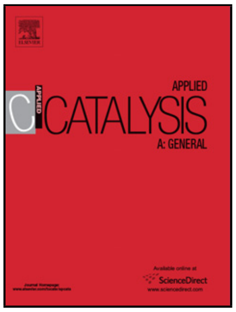

Title: Enhanced Metathesis Activity of low loading Re_2O_7/Al_2O_3 catalysts for Propylene Production by using Aluminum Nitrate as Al_2O_3 Precursor

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Enhanced Metathesis Activity of low loading Re_2O_7/Al_2O_3 catalysts for Propylene Production by using Aluminum Nitrate as Al_2O_3 Precursor

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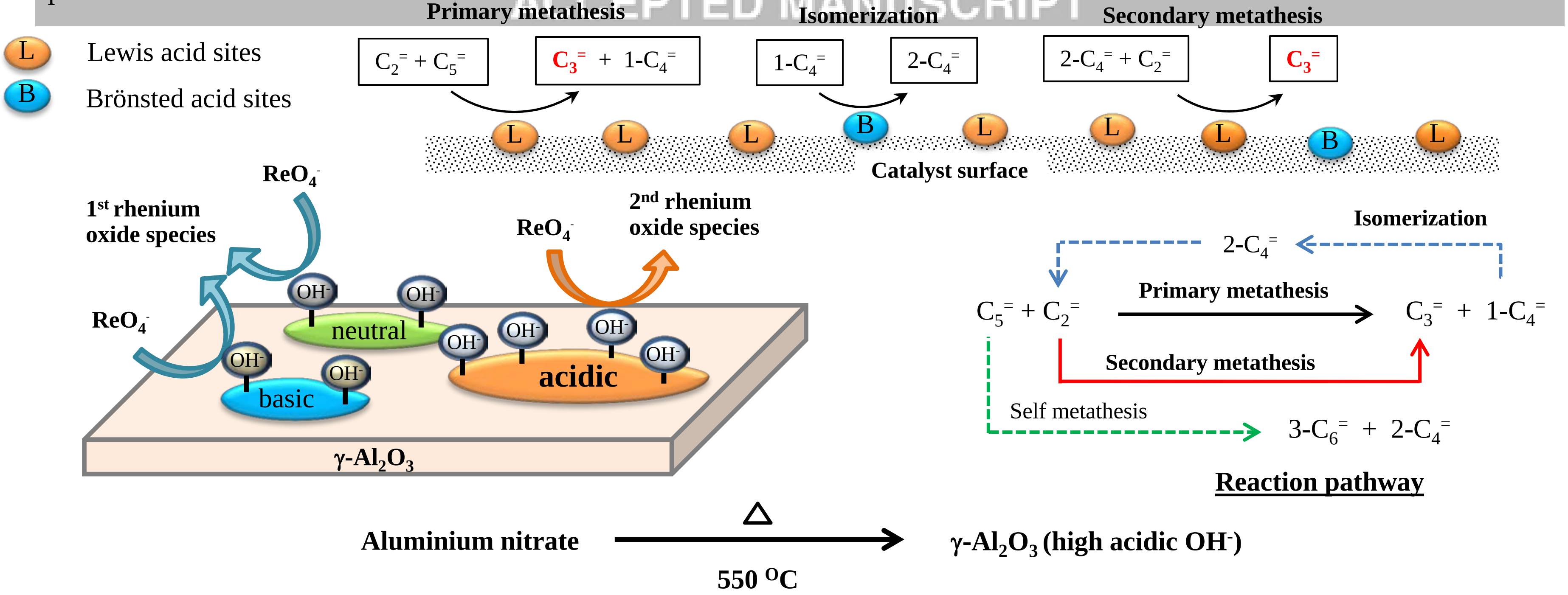
Graphical Abstract



Highlights

- Metathesis of ethylene and 2-pentene over low loading Re_2O_3/Al_2O_3 (4 wt%).
- $Al(NO)_3$ precursor calcined at 550^oC provided higher acidic -OH than the Al-com.
- The 2nd rhenium oxide active species could be formed at relatively low Re loading.
- Amount and strength of the Lewis acid sites play important role in metathesis.
- Bronsted acidity was responsible for the formation of coke and C_{5+} products.

Abstract

A series of alumina supported Re_2O_7 catalysts (4 wt% Re loading) were prepared by using aluminium nitrate (ANN) calcined at different temperatures (400, 550, and 750 ^oC) as the supports and impregnated with ammonium perrhenate solution. Despite their lower pore volume and smaller average pore size, the catalyst performances in the metathesis of ethylene and 2-pentene in terms of 2-pentene conversion and propylene selectivity of all the Re_2O_7/ANN were much improved as compared to the commercial γ-Al_2O_3 supported one (Re_2O_7/Al-com) with the Re_2O_7/ANN-550 exhibited the best performances. Based on the *in situ* Infrared spectroscopy, the *in situ* Raman spectroscopy, and the *in-situ* IR spectroscopy of chemisorbed ammonia and thermodesorption results, the use of ANN as Al_2O_3 precursors provided higher acidic OH group and higher Lewis acid sites, which were necessary for the formation of the 2nd rhenium oxide active species especially for low Re loading. The higher Bronsted acidity on the Re_2O_7/Al-com, on the other hand, produced higher amount of coke and C_{5+} products. In addition, the acid strength of the Lewis acid sites appeared to be another important factor determining metathesis activity of the supported Re_2O_7 catalysts.

Keywords: metathesis; propylene production; rhenium; aluminium nitrate; 2-pentene; Lewis acidity

1. Introduction

Propylene is one of the most important basic chemicals in petrochemical industry, which is used in the production of polypropylene, acrylonitrile, acrylic acid, acrolein, propylene oxide, glycols, plasticizer oxo alcohols, cumene, isopropyl alcohol, and acetone. The growth in propylene production is primarily driven by the industry demand for polypropylene and is expected to be about 5.7% per year in the near future [1].

The majority of propylene is produced as a byproduct of petroleum refineries and olefin plant steam crackers. Due to the possibility of a supply/demand imbalance, the catalytic, on-purpose technology for propylene production such as metathesis and propane dehydrogenation has gained more interest recently. Supported rhenium oxide-based catalyst is known to be active for olefin metathesis at low temperatures (i.e., 25 ^{o}C), whereas, molybdenum oxide- or tungsten oxide-based catalysts require much higher reaction temperatures (100-500 ^{o}C) [2-4]. The catalytic performance of $Re_2O_7/\gamma\text{-}Al_2O_3$ with low rhenium loading can be further improved by addition of the third metal oxides such as MoO_3, V_2O_5, or WO_3. The MoO_3-, V_2O_5-, or WO_3-modified low rhenium loading catalysts were reported to be active and highly selective for the metathesis of methyl oleate. Moreover, their price is lower than the $Re_2O_7/Al_2O_3\text{-}SnR_4$ catalyst for the same reaction [5]. The use of mixed supports such as silica-alumina and alumina-borate also improved the performances of Re-based catalysts in the metathesis reaction because of their high acidity and appropriate amount of Bronsted acidity compared to alumina-supported ones [6]. The alumina-borate-supported rhenium oxide catalysts were tested in both the metathesis of functionalized alkenes [7] and the metathesis of propylene [8]. The $Re_2O_7/Al_2O_3\text{-}B_2O_3$ catalysts showed high activity and selectivity than the conventional $Re_2O_7/A1_2O_3$ catalyst and was attributed to the increase in support acidity and their strong Bronsted acidity. Andreini et al. [9], treated the catalyst based on silica-alumina with hexamethyldisilazane in order to remove surface OH groups and concluded that the acid-base function of these catalysts (mainly their Bronsted acidity) is involved in the reaction. In our recent studies, a relatively high propylene yield (88%) was obtained under mild reaction conditions using the unconventional feed of ethylene and 2-pentene over SiO_2-Al_2O_3 supported Re_2O_7-based catalysts [4, 10-12]. The catalyst performances were found to be influenced by the properties of the SiO_2-Al_2O_3 supports, which were modified by the SiO_2-Al_2O_3 compositions [11] and/or the preparation methods [12]. The treating of Al_2O_3 with phosphate also resulted in more acidic surface, belonging to acidic phosphorus-bonded OH groups [13]. At low Re loadings, these supports have also reacted with the ReO_4^- ions resulting in active metathesis sites.

