RESEARCH PAPER

A Novel Approach for Preparation of Acetylacetonate Complex Anchored to High Order Nanoporous Silica (LUS-1)

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ABSTRACT

Tris(3-bromo-acetylacetonato) chromium(III) as an inert and very stable complex with a good leaving group was synthesized using as-prepared $Cr(acetylacetonate)_3$. Highly ordered nanoporous silica (LUS-1), with some great features, was functionalized with 3-aminopropyltriethoxysilane. Then the as-prepared product was modified with tris(3-bromo-acetylacetonato) chromium(III) under mild reaction condition. Results obtained from N_2 adsorption desorption, and X-ray powder diffraction proved the successful anchoring of the Cr(III) complex inside the pores of LUS-1 without any distortion in the structure. The morphology and configuration of LUS-1 with Scanning electron microscope and Transmission electron microscopy and Energy-dispersive X-ray spectrum of the product were prepared. Mid and Far Infrared spectroscopy confirmed that the product was possibly an amine, formed by substitution addition of NH_2 group on LUS-1, to C-Br in acac ligands and not a weak and non-stable Schiff base. Thermal stability of the species was assessed by thermogravimetric analysis. This novel method resulted in the formation of a stable covalently bonded acetylacetonate to the support that it can be used in acidic media or even in polar solvents without altering the structure.

How to cite this article

INTRODUCTION

$Cr(acac)_3$ (acac=acetylacetonate) is an inert, highly stable and coordinatively saturated complex, that is of great interest because of its different applications such as catalytic uses for reactions like polymerization of ethylene[1], and oxidation of alcohols to aldehydes and ketones[2]. Addition of $Cr(acac)_3$ to different kinds of supports, makes it a well-dispersed product with high surface area that will show better performance in its applications.

Inorganic oxide materials such as silica received increasingly more attention during the last years, because of their high surface area and high thermal, mechanical and chemical stability in comparison to other supports. Mesoporous silica supports, synthesized by Kresge and co-workers in 1992[3] such as MCM-41, SBA-15 and LUS-1 possess high order porosity and very narrow pore size distribution in the range of 2-10 nm. Silica nanomaterials were the first choice for the preparation of functionalized nanosensors[4]. These grafted materials were also used as nanocarriers for anticancer drug[5]. SBA-15 has large pores and thick walls (3–6 nm), leading to high hydrothermal stability. MCM-41 with higher surface area is a good support, although low hydrothermal stability has limited its applications. LUS-1 contains surface area of about 1000 m^2/g, high hydrothermal stability and special textured morphology[6], which allows it to have a good mass transfer, meet both requirements and is an appropriate support for immobilization.

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Several procedures have been carried out for adsorption of metal acac complexes to supports. They include hydrogen bonding between pseudo π system of the ligand and the surface hydroxyl groups[7], ligand exchange reactions[8], that are in danger of leaching in applications, Schiff-base condensation between the free amine groups grafted to the support and the carbonyl of the acac ligand[9]. The latter is a good procedure for covalently attachments of metal acetylacetonate, but the products are not stable in acidic media or in the presence of strong nucleophiles.

In the present work, a different attitude towards preparation of acac complex, anchored onto support was investigated. As Fig. 1 illustrates, first, 3-aminopropyltriethoxysilane was grafted to the surface of LUS-1 and then, the prepared APT/LUS reacted with Cr(Br-acac)$_3$. It is suggested that a nucleophilic substitution has been occurred by replacement of Br with amine groups, providing a stable product that can be applied in acidic media without altering the structure. To assess this claim, it was treated with EDTA, a hexadentate ligand with high tendency towards chelation and acid.

