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ROLE OF ACTIVE CHROMIUM SPECIES ON DIFFERENT SUPPORT FOR DEHYDROGENATION OF PROPANE

(Peranan Spesies Kromium Aktif pada Penyokong yang Berbeza dalam Tindak balas Penyahhidrogenan Gas Propana)

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Abstract

Dehydrogenation of propane (DHP) was studied over a series of Cr_2O_3–Al_2O_3 and Cr_2O_3-SiO_2 catalysts, prepared by incipient wetness impregnation and sol gel (SG) method, respectively, to gain a better understanding of the nature and distribution of chromium (Cr) species and their catalytic function. To this end, the catalysts were characterized by N_2-physisorption and X-ray diffraction (XRD). N_2-physisorption analysis of Cr_2O_3-SiO_2 showed the relatively higher surface area of 391.1 m^2/g, compared with Cr_2O_3-Al_2O_3 of 224.3 m^2/g. The combination method of sol gel and sonothermal also produced smaller particles size of catalyst with higher microporosity of 23.5% and smaller pores size of 6 nm. The good surface properties of Cr_2O_3-SiO_2 enabled the high conversion of propane of 55% at 550 °C. At higher temperature of 600 °C, the Cr species might be reduced into lower oxidation state and inhibit the catalytic behavior to produce hydrogen.

Keywords: chromium (II) oxide, thermodynamic consideration, sonothermal, catalytic behavior, hydrogen energy

Abstrak

Tindak balas penyah-hidrogenan gas propana (DPP) telah dikaji menggunakan beberapa siri mangkin Cr_2O_3–Al_2O_3 dan Cr_2O_3-SiO_2 yang dihasilkan melalui kaedah impregnasi basah dan sol gel (SG) method, untuk memahami sifat dan serakan spesies logam Cr dan fungsi pemangkinannya. Dalam kajian ini, mangkin diciri menggunakan kaedah jerapan gas N_2 dan pembelauan sinar X (XRD). Analisis jerapan N_2 bagi mangkin Cr_2O_3-SiO_2 menunjukkan ia mempunyai luas permukaan yang paling tinggi sebanyak 391.1 m^2/g, berbanding mangkin Cr_2O_3-Al_2O_3 sebanyak 224.3 m^2/g. Kombinasi kaedah sol gel (SG) dan sonotermal menghasilkan mangkin yang bersaiz lebih kecil dengan keporosan mikro sebanyak 23.5% dan saiz liang sebanyak 6 nm. Ciri-ciri permukaan yang baik ditunjukkan oleh mangkin Cr_2O_3-SiO_2 menyumbang kepada aktiviti tindak balas yang baik dengan peratus penukaran propana yang tinggi sebanyak 55% pada suhu 550 °C. Pada suhu tindak balas 600 °C pula, spesies logam Cr boleh terturun kepada keadaan pengoksidaan yang lebih rendah dan merencat tindak balas pemangkin bagi menghasilkan gas hidrogen sebagai produk utama.

Kata kunci: kromium (II) oksida, pendekatan termodinamik, sonotermal, sifat pemangkinan, tenaga hidrogen

Introduction

Propane is produced as a by-product of two other processes, natural gas processing and petroleum refining. The processing of natural gas involves removal of butane, propane, and large amounts of ethane from the raw gas, in order to prevent condensation of these volatiles in natural gas pipelines. Commonly, the dehydrogenation of propane can produce propene and hydrogen as a greener and future fuel sources and carried higher energy [1]. The reaction conditions play a major role to direct the reaction route and selected products. It is possible to produce hydrogen by catalytic dehydrogenation of propane, according to the following reaction (equation 1 and 2):

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^o = 124\ kJ.mol^{-1} \tag{1}$$

$$C_3H_8\ (g) \rightarrow C\ (s) + C_2H_6\ (g) + H_2\ (g) \qquad \Delta H^o = 19.1\ kJ.mol^{-1} \tag{2}$$

However, this reaction cannot be carried out easily due to its strong endothermicity ($\Delta H^o_r = 124\ kJ.mol^{-1}$). Sattler et al. [2] were reviewed various type of catalytic dehydrogenation of light alkanes into other products namely methane, hydrogen, ethane and other series of alkenes. Several type of catalyst have been studied by researchers such as platinum-based, gallium oxide-based and vanadium oxide-based catalysts. In other work, Lee et al. [3] was reported the Sn addition to the $Pt_{0.5}/\theta\text{-}Al_2O_3$ catalyst can decreased the cracking products of C_1-C_3 and increase the stability and olefin selectivity.

