

A Novel Method for Preparation of Alumina-Supported Rhenium-Cesium Catalyst, Re-Cs/ γ -Al₂O₃

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ABSTRACT: Alumina-supported Cs₃[Re(C₂O₄)₃] precursor has been synthesized for preparation of Re-Cs/ γ -Al₂O₃ catalyst. Cs₃[Re(C₂O₄)₃] has been prepared from the reaction of ReCl₃ with H₂C₂O₄.2H₂O and CsCl in water. The complex has been characterized by elemental analysis and various spectroscopy techniques such as FT-IR, UV-Vis and ¹³C-NMR. The complex was supported on γ -Al₂O₃ by column chromatography. Cs₃[Re(C₂O₄)₃]/Al₂O₃ was calcined at 600 °C for 6 h. Characterization of both precursor and calcined catalyst were carried out using XRD, BET specific surface area and thermal analysis methods (TGA/DSC).

KEY WORDS: Alumina, BET, Rhenium catalyst, XRD, Precursor, Thermal analysis.

INTRODUCTION

Rhenium has not been studied extensively for any kind of catalytic reaction, since this element was not discovered until 1925 and was not readily available until many years later. Another problem was that the crustal abundance of this element is very low. However, rhenium-containing catalysts have received much attention over the last three decades due to their use for hydrocarbon transformation and cracking [1-4], selective reduction of NO_x to N₂ [5], hydrodesulfurization and hydrodenitrogenation of heavy crude oil [6,7], metathesis

of alkene [8], selective hydrogenation [9], selective dehydroaromatization of methane and ethane to benzene [10, 11], selective catalytic oxidation of methanol and ethanol [12], and for ammonia synthesis [13-16]. It was discovered that H-ZSM-5 supported [ReO₄] catalyst is active in the selective oxidation of benzene to phenol [17]. Recently, it was found that rhenium oxide supported on organized mesoporous alumina exhibits excellent activity and selectivity in metathesis of higher α -olefins at room temperature without the presence of a cocatalyst

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[18-20]. Whereas characterization of the supported Re catalysts was the subject of several detailed studies [21-25] little information can be found in the literature on the new methods for preparation of γ -alumina-supported rhenium-containing catalysts with or without promoters. The aim of this work is to report a novel method for preparation of alumina-supported rhenium-cesium catalyst, Re-Cs/ γ -Al₂O₃.

EXPERIMENTAL

Materials

All of the chemicals and solvents were reagent grade and used without further purification. Oxalic acid dihydrate, γ -Al₂O₃ (activated, acidic, Brockmann I), CsCl and ReCl₃ were purchased from Aldrich.

Preparation of Cs₃/Re(C₂O₄)₃

A mixture of ReCl₃ (1g, 3.42 mmol) and H₂C₂O₄.2H₂O (1.94 g, 15.38 mmol) dissolved in water (100 cm³) was stirred at room temperature for 24 h. To the reaction mixture was then added CsCl (1.72 g, 10.25 mmol). The solution was evaporated to dryness by rotary evaporator. The dark brown powder, Cs₃[Re(C₂O₄)₃], was collected, washed twice with cold water, ethanol, and ether, and then vacuum dried. Yield 86 %. ¹³C-NMR (DMSO-d₆, 500 MHz, δ): 160.88 ppm; FT-IR (cm⁻¹, KBr pellet): 1686 (strong band, C=O); Anal. Calc. for Cs₃[Re(C₂O₄)₃] (FW=849): C, 8.49 %. Found: C, 8.60 %.

Preparation of Cs₃/Re(C₂O₄)₃/Al₂O₃ precursor

Cs₃[Re(C₂O₄)₃] (2 g, 2.36 mmol) was dissolved in 20 cm³ DMF and injected into a 10 cm \times 0.4 cm column containing 40 g grade I γ -alumina (Brockmann I, acidic, 150 mesh). Elution with toluene yielded a dark green band containing alumina-supported complex, Cs₃[Re(C₂O₄)₃]/Al₂O₃, along the column. Cs₃[Re(C₂O₄)₃]/Al₂O₃ was dried in air at room temperature for 72 h.