In the present work, the catalytic properties of Re_2O_7/γ-Al_2O_3 in the metathesis of ethylene and 2-pentene were enhanced by using aluminium nitrate supports calcined at different calcination temperatures. The catalyst performances were correlated with the formation of well-dispersed active rhenium species. The catalyst properties were further characterized by N_2 physisorption, X-ray diffraction (XRD), inductively-coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), *in situ* Infrared spectroscopy (*in situ* IR), and *in situ* Raman spectroscopy (*in situ* Raman), and *in situ* IR spectroscopy of chemisorbed ammonia and thermodesorption (*in situ* NH_3-IR)

2. Experimental

2.1 Catalyst preparation

The catalyst supports were prepared by calcination of $Al(NO_3)_3{\cdot}9H_2O$ under air at 400, 550, and 750 ^{o}C for 4 h and were denoted as ANN-400, ANN-550, and ANN-750, respectively. The supports were impregnated with an aqueous solution of ammonium perrhenate (NH_4ReO_4, Aldrich) several times to obtain the 4 wt% of rhenium loading.

Between impregnation steps the catalyst was held for 2 h at room temperature and then dried at 110 ^{o}C for 12 h. After the impregnation step, the catalyst was calcined in dry air at 550 ^{o}C for 8 h. For comparison purposes, a commercial γ-Al_2O_3 (Fluka) was also used for preparation of 4 wt% Re_2O_7/γ-Al_2O_3 catalyst. The catalyst was denoted as Re_2O_7/Al-com.

2.2 Catalyst characterization

The specific surface area, the pore volume, and the pore size of the supports and the catalysts were measured by N_2 physisorption at -196 ^{o}C using a Micromeritics ASAP 2020 automated system. The specific surface area was calculated according to Brunauer-Emmett-Teller (BET) method and the pore volume and pore size were determined from Barret-Joyner-Halenda (BJH) method. The XRD patterns were collected using a SIEMENS D5000 X-ray diffractometer with Cu K_{α} radiation and Ni filter. The scans were recorded in the 2θ range of 20-80^{o} using a step size of 0.04^{o}. The actual metal loading for each catalyst were measured by by ICP-OES on a Perkin Elmer Optima 2100DV instrument. The sample was performed by digestion with a mixture of hydrofluoric and nitric acids at 60 ^{o}C. The *in situ* IR spectra were acquired with a Thermo Nicolet 8700 FT-IR spectrometer equipped with a Harrick Praying Mantis attachment for diffuse reflectance spectroscopy. The sample was placed in a Harrick cell, which were cooled by flowing water. Then the sample was heated from room temperature to 500 ^{o}C at a heating rate 10 ^{o}C/min and holding the temperature for 1 h. After that the sample was cooled to 60 ^{o}C. The spectra were collected using a DTGS detector with a resolution of 4 cm-1 and an accumulation of 72 scans. The collection of the initial IR gas phase background was performed by placing a reflective mirror in the laser path. For *in-situ* IR spectroscopy of chemisorbed ammonia and thermodesorption, after pretreatment procedure the sample was saturated with 15% NH_3/He. After saturation, the physisorbed ammonia was desorbed in a helium gas flow about 1 h. Then the sample was heated from 60

^{o}C temperature to 500 ^{o}C at a heating rate 10 ^{o}C/min. The spectra were collected every minute. For *in-situ* Raman spectroscopy, the Raman spectra of catalysts were collected by a high resolution Raman spectrometer system (Horiba-Jobin Yvon Labram-IR) equipped with the visible laser at 532 nm. The LabSpec 5 software was used to operate the experiment and collect the Raman spectra. The laser calibration was performed with a silica slide at 520.7 cm^{-1}. The sample was loaded into the same cell used for IR measurements. The same pretreatment procedure as in the IR experiments was followed. The dehydrated Raman spectra of catalysts were collected at 60 ^{o}C. The TEM micrographs were obtained using a JEOL JEM-2100 transmission electron microscope with an accelerating voltage of 120 kV. The amount of coke was examined by the temperature programmed oxidation (TPO). The spent catalyst was in a quartz tube under the 1% O_2/He flow and heated with the heat rate of 5 ^{o}C/min until the temperature reached 900 ^{o}C, analyzed by GC-8AIT.

2.3 Reaction test

The catalyst performances were tested in the gas-phase metathesis reaction between ethylene and 2-pentene with the molar ratio of ethylene: 2-pentene 3:1, weight hourly space velocity (WHSV) 5.33 h^{-1}, and 1 g catalyst in a fixed-bed reactor (ID tube = 7.5 mm) under atmospheric pressure. In a typical run, the catalyst was pretreated at 500 ^{o}C for 1 h and then cooled down to reaction temperature at 60 ^{o}C under nitrogen flow. During the reaction, the products were analyzed by an on-line Agilent 7820A gas chromatograph equipped with a GS-Gaspro 113-4362 capillary column, 0.32 mm diameter and 60 m in length. The GC signals were processed by an EZChrom Elite integrated peak program integrator.

The conversion of the limiting reactant (2-pentene), the selectivity of products, and the yield of products were calculated by the following equations:

$$\text{2-Pentene conversion (\%)} = \frac{\text{Amount of 2-pentene in feed - amount of 2-pentene remained in product}}{\text{Amount of 2-pentene in feed}} \times 100$$

$$\text{Selectivity of component i (\%)} = \frac{\text{Amount of component i in products}}{\text{Amount of total products}} \times 100$$

$$\text{Yield of component i (\%)} = \text{2-Pentene conversion} \times \frac{\text{Amount of component i in products}}{\text{Amount of total products}}$$

3. Results and discussion

3.1 Catalyst characterization

The physical properties of the various Al_2O_3 supported Re_2O_7 catalysts are shown in **Table 1**. The surface area of the Re_2O_7/Al-com was 136 m^2/g whereas those of the Re_2O_7/ANN catalysts were ranging between 130-170 m^2/g. The pore volume and the average pore size of the Re_2O_7/Al-com were slightly higher than those of the Re_2O_7/ANN catalysts. The actual Re contents were ranged between 3.70-3.94 wt% which were closed to the expected values (4 wt%). **Figure 1** shows the XRD patterns of all the prepared catalysts. The major XRD peaks at 37^o, 39^o, 46^o, 61^o and 67^o were attribtued to the γ-phase alumina [14]. The characteristic peaks corresponding to Re_2O_7 crystals were absent on all the catalysts because of the low amount of rhenium loading and the Re_2O_7 crystals could be volatile at the calcination temperature above 300 ^oC [3, 15, 16]. However, from the ICP results, the values of actual Re loadings on all the catalysts were closed to the desired amount, suggesting that most of the Re were well dispersed on the alumina support.

