The Production of Hydrogen by Catalytic Oxidation of Hydrocarbons using a Rice Husk Based Cobalt Phyllosilicate Catalyst

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Abstract: *Cobalt phyllosilicate was successfully synthesised via a simple template-free sol-gel technique at room temperature. The synthesised catalyst had been characterised by various physico-chemical analyses. The X-ray diffraction (XRD) pattern confirmed the formation of phyllosilicate as supporting material. Co-O bending vibration was detected in the Fourier-transform Infrared (FTIR) spectrum. The presence of cobalt in the silica matrix was confirmed by Energy-dispersive X-ray (EDX) analysis and atomic absorption analysis (AAS analysis). The sample showed a high specific surface area with 350.3 m^2 g^{-1} and a bimodal pore size distribution. The solvent free mineralisation of cyclohexene was carried out in the temperature range 303–353K over cobalt phyllosilicate at atmospheric pressure resulting in 99.6% conversion and 98.2% selectivity to syngas at 353K. The catalyst can be reused for four cycles in the oxidation of cyclohexene. The catalyst was calcined to regain a good conversion. Cobalt phyllosilicate also showed excellent activity in the mineralisation of iso-octane and toluene.*

Keywords: Cobalt phyllosilicate, oxidation, hydrogen production, syngas production, sol gel technique.

1. INTRODUCTION

Syngas is a mixture of hydrogen and carbon monoxide. It is very useful for manufacturing ammonia, methanol, pure hydrogen and hydrocarbon through Fischer Tropsch reaction.[1–4] Hydrogen is an ideal energy carrier that does not contain nitrogen and sulphur compounds and is the by-product of splitting steam or water.[5] Hydrogen has been used for power generation in fuel cell technologies.[6] Hence, an efficient method to generate hydrogen can reduce the need of petroleum and natural gas.

The technologies for producing syngas are catalytic partial oxidation,[7] CO_2 reforming[8] and steam reforming[9] as shown in Equation 1 to 3.

$$CH_4 + 0.5\,O_2 \rightarrow CO + 2\,H_2 \tag{1}$$
$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \tag{2}$$
$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \tag{3}$$

All these methods have the ability for C–H bond cleavage to form syngas. However, all these technologies require high temperature[10–14] (973–1273K) and sometimes even high pressure[13,14] (8–20 atm) to convert the hydrocarbon to syngas.

Phyllosilicate is a class of material that has layer dimension, shape selectivity and small particle size.[15] It has a high thermal stability and does not alter its physical nature after incorporating with metals.[16] The inertness of phyllosilicate towards chemical reaction makes it a suitable material to be used as a catalyst support.

In this study, rice husk[17] was used as a source of silica to synthesise cobalt–phyllosilicate heterogeneous catalyst. The prepared catalyst was used for the solvent-free catalytic oxidation of cyclohexene to syngas at ambient reaction condition. The oxidation of cyclohexene to syngas was accidentally discovered while trying to oxidise it to allylic alcohols and ketones using H_2O_2 as shown in Equation 4.

$$(4)$$
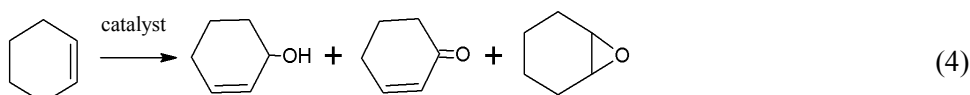
2.   EXPERIMENTAL

2.1   Raw Materials

Rice husk (RH) was obtained from a local rice mill in Penang. Nitric acid (QreC, 65%), sodium hydroxide (QReC, 99%) and cobalt(II) nitrate (R&M Chemical) were used as received. All chemicals were AR grade.

