ตัวเร่งปฏิกิริยาออกไซด์ NiCr และ NiAl สำหรับออกซิเดชันของเอทิลเบนซิน

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บทคัดย่อ

ได้สังเคราะห์พรีเคอเซอร์เลเยอร์ดับเบิลไฮดรอกไซด์ NiCr และ NiAl และทำการเผาให้กลายเป็นออกไซด์โลหะ ทำการตรวจพิสูจน์เอกลักษณ์ด้วยการวิเคราะห์ทางเคมี การเลี้ยวเบนรังสีเอ็กซ์ ฟูเรียร์ทรานสฟอร์มอินฟราเรดสปกโทรสโคปี และวัดพื้นที่ผิว (BET) ทดสอบประสิทธิภาพการเร่งปฏิกิริยาอย่างเลือกจำเพาะสำหรับออกซิเดชันของเอทิลเบนซิน เป็นอะซิโทฟีโนนโดยใช้เทอร์เชียรีบิวทิลไฮโดรเปอร์ออกไซด์เป็นสารออกซิไดซ์ ทำการศึกษาผลกระทบของพารามิเตอร์ ของการเกิดปฏิกิริยา ได้แก่ ชนิดของโลหะ สัดส่วนโดยโมลของสารออกซิไดซ์ต่อเอทิลเบนซิน และปริมาณของตัวเร่ง ปฏิกิริยาต่อประสิทธิภาพและความเลือกจำเพาะของปฏิกิริยาออกซิเดชัน ผลการทดลองแสดงว่า ที่ภาวะการทดลอง คือ ตัวเร่งปฏิกิริยา 0.2 กรัม สัดส่วนโดยโมล สารออกซิไดซ์/เอทิลเบนซิน = 3 อุณหภูมิ 130 °ซ และเวลาการทำปฏิกิริยา 12 ชั่วโมง NiCr-ออกไซด์ และ NiAl-ออกไซด์ ให้เปอร์เซ็นต์การเปลี่ยนรูปของเอทิลเบนซินที่สูง (77% และ 75%) เมื่อเทียบกับของ MgAl-ออกไซด์ (50%) NiAl-ออกไซด์แสดงความเลือกจำเพาะต่อการเกิดอะซิโตฟีโนน (98%) สูงกว่า NiCr-ออกไซด์ (75%) สปีชีส์โลหะที่เกิดรีดอกซ์มีบทบาทเป็นศูนย์กลางของการเร่งปฏิกิริยาออกซิเดชัน สามารถเพิ่มการ เปลี่ยนรูปขึ้นได้เมื่อเพิ่มปริมาณของตัวเร่งปฏิกิริยากลไกการเกิดปฏิกิริยาเกิดผ่านอนุมูลอิสระบางส่วน นอกจากนี้ ตัวเร่ง ปฏิกิริยาสามารถนำมาใช้ซ้ำได้

คำสำคัญ : เอทิลเบนซิน / ออกซิเดชัน / เลเยอร์ดับเบิลไฮดรอกไซด์ / ออกไซด์โลหะ / นิกเกิล / โครเมียม

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หลักสูตรปิโตรเคมี ภาควิชาเคมี คณะวิทยาศาสตร์ และศูนย์ความเป็นเลิศด้านปิโตรเลียม ปิโตรเคมีและวัสดุขั้นสูง