The TEM images of 4Re/Al-com, 4Re/ANN-400, 4Re/ANN-550, and 4Re/ANN-750 are shown in **Fig. 2**. The rhenium oxides or rhenium metal species could not be distinguished from the alumina supports. The TEM results were consistent with the XRD results, in which the diffraction patterns corresponding to Re_2O_7 crystals were not detected. Such results suggested that non-crystalline rhenium oxide species were well dispersed on the alumina surface in the form of isolated active Re species [17].

According to previous studies [13, 18-21], the surface OH groups of alumina support consists of five different types: two types with basic characteristic, one neutral type, and two types with acidic characteristic. Normally, during the catalyst preparation, the reaction between ions and surface OH groups of support occurs and then ReO_4^- ions turn into rhenium oxide on the support. The properties of these rhenium oxides depend on the type of OH groups that they replace. At low rhenium oxide loading, ReO_4^- ions first replace the most basic OH groups, resulting in inactive sites, whereas ReO_4^- ions that replace more acidic OH groups at higher loading results in active sites for metathesis reaction.

The *in-situ* IR spectra representing the OH stretching of the dehydrated Al_2O_3 supports are shown in **Figure 2**. The IR bands at 3775 cm^{-1}, 3730 cm^{-1}, and 3690 cm^{-1} corresponded to the basic, neutral, and acidic OH groups, respectively [22]. It was found that the Al-com support showed much higher peak area at 3775 cm^{-1}, compared to the ANN supports. This indicates that most ReO_4^- ions of the Re_2O_7/Al-com probably reacted with basic OH groups and turned into inactive sites. On contrary, the IR band at 3775 cm^{-1} was not detected on the ANN-550 support. Therefore, the ReO_4^- ions of the Re_2O_7/ANN mostly replaced the acidic OH groups, forming metathesis active sites.

The influence of rhenium loading on the formation of surface rhenium oxide structures under dehydrated conditions was studied by Vuurman et al. [23]. The first species were observed at low Re loading by the *in situ* Raman spectra at 1002, 970, 879 and 340 cm^{-1}, which were assigned to ν_s(Re=O), ν_{as}(Re=O), ν_s(Re−O−Al), and δ(O−Re−O), respectively. The second species were observed at high Re loading at 1012, 976, 890 and 340 cm^{-1} Raman bands, which were specified to ν_s(Re=O), ν_{as}(Re=O), ν_s(Re−O−Al), and δ(O−Re−O), respectively [23, 24]. At low rhenium loading the catalytic performace was extremely low due to the presence of the first species. When Re_2O_7 loading was increased to about 6 wt%, the second species were formed and as a consequence, the catalytic performaces increased [20].

The *in situ* Raman spectra of the different alumina supported Re_2O_7 catalysts under dehydrated condition at 60 °C are shown in **Figure 3**. The Re_2O_7/Al-com showed the Raman bands at 1001, 967, 882 and 339 cm^{-1}, which were attributed to the first surface rhenium oxide species whereas all the Re_2O_7/ANN exhibited the Raman bands at 1009, 976, 890 and 338 cm^{-1}, which were attribtued to the second surface rhenium oxide species.

Based on the *in situ* IR and the *in situ* Raman data under dehydrated conditions at 60 ^{o}C results, it is revealed that the rhenium oxides on the Al-com support were the first surface rhenium oxide species,which were formed by the reaction of ReO_4^- ions and basic OH group, while the rhenium oxide on ANN support was a result of the reaction of ReO_4^- ions with more acidic OH group forming the second surface rhenium oxide species. It should be noted that the active rhenium oxide species can be formed on the ANN supports at relatively low Re loading (4% Re metal) compared to those reported in the literature [23].

The Lewis/Bronsted nature of surface acidity of all the catalysts was further investigated by the *in situ* IR spectroscopy of ammonia adsorption. The *in-situ* IR substracted spectra of the chemisorbed ammonia over the catalysts are shown in **Figure 4**. The presence of Lewis acid sites was confirmed by the bands at 1621 and 1280 cm^{-1} whereas the Bronsted acid sites were detected by the IR bands at 1682 and 1460 cm^{-1} [25]. The amount of Lewis/Bronsted acidity, which were calculated from the integrated peak areas, are given in **Table 1**. It appears that Lewis acidity on the Re_2O_7/ANN catalysts were much higher than those on the Re_2O_7/Al-com. Moreover, the Bronsted acidity of the Re_2O_7/ANN catalysts was lower than the Re_2O_7/Al-com. The strength of Lewis/Bronsted acidity was also considered by the *in-situ* IR spectroscopy and ammonia thermodesorption. The *in-situ* IR spectra of chemisorbed ammonia results over the Re_2O_7/ANN catalysts at 250 ^oC are shown in **Figure 5**. The peaks at 1621, 1460 and 1280 cm^{-1} were observed on the Re_2O_7/ANN-400 and Re_2O_7/ANN-750 catalysts whereas there was no signal for the Re_2O_7/ANN-550 catalyst. Such results suggest that the Lewis and Bronsted acidity of the Re_2O_7/ANN-550 catalyst was weaker than those on the Re_2O_7/ANN-400 and Re_2O_7/ANN-750 catalysts.

3.2 Reaction results

The metathesis activity of the different alumina-supported Re_2O_7 catalysts was evaluated in the gas-phase metathesis of ethylene and 2-pentene at 60 °C. **Figure 6** shows the conversion of 2-pentene as a function of time-on-stream during the 11 h reaction time. The 2-pentene conversion of the Re_2O_7/ANN was much higher than the Re_2O_7/Al-com with the Re_2O_7/ANN-550 showed the highest yield of propylene. The metathesis activity results corresponded well with the *in situ* IR and the *in situ* Raman results that the ANN supported Re_2O_7 catalysts contained higher amount of the more active second surface rhenium oxide species, which were formed in the presence of more acidic OH groups.