Preparation of alumina-supported rhenium-cesium catalyst, Re-Cs/ γ -Al₂O₃

The Cs₃[Re(C₂O₄)₃]/Al₂O₃ precursor was heated up to 600 °C in static air in the electric furnace and kept at this temperature for 4 h. The grey powder, Re-Cs/ γ -Al₂O₃, was formed and kept in desicator.

Catalyst Characterization

X-Ray Diffraction (XRD)

Powder XRD measurements were performed using D8 Advance diffractometer made by Bruker Company in Germany. Scans were taken with a 2θ step size of 0.02 and a counting time of 1.0 s using Cu K_α radiation source generated at 40 KV and 30 mA. Specimens for XRD were prepared by compaction into a glass-backed aluminum sample holder. Data were collected over a 2θ range from 4° to 70° and phases were identified by matching experimental patterns to entries in the Diffract ^{plus} version 6.0 indexing software.

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The weight changes of catalyst precursors were measured using a TGA/DSC simultaneous thermal analyzer apparatus of Rheometric Scientific Company (STA 1500+ Model) under a flow of dry air. The temperature was raised from room temperature to 600 °C using a linear programmer at a heating rate of 10 °C per min. The samples weights were between 15 and 20 mg.

Scanning Electron Microscopy (SEM)

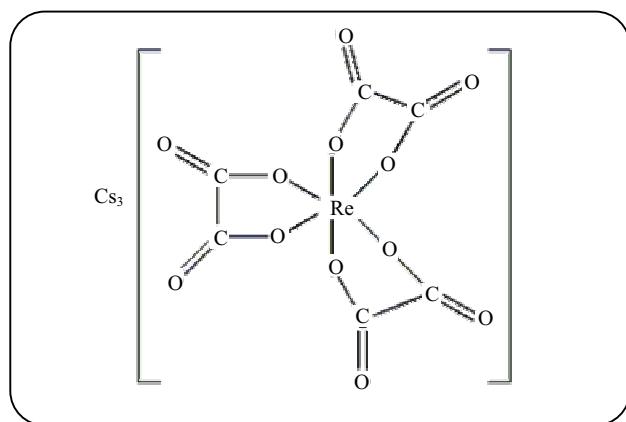
The morphology of catalyst and its precursor was observed by means of a Philips XL30 scanning electron microscopy.

Brunauer-Emmett-Teller (BET) surface area measurements

Brunauer-Emmett-Teller surface area (BET) measurements were conducted using micrometrics adsorption equipment (Quantachrome Instrument, Model Nova 2000, USA) determining nitrogen (99.99 % purity) as the analysis gas and the catalyst samples were slowly heated to 300 °C for 3 h under nitrogen atmosphere. The BET specific surface area measurements of different precursors and catalysts were evacuated at -196 °C for 66 min.

X-ray Fluorescence (XRF)

The X-ray fluorescence analysis of both precursor and calcined catalyst was determined using a Philips PW2404 spectrometer.



Scheme 1.

FT-IR, ^{13}C -NMR, UV-Vis, and Elemental analysis

Elemental analysis was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra ($4000\text{-}400\text{ cm}^{-1}$) were measured on a FT-IR JASCO 460 spectrophotometer with KBr pellets. UV-Vis spectroscopy was performed on a JASCO 7850 spectrophotometer. The ^{13}C -NMR spectrum was recorded on a Bruker DRX-500 MHz, Avance spectrometer at ambient temperature.

RESULTS AND DISCUSSION

The Re(III) complex, $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ (Scheme 1), was synthesized in good yield from the reaction of ReCl_3 and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the presence of CsCl at room temperature in water. The oxalate ion is a bidentate, chelate ligand that can form complex with Re(III) ion. The complex appeared stability in solution for days at a time and no evidence of decomposition was seen in the solid state. The elemental analysis of the complex is entirely consistent with its formulation as is the following spectroscopic characterization. The ^{13}C -NMR of $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ was recorded at ambient temperature in DMSO-d_6 . The three oxalato ligands in the complex have similar magnetically environment and show one chemical shift at 160.88 ppm (Fig. 1).