MATERIALS AND METHODS

The materials used in this study including 3-aminopropyltriethoxysilane (APTS), Cr(III) nitrate nonahydrate (Cr(NO$_3$)$_3$.9H$_2$O), urea, acetylacetone, silica gel (SiO$_2$), cetyl-trimethylammonium bromide (CTMABr) as a surfactant, N-Bromosuccinimide

(NBS), and hydrochloric acid (HCl) all were purchased from Merck Company. p-toluenesulfonic acid monohydrate (TSOH) was obtained from Aldrich and used without further purification. Petroleum ether and toluene were purified and dried prior to use, according to standard purification methods[10]. FTIR spectra in the region of 4000-600 cm^{-1} as Mid-IR and 500-50 cm^{-1} as Far-IR analysis with a little modification on the system were measured on Equinox 55 BRUKER model infrared spectrophotometer. SEM analysis was performed on a Philips XL-30 field emission scanning electron microscope operated at 16 kV. TEM was performed on Zeiss EM900 instrument at an accelerating voltage of 80 kV. The energy dispersive X-ray (EDX) spectrometer was operated at an accelerating voltage of 10 kV. Nitrogen physisorption isotherms were obtained at 77 K using a BELSORP-miniII porosimeter. BET (Brunauer–Emmett–Teller) equation was performed to calculate specific surface area and BJH (Barret, Joyner and Halenda)[11] method was applied to obtain pore size distribution and total pore volume. UV–visible analysis in 190-1100 nm range was measured by spectrophotometer model Raylight UV-1600. The low angle X-ray scattering spectrum was recorded by model X'Pert Pro MPD diffractometer at room temperature (40 mA, 40 kV) with Cu K$_\alpha$ radiation within a range of 2θ of 0.6 - 10 degree. Thermogravimetric analysis was performed at a heating rate of 20 °C.min^{-1} in the
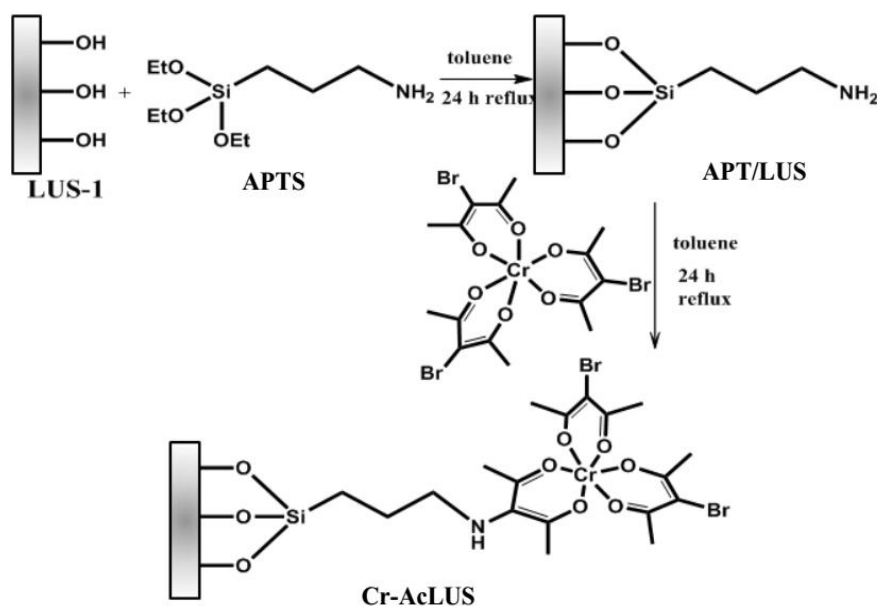

Fig. 1. Proposed procedure for anchoring Cr(Br-acac)3 onto amine-functionalized LUS-1

temperature range of 25 to 600 °C under Argon by TGA instrument model Q50.

Synthesis of nanoporous silica (LUS-1)

LUS-1 was synthesized according to the reported literature[6], with a molar ratio of SiO_2: 0.054 CTMABr: 0.054 TSOH: 80 H_2O. As-made LUS-1 was washed with a solution of HCl (2 M) and ethanol, with a ratio of 1:9 for 2 hours, in order to eliminate the surfactants and increase the surface area of LUS-1, and then was filtered off under vacuum and dried in an oven overnight. It was calcined at 600 °C for 6 hours.