The metathesis of 2-pentene and ethylene produces propylene and 1-butene as by products. In this study, excess ethylene in the feed was used because it has been found that 1-butene product from the metathesis of 2-pentene and ethylene can isomerize to 2-butenes and react with excess ethylene, resulting in more propylene formation [4]. **Figure 7** shows the product distribution at 1 and 11 h reaction time while the product distribution of the prepared catalysts as a function of reaction time is also shown in **Figure 8**. It can be seen that the propylene yield obtained over the Re_2O_7/ANN exceeded the theoretical stoichiometric value (43 wt% based on the complete conversion of 2-pentene) whereas the propylene yield of the Re_2O_7/Al-com catalyst remained close to its stoichiometric values. In addition, the 1-butene yield decreased with increasing 2-butene yield, suggesting that 1-butene isomerized to 2-

butenes and reacted with excess ethylene to produce additional propylene. From the *in-situ* IR of chemisorbed ammonia results, the Re_2O_7/ANN catalysts contained much higher Lewis acidity than the Re_2O_7/Al-com. It is suggested that Lewis acidity plays an important role in metathesis activity. Such results were in good agreement with Schekler-Nahama et al., in which Lewis acidity was reported to be the key for the metathesis reaction [25]. Comparing the streght of acidity among the Re_2O_7/ANN catalysts, the weaker acidity of the Re_2O_7/ANN-550 seemed to be appropriate for the reaction so that it exhibited the best catalytic performance.

The amount of coke deposited on the spent catalysts after the metathesis reaction of ethylene and 2-pentene at 60 °C for 11 h was determined by TPO and the results are shown in **Figure 9**. The TPO profiles of the Al-com and ANN supported rhenium catalysts after being used in the reaction as a function of CO_2 formation are displayed in **Figure 10**. The areas under the TPO profiles were directly correlated with the amount of coke deposit. It is demonstrated that the total amounts of coke deposit increased in the order: Re_2O_7/ANN-550 < Re_2O_7/ANN-750 < Re_2O_7/ANN-400 < Re_2O_7/Al-com. From the metathesis reaction and coke formation results, it can be further suggested that the presence of Bronsted acidity on the Re_2O_7/Al-com facilitated oligomerisation and/or polymerisation side-reactions [25]. The yield of C_{5+} and coke formation over the Re_2O_7/Al-com was higher than on the Re_2O_7/ANN. In addition, the two main peaks of coke burning in the TPO profiles (Figure 10) can be assigned to coke deposited on different locations. The low temperature peak was attributed to the oxidation of coke deposited on the metal species whereas the higher temperature peak corresponded to coke deposited on acid sites of the support, mostly Bronsted acid sites [26]. It was found that the Re_2O_7/Al-com contained higher amount of coke deposited on the acid sites of the alumina support than the Re_2O_7/ANN catalysts. For all the Re_2O_7/ANN catalysts, it appears that the major of coke deposit was on the metal species, leading to blocking of the active sites. Therefore, the Re/Al-com was found to be more stable compared to the ANN-supported ones.

4. Conclusions

The catalytic activity in the metathesis of ethylene and 2-pentene over Re_2O_7/Al_2O_3 catalysts was significantly enhanced by using aluminium nitrate calcined at 550 °C as the support. The catalyst performances were correlated well with the presence of the 2nd surface rhenium oxide species. As revealed by the *in situ* IR, the *in situ* Raman, and the *in-situ* IR spectroscopy of chemisorbed ammonia and thermodesorption results, the use of aluminium nitrate as the Al_2O_3 precursor provided acidic OH group rather than basic OH and higher Lewis acidity, compared to the commercial γ-Al_2O_3, which were important for the formation of active rhenium oxide species. Among the various Re_2O_7/ANN catalysts, the Re_2O_7/ANN-550 showed the best catalyst performances in terms of 2-pentene conversion and selectivity to propylene. On the other hand, the higher Bronsted acidity observed on the Re_2O_7/Al-com was responsible for higher coke formation and C_{5+} selectivity.

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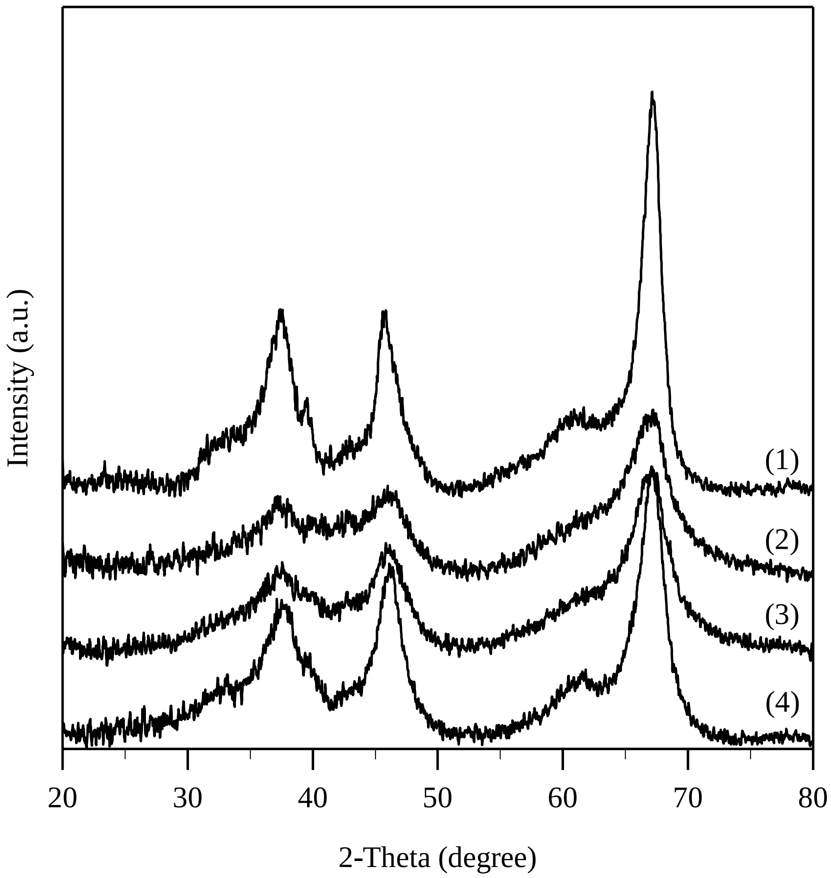
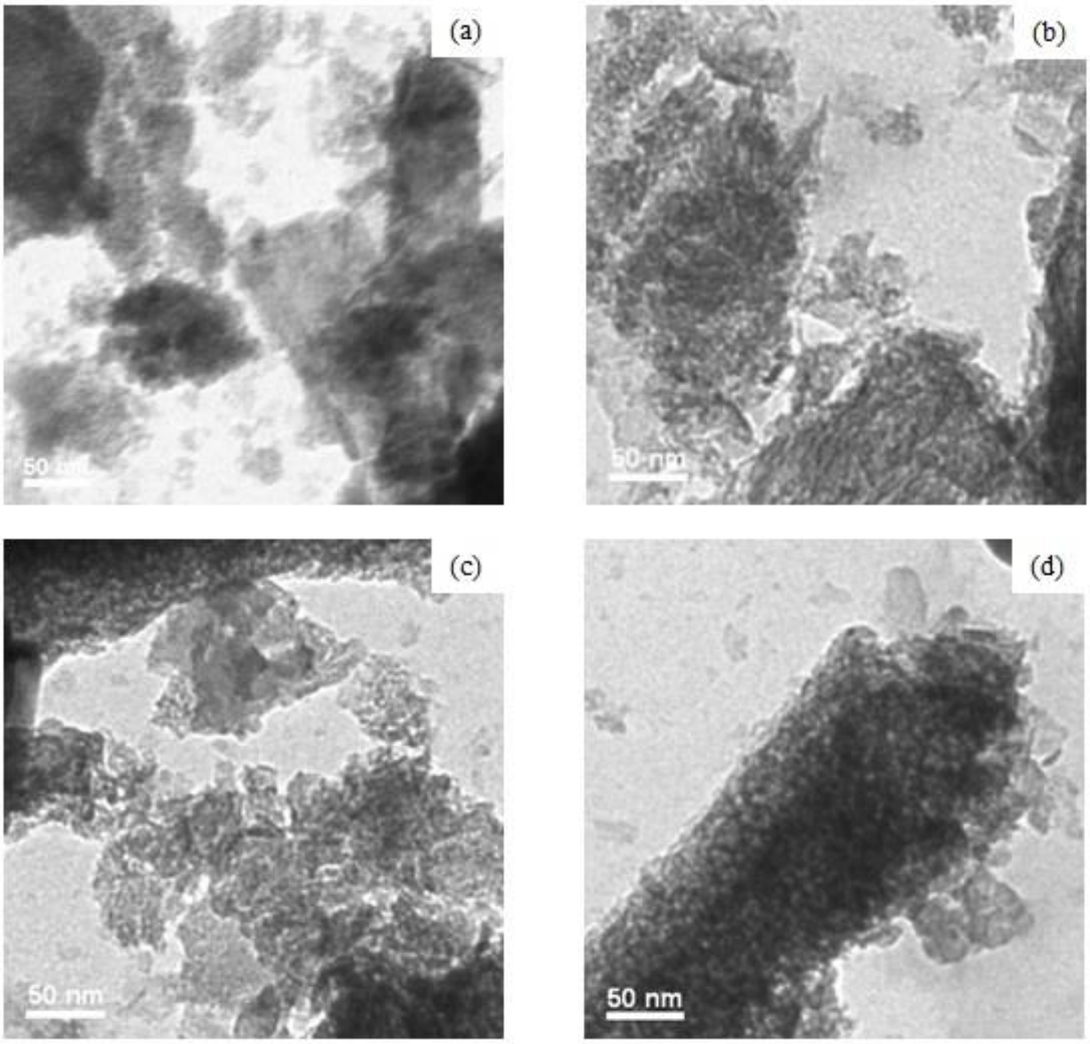