2.2   Preparation of Cobalt Phyllosilicates

The sodium silicate was prepared according to the procedure by Adam et al.[18] 30.0 g of dried RH was weighed and transferred into a plastic container. 600 mL of 1.0 M HNO_3 was added in the container and was stirred for 24 h in order to remove unwanted metal ions. The acid washed RH was filtered and washed with distilled water until it reached a constant pH (4.5–5.0) and dried in an oven at 383K overnight. The dried RH was stirred in 500 mL of 1.0 M NaOH for 24 h. The mixture was suction filtered to obtain a dark brown filtrate (sodium silicate), which was kept in a covered plastic container. The prepared sodium silicate was titrated slowly with a mixture of $Co(NO_3)_2$ and 3.0 M HNO_3 until it reached pH 9. The obtained colloid gel was aged in a covered container for two

days. The prepared gel was recovered by centrifuge (Zentrifugen Hettich) at 4000 rpm, suction filtered and finally followed by washing with distilled water. It was dried in an oven at 383K for 24 h. The hot solid was allowed to cool in a desiccator. Finally, the product was hand ground into fine powder and labeled as cobalt phyllosilicate.

2.3   Characterisation of Catalyst

The cobalt phyllosilicate was characterised by Fourier-transform infrared (FTIR) spectroscopy (Perkin Elmer system 2000), powder X-ray diffraction (Siemens diffractometer D5000, Kristalloflex), nitrogen sorption analysis (Nova 2200e, surface area and pore size analyser), transmission electron microscopy (TEM) analysis (FEI CM12), scanning electron microscope (SEM) (LEICA Cambridge S360) and energy dispersive X-ray – mapping analysis (Edax Falcon system).

2.4   Catalytic Activity

Typically, prior to the reaction, cobalt phyllosilicate was activated at 383K overnight. The round bottom flask equipped with a condenser was set up in a temperature controllable oil bath at 343K. 2.46 g (30 mmol) of cyclohexene was placed into the flask. 6.80 g (60 mmol) H_2O_2 (30%) was added drop wise into the reaction vessel. The reaction was carried out for 4 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 (30 m × 0.2 mm ID) column and further confirmed by GCMS (Perkin Elmer, Clarus 600) analysis. The following are the GC and GCMS condition used: initial temperature = 333K, final temperature = 503K, ramp 1 = 10K min^{-1} to 403K, ramp 2 = 20K min^{-1} to 503K, total run time = 13 min.

Reusability of cobalt phyllosilicate was studied for 4 cycles under the optimum reaction conditions. The first three cycles of catalyst was regenerated by washing with water. The 3rd reused catalyst was regenerated by calcination at 773K for 5 h to remove organic moieties.

For the qualitative identification of the gaseous products, two common and simple procedures were used. For the determination of the presence of hydrogen gas, the burning splint test was carried out. While, the limewater test was used to confirm the presence of carbon dioxide in the reaction. The evidence for these can be found in the supplementary files supplied.

The water displacement method (Figure 1) was used to collect and quantify the hydrogen gas. The reaction was carried out under the optimised

reaction conditions and the resulting gases were collected in an inverted measuring cylinder in downward displacement of limewater. The use of limewater instead of water was to dissolve the carbon dioxide and collect the hydrogen gas. Carbon dioxide is easily removed by absorption into water[3] and limewater was used as an added measure to remove it completely.

Figure 1: The reaction set up (on the right) and the arrangement for the downward displaced collection of the hydrogen gas (left measuring cylinder).

3.   RESULTS AND DISCUSSION

Cobalt phyllosilicate was examined by FTIR in the range of 4000–400 cm^{-1} (Figure 2). The adsorption band around 1016, 793 and 462 cm^{-1} belong to Si–O–Si bending and stretching vibrations.[19] A previous investigation involving the synthesis of phyllosilicate showed that a band ca. 1020 cm^{-1} is responsible for 2:1 phyllosilicate structural arrangement[15] (evidenced later). A bending vibration appeared for the trapped water molecules in the silica matrix at 1630 cm^{-1}. While the presence of a broad band at ~3462 cm^{-1} is due to O–H stretching vibration of the silanol or adsorbed water molecules on the silica surface. The Co-O bending vibration mode is responsible for the band at ca. 662 cm^{-1}.[20,21] This is a reasonable evidence for the successfully incorporated of cobalt into the layered silica matrix. No such band was observed in pure silica in our previous research study.[17]
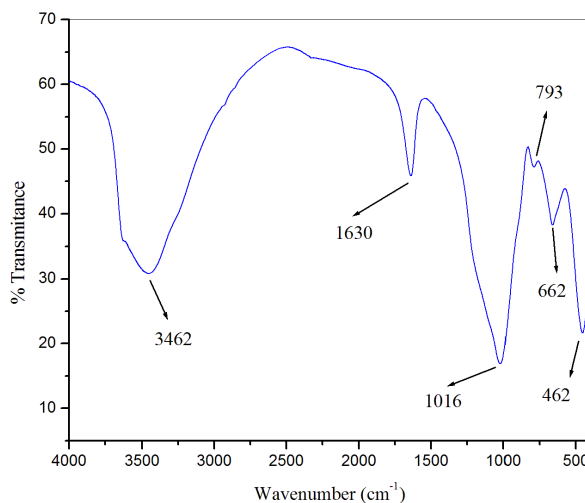
Figure 2: The FTIR spectra of cobalt phyllosilicate.