This paper was focused on the hydrogen formation by catalytic dehydrogenation of propane. The effect of chromium species was also studied. The pure hydrogen can be produced from this reaction.

Materials and Methods

Thermodynamic consideration

The catalyst selection was performed using a simple thermodynamic approach based on thermodynamic data. Several pyrolysis routes have been selected to study the possibility. For example, the propane gas can be pyrolyzed into methane and hydrogen. There was some possible route for propane dehydrogenation reaction (equation 3 - 5).

$$C_3H_8 \rightarrow C_3H_6 + H_2 \tag{3}$$

$$C_3H_8 \rightarrow 2C + CH_4 + 2H_2 \tag{4}$$

$$C_3H_8 \rightarrow 3C + 4H_2 \tag{5}$$

Synthesis of catalyst

The catalyst $15\%Cr_2O_3/\gamma\text{-}Al_2O_3$ was synthesized by using the wet impregnation method. 3.95g of $Cr(NO_2)_3{\cdot}9H_2O$ was dissolved in 10 ml of distilled water. Then, 8.5g of $\gamma\text{-}Al_2O_3$ was added into the solution and stir for 1 hour. The mixed sample was introduced to ultrasonicator for 10 minutes. The sample was dried at 110 °C and calcine at 400 °C for 3 hours before the catalyst is ready to test in reaction.

The $15\%Cr_2O_3/SiO_2$-sol gel (SG) was prepared by sol gel method by mixing the tetraethyl orthosilicate (TEOS) and ethanol with molar ratio of 1:1 to obtain a sol gel precursor solution. Then, several amount of $Cr(NO_2)_3{\cdot}9H_2O$ was dissolved in distilled water followed by some nitric acid addition. Both mixtures were stirred by vigorous magnetic stirring separately at room temperature until the pH 2 was observed. The solution was lifted for 24 hours until gelation is complete. The samples were dried at 110 °C and calcined at 400 °C for 3 hours before ready for use.

Characterization of catalyst

Nitrogen adsorption at 77K (liquid nitrogen) was conducted using a Micromeritics ASAP 2010 instrument to obtain the adsorption isotherm of each sample. The Brunauer-Emmett-Teller (BET) surface area, micropore volume and micropore area were calculated from the isotherms. Before analysis was conducted, the samples were degassed at 350 °C for 6 hours. The crystallinity analyses of the samples were performed using a Bruker DB-Advance X-ray Diffractometer (XRD), Germany. The analyses were performed with 1-g samples, employing Cu Kα radiation at 2θ ranging from 10° to 80°.

Propane pyrolysis reaction

The propane pyrolysis was conducted using fluidized bed reactor under propane gas flows at ranging of 30 – 70 mL/min. The output gas was analyzed using GC-FID.

Results and Discussion

Thermodynamic consideration

There were several possible reactions might be occurred during the pyrolysis of propane as showed in Table 1. The reactions 3 to 5 (R1-R5) are very favorable at low temperature. However, the possible R1 and R2 is need high temperature to occur (more than 972 k). Theoretically, R3 to R5 can occur at relatively low ranging temperature of 180 – 402 K. However, the presence of energy barrier or high activation energy during the reaction contributed the sum of error around 30 kJ/mol^{-1} or 500 K. It was noted that the tendency to produce carbon during propane pyrolysis is high in the present of metal oxide catalyst [4,5].

Table 1. Thermodynamics data of possible reactions for propane pyrolysis

Reaction Involved	ΔH (Kj·Mol^{-1})	ΔS (J·Mol^{-1}·K^{-1})	ΔG (Kj·Mol^{-1})	T (K)	Reaction Possibility
C_3H_6 (g) → C_3H_6 (g) + H_2 (g) **R1**	124.2	127.8	0	972	Favourable at high temperature
C_3H_8 (g) → C_2H_2 (g) + CH_4 (g) + H_2 (g) **R2**	-197.7	-153.8	-5	1253	Favourable at very high temperature
C_3H_8 (g) → C (s) + C_2H_6 (g) + H_2 (g) **R3**	19.1	84.7	-5	285	Favourable
C_3H_8 (g) → 2C (s) + CH_4 (g) + 2H_2 (g) **R4**	29.0	189.3	-5	180	Favourable
C_3H_8 (g) → 3C (s) + 4H_2 (g) **R5**	103.8	270.9	-5	402	Favourable

