1) concentration on the % conversion of reactant to the product after regular intervals

Oxidation studies

Methyl phenyl sulfide (thioanisole, 1 mmol) was oxidized to methyl phenyl sulfoxide and methyl phenyl sulfone, when reacted to H_2O_2 (1 mmol) in ACN (10 ml) at room temperature in the presence of a catalyst (rGO/V_2O_5, 5 mg) in 1:1, 2:1, 1:2 ratio, respectively. Product samples were taken every ½ h (30, 60, 90, 120, 150, and 180 min). The results were analyzed through TLC and GC. The sulfur present in the reagent is an electron-rich species and produces sulfoxide and sulfone products by undergoing electrophilic oxidation. The ratio of the catalyst is important to determine the amount of the product. It was found that the 2:1 rGO: V_2O_5 was the best to generate the maximum yield among all three ratios (Fig. 5a). The effect of the varying amount of oxidant (H_2O_2, 1, 1.5, and 2 mmol) on the % conversion was also studied by stabilizing the rGO:V_2O_5 in 2:1 ratio. It was found that with increasing ratio of oxidant in the reaction site the % conversion also increased (Fig. 5b).

CONCLUSIONS

rGO/V_2O_5 heterogenous catalyst was prepared by *ex-situ* method and was used for oxidation of methyl phenyl sulfide to produce methyl phenyl sulfoxide and methyl phenyl sulfone. The rGO:V_2O_5 in 2:1 ratio was found to have the best result (88.3% conversion). The effect of amount of oxidising agent was also determined which shows that with increasing concentration of H_2O_2 the % conversion increased.

Conflict of interest: The authors declared no conflicts of interest.

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