Functionalization of LUS-1 with 3-aminopropyl-triethoxysilane (APT/LUS)

Prior to using LUS-1, it was activated under vacuum at 120 ºC. The activated LUS-1 (1 g) and anhydrous toluene (20 mL) were added to a two-necked, round bottom flask equipped with a magnetic stirrer. Then, 3-aminopropyltriethoxysilane (APTS) was added dropwise via syringe and the mixture was refluxed under N_2 atmosphere for 24 hours. APT/LUS was filtered off under vacuum and washed with excess amount of toluene and then dried in an oven overnight.

Preparation of tris-(3-bromo-acetylacetonato)Cr(III) (Cr(Br-acac)₃)

First Cr(acac)₃ was synthesized according to a reported method[12]. Cr(NO₃)₃.9H₂O solution (consists of 4.01 g (0.01 mol), in 100 mL of distilled water), urea (20 g) and acetylacetone (6 g, 0.06 mol) were used for reaching the product. The resultant was recrystallized from toluene and petroleum ether. The obtained melting point was 214 ºC that is similar to the literature[12]. The recrystallized Cr(acac)₃ with three λ_{max} at 328, 381 and 566 nm was brominated by NBS as mentioned in literature[13] to prepare tris-(3-bromo-acetylacetonato) Cr(III) named as Cr(Br-acac)₃. The obtained melting point was 225 ºC, which is in a good agreement with the reported procedure[13]. Cr(Br-acac)₃ shows three λ_{max} at 360, 414 and 571 nm.

Anchoring Cr(Br-acac)₃ onto APT/LUS (Cr-AcLUS)

Grafting the Cr(III) complex(Cr(Br-acac)₃) onto LUS-1 has been carried out by adding 20 mL of dried toluene to 1 g of dried APT/LUS, activated under vacuum at 120 ºC for 1 hour. Solution of Cr(Br-acac)₃ in 10 mL of hot toluene, was added slowly to the suspension and refluxed for 24 hours. Finally, it was filtered under vacuum, washed with excess amount of toluene, and dried in an oven for 1 day.

RESULTS AND DISCUSSION

Fig. 2 shows Cr-AcLUS X-ray diffraction pattern. Three well-known and characteristic reflection peaks at 2θ = 2.33º, 3.90º, and 4.49º are due to diffraction peaks of (100), (110), and (200) planes, respectively, confirming the hexagonal P6mm symmetry for mesoporous structures[14, 15]. It clearly confirmed that amine-functionalization
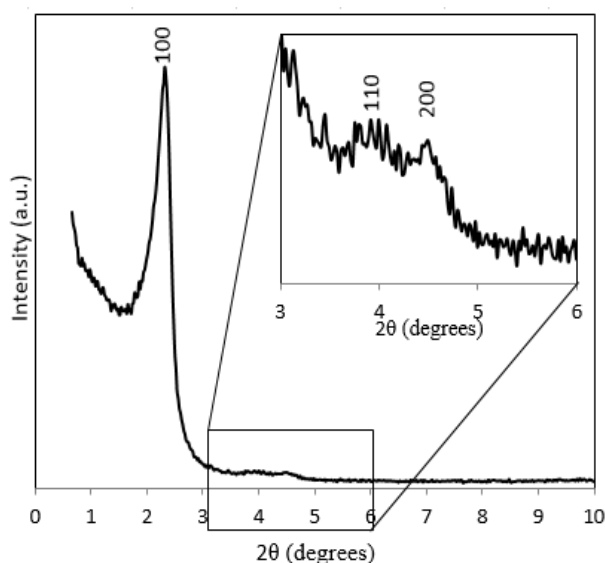