The cesium salt of the complex, $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$, was readily adsorbed on $\gamma\text{-Al}_2\text{O}_3$ by column chromatography. The $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]/\text{Al}_2\text{O}_3$ precursor was calcined in air at $600\text{ }^\circ\text{C}$ for 4 h. The rhenium content of the catalyst was measured by XRF and it appears that all rhenium remains on the surface of the catalyst after calcinations at $600\text{ }^\circ\text{C}$. This temperature is below volatilization temperature of bulk rhenium oxide.

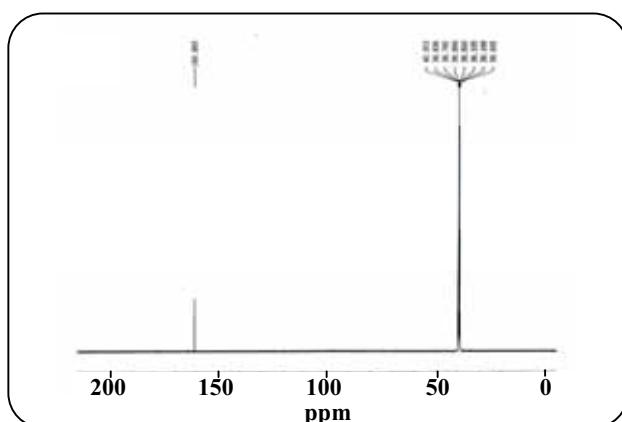


Fig. 1: The ^{13}C -NMR spectrum of $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ in DMSO-d_6

Cesium chloride was used as a Cs precursor and it was introduced to the anionic complex, $[\text{Re}(\text{C}_2\text{O}_4)_3]^{3-}$, by the precipitation method with an aqueous solution of this compound. Cesium is an alkali promoter for some rhenium-containing catalysts [13]. For example, in the ammonia synthesis process, it is known that alkali addition promotes the catalytic activity. This effect is also drastic for ruthenium catalysts [26-28]. Kojima and co-workers reported that cesium as an alkali promoter is usually the most effective promoter among the elements in the first group of the periodic table for rhenium catalysts [13]. Alkali promoters are also added to many transition metal catalysts, although the electronic effect is less important than the surface structural effect [13, 29].

The FT-IR spectrum of the complex, $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$, shows a strong band at 1686 cm^{-1} that is assigned to $\nu(\text{C=O})$ of the oxalato ligands (Fig. 2A) [30]. The absorption bands corresponding to the vibrations C-C, O-C and O-C-O (bending) are also related to the oxalate ligands [30]. The calcined catalyst was also characterized by FT-IR and due to thermal decomposition of oxalate ligands, no vibration band for C=O stretching is seen (Fig. 2B). The electronic spectrum of the complex in DMF shows only one intense band at 270 nm for LMCT transition [31].

The phase analysis of precursor and calcined catalyst were done by XRD technique. The XRD patterns of both precursor and calcined catalyst showed crystalline phases (Fig. 3). Comparing the precursor and calcined catalysts phases, indicated that new phases containing Al_2O_3 (cubic), ReO_2 (monoclinic) and $\text{Cs}_2\text{Al}_2\text{O}_4/\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3$ (cubic) in the calcined catalyst were created.