Figure 1 XRD patterns of the prepared catalysts: (1) 4Re/Al-com, (2) 4Re/ANN-400, (3) 4Re/ANN-550 and (4) 4Re/ANN-750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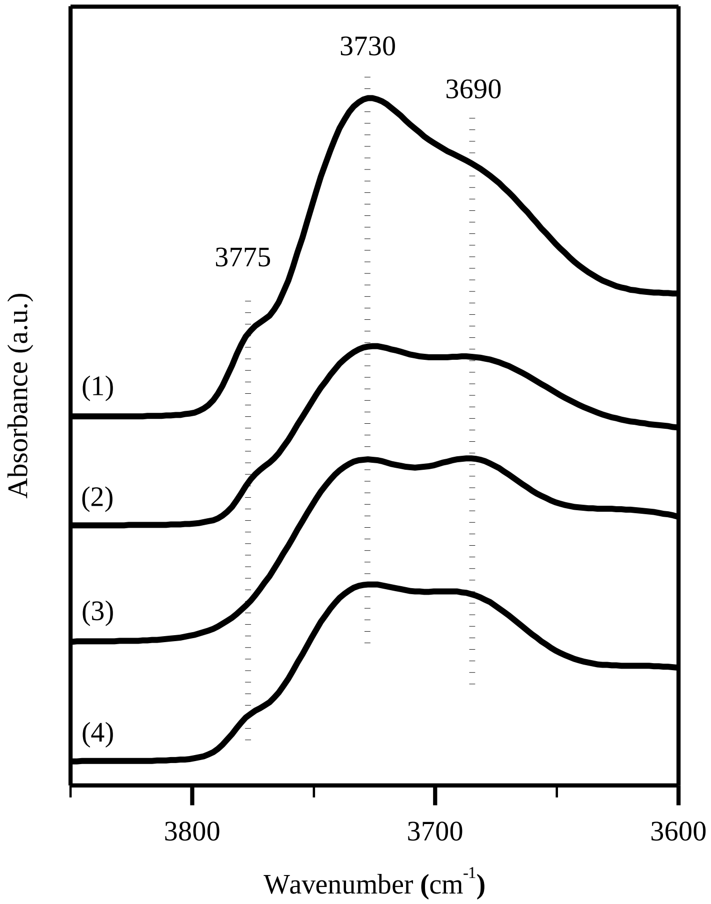

Figure 2 In situ IR spectra in the OH stretching region of supports under dehydrated condition at 60°C: (1) Al-com, (2) ANN-400, (3) ANN-550 and (4) ANN-750

