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Graphical abstract



Synthesis and characterization of nano acid catalyst derived from rice husk silica and its application for the synthesis of 3,4-Dihydropyrimidinones/thiones compounds

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Abstract

In the present work, the extraction of silica nanoparticles from the rice husk followed by the modification using an acidic ionic liquid containing imidazolium butyl sulfonic acid through a sol-gel method (RH@[SiPrImBuSO₃H]Cl) has been investigated. The composition, morphology and structural properties of the synthesized solid acid were analyzed by fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal gravimetric analysis-derivative thermogravimetric (TGA-DTG), and nitrogen adsorption-desorption. The catalytic activity of the nanocomposite was examined through the one-pot condensation of aromatic aldehyde, β -diketone, urea or thiourea under reflux condition. Diverse 3,4-dihydropyrimidinones/thiones derivatives were produced up to excellent yields in a short period of time. This nanocatalyst could be easily recovered, and reused without considerable loss of catalytic activity. This method seems to be a promising method for synthesizing organic chemicals. In addition to the conducted experiments, the ¹H and ¹³C chemical shift and X-ray spectra values together with the structural parameters of 3,4-dihydropyrimidinones/thiones were computed and compared to the corresponding experimental values. As a result, the calculated ¹H and ¹³C chemical shift and X-ray spectra show a good agreement with the experimental results.

Keywords: Three component reaction; 3,4-dihydropyrimidinones/thiones; Solid acid; Rice husk ash; Theoretical NMR and X-ray simulation.

1. Introduction

Ever growing demands of acidic ionic liquid catalysts (AILCs) in a variety of organic transformations, separation problems, reactor corrosion, waste neutralization, and incapability to reuse still remains a great challenge [1-3]. Immobilization of the AILC on the solid supports like silica shows the synergetic effects along with the advantages of immobilizations such as ability to design, great solubility of the catalytic site, ease of handling, separation, and recycling. AILCs are dissolved in both water and an organic solvent making them appropriate catalysts for industrial application [4-6]. Surface functionalized rice husk silica nanoparticles are unprecedented functional materials that can be used in and catalysis industry [7-9]. silane agents, especially 3biotechnology The chloropropyltriethyloxysilane (CPTES) and 3-aminopropyltriethyloxysilane (APTES), are mainly used for modifying the surface of silica nanopatricles. The presence of hydroxyl groups on the surface of silica leads to the reaction with alkoxysilane reagents and formation of Si-O bonds, which supports the availability of terminal functional groups to immobilize other substances [10-12]. Ring opening reaction of 1,3 and 1,4-propanesultone, and oxidation of immobilized thiols to sulfonic acids are the most common approaches for covalently bonded sulfonic acid sites on the solid supports [13-15].

Since the synthetic procedure should be facile, fast, and efficient [16-18], multicomponent condensation reactions (MCRs) could be a good candidate for molecular diversity per step with reduction of the steps for synthesis of bioactive and complex molecules. In addition, 3,4-dihydropyrimidinones and their derivatives are very well known for their wide range of biological activities, such as calcium channel blockers, antihypertensive agents, and neuropeptide Y antagonists [19-21]. Herein, several methods have been reported for the

promoting preparation 3,4-dihydropyrimidinones /thiones derivatives. Most of the reported processes offer unique advantages while suffer from low yields production, extended reaction times, harsh reaction conditions, tedious work up procedures, toxic solvents, and using expensive or unavailable catalysts. Moreover, the catalysts lose their activities and cannot be reused [22-24]. In this work, synthesis of 3,4-dihydropyrimidinones/thiones derivatives by inorganic-organic hybrid containing imidazolium chloride-butyl sulfonic acid supported on the rice husk silica, RH@[SiPrImBuSO₃H]Cl, as a proficient, mild, eco-friendly, recyclable, and non-toxic solid Brönsted acid catalyst was investigated.

2. Experimental Section

2.1. Chemicals and Equipment

All Chemical were purchased from Fluka and Merck companies and used without further purification. Products were characterized by comparison of their physical data, IR and ¹H NMR and ¹³C NMR spectra with known samples.