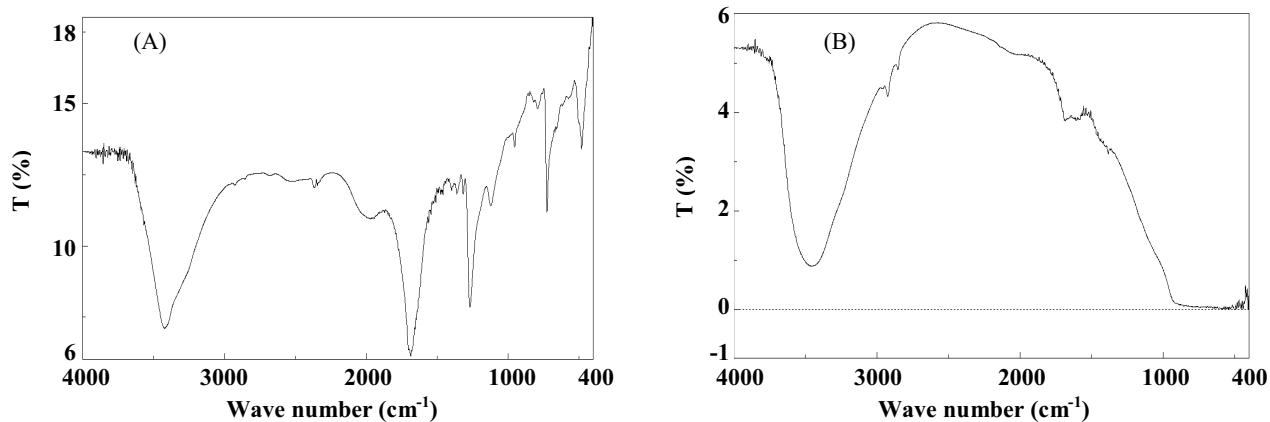


Fig. 2: The FT-IR spectra of A) $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ and B) calcined catalyst.

The precursor, $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]/\text{Al}_2\text{O}_3$, was also characterized by TGA, to indicate decomposition of $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ complex (Fig. 4). The thermal gravimetric curve of the precursor seems to indicate two-stages of mass loss, which is considered to be due to removal of physisorbed water on the surface of the precursor (40–110 °C). The second mass loss is due to thermal decomposition of oxalato complex. Thermal decomposition of oxalate complexes are typical model reactions accompanied by the migration of anionic ligands over the lattice. Boldyrev proposed a classification for oxalate thermal decompositions according to which all oxalate salts and complexes can be divided into three groups [32]. The first group comprises the thermal decomposition of oxalates of alkaline and alkaline earth metals. They usually decompose to form a carbonate and carbon oxide. The second group includes the thermal decomposition of the oxalates giving rise to metal as the solid product and carbon dioxide as the gaseous product. Finally, the third group incorporates the thermal decomposition of the oxalates that decompose forming metal oxide as a solid phase and a mixture of carbon monoxide and carbon dioxide as gaseous products:



In the presence work, the XRD pattern of calcined catalyst showed rhenium (IV) oxide (ReO_2) and the large scale decomposition of oxalate complex, $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ released a mixture of carbon dioxide and carbon monoxide. The released CO_2 can trap by alkaline solutions. The presence of CO_2 in the gaseous product of decomposition of $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ can be detected by milk of lime. It turns milky if carbon dioxide is

passed through, due to precipitation of calcium carbonate. The strong band at 2142 cm^{-1} in the FT-IR spectrum of the gaseous products of thermal decomposition of $\text{Cs}_3[\text{Re}(\text{C}_2\text{O}_4)_3]$ is assigned to $\nu(\text{C}\equiv\text{O})$ of free carbon monoxide [30]. After 420 °C, no observable mass loss in this precursor means that all of the compositions of the catalyst converted to the stable oxides forms. DSC was performed in order to provide further evidence for the presence of the various species and evaluate their thermal behavior.

The DSC curve of this precursor (Fig. 4) exhibits a endothermic peak between 40–110 °C attributed to the removal of the physically adsorbed water and one exothermic peak around 280–360 °C that is due to the burning of the sample.

Characterization of both precursor and calcined catalyst was also carried out using scanning electron microscopy (SEM). All the electron micrographs were obtained from powder specimens of these materials. SEM observations (Fig. 5) have shown differences in morphology of both precursor and calcined catalyst. The electron micrograph obtained from catalyst precursor (Fig. 5A) depicts several agglomerations of crystalline particles. This is in agreement with XRD pattern which showed the crystalline phase.

The morphological features of calcined catalyst (Fig. 5B) are quite different with the precursor and show that the agglomerate size is greatly increased in compared to the precursor sample described above.