NiCr- and NiAl-Oxides Catalysts for Oxidation of Ethylbenzene

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Abstract

NiCr- and NiAl- layered double hydroxide (LDH) precursors were synthesized and calcined to metal oxides. They were characterized by chemical analysis, X-ray diffraction, Fourier transform infrared spectroscopy and surface area (BET) measurement. Their catalytic activity was tested in the selective oxidation of selective ethylbenzene to acetophenone using tert-butylhydroperoxide as an oxidant. The influence of various reaction parameters: type of metal, oxidant/ethylbenzene molar ratio and catalyst amount on the activity and selectivity for the oxidation reaction were evaluated. Experimental results show that under the reaction condition of 0.2 g catalyst, TBHP/ethylbenzene molar ratio = 3, temperature at 130 °C and reaction time 12 h, the NiCr-oxide and the NiAl-oxide show high conversion of ethylbenzene (75 and 77%), compared to that from the MgAl-oxide (50%). The NiAl-oxide shows much higher selectivity for acetophenone (98%) than the NiCr-oxide (75%). Redox metal species plays the role as the active centers in the oxidation process. Higher conversion can be obtained when the catalyst amount was increased. A reaction mechanism was proved to be partly via free radicals. Moreover the heterogeneous catalysts are reusable.

Keywords : Ethylbenzene / Oxidation/ Layered Double Hydroxides / Metal Oxides / Nickel / Chromium

1. Introduction

Oxidation of ethylbenzene is of importance for the production of acetophenone, which is a key industrial product. It is used as a component of perfumes and as an intermediate for the manufacture of pharmaceuticals, resins and alcohols. The current industrial production of benzylic ketones is based on the oxidation of alkylbenzenes with molecular oxygen using cobalt acetate as the catalyst in acetic acid [1]. Oxidation of ethylbenzene via homogeneous catalysis has been reported using Co, Mn and Fe fluorinated metalloporphyrins, resulting in a 38% conversion and 94% selectivity to acetophenone [2]. However, in this procedure catalyst recovery and recycling are problematic. The use of heterogeneous catalysts has also been reported using oxygen as an oxidant [3-5]. However, in view of safety considerations and the low selectivity to this reaction, molecular oxygen is not viewed as a plausible reactant in an industrial process.

Metal oxides containing transition metal cations with oxidative, or reductive properties are often used as heterogeneous catalysts for many chemical reactions due to their unique combination of acid-base and redox properties [6,7]. They can be obtained by controlled thermal decomposition of layered double hydroxides (LDHs): $(M^{2+}_{1-x} M^{3+}_{x}(OH)_2)^{x+}(A^{n-})_{x/n} \cdot yH_2O$. LDHs containing carbonate as interlayer anion are usually calcined at intermediate temperatures (450-600 ºC) giving poorly crystallized mixed oxides which were used as catalysts and catalyst supports [8] due to their remarkable properties, such as high thermal stability, high surface area, basicity, good metal dispersion and small crystallite size. Chromium-containing solid catalysts also are currently used in catalytic liquid-phase oxidations [9]. It was reported that nickel substituted copper chromite spinel ($Cu_{0.5}Ni_{0.5}Cr_2O_4$) catalyzed oxidation of ethylbenzene using *tert*-butylhydroperoxide gave 56% conversion and 69% selectivity of acetophenone [10]. There have also been some reports on supported metal oxide catalysts for this system using oxygen or *tert*-butylhydroperoxide oxidant [11-13].

In this work, NiCr- and NiAl-oxides were synthesized from calcination of their corresponding layered double hydroxide (LDH) precursors. The catalytic activities were tested for the selective oxidation of ethylbenzene to acetophenone using tert-butylhydroperoxide as an oxidant, the reusability of the catalysts also being investigated.

2. Experimental

2.1 Catalyst Preparation

NiCr-and NiAl-oxides were prepared by a modified literature method [11, 12]. An aqueous mixture (60 ml) of nickel nitrate (90 and 72 mmol) and aluminium or chromium nitrates solution (M^{2+}/M^{3+} molar ratio of 5 and 4) (18 mmol) was added slowly to 0.4 M aqueous Na_2CO_3 (100 mL). The pH of the mixture was held at pH 10 through the dropwise addition of 1 M NaOH. The resulting gel-like material was heated to 60 ºC and stirred for 18 h at this temperature, then filtered and thoroughly washed with distilled water until the filtrate was neutral. The solid was dried in an oven at 110 ºC for 12 h. It was then calcined at 500 ºC for 5 h in a muffle (static air atmosphere) with a heating rate of 5 ºC/min, yielding the corresponding oxides.