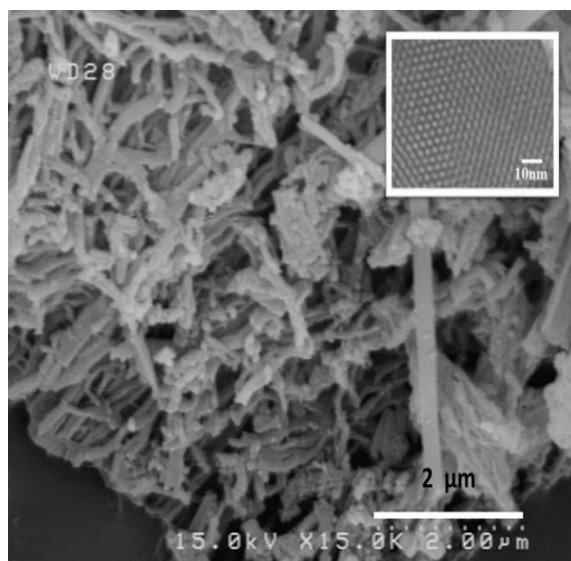Fig. 2. Low angel X-Ray Diffraction pattern of Cr-AcLUS.

Fig. 3. SEM and (inset)TEM images of LUS-1.

and anchoring of $Cr(Br\text{-}acac)_3$ onto LUS-1, have not changed the hexagonal structure of LUS-1.

The surface morphology of LUS-1 was examined using a scanning electron microscope. Fig. 3 gives the SEM and TEM images of LUS-1. SEM image showed long rod shape particles and TEM image demonstrated the parallel channels, which resembled the configuration of the pores in LUS-1.

Fig. 4 shows the energy dispersive analysis of X-ray spectrum from Cr-AcLUS. The spectrum confirmed the presence of Cr and Br in the films.

Nitrogen physisorption isotherms of calcined LUS-1, APT/LUS and Cr-AcLUS at 77 K showed a type IV standard IUPAC isotherm[16] that is typical of mesoporous materials as depicted in Fig. 5. All the isotherms showed a step in the range of $0.1 < P/P^0 < 0.4$, which its height is attributed to uniformity of the pores. As it can be seen, the height in LUS-1 isotherm is longer than APT/LUS and for APT/LUS is longer than Cr-AcLUS, that can be interpreted as pore filling by APTS and $Cr(Br\text{-}acac)_3$, respectively. This explanation was confirmed by Fig. 3, inset that shows a narrow pore size distribution in APT/LUS in comparison with Cr-AcLUS. As it is collected in Table 1, gradual reducing in the specific surface

area and total pore volume indicated that APTS and $Cr(Br\text{-}acac)_3$ entered successfully inside the pores of LUS-1.

Mid IR spectra of $Cr(Br\text{-}acac)_3$, LUS-1, APT/LUS and Cr-AcLUS were measured [Fig. 6]. The spectra of LUS-1 based materials exhibit well defined peaks of silica supports including a very strong and broad band at 1110-1010 cm^{-1}, representing stretching vibrations of Si-O-Si and a very broad band in the range of 3700-3200 cm^{-1} ascribed to surface hydroxyl groups. The peak at 1580 cm^{-1} in APT/LUS spectrum might be due to NH_2, shifted to 1570 cm^{-1} for NH, because of possible conversion of primary amine to a secondary pseudo aromatic amine. After tethering $Cr(Br\text{-}acac)_3$ to amine-functionalised LUS-1, two new and strong peaks at 1556 and 1658 cm^{-1} appear in Cr-AcLUS spectrum that can be assigned to $\upsilon(C=O)$ in acac complex, which are the evidence for anchoring the complex onto LUS-1 support.