Powder XRD pattern of cobalt phyllosilicate is shown in Figure 3. It shows a small peak at $2\theta = 22°$ which indicate the amorphous nature of the silica.[22] While the presence of $2\theta = 34°$ and $2\theta = 59°$ are characteristic of the typical 2:1 layered phyllosilicate-like structure.[23,24] Similar observation was made by Carta et al. for synthesising phyllosilicate structure.[25] The absence of crystalline peak indicates a good dispersion of cobalt in the silica matrix. This is in accordance with EDX-Mapping result (evidenced later). The (001) line corresponding to the basal spacing was not detected at low angle XRD pattern (not shown), this may be due to the weak c–axis of phyllosilicate which contains two layer at most. This was typical for the phyllosilicate synthesised at room temperature. A similar observation was reported by Trujillano's research group.[24]

Nitrogen adsorption-desorption isotherm of cobalt phyllosilicate is shown in Figure 4. The sample exhibited type IV isotherm and H3 hysteresis loop according to IUPAC classification.[26] H3 hysteresis loop is a characteristic of mesoporous material consisting of slit-shape capillaries.[27] This is in accordance with TEM result (evidenced later). The sample possessed high BET specific surface area of 350 $m^2\,g^{-1}$ and pore volume of 0.51 cc g^{-1}. It showed a bimodal pore size distribution (PSD) centred at 3.7 nm and 15.8 nm respectively, which was derived from BJH model.
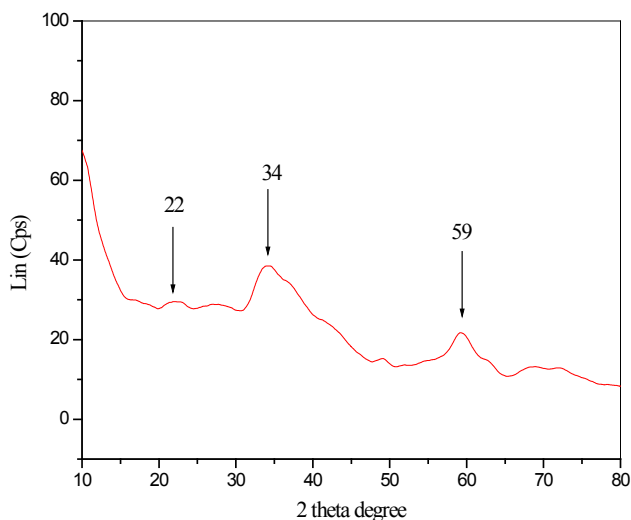
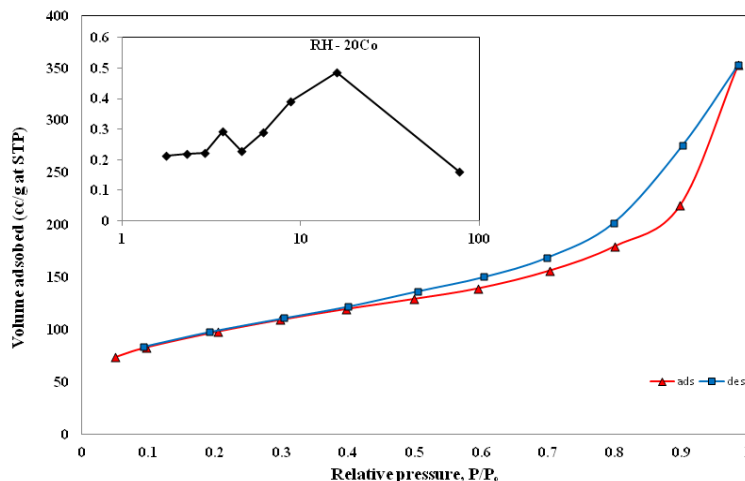Figure 3: X-ray diffractogram of cobalt phyllosilicate.