2.2 Characterization

The atomic ratio of metals was determined by ICP-AES analysis using a LIBERTY 200-VARIAN instrument. Powder X-ray diffraction (XRD)

spectra were recorded on a Rigaku RINT 2200 spectrometer using filtered CuKα radiation. The specific surface area determination and pore volume and size analysis were performed by BET and BJH methods using a Quantachrome Autosorb-IC-VP Analyzer. Prior to the measurements, the samples were degassed at 100 ºC for 2 h. FT-IR spectra (KBr discs) were recorded on a Nicolet FT-IR Impact 410 Spectrophotometer. Temperature programmed reduction (TPR) measurements were carried out on a TPR MODEL BEL-CAT instrument equipped with a thermoconductivity detector (TCD). The sample (50 mg) was placed in a quartz reactor and reduced in a stream (flow rate 50 ml/min) of H_2 (3% H_2+ 97% He) with a heating rate of 15 ºC/min over the range 25-900 ºC and held at this temperature for 20 min.

2.3 Catalytic Oxidation

The catalytic oxidation of ethylbenzene was carried out in a magnetically stirred stainless steel reactor. Ethylbenzene (2.4 ml, 20 mmol) and catalyst (0.2 g) were added followed by *tert*-butylhydroperoxide (TBHP) (60 mmol). The mixture was heated to 130 ºC and stirred for 12 h. The reaction products were analyzed with a gas chromatograph (GC) equipped with a flame ionization detector using the internal standard method. Quantification

was done by determining the response factors of the reagents and products obtained using standard mixtures. The selectivity was calculated based on ethylbenzene.

2.4 Reusability of Catalysts

After the reaction, the catalyst was filtered and washed with acetone. The oxidation was performed with the washed catalyst for the second and third runs.

2.5 Reaction Mechanism

In order to prove whether the oxidation reaction occurs via free radical pathway, the oxidation reaction was also conducted in the presence of hydroquinone as a radical trap.

## 3. Results and Discussion

3.1 Catalyst Characterization

As shown in Table 1 from elemental analysis, the LDHs show a reasonable correspondence between M^{2+}/M^{3+} molar ratios of the solids and the starting solutions. Thermal decomposition of LDH precursors at 500 ºC led to the formation of mixed oxides possessing higher surface area and pore volume due to dehydration and decarbonylation which leave more spacing.

Table 1 Characteristics of LDHs and oxides

Sample	Composition M^{2+}/M^{3+}		LDH		Oxide	
	Solution	Solid	Surface area (m^2/g)	Pore volume (cm^3/g)	Surface area (m^2/g)	Pore volume (cm^3/g)
Ni4Al	4.0	3.9	80	0.27	105	0.30
Ni5Al	5.0	4.8	90	0.28	114	0.39
Ni5Cr	5.0	5.1	108	0.29	122	0.40

Fig. 1 shows XRD patterns of Ni5Al- and Ni5Cr-LDHs as well as their corresponding oxides. The LDH samples (Fig. 1, a and b) show sharp and intense peaks at low diffraction angles of $2\theta = 11º$, 24º and 35º; ascribed to diffraction by basal planes (003), (006) and (009) of LDHs, respectively. The broad and less intense peaks at higher angles of 2θ = 38º, 46º, 60º and 61º ascribed to diffraction by (105), (108), (110) and (113) planes, respectively (JCPDS 41-1428). The values of parameters a and c in the Ni5Al-LDH are 3.040 and 23.358 Å, respectively. The Ni5Cr-LDH has higher a parameter (3.046 Å) due to the larger ionic radius of