The stablility of Cr-AcLUS was assessed by treatment with EDTA. In this way the sample was suspended in EDTA for 1 day. It was followed by soxhlet with ethanol, and then washed with HCl (0.1 M). As can be seen in Fig. 6, the bands

Table 1. Textural properties for LUS-1 based materials

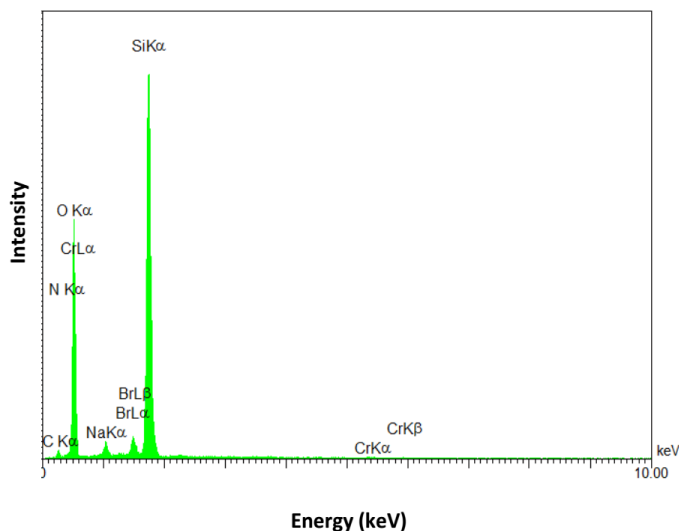| Nanopore	a_{BET} (m^2/g)	Total pore volume (mL/g)	Pore diameter (nm)
LUS-1	842	0.939	2.4
APT-LUS	589	0.588	2.35
Cr-AcLUS	232	0.367	2.27

Fig. 4 shows the energy dispersive analysis of X-ray spectrum from Cr-AcLUS.
The spectrum confirmed the presence of Cr and Br in the films.
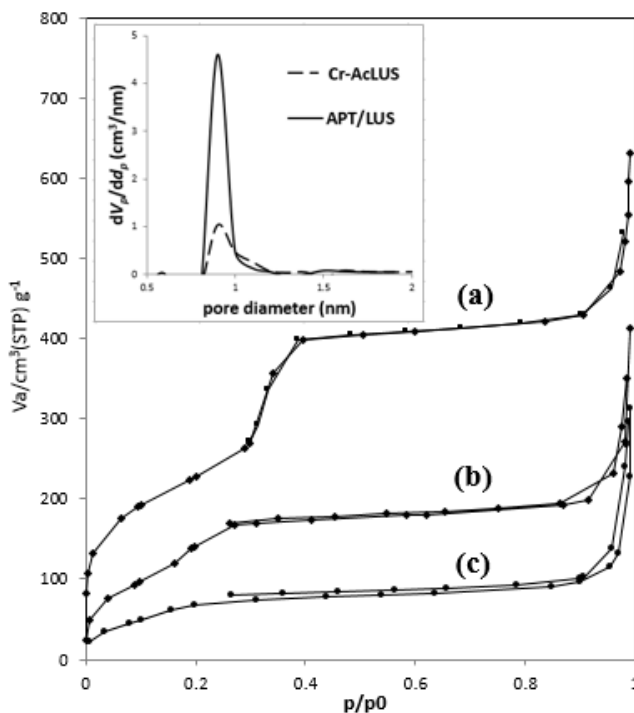

Fig. 5. N_2 adsorption-desorption isotherms of (a)LUS-1, (b)APT/LUS and (c)Cr-AcLUS. Inset: Pore diameter distribution in APT/LUS and Cr-AcLUS at77 K.

in Cr-AcLUS spectrum and test, related to after treatment with EDTA, have not changed or shifted, confirming Cr-AcLUS is a stable product even in acidic media or in presence of strong polydentate ligands such as EDTA.

