

Oxidation of *n*-heptane over Functionalised Chromium/Silver Bimetallic Heterogeneous Catalyst

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Abstract: Rice husk ash silica bimetallic heterogeneous catalyst loaded with 5 wt% chromium and 5 wt% silver was synthesised via a simple sol-gel, template free method at pH 3. The energy dispersive X-ray (EDX) analysis confirmed the presence of chromium and silver in the silica catalyst. The X-ray diffractogram showed that the catalyst was semi-crystalline. The catalyst exhibited a high specific surface area of $429 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore size distribution. The catalytic activity of RHA-5Cr5Ag was tested in the liquid phase oxidation of *n*-heptane in the presence of H_2O_2 as oxidant and acetonitrile as solvent at 353K. The catalyst was found to be active in the oxidation of *n*-heptane with a high *n*-heptane conversion of 89.54% with good selectivity towards heptanones. The products obtained from the oxidation of *n*-heptane were identified as 2-heptanone, 3-heptanone, 4-heptanone, 1-heptanol, 2-heptanol, 3-heptanol, 4-heptanol and heptanal.

Keywords: Rice husk ash silica, bimetallic catalyst, sol-gel technique, oxidative functionalised, *n*-heptane.

1. INTRODUCTION

Oxidative functionalisation of alkanes (saturated hydrocarbon) to oxygen containing compounds is very important for chemical and pharmaceutical industry.¹ Only few reports are available on the oxidation of heptane.²⁻⁴ This is presumably due to the un-reactive nature of alkanes which is a saturated hydrocarbon.⁵ The high ionisation energy and low electron affinity of alkanes make it less reactive and result in low selectivity.⁶

Several studies on the oxidation of *n*-heptane have been reported. Liu et al.² had investigated the plasma phase oxidation of *n*-heptane at 188K and reported a yield of 16% conversion and ca. 66% and 31% selectivity to heptanol (mixture of 2-heptanol, 3-heptanol and 4-heptanol) and heptanone (mixture of 2-heptanone and 3-heptanone) respectively. Molecular sieves (SAPO-5, SAPO-11, BEA and MCM-41) were used for the oxidation of *n*-heptane at 573K and 6.8 bar pressure to yield 2-heptanone, 3-heptanone, 4-heptanone and heterocyclic compounds.³ Anisia and Kumar⁴ had reported the oxidation of *n*-heptane at 523K using [1, 2-bis(salicylideneamino)phenylene] zirconium complex as

heterogeneous catalyst to yield cyclohexanone, 2-methylpentane, methylcyclopentane, 4-methylpent-1-ene and toluene.

Chromium and silver are known to be active in various oxidation reactions.^{7,8} We thought that it would be interesting to prepare a chromium-silver bimetallic heterogeneous catalyst and evaluate it in the oxidation of *n*-heptane. Rice husk ash silica exhibits high surface area and high porosity,⁹ hence it was used as the catalyst support for the chromium and silver bimetallic catalyst in this study. The supported bimetallic catalyst was tested in the oxidation of *n*-heptane under mild reaction conditions.

2. EXPERIMENTAL

2.1 Preparation of RHA-5Cr5Ag Catalyst

The preparation of RHA and the catalyst was carried out following published procedures.¹⁰ In a typical preparation, 3.0 g of RHA was dissolved in 0.8 M NaOH and filtered. The filtrate (sodium silicate) was titrated with 3.0 M HNO₃ containing 5 wt% Cr³⁺ and 5 wt% Ag⁺ ions with constant stirring till pH 3.0. The apple green gel formed was aged for 2 days. The gel was recovered by centrifuging, washing with water followed by acetone. The recovered gel was dried at room temperature and calcined at 773K for 5 h. The Cr-Ag ions modified silica was ground to powder and labelled as RHA-5Cr5Ag. The yield was 2.38 g.

2.2 Catalyst Characterisation

The as-synthesised catalysts were characterised by FTIR spectroscopy (Perkin Elmer System 2000), Nitrogen adsorption-desorption analysis (Micromeritics Instrument Corporation model ASAP 2000, Norcross), powder X-ray Diffractometry (XRD), Siemens Diffractometer D5000, Kristalloflex), Scanning electron microscopy – Energy dispersive X-ray (Leica Cambridge S360 with EDX Falcon system) and Atomic adsorption spectroscopy (Perkin Elmer AAnalyst 100).