Cr^{3+} (0.62 Å), compared to that of Al^{3+} (0.54 Å). The layered structure was destroyed upon calcination at 500 ºC. Calcination of well-crystallized LDHs leads to formation of metal oxides (Fig. 1, c and d) with the trivalent cations Al (or Cr) occupation in the NiO matrix. Meanwhile, based on the similar diffraction angles in XRD to NiO phase (JCPDS 4-0835), spinel phase $NiAl_2O_4$ or $NiCr_2O_4$ may be contained with NiO in the Ni5Al-oxide and Ni5Cr-oxide samples, respectively. In addition, no peaks ascribed to chromium oxides are identified by XRD, most probably, owing to complete dissolution of Cr^{3+} ions to the matrix of spinel phase.
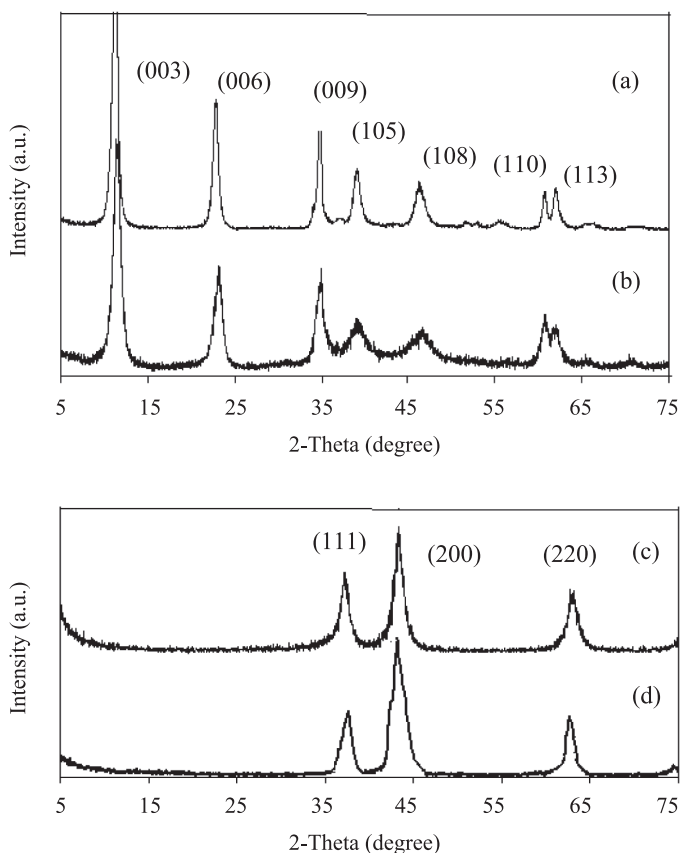
Fig. 1 XRD patterns of (a) Ni5Al-LDH (b) Ni5Cr-LDH (c) Ni5Al-oxide and (d) Ni5Cr-oxide.

Fig. 2 shows the FTIR spectra of the LDHs and their corresponding oxides. In the LDHs (a and b), a strong absorption band in the range 3500-3400 cm^{-1} is attributed to the O-H stretching. A shoulder at 1625 cm^{-1} may be ascribed to the bending mode of interlayer water molecules. The sharp absorption appeared around 1380 cm^{-1} is due to antisymmetric stretching of carbonate at interlayer vibrations. The bands observed in the low-frequency region, 850-650 cm^{-1} correspond to metal-oxygen (M-O)