To determine the Cr-O vibrations and possible the presence of Cr-N ones, Far-IR spectra of LUS-1, Cr-AcLUS and $Cr(Br\text{-}acac)_3$ were obtained (Fig. 7). Two strong peaks at 466 and 354 cm^{-1} in $Cr(Br\text{-}acac)_3$ spectrum could be ascribed to the Cr-O vibrations[17]. Both spectra of $Cr(Br\text{-}acac)_3$ and Cr-AcLUS demonstrate a medium peak at 440 cm^{-1} possibly due to acetylacetonate, bound to Cr(III) that was masked in Cr-AcLUS spectrum by
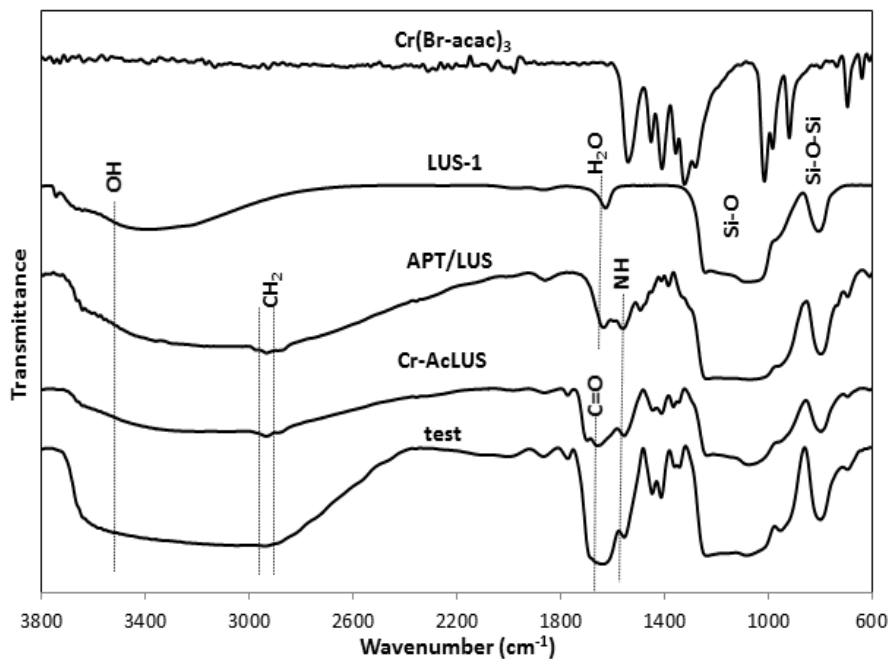
Fig. 6. Mid Infrared spectra of Cr(Br-acac)3, LUS-1, APT/LUS, Cr-AcLUS, and Test.
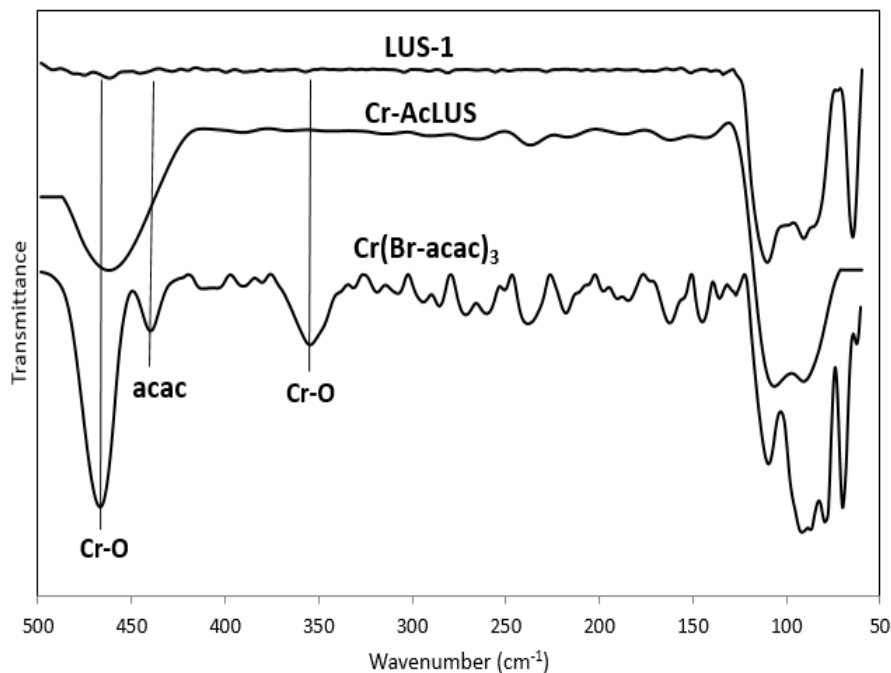

Fig. 7. Far-IR spectra of LUS-1, Cr(Br-acac)3 and Cr-AcLUS.