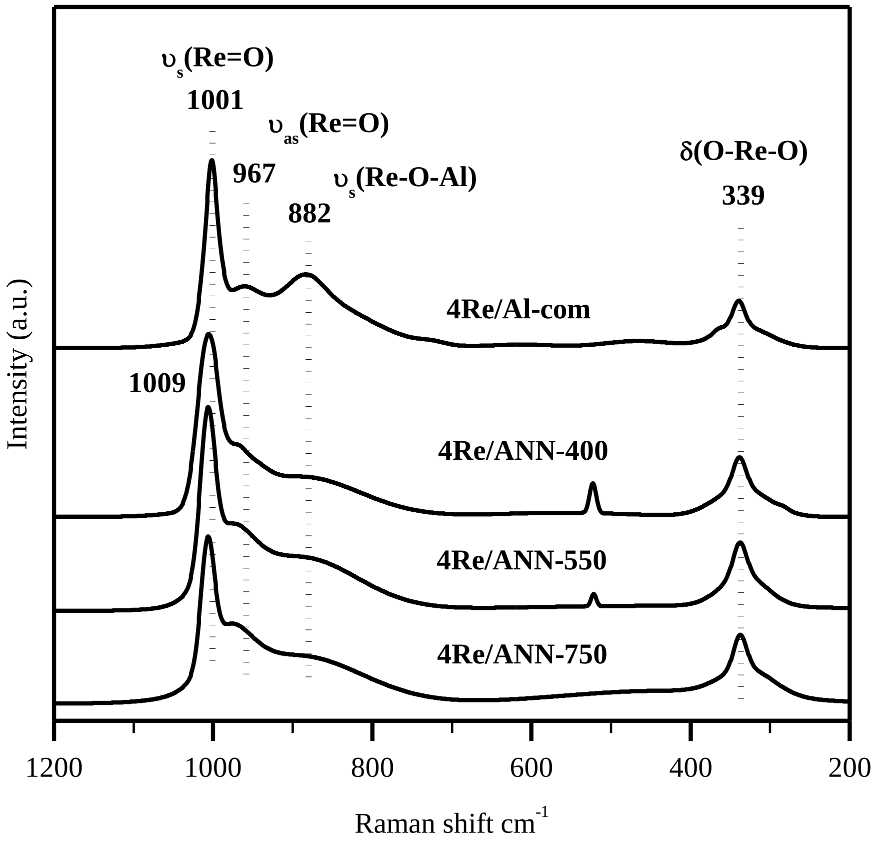

Figure 3 In situ Raman spectra of catalysts under dehydrated condition at 60 °C

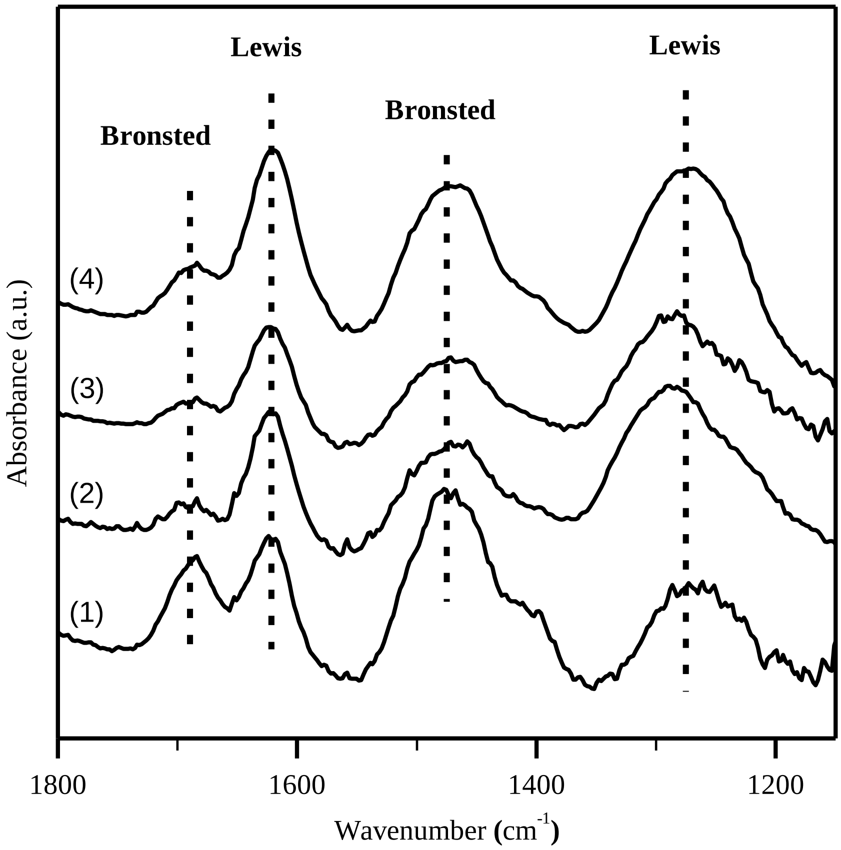

Figure 4 In situ IR substracted spectra of chemisorbed ammonia over the catalysts at 60 ^{o}C: (1) 4Re/Al-com, (2) 4Re/ANN-400, (3) 4Re/ANN-550 and (4) 4Re/ANN-750

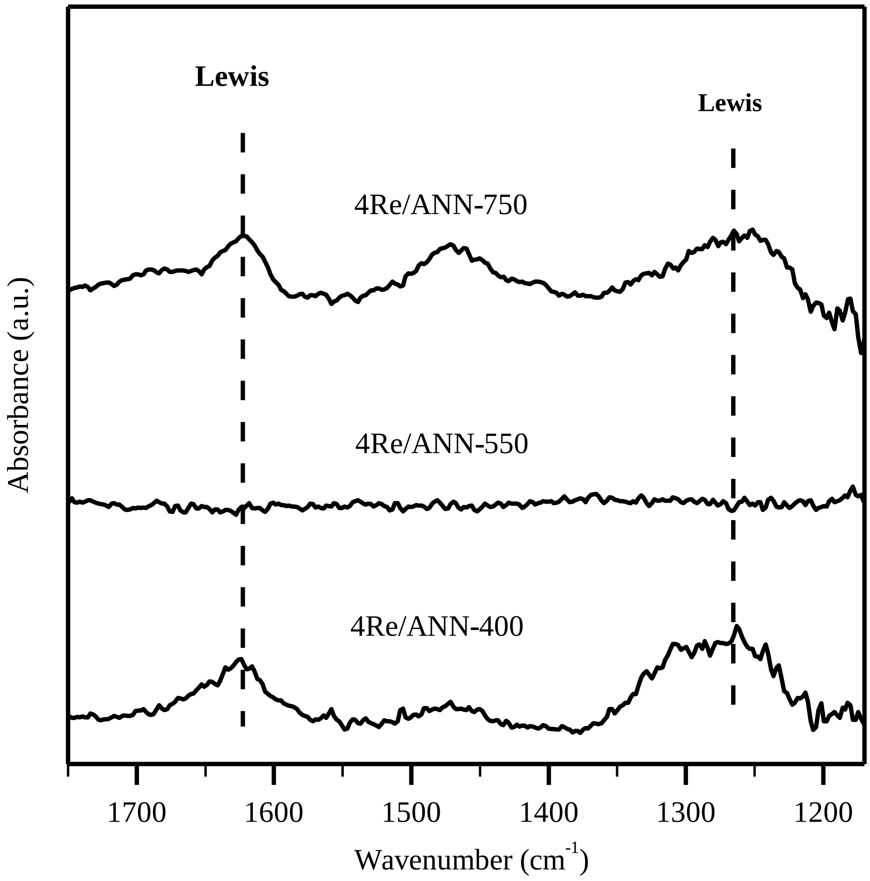

Figure 5 In situ IR substracted spectra of chemisorbed ammonia over the catalysts at 250 °C

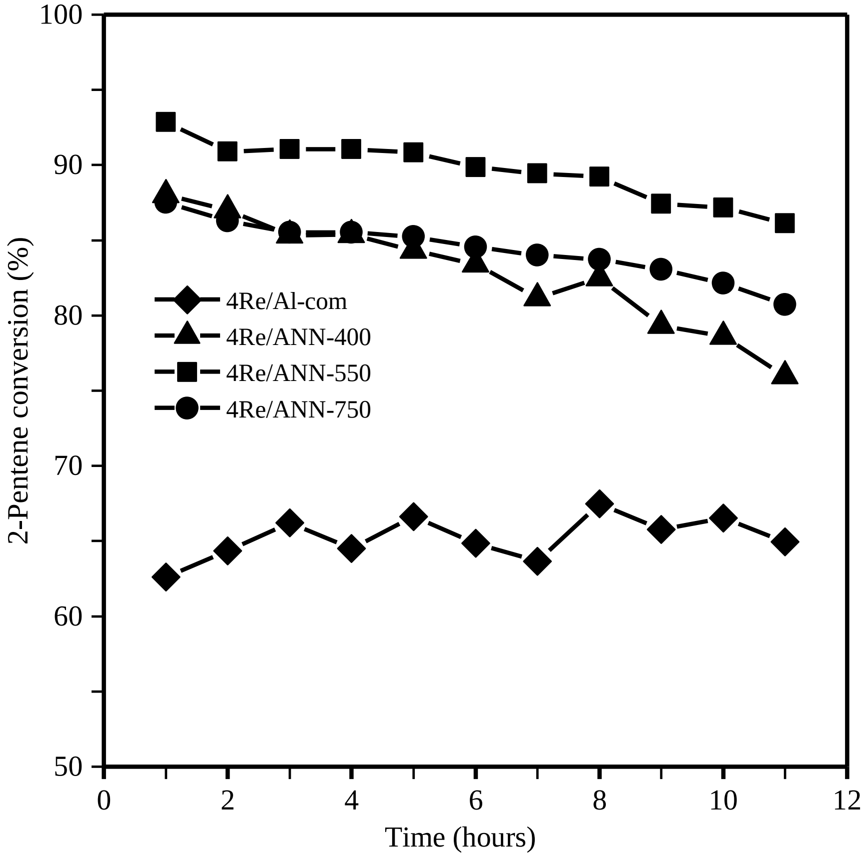

Figure 6 The 2-pentene conversion of the prepared catalysts over the metathesis reaction as a function of reaction time