Figure 4: Nitrogen adsorption analysis of isotherm and pore size distribution.

The morphology of cobalt phyllosilicate was examined by transmission electron microscope and shown in Figure 5. The silica/cobalt complex showed a nano-needle like morphology. Similar morphology of the complex was reported by Carta et al.[25] The formation of the nanoneedle structure may be due to the strong electrostatic adsorption which is maximising the interaction between cobalt ion and negatively charged silicate in basic condition.[28]
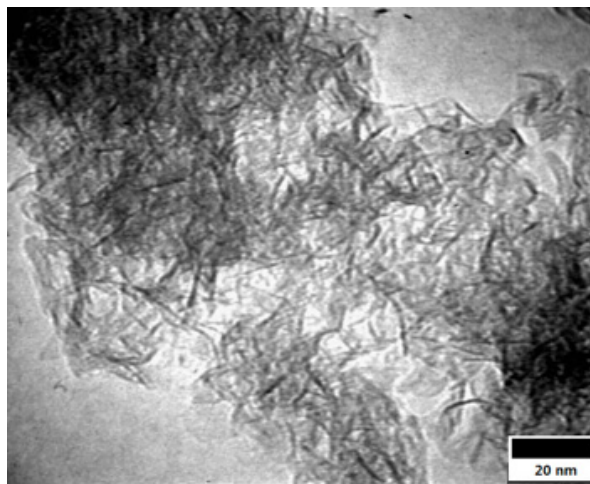
Figure 5: TEM micrographs of cobalt phyllosilicate with 650 K magnification.

The surface analysis for cobalt phyllosilicate was investigated by SEM and shown in Figure 6a. The SEM showed that the complex is granular and porous. The chemical composition of cobalt phyllosilicate was determined by energy dispersion X-ray (EDX) – Mapping. The EDX showed the presence of cobalt, silicon, oxygen (and carbon which may be impurities from RH). EDX-Mapping (Figure 6b) showed cobalt particles were homogeneously dispersed. To further confirm, atomic absorption analysis (AAS) was carried out for the cobalt phyllosilicate. This analysis showed an average cobalt loading of 18.8%.

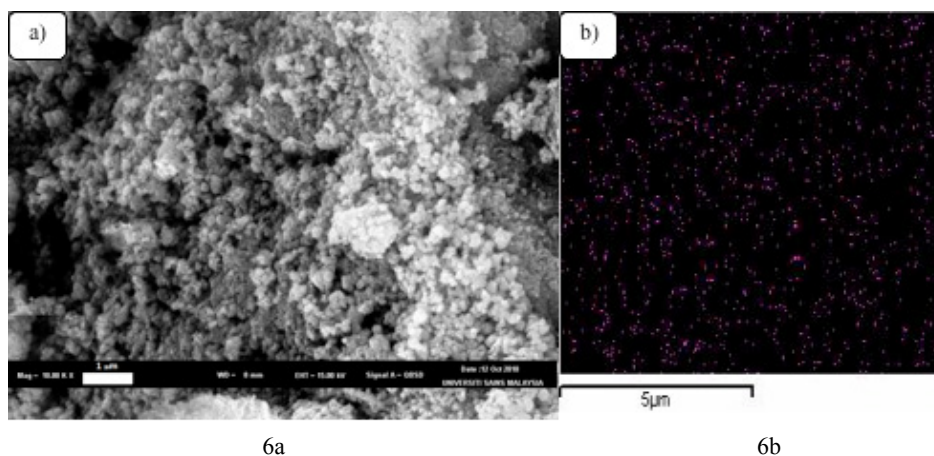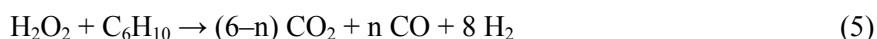6a   6b

Figure 6(a):   SEM micrograph of cobalt phyllosilicate and Figure 6 (b): Elemental mapping of cobalt phyllosilicate.