vibrations. After calcinations, the LDH structure was destroyed to the mixed metal oxides (c and d). The bands observed in the low-frequency around 550-800 cm^{-1} region of the spectrum, are attributed to metal-oxygen and metal-hydroxyl vibration modes in the lattice of LDHs. The minor remaining carbonate band may arise from the adsorption of carbon dioxide from air on the surface of the metal oxide.
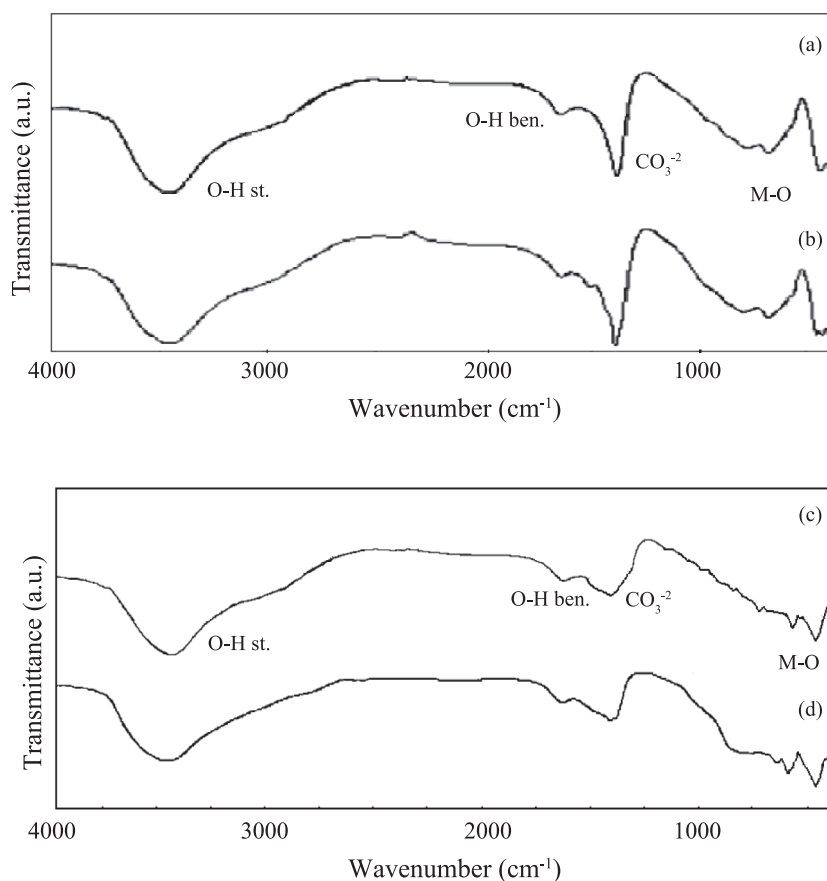
Fig. 2 FTIR spectra of (a) Ni5Al-LDH (b) Ni5Cr-LDH (c) Ni5Al-oxide and (d) Ni5Cr-oxide.

The reducibility of the metal oxides was studied by TPR experiments as shown in Fig.3. The reduction peaks at various temperatures are attributed to the reduction of the metal ion in different phases or environments. The Ni5Al-oxide sample showed two broad peaks. The first big peak at 370-470 can be attributed to the reduction of NiO and the second small peak at higher temperature, 500-550 ℃ is from reduction of Ni species which have weak interaction with aluminium oxide [14].

In this TPR profile, a peak from $NiAl_2O_4$ which usually occurs at 800-850 ℃ was not observed [15]. The TPR result of the Ni4Al-oxide is similar to that of the Ni5Al-oxide but with lower signal intensity. The Ni5Cr-oxide was reduced at 450-560 ℃, this high temperature reduction might be because Cr^{3+} ion polarizes the covalent Ni^{2+}-O bonds thereby increasing the effective charge of the Ni^{2+} ion in the $NiCr_2O_4$.
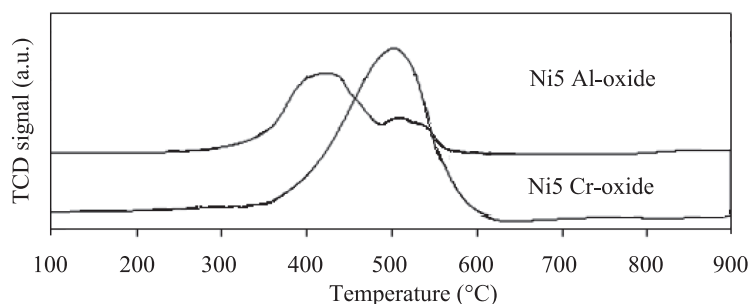

Fig. 3 TPR profiles of Ni5Al-oxide and Ni5Cr-oxide.