The BET specific surface area measurements for both precursor and calcined catalyst were carried out and the precursor showed a higher surface area (174.77 m^2/g)

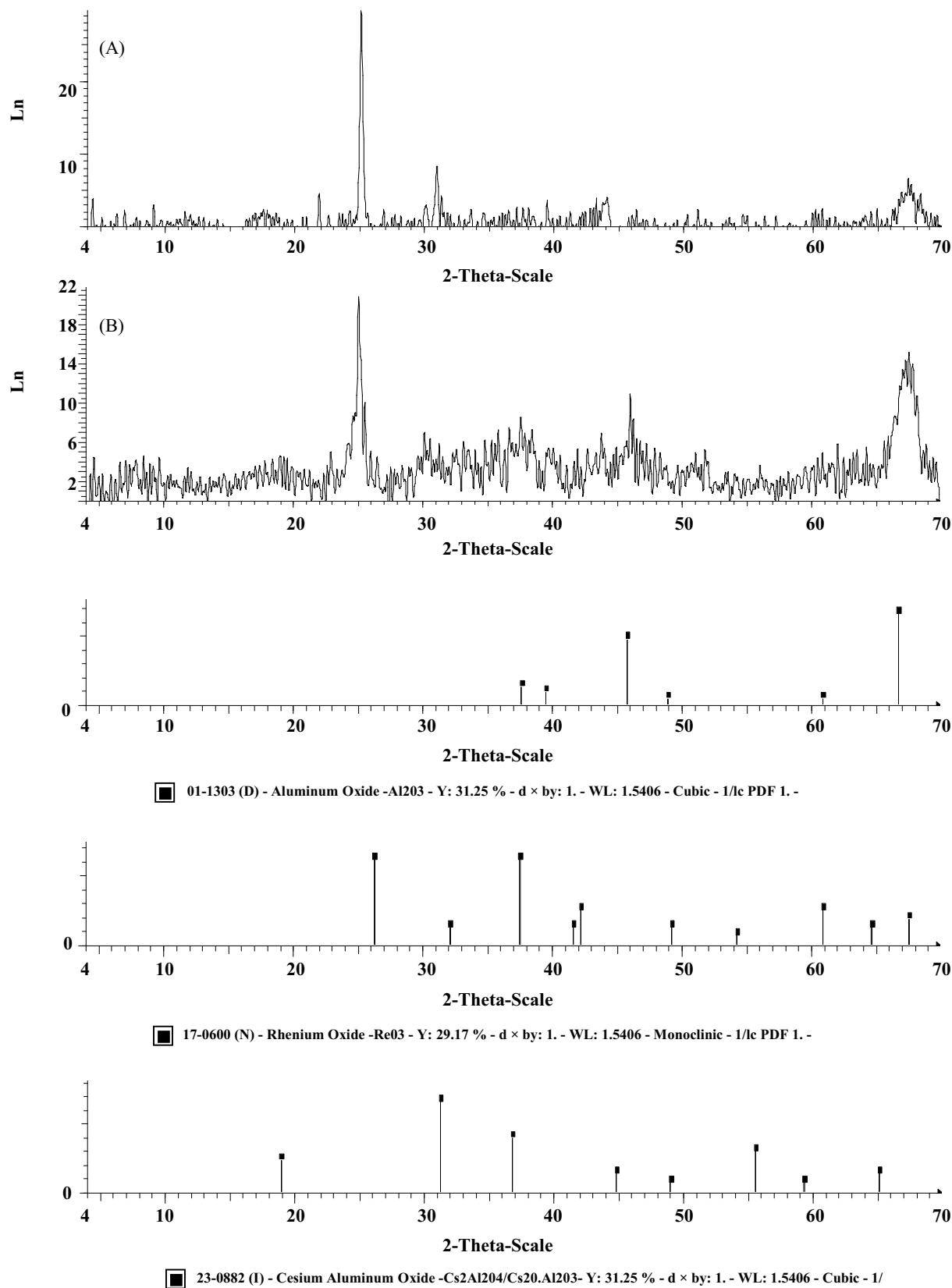
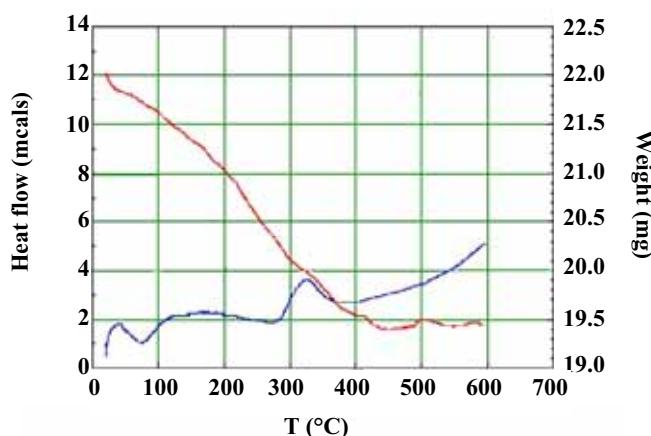
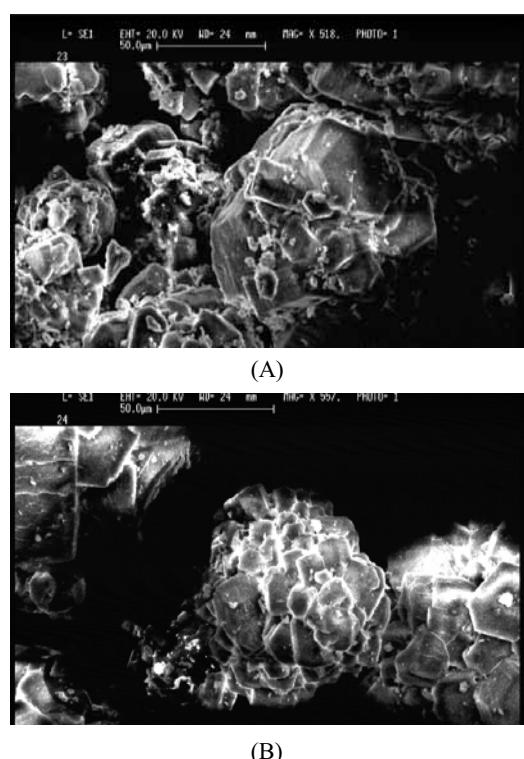