2.3 Catalytic Activity

Typically, prior to the reaction, 0.1 g of RHA-5Cr5Ag was preheated overnight at 110°C. The round bottom flask equipped with a condenser was set up in a temperature controllable oil bath at 353K. 2.0 g of *n*-heptane in 10.0 mL of acetonitrile was placed into the flask. 2.27 g H₂O₂ (30%) was added drop wise into the reaction vessel. The reaction was carried out for 6 h. During the reaction, 0.5 mL of sample was withdrawn periodically, filtered and analysed by gas

chromatography (Perkin Elmer Clarus 500) equipped with Elite Wax column (30 m \times 0.2 mm ID) and further confirmed by GCMS (Perkin Elmer, Clarus 600) analysis. The following are the GC and GCMS conditions used: initial temperature = 313K, final temperature = 388K, ramp 1 = 5K min⁻¹, total run time = 15 min.

3. RESULTS AND DISCUSSION

3.1 Characterisation of RHA-5Cr5Ag

Figure 1 shows the FTIR spectrum of the prepared catalyst. The transmission band at 1641 cm⁻¹ was attributed to trapped water molecules in the silica matrix. The band at ca. 1080 cm⁻¹ was due to the structural siloxane bond (Si–O–Si). A shoulder at 964 cm⁻¹ was attributed to the stretching vibration of silanol group. The bands around 804 cm⁻¹ and 467 cm⁻¹ were due to the stretching and bending modes of Si–O bond. The band observed at 576 cm⁻¹ could be attributed to the stretching vibration of Ag/Cr–O bond. This band was not observed in the pure RH-silica.¹¹

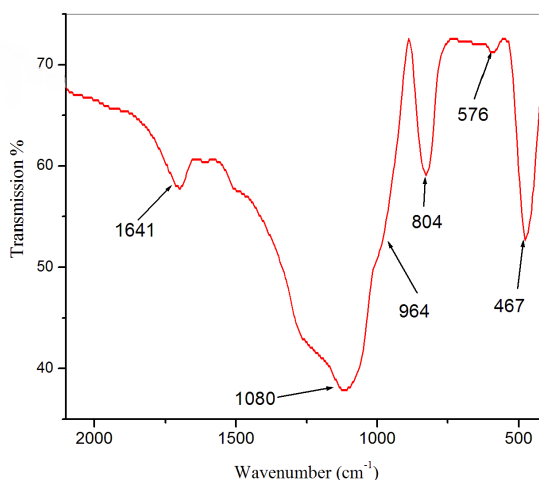


Figure 1: The FTIR spectrum of RHA-5Cr5Ag.

The XRD diffraction pattern of RHA-5Cr5Ag is shown in Figure 2. It shows a broad peak at $2\theta = 23^\circ$ which indicated the formation of amorphous silica.¹¹ However, there were several diffraction peaks found at 2θ of 32° , 35° , 38° , 45° and 55° . The peaks at $2\theta = 32^\circ$ and $2\theta = 35^\circ$ assigned as Ag_2O_3 . Whereas, the peaks at $2\theta = 38^\circ$ and $2\theta = 45^\circ$ were attributed to crystallised silver

metal.¹² The peak at $2\theta = 55^\circ$ can be attributed to Cr_2O_3 . Thus, the catalyst was found to be a semi-crystalline amorphous powder.

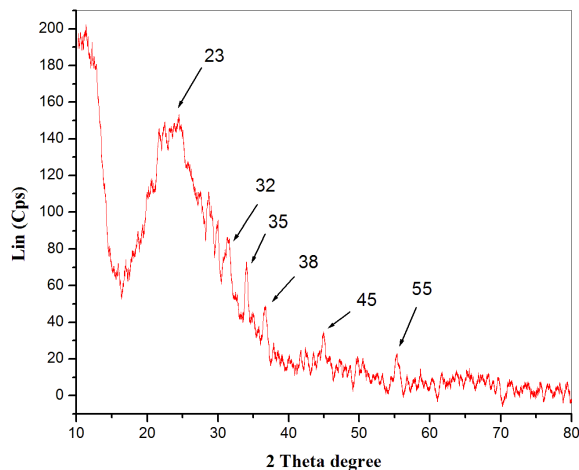


Figure 2: The X-ray diffractogram of RHA-5Cr5Ag.

The textural properties of RHA-5Cr5Ag was determined by N_2 sorption analysis and BET analysis. Figure 3 shows the nitrogen sorption isotherms and the pore size distribution of the catalyst (shown inset). According to IUPAC classification, the isotherm obtained was attributed to Type VI with H2 hysteresis loop, which is characteristic of an ink bottle shaped mesopores.¹³ The specific surface area of the catalyst was found to be $429 \text{ m}^2 \text{ g}^{-1}$ and the pore volume was $0.3 \text{ cm}^3 \text{ g}^{-1}$. The catalyst showed a narrow pore size distribution centred at ca. 2 \AA .