The formation of syngas was detected as soon as the H_2O_2 was added into the reaction. After 4 h, 99.5% of cyclohexene was converted to syngas. The hydrogen produced was detected by the simple burning splint test. A popping noise was heard as the hydrogen began to evolve. The formation of the products are shown in Equation 5. This is different from the typical catalytic oxidation process used in closed systems, i.e., autoclave. Carbon dioxide was detected by the limewater test (see supplementary Figure 1). Hence, the carbon monoxide formed from the oxidation was believed to undergo the water shift gas reaction[29] as shown in Equation 6. The enthalpy change of equation 6 was calculated by Hess' law. It is a mild endothermic reaction.

$$H_2O_2 + C_6H_{10} \rightarrow (6\text{–}n)\ CO_2 + n\ CO + 8\ H_2 \tag{5}$$
$$n\ CO\ (g) + H_2O\ (l) \rightarrow n\ CO_2 + H_2\ \Delta H = +\ 2.95\ kJ\ mol^{-1} \tag{6}$$

The other possibility resulting in the formation of the excess hydrogen can come from the splitting of water.

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \tag{7}$$
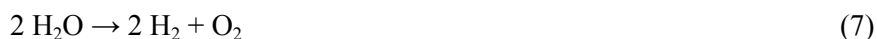
However, this possibility can be ruled out in this work, because oxygen was never detected. Therefore it is safe to say that the excess hydrogen comes from the reaction shown in equation 6. Neverthless, literature review indicates the reaction shown in Equation 6 occurs only at high temperature (473K).[29] In this work, the reaction in Equation 6 takes place easily at 343K although the enthalpy of the reaction in slightly endothermic. Apparently this small positive enthalpy was easily overcome with the catalyst employed in this study.

Literature reviews[30–32] showed that cyclohexene can undergo allylic oxidation as well as epoxidation to yield cyclohexen-1-ol, cyclohexen-1-one and cyclohexane epoxide. Surprisingly, in our study, we only detected trace amounts of these expected products (ca. 2%) in the gas chromatogram with the selectivity being cyclohexen-1-ol, cyclohexen-1-one and cyclohexene epoxide.

The effect of reaction time on the conversion of cyclohexene over cobalt phyllosilicate is shown in Table 1. The reaction was carried out with 50 mg of the catalyst using a cyclohexene:H_2O_2 ratio of 1:2 at 353K. The initial conversion of cyclohexene during the first hour was 34.8% and it gradually increased to 99.6% in 4 h. Hence, 4 h is the optimum reaction time for the reaction to achieve maximum catalytic conversion.

The effect of reaction temperature in the range of 303–353K at a fixed contact time of 4 h was investigated. On increasing the reaction temperature, the conversion of cyclohexene increased. The selectivity to the syngas was $\geq 98\%$

with some traces of by-products (Equation 4) detected in the reaction. The product variation with temperature is shown in Table 2. No reaction was carried out above 353K as H_2O_2 will dissociate too rapidly.

Table 1: The effect of reaction time.

Reaction time (h)	Conversion (%)
1	34.8
2	78.2
3	98.7
4	99.6

Reaction conditions: 50 mg of catalyst, cyclohexene (30 mmol), H_2O_2 (60 mmol), refluxed for 4 h at 353K.

Table 2: The effect of reaction temperature toward conversion and selectivity.

Temperature (K)	Conversion (%)	Selectivity to syngas (%)
303	87.6	99.0
323	98.6	98.8
343	99.5	99.1
353	99.6	98.2

Reaction conditions: 50 mg of catalyst, cyclohexene (30 mmol), H_2O_2 (60 mmol), refluxed for 4 h.

Table 3: The effect of molar ratio of H_2O_2 toward conversion and selectivity of syngas. The selectivity of syngas was calculated based on the difference with the minor organic products from the GC.

Molar ratio of cyclohexene: H_2O_2	Conversion (%)	Selectivity to syngas (%)
1:1	78.3	99.6
1:2	99.5	99.1
1:3	96.0	99.8

Reaction conditions: 50 mg of catalyst refluxed at 343K for 4h.