Catalysts surface properties

Figure 1 showed the adsorption-desorption isotherm of the fresh support and modified catalyst. The fresh SiO_2 (Figure 1 (a)) and Al_2O_3 (Figure 1 (b)) showed the adsorption isotherms type II and IV, respectively. However, the dispersion of Cr_2O_3 on SiO_2 (in Figure 1 (c)) was changed the adsorption isotherm into type I. Type I isotherms are observed for the adsorption of gases on microporous solids whose pore sizes are not much larger than the molecular diameter of the adsorbate. This property can bring forward the solid-gases reaction which is most of the reaction occurs in pores and surfaces [6]. On the other hand, the Cr_2O_3/SiO_2 catalyst (Figure 1 (d)) showed the hysteresis type IV represented to slit-shaped pores with uniform in size [7]. This type of hysteresis can maximize the reactant adsorption during reaction and desorbed the products easily. Table 2 showed the better surface properties of Cr_2O_3/SiO_2 with higher surface area and microporosity of 391.1 m^2/g and 23.5%, respectively. The higher surface area with maximum metal oxide dispersion would lead the higher active sites and subsequently contribute to good catalytic activity.

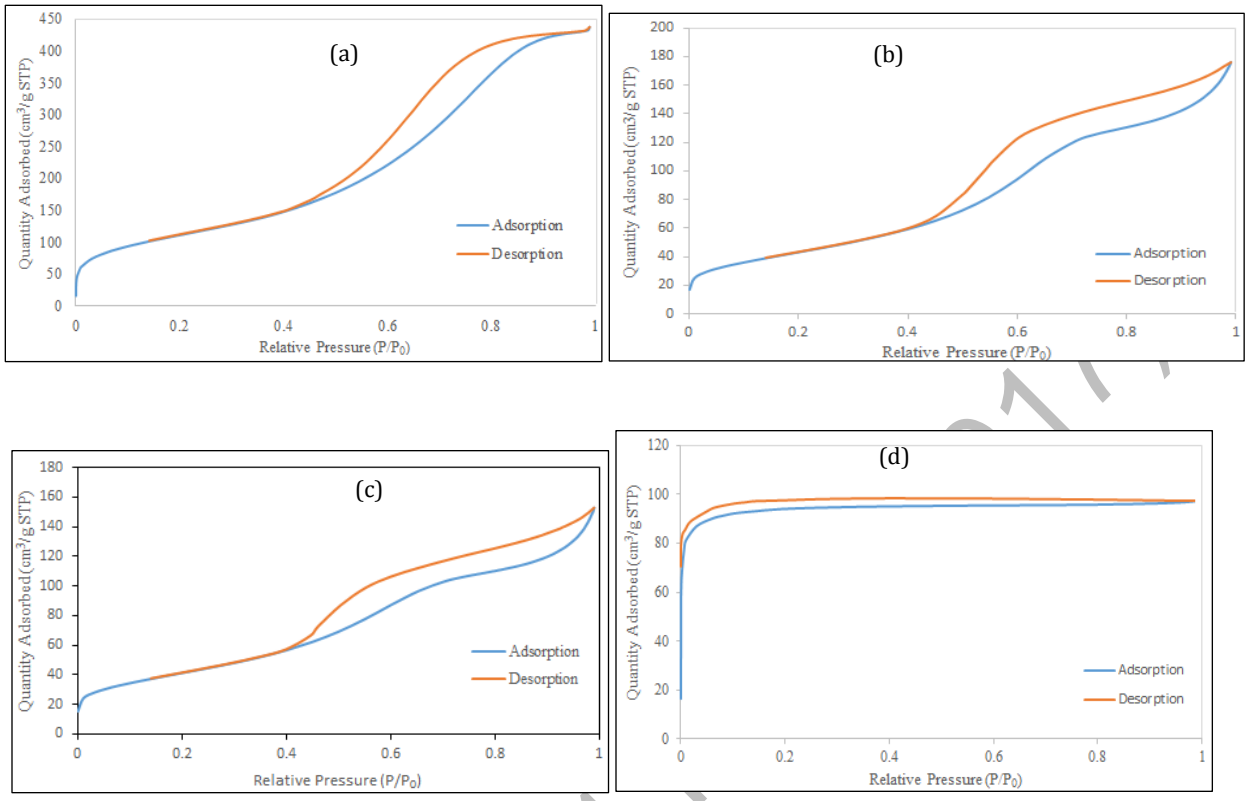


Figure 1. The isotherms of a) SiO_2, b) Al_2O_3, c) Cr_2O_3-Al_2O_3 and d) Cr_2O_3-SiO_2 SG