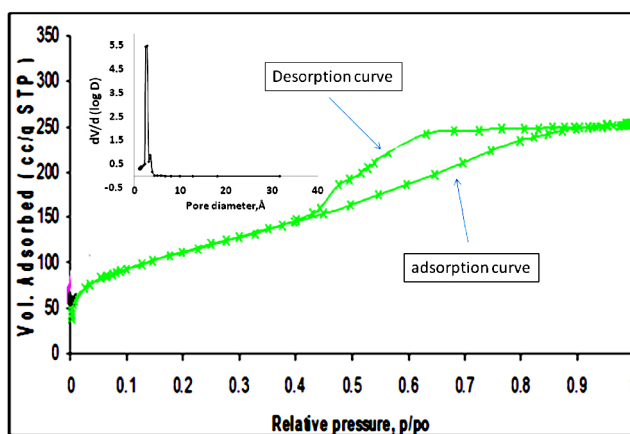


Figure 3: The nitrogen sorption isotherm and the pore size distribution of the catalyst (inset).

Figure 4 presents the SE micrograph of RHA-5Cr5Ag. It revealed small particles which were well distributed in a smooth surface. The nanoparticles lead to the formation of high specific surface area. From the EDX analysis, the catalyst was made up of Ag and Cr which were distributed homogeneously on the surface of the silica matrix. This analysis showed that Cr and Ag were well incorporated onto the silica.

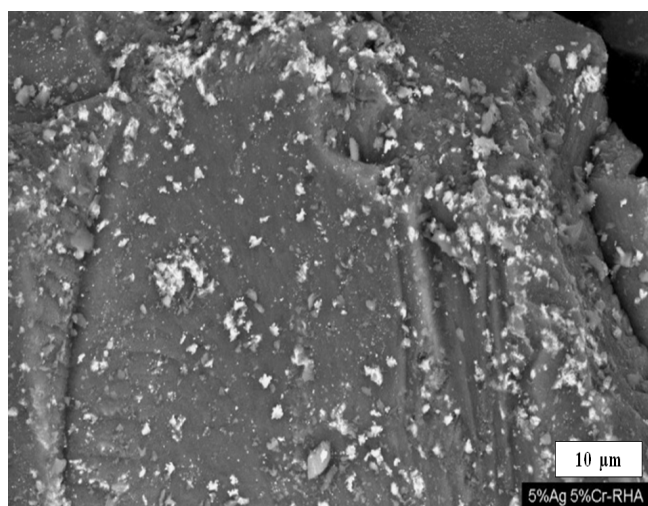


Figure 4: The scanning electron micrograph of RHA-5Cr5Ag at 10,000 times magnification.

3.2 Catalytic Activity

The main products from the oxidation of *n*-heptane with H_2O_2 are 2-, 3-, 4-heptanones, 1-, 2-, 3-, 4-heptanol and heptanal. The identification of these compounds was done by GC-MS analysis. In this study, reaction temperature, mass of catalyst molar ratio of substrate to oxidant and the reusability of the catalyst were studied to optimise the catalytic activity of the prepared catalyst.

The effect of reaction temperature on the oxidation of *n*-heptane was studied by varying the temperature from 333K to 353K over RHA-5Cr5Ag (100 mg) with other parameters kept constant ($\text{H}_2\text{O}_2 = 2.27$ g, *n*-heptane = 2.00 g, acetonitrile = 10 mL and reaction time of 6 h). The conversion of *n*-heptane increased with an increase in temperature as shown in Table 1. The catalyst was found to have higher selectivity toward heptanone with 76.45% compared to heptanol and heptanal with 19.08% and 4.47% respectively. Since H_2O_2 decomposed very fast at high temperature, temperature above 353K was not studied. Thus, the optimum reaction temperature was found to be at 353K.

Table 1: The effect temperature on the oxidation of *n*-heptane.

Temperature (K)	Conversion (%)	Selectivity (%)		
		Heptanone	Heptanol	Heptanal
333	61.02	87.73	9.49	2.78
343	86.45	71.05	22.52	6.43
353	89.54	76.45	19.08	4.47

Note: Reaction conditions: molar ratio of *n*-heptane:H₂O₂ = 1:1, catalyst mass = 100 mg, solvent = 10 mL of acetonitrile, reaction time = 6 h.

The oxidation of *n*-heptane was studied with various catalyst weights (50–100 mg) and the results are presented in Table 2. The conversion was found to increase as the mass of the catalyst increased from 50 mg to 100 mg. Increase in mass of the catalyst could increase the amount of active sites which participated in the reaction, thus promoted the conversion of *n*-heptane.¹⁴ Moreover, the selectivity of heptanone was increased from 50.35% to 76.45% as the mass of the catalyst increased from 50 mg to 100 mg. Hence, 100 mg was chosen as the optimum catalyst mass.

Table 2: The effect of catalyst's mass on the oxidation of *n*-heptane.