The effect of H_2O_2 was studied by varying H_2O_2 molar ratio from 1 to 3 at a fixed molar amount of cyclohexene as shown in Table 3. The conversion increased from 78.3% to 99.5% for 1:1 and 1:2 molar ratios respectively. With the molar ratio of 3:1, the conversion decreased slightly. Two layers of reactants were observed up to the first hour of reaction. However, at the end of 4 h, only the aqueous phase remained, which contained the expected organic products. Generally, decomposition of H_2O_2 produces water as a by-product. The water and oxidant can compete for the cobalt active sites and the excess of water might inhibit the reaction.[33]

The influence of mass of catalyst (Table 4) was also studied by varying the catalyst mass from 30 mg to 80 mg at constant reaction temperature of 343K. The conversion of cyclohexene was found to increase from 95.3 to 99.5% for 30 and 50 mg. However, further increase in the catalyst mass to 80 mg resulted in a decrease in conversion of cyclohexene to 91.8%. This could be due to the decomposition of H_2O_2 at higher mass of catalyst.[34] The higher mass of catalyst provides more surface area for the decomposition of H_2O_2 to occur and retard its catalytic activity. There was however, no noticeable change in the selectivity for syngas.

Table 4: The effect of mass of catalyst towards conversion and selectivity.

Mass (mg)	Conversion (%)	Selectivity to syngas (%)
30	93.5	99.3
50	99.5	99.1
80	91.8	99.4

Reaction conditions: cyclohexene (30 mmol), H_2O_2 (60 mmol) re fluxed at 343K for 4 h.

Reusability of the catalyst was studied for 4 cycles at the optimum reaction condition and the results are shown in Table 5. From the fresh catalyst's reaction till the 3rd cycle, the conversion of the catalyst decreased slightly from 99.4% to 92.5%. Some organic impurities were expected to adsorb onto the silica matrix, hence resulting in blockage of the pore and caused lower conversion. The used catalyst was calcined at 773K in order to remove the impurities. The calcined catalyst showed good catalytic activity with conversion of 98.4%. An experiment without the catalyst was also carried out. However, no product was observed when the catalyst was not present.

Table 5: The reusability of the catalyst. The first three cycles of catalyst were regenerated by washing with water. The 3rd reused catalyst was regenerated by calcination at 773K for 5 h.

Cycle	Conversion (%)
Fresh catalyst	99.5
1st reuse	99.1
2nd reuse	92.2
3rd reuse	98.4

Reaction conditions: 50 mg catalyst, cyclohexene (30 mmol), H_2O_2 (60 mmol) were refluxed at 343K for 4 h.

To test the universality of the catalyst, a variety of hydrocarbons were used in the study. Since cyclohexene is too valuable a chemical to be used as liquid fuel and as a chemical intermediate, we tried other hydrocarbons to form

syngas. At the optimum reaction condition, iso-octane and toluene were used as reactants for producing syngas. The cobalt phyllosilicate showed good catalytic activities with conversion of 97.4% and 99.2% respectively. For these two studies, no minor product was detected. Cobalt phyllosilicate was effective as a catalyst for the oxidation of hydrocarbons to syngas at ambient reaction condition. The experiments were carried out in triplicate and the results are shown in Table 6. Toluene produced the highest amount of hydrogen, and followed by cyclohexene and iso-octane.

However, it was found that the hydrogen produced was not stoichiometric with respect to the reactants used. The volume of hydrogen produced was found to be always in excess of the stoichiometric amount. This may be due to the formation of hydrogen via Equation 6. It may also be due to other unknown phenomena which need to be investigated in greater depth.

Table 6: The volume of hydrogen gas produced from different hydrocarbons in the oxidation using the Co-phylosilicate.

Hydrocarbon Used	*Average volume of hydrogen produced (mL)	*Average mole of hydrogen produced (mmol)
Cyclohexene (5 mmol)	833.3	33.5
Toluene (5 mmol)	880	35.4
Iso-octane (3 mmol)	725	29.2

*All data are average for 3 runs. Reaction condition: 50 mg catalyst, 1:2 molar ratio of reactant and H_2O_2 were refluxed at 343K for 4 h.