Table 2. The physical properties of catalysts

Selected Catalysts	Microporosity (%)	Pores Size (nm)	Surface area (m^2/g)
SiO_2	4.8	6.83	391.1
Al_2O_3	1.3	6.85	154.4
Cr_2O_3-Al_2O_3	1.4	6.02	308.8
Cr_2O_3-SiO_2	23.5	6.19	224.3

Crystallinity of catalyst

XRD analyses were performed for the Cr_2O_3/Al_2O_3, Cr_2O_3/SiO_2, SiO_2 and Al_2O_3 as a support. Figure 2 (a) and 2 (b) showed the XRD patterns for semicrystalline SiO_2 and crystalline Al_2O_3, respectively. Figure 2(c) showed the low intensity of Cr_2O_3 phase which detected at 34.8° and 54.4° with rhombohedral lattice system and the diffraction data match very well with JCPDS card of Cr_2O_3 (JCPDS 70-3765). No CrO_2 phase was detected in this catalyst. The Cr_2O_3/SiO_2 catalyst (Figure 2 (d)) showed three phases of Cr_2O_3 at 32.6°, 34.7° and 54.3° with rhombohedral lattice system. The single phase of CrO_2 was detected at 64.1° with orthorhombic lattice system and the diffraction data match very well with the JCPDS card of CrO_2 (JCPDS 75-7969). The high oxygen level of CrO_2 phase can accelerate the propane cracking into hydrogen, propene, methane and carbon deposition [8]. After reaction, the graphite phase was detected in the catalyst due to carbon deposition as one of the product of the reaction at relatively high temperature. Besides, the Cr(IV) was fully reduced into Cr(III) due to high temperature reaction of 600 °C.

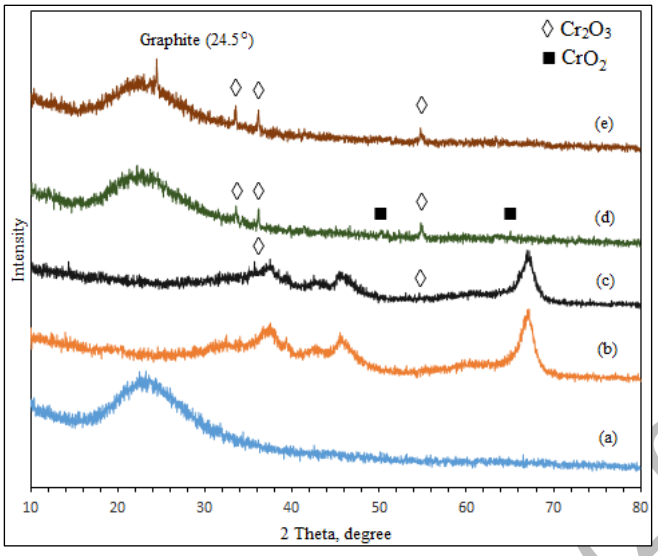


Figure 2. XRD diffractogram of (a) fresh SiO_2, (b) fresh Al_2O_3, (c) 15%Cr_2O_3/Al_2O_3, (d) 15%Cr_2O_3/SiO_2 and (e) 15%Cr_2O_3/SiO_2 after reaction

Catalytic performances

The pyrolysis reaction of propane gas was studied based on several parameters such as the effect of reaction temperature, reactant flowrate, reaction time and catalysts type. This reaction was performed in the range of temperature of 450 – 600 °C. The range was selected by calculation of thermodynamic data which was favorable to occur. Figure 3 showed the effect of reaction temperature on propane pyrolysis into hydrogen and other hydrocarbon or carbon due to highly dispersion of Cr species on SiO_2 surfaces. However, at 600 °C, the propane conversion was relatively decreases due to Cr_2O_3 fully converted to CrO_2 which decrease the catalyst activity of dehydration reaction with C_3H_6 and H_2 are dominant products. Figure 4 showed the effect of residence time to propane conversion. The residence time is depended to the flowrate of the reactant which reacted to the catalyst. In this reaction, it was noted that higher residence time of 30 seconds gave the longer time for reaction to be occurred and achieved the completion.