Mass (mg)	Conversion (%)	Selectivity (%)		
		Heptanone	Heptanol	Heptanal
50	75.85	50.35	32.55	17.10
70	82.07	71.85	23.93	4.22
100	89.54	76.45	19.08	4.47

Note: Reaction conditions: molar ratio of *n*-heptane:H₂O₂ = 1:1, temperature = 353K, solvent = 10 mL of acetonitrile, reaction time = 6 h.

The conversion of *n*-heptane at different molar ratio of *n*-heptane to H₂O₂ was studied and the results are tabulated in Table 3. With 1:1 molar ratio of *n*-heptane to H₂O₂, the catalyst exhibited an excellence catalytic activity with the conversion of 89.54%. The *n*-heptane conversion decreased to 77.85% as the molar ratio of *n*-heptane to H₂O₂ was increased to 1:3. Lower conversion of *n*-heptane was observed at high amount of H₂O₂. This may be due to the catalyst poisoning by the water formed from the decomposition of H₂O₂.¹⁵ The deactivated catalyst decreased the efficiency of the catalytic activity. Thus, the 1:1 molar ratio of *n*-heptane to H₂O₂ was fixed as the optimum molar ratio.

Table 3: The effect *n*-heptane to H₂O₂ molar ratio on the oxidation of *n*-heptane.

Molar ratio	Conversion (%)	Selectivity (%)		
		Heptanone	Heptanol	Heptanal
1:1	89.54	76.54	19.08	4.47
1:2	80.63	52.62	27.72	19.66
1:3	77.58	52.17	27.48	20.35

Note: Reaction condition: catalyst mass = 100 mg, temperature = 353K, solvent = 10 mL of acetonitrile, reaction time = 6 h.

Under the optimised reaction conditions, the catalyst showed excellent catalytic activity towards the oxidation of *n*-heptane. The product selectivity towards heptanone, heptanol and heptanal at this optimum condition were 76.45%, 19.08% and 4.47% respectively. In a previous study, Liu et al.² reported 15.1% conversion with ~ 66% and 31% selectivity for heptanol and heptanone under plasma oxidation of *n*-heptane in the liquid phase. Since no catalyst was used in the reaction, it resulted in low conversion. Moreover, a low temperature (188K) was used for the reaction, which is not suitable in the industrial. Stoylkova's research group³ had investigated the oxidation of *n*-heptane over different molecular sieves (SAPO-11 BEA and MCM41). They found that SAPO-11 was the most active catalyst for the oxidation of *n*-heptane with 55.3% conversion. However, a high reaction temperature (523K) coke formation occurred, resulting in low efficiency of the catalyst. Anisia and Kumar⁴ had synthesised zirconium complex incorporated onto silica for the oxidation of *n*-heptane. The catalyst showed good catalytic activity with ~80% conversion in 8 h. However, the multi step preparation of the zirconium complex is complicated and the reactor pressure of 100 psi was not economical. It is quite clear that RHA-5Cr5Ag is a better catalyst for the oxidation of *n*-heptane under mild reaction conditions.

The reusability of RHA-5Cr5Ag for the oxidation of *n*-heptane was tested for 2 cycles and the results are shown in Table 4. After the second reuse of the catalyst, the conversion of *n*-heptane dropped about 18%. Hence, a leaching test of the catalyst was carried out by AAS analysis to identify the heterogeneity of this catalytic system. The result showed that only 0.02% of Cr was leached. However, Ag was found to be completely leached out after the reaction. Thus, it can be said that Ag was not incorporated well in the catalyst. This may cause the lower catalytic activity. The objective of the present study did not involve any attempt to improve the incorporation of Ag in the silica matrix. However, further work is in progress to improve the preparation of well incorporated metal/silica catalysts.

Table 4: The reusability of RHA-5Cr5Ag catalyst for the oxidation of *n*-heptane.

Catalyst	Conversion (%)	Selectivity (%)		
		Heptanone	Heptanol	Heptanal
Fresh	89.54	76.54	19.08	4.47
1 st used	75.00	94.74	–	5.27
2 nd used	71.54	81.94	–	18.06

Note: Reaction conditions: catalyst mass = 100 mg, temperature = 353K, molar ratio of *n*-heptane:H₂O₂ = 1:1, solvent = 10 mL of acetonitrile, reaction time = 6 h.

4. CONCLUSION

In summary, a Cr/Ag bimetallic heterogeneous catalyst had been successfully synthesised from the biomass (RHA-silica) via simple sol-gel technique. We have developed a simple, cost-effective and green route to investigate the liquid phase oxidation of *n*-heptane using RHA-5Cr5Ag as the catalyst and H₂O₂ as the oxidant under mild condition. The product selectivity toward heptanone, heptanol and heptanal at the optimum condition were 76.45%, 19.08% and 4.47% respectively. This study showed that using an appropriate catalyst, alkanes (which are unreactive) can be oxidised into beneficial compounds under mild reaction conditions.

5. ACKNOWLEDGEMENT

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