3.2 Catalytic activity

Oxidation of ethylbenzene was performed using ethylbenzene 2.4 ml (20 mmol), catalyst 0.2 g, different molar ratios of TBHP/ethylbenzene at 130 ℃ in 12 h. The results are reported as conversion of ethylbenzene and product selectivity as shown in Table 2. Products detected are benzaldehyde, acetophenone, 1-phenylethanol and benzoic acid. No product was obtained for the blank reaction (without catalyst).
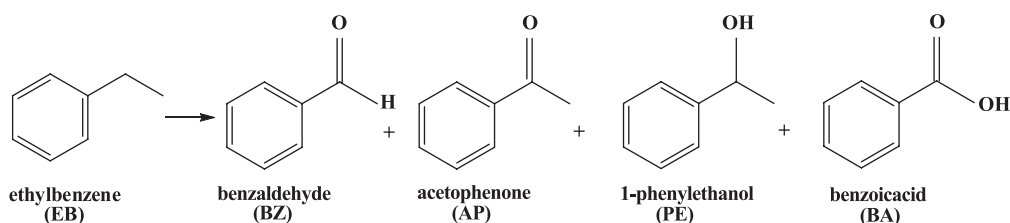
Table 2 Catalytic oxidation of ethylbenzene

Catalyst	TBHP/ ethylbenzene molar ratio	Conv. (%)	Selectivity (%)			
			AP	PE	BZ	BA
-	2	0	-	-	-	-
Ni4Al-oxide	2	70	98	1	1	0
	3	73	98	1	1	0
Ni5Al-oxide	2	72	98	1	1	0
	3	75	98	2	0	0
Ni5Cr-oxide	2	74	76	10	11	3
	3	77	75	9	13	3
Mg4Al-oxide*	2	50	98	1	1	0

AP= acetophenone, PE = 1-phenylethanol, BZ = benzaldehyde, BA = benzoic acid

*From reference [16].

Effect of type of catalyst: The oxidation of ethylbenzene was conducted using the Ni5Cr-oxide and Ni5Al-oxide, compared to the Mg4Al-oxide from our previous work [16]. It is well known that transition metal oxides operate in hydrocarbon oxidation by a redox type mechanism. So the catalytic behaviour can be correlated with the metal oxide reducibility. In this work the experimental results show that the Ni5Cr-oxide and Ni5Al-oxide show higher activity (77 and 75% conversion) than that obtained from the Mg4Al-oxide (50% conversion). This revealed that redox Ni, Cr species play the role as the active centers in the oxidation process, as seen from reducibility of these two oxides in Fig. 3. One possible oxidation reaction pathway (proved in section 3.4) is formation of free radicals, t-BuOO and/or t-BuO radicals from an activation of TBHP by coordination to the active redox site of the oxide catalyst.

As for the product selectivity, the Ni5Al-oxide gave much higher selectivity to acetophenone (98%) than the Ni5Cr-oxide (75-76%). Significant

amounts of other side products, 1-phenylethanol and benzaldehyde were also formed in case of the Ni5Cr-oxide. The different product selectivity might be due to different basicity-acidity of the two oxides. Formation of acetophenone requires chemisorption of alkyl hydroperoxide on the Lewis acidic and basic sites of the oxide catalyst whereas formation of benzaldehyde requires chemisorption of alkyl hydroperoxide on Lewis acid sites alone [6]. Order of acidity of the metal oxide follows the electronegativity of the cationic metals which increases in the following order: Mg (0.9) < Al (1.6) < Cr (1.7) < Ni (1.9). Therefore the selectivity to acetophenone from the NiCr-oxide (more acidic) is lower than that from the NiAl-oxide.