2.2. Synthesis of RHA@[SiPrImBuSO₃H]Cl

Amorphous silica nanoparticles were extracted from rice husk (RH-SiO₂)[7]. About 3.0 g of the nanosilica (obtained from RH) was stirred in 350 mL of the NaOH solution (1.0 M) at the room temperature. The solution was filtered to remove the undissolved particles, and about 1.0 mL of CPTMS was added to the resulting sodium silicate. The solution was then titrated slowly (1.0 mL min⁻¹) with nitric acid (3.0 M) with constant stirring. The acid solution was added at a slow rate of ca. 1.0 mL min⁻¹ with constant stirring. The silica gels started to precipitate when the pH decreased to the values less than 11. The titration was continued until the pH of solution reached 5.0 and aged for 24 h. The filtered silica gel

washed thoroughly with distilled water and dried at 100 °C for 18 h (RH-PrCl). RH-PrCl (3.0 g) was added to a flask containing 30 mL of ethanol and an excess of imidazole (6 mmol). The reaction mixture was refluxed with stirring for 24 h. Then, the reaction mixture was cooled down to the room temperature, transferred to a vacuum glass filter, and washed with water and acetone. The rice husk which is chemically bonded to imidazole (RH@SiPrIm) was dried at 50 °C for 8 h. For target catalyst preparation, 1,4-Butanesultone (6 mmol) was slowly added into the mixture of RH@SiPrIm (3.0 g) and toluene (100 mL). The mixture was stirred at 100 °C for 12 h and toluene was removed by rotary evaporation under reduced pressure. The formed RH@[SiPrImBuSO₃H]Cl then was washed with ether for 3 times and dried in vacuum at 50 °C for 3 h.

2.3. pH-analysis of RHA@[SiPrImBuSO₃H]Cl

To an aqueous solution of NaCl (1 M, 25 mL) with an initial pH 5.9, the RHA@[SiPrImBuSO₃H]Cl (100 mg) was added and the resulting mixture stirred for 24 h after which the pH of solution decreased to 2.2. This is equal to a loading of 1.58 mmol SO₃H/g of acidic catalyst. Additionally, this result confirmed by back-titration analysis of the catalyst.

2.4. Typical procedure for the preparation of 3,4-dihydropyrimidin-2(1H)-ones/thiones

A mixture of aromatic aldehyde (1.0 mmol), β -diketone (1.0 mmol), urea or thiourea (2 mmol) and 0.1 g of RHA@[SiPrImBuSO₃H]Cl was refluxed in ethanol for the time shown in Table 3. After complete consumption of aromatic aldehyde as judged by TLC (using n-hexane-ethylacetate as eluent), the mixture was washed with distilled water to separate the excess of urea or thiourea. The crude product was dissolved in hot ethanol and the catalyst

was filtered. The crude product was purified by recrystallization in aqueous ethanol to afford the pure product.

3. Results and Discussion

3.1. Investigation around the approach of RH@[SiPrImBuSO₃H]Cl preparation and its structural and morphological analysis

Inorganic-organic hybrid which contains imidazolium chloride-butyl sulfonic acid supported on rice husk silica, RH@[SiPrImBuSO₃H]Cl, with high surface area was prepared by the direct incorporation of chloropropyl groups through co-condensation of RH-SiO₂ and CPTMS (Scheme 1). Thereafter, a simple nucleophilic substitution reaction of imidazole with propyl chloride groups (RH@SiPrIm) takes place, and the last step exhibits the ring opening of 1,4-butanesultone with imidazole (Scheme 1). The catalyst has been characterized by SEM, FT-IR, TGA, XRD and BET methods (Figs 1-5). Additionally, characterization shows the promising results revealing the advantages of the RH@[SiPrImBuSO₃H]Cl as a heterogeneous catalyst. We have examined the catalytic activity in the preparation of 3,4dihydropyrimidinones/thiones derivatives.



RH@[SiPrImBuSO₃H]Cl Scheme 1 Synthesis of RH@[SiPrImBuSO₃H]Cl

The FT-IR spectra of RH@[SiPrImBuSO₃H]Cl and RH-SiO₂ are shown in Fig. 1. In two materials, the typical bands around 990-1220, 801 and 473 cm⁻¹ were attributed to the presence of Si-O group. The band around 1635 cm⁻¹ is also due to the bending vibration of water molecules bound to the silica matrix. The presence of peaks at 1200-1500 and 2870-3040 cm⁻¹ in the RH@[SiPrImBuSO₃H]Cl were most probably due to the C-H bonds and also a band around 1465 cm⁻¹ is characteristic for the tertiary amine group.