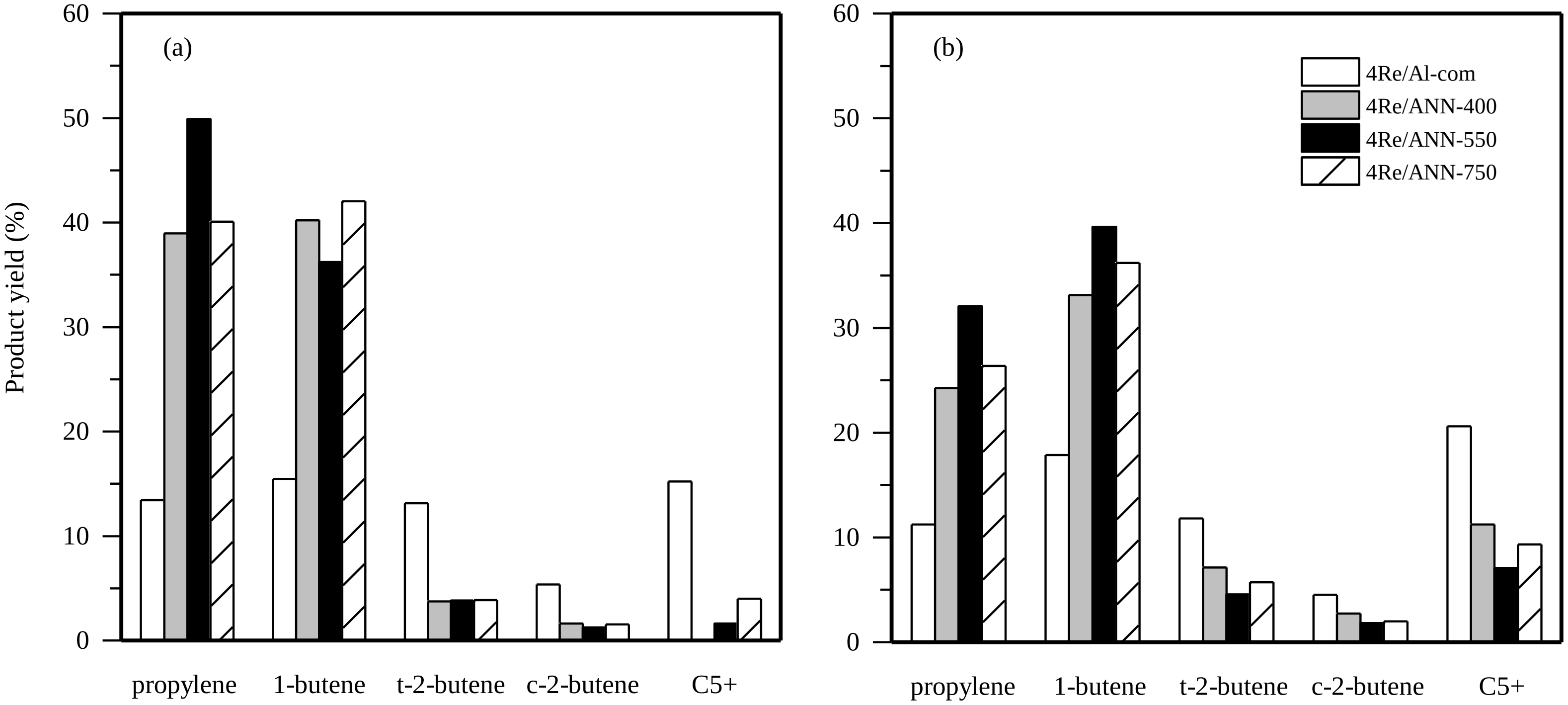

Figure 7 Product distributions of different catalysts at (a) 1 h and (b) 11 h reaction time

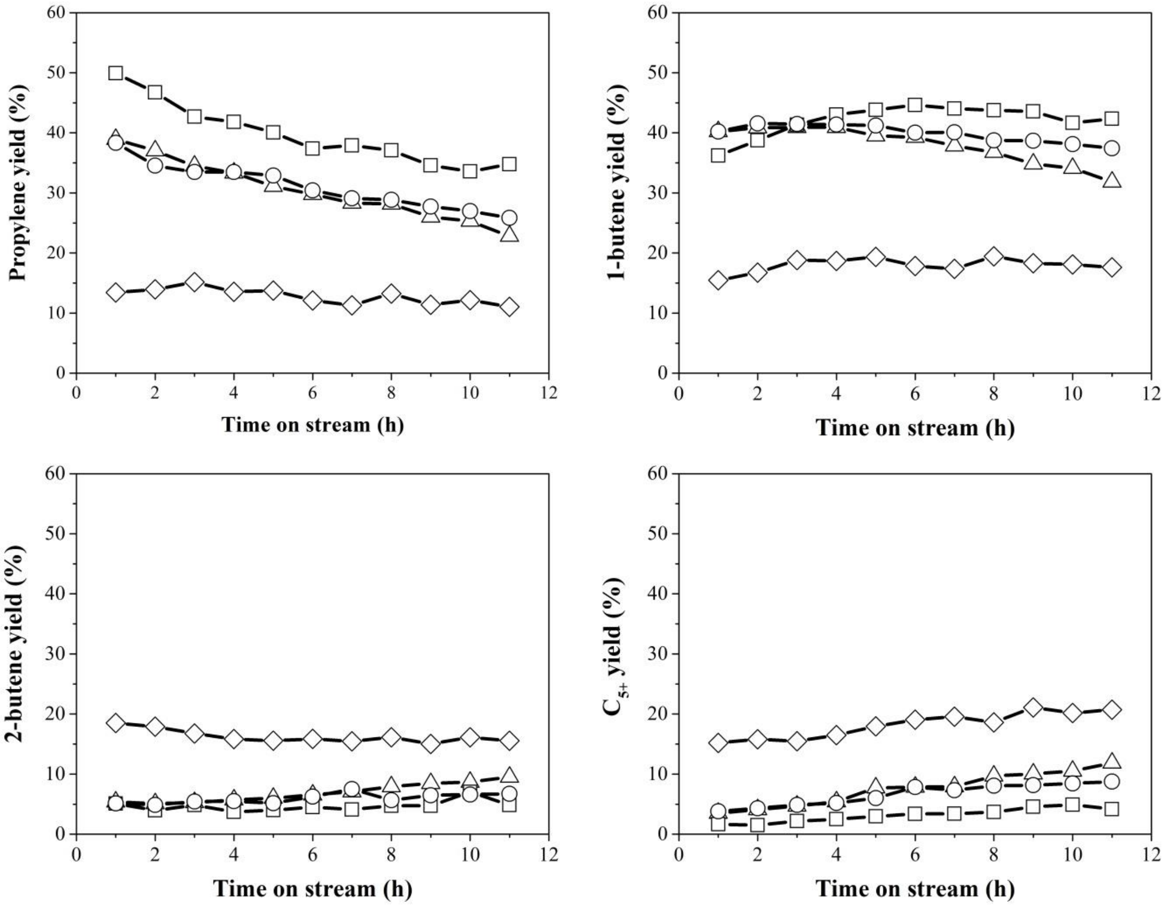

Figure 8 The product distribution of the prepared catalysts over the metathesis reaction as a function of reaction time ◊: 4Re/Al-com, Δ: 4Re/ANN-400, □: 4Re/ANN-550, ○: 4Re/ANN-750