O-Si-O vibrations at 469 cm^{-1} observed in LUS-1 spectrum. To the best of our knowledge, LUS-1 has no characteristic band in wavenumber below 400 cm^{-1}, therefore the bands observed in the range of <150 cm^{-1} in LUS-1 spectrum must be objects of the disk[18]. Cr(Br-acac)$_3$ has further bands below 200 cm^{-1} other than those, assumed to be objects of the disk, that could be ascribed to the lattice vibrations of the complex. Aranha [19] pointed out that a band at 260–390 cm^{-1} is due to Cr–N
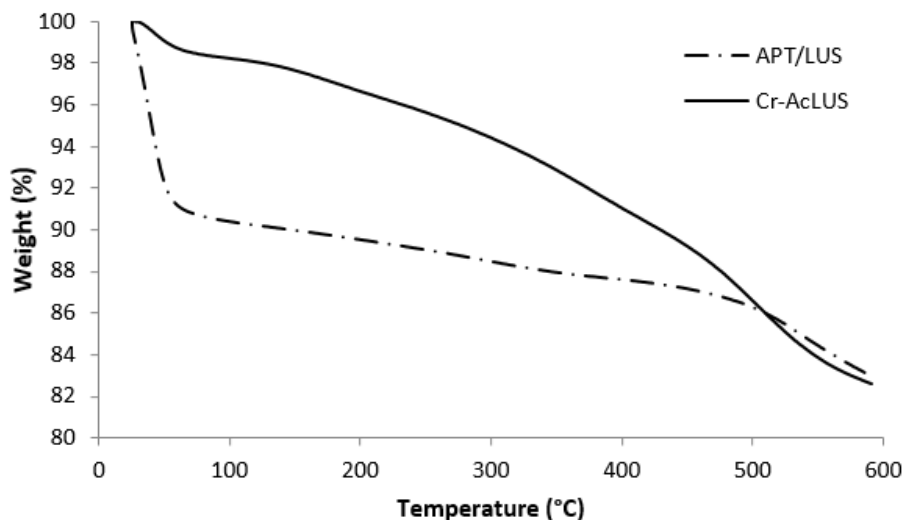
Fig. 8. Thermogravimetric analysis of APT/LUS and Cr-AcLUS.

vibrations in Schiff base, and there is no such band in this region for Cr-AcLUS spectrum, thereby no Cr–N bond has been formed, confirming no formation of Schiff base product.

The thermogravimetry analysis of APT/LUS and Cr-AcLUS were performed [Fig. 8] to estimate the amount of APTS and Cr(Br-acac)$_3$ grafted on LUS-1, respectively. In both curves two clear steps can be seen. The first weight loss, observed below T = 150 ºC commonly interpreted as the evaporating of adsorbed and bound water that is lower in Cr-AcLUS curve compared to APT/LUS. It suggests that anchoring of Cr(Br-acac)$_3$ descended the water amount of LUS-1 that is due to hydrophobicity of Cr(Br-acac)$_3$ in contrast to hydrophilicity of amine. Another weight loss is at about 500 ºC that probably is the resultant of decomposition of functional groups. As a result, loading of grafted amine group and Cr(Br-acac)$_3$ was estimated to be 6 and 5 %, respectively. Steric hindrance is a major controller for the amount of loaded complex onto APT/LUS.

CONCLUSION

In present research, a novel method for the preparation of acetylacetonate complex tethered onto LUS-1 was investigated. Cr(Br-acac)$_3$, synthesized by using Cr(acac)$_3$, was incorporated into the amine-functionalised LUS-1. The results proved two points: 1. The successful grafting in both two steps and remaining the structures unchanged after immobilization, and 2. Cr-AcLUS

was possibly an amine, formed by substitution addition of NH$_2$ group on LUS-1, to C-Br in acac ligands, and not a Schiff-base. Thus the suggestion was verified. This product was very stable, so that it can be used in acidic media or even in polar solvents without altering the structure.