4.   CONCLUSION

A solvent-free oxidation process at low temperature and atmospheric pressure was developed to convert cyclohexene to syngas. The cobalt phyllosilicate was shown to effectively act as the catalyst for the mineralisation of cyclohexene as well as toluene and isooctane. A range of reaction temperature, the effect of molar ratio, mass of catalyst and reusability of catalyst were studied and a high conversion of cyclohexene and high selectivity to syngas was obtained. This novel method offers a new and cost effective approach for mass production of hydrogen from hydrocarbon. It is believed that this process has important implication in future green energy production and in the possible elimination of hydrocarbon pollutants from the environment.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

1.   Mukhopadhyay, S., Zerella, M. & Bell, A. T. (2005). A high-yield, liquid-phase approach for the partial oxidation of methane to methanol using SO_3 as the oxidant. *Adv. Synth. Catal.*, 347, 1203–1206.

2.   Udengaard, N. R. (2004). Hydrogen production by steam reforming of hydrocarbons. *Prep. Pap-Am. Chem. Soc. Div. Fuel Chem.*, 49, 906–907.

3.   Ratnasam, C. & Wagner, J. P. (2009). Water gas shift catalysis. *Catal. Rev.*, 51, 325–440.

4.   Cormier, J. M. & Rusu, I. (2001). Syngas production via methane steam reforming with oxygen: Plasma reactors versus chemical reactors. *J. Phys. D: Appl. Phys.*, 34, 2798–2803.

5.   Datta, P., Rihko-Struckmann, L. K. & Sundmacher, K. (2011). Influence of molybdenum on the stability of iron oxide materials for hydrogen production with cyclic water gas shift process. *Mater. Chem. Phys.*, 129, 1089–1095.

6.   Zhu, X. et al. (2010). Hydrogen and syngas production from two-step steam reforming of methane over CeO_2-Fe_2O_3 oxygen carrier. *J. Rare Earths*, 28, 907–913.

7.   Sun, W. Z., Jin, G. Q. & Guo, X. Y. (2005). Partial oxidation of methane to syngas over Ni/SiC catalysts. *Catal. Comm.*, 6, 135–139.

8.   Daza, C. E. et. al. (2011). High-stable mesoporous Ni-Ce/Clay catalysts for syngas production. *Catal. Lett.*, 141, 1037–1046.

9.   Ruiz, J. A. C. et al. (2008). Syngas production by autothermal reforming of methane on supported platinum catalysts. *Appl. Catal. A Gen.*, 334, 259–267.

10.   Shen, S., Li, C. & Yu, C. (1998). Mechanistic study of partial oxidation of methane to syngas over a Ni/Al_2O_3. *Stud. Surf. Sci. Catal.,* 119, 765–770.

11.   Choudhary, V. R., Mondal, K. C. & Choudhary, T. V. (2006). Partial oxidation of methane to syngas with or without simultaneous steam or CO_2 reforming over a high-temperature stable-$NiCoMgCeO_x$ supported in zirconia-hafnia catalyst. *Appl. Catal. A Gen.*, 306, 45–50.

12. Chu, W., Yang, W. & Lin, L. (2002). The partial oxidation of methane to syngas over the nickel modified hexaaluminate catalysts $BaNi_yAl_{12-y}O_{19-\delta}$. *Appl. Catal. A Gen.*, 235, 39–45.

13. Schmidt, L. D., Deutschmann, O. & Goralski, C. T. (1998). Modelling the partial oxidation of methane to syngas at millisecond contact times. *Stud. Surf. Sci. Catal.*, 119, 685–692.

14. Lyubovsky, M., Roychoudhury, S. & LaPierre, R. (2005). Catalytic partial oxidation of methane to syngas at elevated pressures. *Catal. Lett.*, 99, 113–117.

15. Fonseca, M. G., Silva, C. R., Barone, J. S. & Airoldi, C. (2000). Layered hybrid nickel phyllosilicates and reactivity of the gallery space. *J. Mater. Chem.*, 10, 789–795.

16. Park, J. C. et al. (2009). Chemical transformation and morphology change of nickel-silica hybrid nanostructures via nickel phyllosilicates. *Chem. Commun.*, 47, 7345–7347.