Figure 1 FT-IR spectra of RH@[SiPrImBuSO3H]Cl and RH-SiO2

The thermal stability of catalyst was investigated by TGA and DTG. The TGA and DTG thermograms of RH-SiO₂ and RH@[SiPrImBuSO₃H]Cl in N₂ atmosphere is shown in Fig. 2. The 0-4% weight loss below 200 °C might be due to the loss of the adsorbed water as well as dehydration of the surface OH groups. Curve (a) indicates that the nanosilica particles are thermally stable, and no obvious weight loss was observed, while in curve (b), the mass loss of RH@[SiPrImBuSO₃H]Cl at 300-600 °C is attributed to the organic groups. DTG was also shown in Fig. 2 and no transition was observed up to 300 °C for both of them. A sharp endotherm transition in around 300 °C might be due to the breakdown and decomposition of

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organic moieties observed for RH@[SiPrImBuSO₃H]Cl. Thus, the TGA and DTG curves also reveal that the nanosilica particles are successfully coated by imidazolium butyl sulfonic acid groups.



Figure 2 Thermal gravimetric analysis (TGA) of RH@[SiPrImBuSO₃H]Cl

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Fig. 3 shows the XRD spectra of RH@[SiPrImBuSO₃H]Cl. Lack of any sharp peaks in the X-ray diffraction pattern indicates the amorphous nature of the samples in which only a broad diffraction band at 2θ angle of ca. 22 can be observed.



Figure 3 The X-ray diffraction pattern for RH@[SiPrImBuSO₃H]Cl

The BET adsorption isotherm obtained for RH@[SiPrImBuSO₃H]Cl is shown in Fig. 4. The hysteresis loop was observed in the range of $0.4 < P /P_0 < 1.0$, which is associated with capillary condensation taking place within the mesopores. The isotherms present a sharp adsorption step in the P/P₀, which implied that the materials possess large pore size with narrow distributions. The BET surface area of RH@[SiPrImBuSO₃H]Cl was found to be 134 m² g⁻¹, while that of RH-SiO₂ was reported as 347 m² g⁻¹ [25]. This was further confirmed by the pore size distributions calculated by BJH method from the adsorption branches. The average pore diameter of 10.58 nm (BJH model) was obtained for RH@[SiPrImBuSO₃H]Cl. The characteristic data on the sample are summarized in Table 1.

Sample		BET surface $(m^2 a^{-1})$	BET surface area dian $(m^2 e^{-1})$		pore volume $(am^3 a^{-1})$	
DII@[C:D_L			(III g)		(IIII)	(cm g)
		134		10.58	0.744	
						- R
	600					
		(a)				×
						· ·
						t
	400					//
TP) g ^{,1}						#
",/cm ³ (S					J	
2	200					
					100	
	0)	0.5			1
			p / p ₀			
		Adsorp	otion / desorptio	on isotl	herm	
			Adsorptive N2 Adsorption temperature 7	7 fK1		
	~					

 $\begin{array}{l} \textbf{Table 1} Specific \ surface \ area \ (S_{BET}), \ diameter \ pore \ and \ total \ pore \ volume \ of \\ RH@[SiPrImBuSO_3H]Cl \end{array}$



Figure 4 (a) Pore size distributions and (b) nitrogen adsorption-desorption isotherm of RH@[SiPrImBuSO₃H]Cl

SEM is a useful tool for determining the size distribution, particle shape and porosity. It has been a primary tool for characterizing the surface morphology and fundamental physical properties of the surface [26]. According to Fig. 5, both kinds of RH@[SiPrCl] and RH@[SiPrImBuSO₃H]Cl nanoparticles apparently are similar in size and shape and have nano dimension ranging from 90 to 170 nm. Particles are rather uniform in morphology.

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Figure 5 SEM images of (a) RH@[SiPrCl](b) RH@[SiPrImBuSO₃H]Cl

3.2. Application of RH@[SiPrImBuSO₃H]Cl as heterogeneous solid acid catalyst for one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

To evaluate the catalytic activity of RH@[SiPrImBuSO₃H]Cl as heterogeneous solid acid catalyst in the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones through multicomponent condensation reaction (Scheme 2), a model three-component coupling reaction of benzaldehyde (1 mmol), ethylacetoacetate (1 mmol) and urea (2 mmol) was examined to determine whether the use of RH@[SiPrImBuSO₃H]Cl was efficient and to investigate the optimized conditions (Table 2).