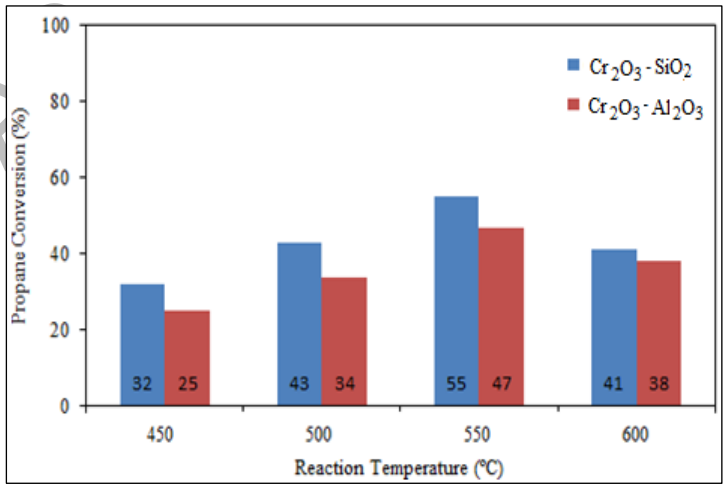


Figure 3. Effect of reaction temperature of (a) Cr_2O_3/SiO_2 SG and (b) Cr_2O_3/Al_2O_3 (Reaction carried out at flowrate of 60 mL/min)

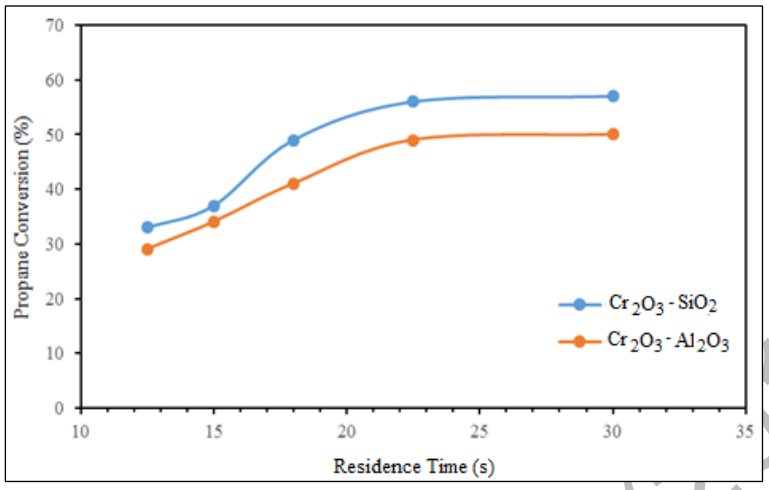


Figure 4. Effect of residence time of the reaction on H_2 production for (a) Cr_2O_3-Al_2O_3 and (b) Cr_2O_3-SiO_2 SG (Reaction carried out at 550 °C)

In Figure 5, at different reaction temperature, the Cr_2O_3-SiO_2 SG showed a series of products. At 550 °C, the hydrogen is a major product followed by carbon deposition and C_3H_6 formation. However, at 600 °C, the propene is significantly increased. It was noted that the high energy supply can bring forward the reaction route which produced hydrogen and propene as major products [3].