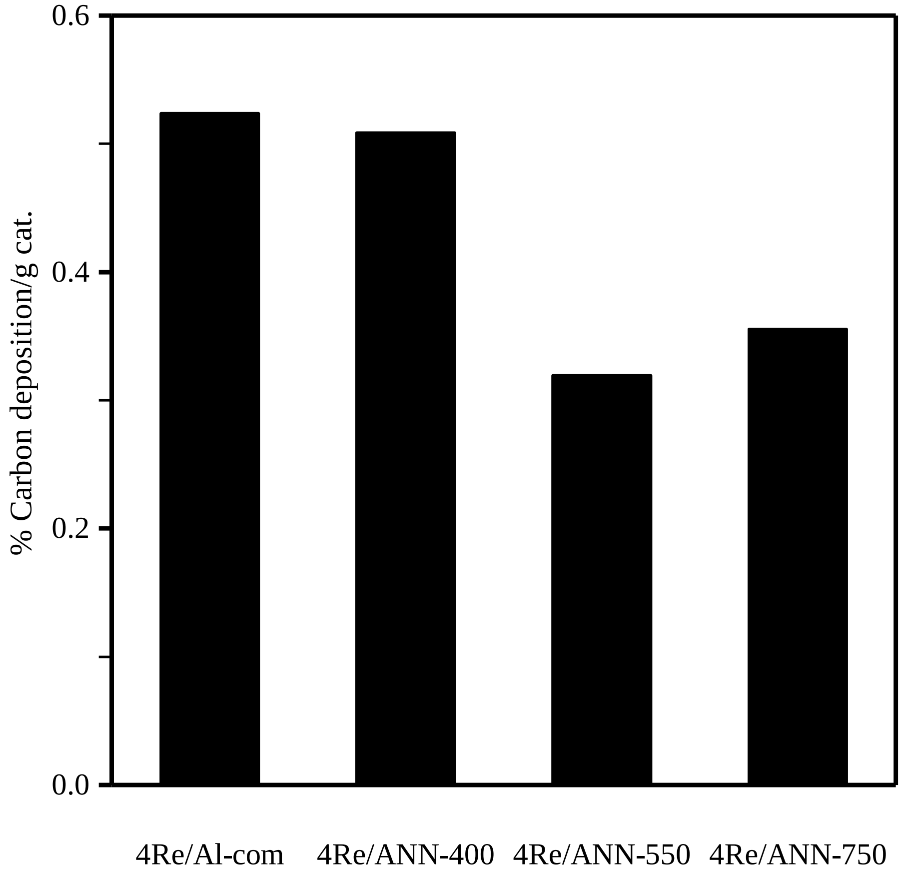

Figure 9 The amount of coke deposit on the spent catalysts

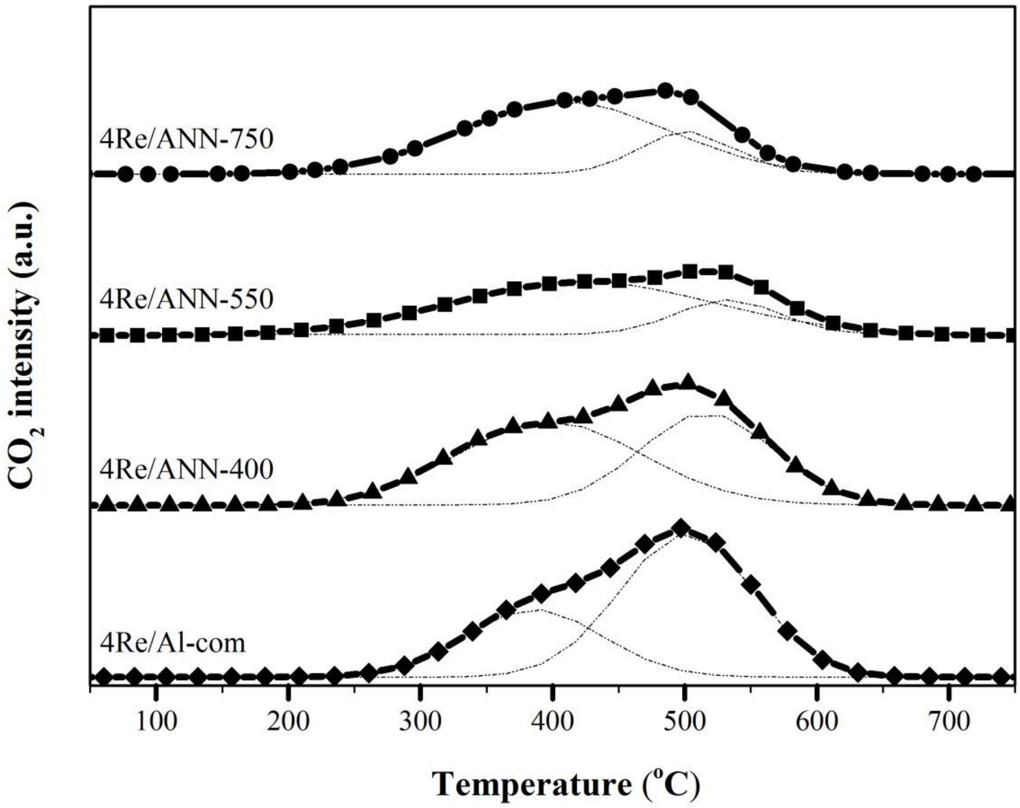

Figure 10 Temperature programmed oxidation (TPO) patterns of the spent catalysts

Table 1 The physicochemical properties of the supported rhenium oxide catalysts

Support	Actual Re-metal loading[a] (wt% Re)	Surface Area (m^2/g)	Pore volume (cm^3/g)	Avg. Pore size (nm)	Normalized amount of	
					Brönsted acid[b] (μmol/m^2)	**Lewis acid[b] (μmol/m^2)**
4Re/Al-com	3.94	136	0.22	4.35	21.52	8.00
4Re/ANN-400	3.94	150	0.18	3.51	10.97	22.18
4Re/ANN-550	3.73	130	0.15	3.50	11.42	21.07
4Re/ANN-750	3.70	170	0.17	3.35	12.20	17.83

[a] Based on the ICP-OES results.

[b] Based on the *in-situ* IR spectroscopy of chemisorbed ammonia results.