Fig. 3: Powder X-ray diffraction patterns for A) $\text{Cs}_3/\text{Re}(\text{C}_2\text{O}_4)_3/\text{Al}_2\text{O}_3$ and B) calcined catalyst.

Table 1: XRF data for precursor and calcined catalyst.

Sample	Al ₂ O ₃	Re	Cs
Precursor	75.744	2.422	3.834
Calcined catalyst	84.978	2.975	2.675

**Fig. 4: The TGA and DSC diagrams for the Cs₃/Re(C₂O₄)₃/Al₂O₃ precursor.****Fig. 5: SEM micrographs of the Cs₃/Re(C₂O₄)₃/Al₂O₃ precursor (A) and the calcined catalyst (B).**

than the calcined catalyst ($168.31\text{ m}^2/\text{g}$). This is in agreement with SEM results, which showed that the size of grains grew larger by agglomeration in the calcined catalyst, and so leads to a decrease in the BET specific surface area.

The XRF data for the both precursor and calcined catalyst are given in (table 1). The XRF results of both precursor and calcined catalyst showed the presence of Al₂O₃, Re and Cs.

CONCLUSIONS

We have firstly reported a simple and easy way to preparation of alumina-supported rhenium-cesium catalyst for industrial catalytic processes. The cesium promoter was added to aqueous solution of anionic complex, $[\text{Re}(\text{C}_2\text{O}_4)_3]^{3-}$, and due to the electroneutrality principle, the stoichiometric ratio of the catalyst and promoter remains constant in the precursor (Cs:Re = 3:1). This stoichiometric ratio is usually accompanied by change in inner-sphere charge of the given complex. Combining the results of the FT-IR spectra, TGA/DSC curves, classical identification method, and XRD patterns for tris(oxalato)rhenate (III) complex, precursor, and calcined catalyst showed that the complex decomposed to form an oxide of Re as the solid product and a mixture of CO and CO₂ as gaseous products. During the calcination operation, the morphological features of calcined catalyst are quite different with the Cs₃[Re(C₂O₄)₃]/Al₂O₃. SEM results showed that the catalyst particles became larger due to agglomeration. Thus, the Re catalysts should be supported on high surface area metal or metalloid oxides such as alumina or on active carbon.

Comparison between the surface area of this prepared Re-Cs catalyst and other supported rhenium catalysts shows a higher surface area for the present catalyst [1-26].

This method could also be useful to preparation other Re, Ru and Os catalysts.

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