Applying Cr-AcLUS as a stable catalyst for reactions such as polymerization of ethylene could be a future view of this project.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publicaton of this manuscript.

REFERENCES

1. Coutinho F.M.B, Iwamoto R.K., Costa M.A.S, de Santa Maria L.C, Polymerization of ethylene by chromium acetylacetonate/methylaluminoxane catalyst system, Polym. Bull. 1998; 40(6): 695-700.
2. Xu L, Trudell M.L, A mild and efficient oxidation of alcohols to aldehydes and ketones with periodic acid catalyzed by chromium(III) acetylacetonate, Tetrahedron Lett. 2003; 44(12): 2553-2555.
3. Kresge C.T, Leonowicz M.E, Roth W.J, Vartuli J.C, Beck J.S, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature. 1992; 359(6397): 710-712.
4. Lashgari N, Badiei A, Mohammadi Ziarani G, Modification of mesoporous silica SBA-15 with different organic molecules to gain chemical sensors: a review, Nanochem. Res. 2016; 1(1): 127-141.

5. Bahrami Z, Badiei A, Atyabi F, Surface functionalization of SBA-15 nanorods for anticancer drug delivery, Chem. Eng. Res. Des. 2014; 92(7): 1296-1303.

6. Bonneviot L, Morin M, Badiei A, mesostructured metal or nonmetal oxides and method for making some, US patent 0133868. 2003.

7. Kenvin J.C, White M.G, Mitchell M.B, Preparation and characterization of supported mononuclear metal complexes as model catalysts, Langmuir. 1991; 7(6): 1198-1205.

8. Haukka S, Lakomaa E.-L, Suntola T., Chemisorption of chromium acetylacetonate on porous high surface area silica, Appl. Surf. Sci. 1994; 75(1–4): 220-227.

9. Oliveira P, Machado A, Ramos A.M, Fonseca I.M, Braz Fernandes F.M, Botelho do Rego A.M, et al., Anchoring manganese acetylacetonate complex on MCM-41: Catalytic testing on limonene oxidation, Catal. Commun. 2007; 8(9): 1366-1372.

10. Armarego W.L.F, Perrin D.D. Purification of laboratory chemicals: Butterworth Heinemann; 1997.

11. Barrett E.P, Joyner L.G, Halenda P.P, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, J. Am. Chem. Soc. 1951; 73(1): 373-380.

12. Moeller T. Inorganic Chemistry: An Advanced Textbook: John Wiley & Sons; 1952.

13. Kleinberg J. Inorganic Syntheses: McGraw-Hill; 1963.

14. Zhao D, Sun J, Li Q, Stucky G.D, Morphological Control of Highly Ordered Mesoporous Silica SBA-15, Chem. Mater. 2000; 12(2): 275-279.

15. Yamada T, Zhou H.S, Hiroishi D, Tomita M, Ueno Y, Asai K, et al., Platinum Surface Modification of SBA-15 by γ-Radiation Treatment, Adv. Mater. 2003; 15(6): 511-513.

16. Rouquerol F, Rouquerol J, Sing K, Adsorption by Powder and Porous Solids: Principles, Methodology and Applications, San Diego: Academic, 1999.

17. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds: Theory and applications in inorganic chemistry: John Wiley; 1997.

18. Shamir J, Raman and infrared spectra of the FeCl 63− anion: Comparison of MCl4 and MCl6 vibrational frequencies, J. Raman Spectrosc. 1991; 22(2): 97-99.

19. Aranha P.E, dos Santos M.P, Romera S, Dockal E.R, Synthesis, characterization, and spectroscopic studies of tetradentate Schiff base chromium(III) complexes, Polyhedron. 2007; 26(7): 1373-1382.