17. Adam, F., Chew, T. S. & Andas, J. (2011). A simple template-free sol-gel synthesis of spherical nanosilica from agricultural biomass. *J. Sol-Gel Sci. Technol.*, 59, 580–583.

18. Adam, F., Chew, T. S. & Andas, J. (2012). Liquid phase oxidation of acetophenone over rice husk silica vanadium catalyst. *Chin. J. Catal.*, 33(3), 518–522.

19. Liou, T. H. & Wu, S. J. (2010). Kinetics study and characteristics of silica nanoparticles produced from biomass-based material. *Ind. Eng. Chem. Res.*, 49, 8379–8387.

20. Chowdhury, A. N. et al. (2010). Cobalt-nickelmixed oxide surface: A promising adsorbent for the removal of PR dye from water. *Appl. Surf. Sci.*, 256, 3718–3724.

21. Ortega-Zarzosa, G., Araujo-andrade, C., Compean-Jasso, M. E. & Martinez, J. R. (2002). Cobalt oxide/silica xerogels powders: X-ray diffraction, infrared and visible absorption studies. *J. Sol-Gel Sci. Technol.*, 24, 23–29.

22. Adam, F. & Iqbal, A. (2011). The liquid phase oxidation of styrene with tungsten modified silica as a catalyst. *Chem. Eng. J.*, 171, 1379–1386.

23. Melo, M. R. & Airoldi, C. (2010). Energetic features of copper and lead sorption by innovative aminoalcohol-functionalized cobalt phyllosilicates. *Dalton Trans.*, 39, 10217–10227.

24. Trujillano, R., Lambert, J. F. & Louis, C. (2008). Chemistry of silica-supported cobalt catalysts prepared by cation adsorption. 2. Neoformation of cobalt phyllosilicate. *J. Phys. Chem. C*, 112, 18551–18558.

25. Carta, D. et al. (2009). Structural and magnetic characterization of Co and Ni silicate hydroxides in bulk and in nanostructures within silica aerogels. *Chem. Mater.*, 21, 945–953.

26.   Khalfaoui, M., Knani, S., Hachicha, M. A. & Lamine, A. B. (2003). New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment. *J. Colloid Interf. Sci.*, 26, 350–356.

27.   Chiang, Y. C., Chiang, P. C. & Chang, E. E. (1998). Comprehensive approach to determining the physical properties of granular activated carbons. *Chemo.*, 37, 237–247.

28.   Job, N. et al. (2010). Preparation of highly loaded Pt/carbon xerogel catalysts for proton exchange membrane fuel cells by the strong electrostatic adsorption method. *Catal. Today.*, 150, 119–127.

29.   Mellor, J. R., Coville, N. J., Sofianos, A. C. & Copperthwaite, R. G. (1997). Raney copper catalysts for the water shft gas reaction II. Initial catalyst optimization. *Appl. Catal. A Gen.*, 164, 185–195.

30.   Liu, J. et al. (2002). The oxidation of cyclohexene with polymer supported Co (II) in supercritical carbon dioxide. *Chin. Chem. Lett.*, 13, 1162–1163.

31.   Poltowicz, J. et al. (2001). Oxidation of cyclohexene over Mn(TMPyP) porphyrin-exchanged Al.Si-mesoporous molecular sieves. *Appl. Catal. A Gen.*, 218, 211–217.

32.   Salavati-Niasari, M. (2009). Synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen over host (nanopores of zeolite-Y)/guest ($[Ni(\{R\}_2\text{-}N_2X_2)]^{2+}$ (R=H, CH_3; X=NH, O, S) nanocatalyst. *J. Coord. Chem.*, 62, 980–995.

33.   Neumann, R. & Elad, M. L. (1995). Vanadium silicate xerogels in hydrogen peroxide catalyzed oxidations. *Appl. Catal. A Gen.*, 122, 85–97.

34.   Singh, A. P. & Selvam, T. (1996). Liquid phase oxidation of para-chlorotoluene to para-chlorobenzaldehyde using vanadium silicate molecular sieves. *Appl. Catal. A Gen.*, 143, 111–124.