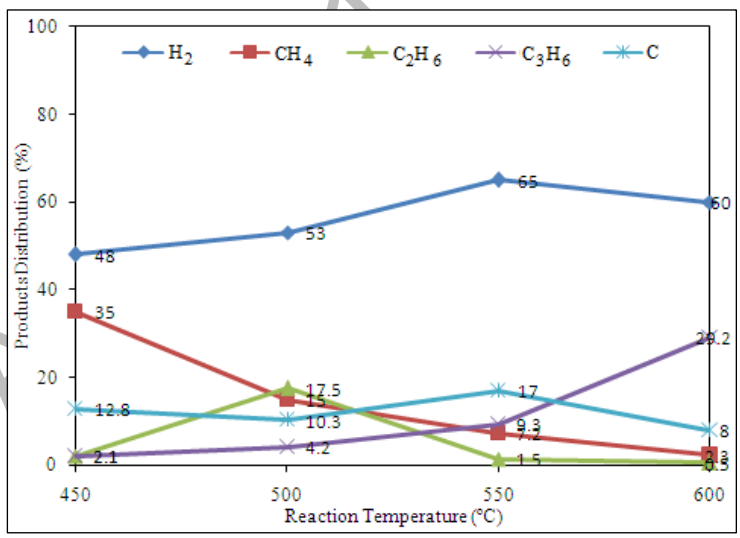
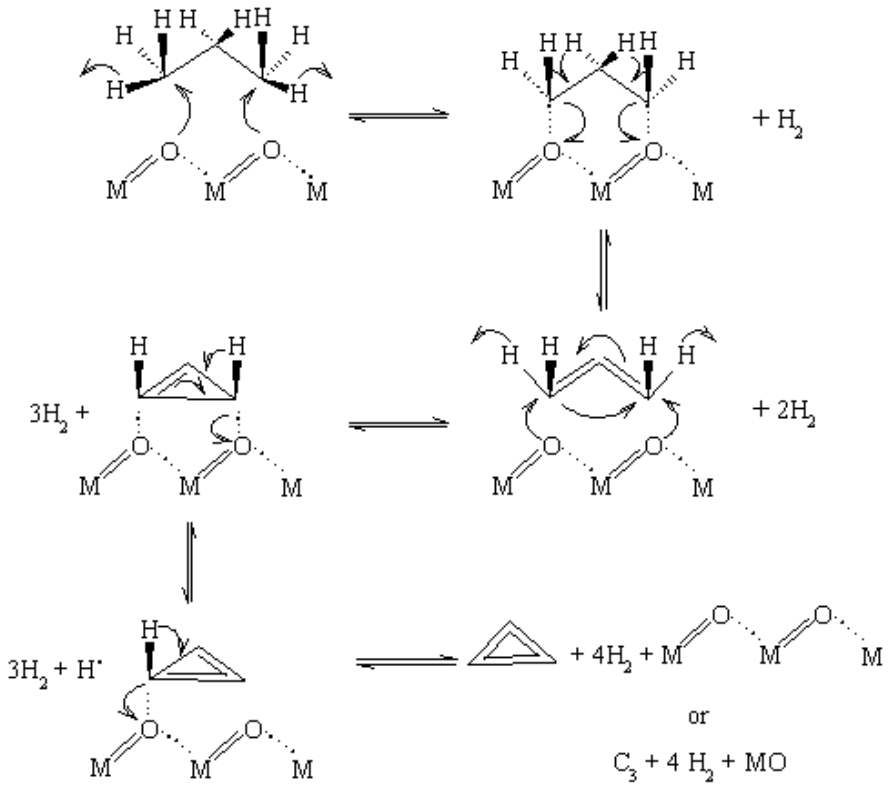


Figure 5. The products distribution from propane pyrolysis using Cr_2O_3-SiO_2 SG at optimum condition (Reaction was carried out at flowrate of 60 mL/min)

Proposed mechanism

Thermodynamics theory approach can be used for evaluation the potential of metal oxide (MO) as catalyst in propane pyrolysis process. Theoretically, the breaking of hydrogen chain from carbon can easier occur if the formation of the new bond between MO and carbon is stronger. The bond between the carbon and MO known as

physical interaction (van der wall bond), where the interaction is weak, but due to the effects of temperature, the heavier atoms (i.e., carbon and MO) tends easier to form a slightly stronger bonds than lighter atoms (i.e., hydrogen), consequently, the hydrogen bonds in the carbon is easier to break at lower temperatures. Thus, the catalyst material is expected to help increase the rate of hydrogen production and reduces the reaction temperature. The reaction mechanism between the MO with propane can be described in several possible routes as showed in Scheme 1.



Scheme 1. Proposed mechanism of propane dehydrogenation over metal oxide catalyst

A thermodynamic calculation to illustrate that the mechanism (1) may only occur at high temperatures (≈ 400 K) due to the entropy of the reaction is very high [9,10] . This due to the process of acquiring C is through the chain termination mechanism of double or triple bonds of C. In this case, all of the hydrogen atom consist of propane has been transformed into four moles of H_2 molecules and created a very stable double or triple bond of carbon which required a relatively high energy to dissociate. However, this mechanism just a form that is closest to clarify the possibility of the mechanism due to this mechanism is very complex which involves the variety of free radicals [11].

Conclusion

Hydrogen as a green fuel was successfully produce by dehydrogenation of propane in the presence of Cr-based catalyst. Thermodynamic calculation showed the feasibility of propane pysolysis into several products such as hydrogen, methane, propene and carbon depends on the reaction temperature. The Cr_2O_3/SiO_2 catalyst showed the better surface properties with high surface area of 393.1 m^2/g, microporosity of 23.5% and slit-shaped micropores. These properties were contributed to the higher propane conversion of due to high catalytic and gas adsorption ability. At 550 °C, the hydrogen, C_3H_6 and carbon were dominant products with 55% of propane conversion. However, in long period, the high carbon deposition can deactivate the catalyst by covering the pores and surface and reduce the selectivity to hydrogen as a major product.

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