Effect of M^{2+}/M^{3+} molar ratio in the catalyst: The experimental results revealed that the Ni5Al-oxide showed higher conversion than the Ni4Al-oxide under the same reaction condi-tion. This can be due to higher amount of Ni in the catalyst, as evidenced by ICP-AES analysis (in

Table 1). It was also reported in the literature that the decrease in Ni content in NiMgAl oxides resulted in decrease in NiO reducibility [17].

Effect of TBHP/ethylbenzene molar ratio: The reaction using TBHP/ethylbenzene molar ratio = 3 yielded a little higher conversion than that using ratio of 2, however the selectivity was unchanged.

Effect of catalyst amount: Effect of catalyst amount was evaluated by conducting reactions using the Ni5Al-oxide as a catalyst (with different weights: 0.1-0.5 g) and 2.4 ml ethylbenzene, molar ratio of TBHP/ethylbenzene = 3, at 130 ºC in 12 h. The results were shown in Fig. 4. The conversion increased with the catalyst quantity: 57, 75%, 85%, 92% and 92% conversions for 0.1, 0.2, 0.3, 0.4 and 0.5 g, respectively. This is due to higher concentration of active sites available for oxidation. The selectivity to acetophenone was 98% but slightly decreased (94%) when the catalyst amount was increased beyond 0.4 g.
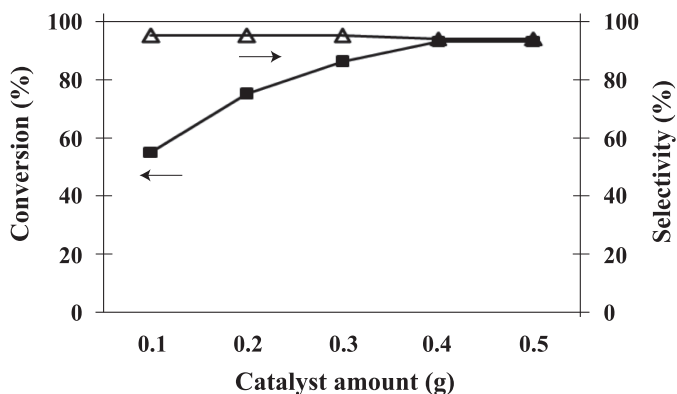

Fig. 4 Effect of catalyst amount on conversion and selectivity using Ni5Al-oxide.

3.3 Reusability of catalysts

After the reaction, the catalyst was filtered and washed with acetone and reused. It was found that the catalyst showed a slight drop in activity after the third run (from 92% to 89% conversion). This might be due to the coverage of active catalyst site on the surface or deactivation of the active catalyst. The coverage of active catalyst site was proved by calcination of the catalyst at 500 ºC for 5 h, the regenerated catalyst showed similar activity (91% conversion of ethylbenzene) as the fresh catalyst.

3.4 Reaction mechanism

When hydroquinone (as a radical scavenger) was added into the reaction, it was found that for all catalysts the conversions decreased to about half (73-77% to 34-38%). This indicates that the oxidation occurs partly via free-radical pathway. Another pathway may be via a metal-oxo intermediate which is formed from oxygen (from decomposition of TBHP) chemisorbed on the metal.

4. Conclusions

The NiCr- and NiAl-oxides can be easily synthesized from calcination of the LDHs precursors.

They showed high activities for the selective oxidation of ethylbenzene to acetophenone with TBHP as an oxidant. The NiAl-oxide catalysts (Ni4Al-oxide and Ni5Al-oxide) were shown to give higher selectivity than the Ni5Cr-oxide. Under the reaction condition of 0.4 g catalyst, TBHP/ethylbenzene molar ratio of 3, 130 °C and 12 h the Ni5Al-oxide gave 92% conversion and 98% selectivity to acetophenone. The catalyst is reusable after the reaction. The reaction mechanism partly involved free radicals formation as the addition of radical scavenger can reduce oxidation taking place to half.

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