Scheme 2 Synthesis of 3,4 -dihydropyrimidin-2(1H)-ones/thiones through multicomponent reaction promoted by RHA@[SiPrImBuSO₃H]Cl
Table 2 Reaction of benzaldehyde, ethylacetoacetate, and urea under different

Entry	Solvent	T(°C)	Catayst (g)	Time (min)	Yield ^a (%)
1	Solvent-free	50	0.1	180	62
2	Solvent-free	80	0.1	180	65
3	Solvent-free	80	0.2	180	65
4	Solvent-free	80	-	180	15
5	Water	Reflux	0.1	180	40
6	Acetonitrile	Reflux	0.1	180	52
7	Ethanol	50	0.1	90	80
8	Ethanol	Reflux	0.05	60	78
9	Ethanol	Reflux	0.1	30	95

conditions

10	Toluene	Reflux	0.1	180	53
11	CH_2Cl_2	Reflux	0.1	180	50

Subsequently, with optimal conditions in hand, 1:1:2 molar ratios of aldehyde, ethylacetoacetate and urea and 0.1 g of RHA@[SiPrImBuSO₃H]Cl under reflux condition, the generality and synthetic scope of this coupling protocol were demonstrated by synthesizing a series of 3,4-dihydropyrimidin-2(1H)-ones (Table 3).

Table 3 Synthesis of 3,4 -dihydropyrimidin-2(1H)-ones/thiones in presence of

Entry	R	X	R ₂	Time (min)	Yield ^a (%)
1	Н	0	OEt	30	95
2	Н	S	OEt	40 🔨	88
3	4-N	0	OEt	20	95
4	$4-O_2N$	S	OEt	25	88
5	4-Cl	0	OEt	30	92
6	4-Cl	S	OEt	30	87
7	$4-CH_3O$	0	OEt	40	88
8	4-CN	0	OEt	20	95
9	2-HO	0	OEt	40	85
10	2-HO	S	OEt	40	82
11	$4-H_3C$	0	OEt	40	82
12	$4-H_3C$	S	OEt	40	81
13	$4-CH_3O$	0	Me	40	88
14	2-HO	0	Me	40	85
15	Н	0	Me	30	95
16	Н	S	Me	30	90
17	$4-O_2N$	0	Me	25	95
18	$4-O_2N$	S	Me	25	90
19	4-C1	0	Me	30	92
20	4-C1	S	Me	30	87

RHA@[SiPrImBuSO₃H]Cl

As it is shown in Table 3, aromatic aldehydes having electron-releasing as well as electron-withdrawing groups were uniformly transformed into the corresponding 3,4-dihydropyrimidin-2(1H)-ones in high yields within 20-40 min. Substituents on the aromatic ring had no obvious effect on yield or reaction time under the above optimal conditions.

The reusability of the catalyst in the reaction of benzaldehyde, ethylacetoacetate and urea, under reflux condition was evaluated. In this procedure, after completion of each reaction, hot ethanol was added to the system and then the catalyst was filtered. The recovered catalyst was washed with ethanol, dried and reused for four times (Fig.6). The pH change during reaction process was also considered for fresh and recovered catalyst, and the pH decrease was not observed after reaction process. Based on titration of the proton-exchanged brine solutions, fresh and recovered catalysts were shown the loading of 1.58 mmol SO_3H/g .



Figure 6 Recyclability of RHA@[SiPrImBuSO₃H]Cl

To evaluate the generality and synthetic scope of this coupling protocol this three component condensation reaction also proceeded with acetyl acetone and thiourea (Table 3). In order to show the merit of the presented protocol in DHPMs synthesis, we have compared the results of RHA@[SiPrImBuSO₃H]Cl catalyst with some of those reported in the literatures. The model reaction of benzaldehyde, ethyl acetoacetate and urea was considered as a representative example (Table 4).

Entry	Catalyst	Catalyst loading (g or wt. %)	Time (h)	Yield (%)	Ref
1	RHA@[SiPrImBuSO ₃ H]Cl	0.1 g	0.5	95	This work
2	Montmorillonite KSF	15%	48	77	[27]
3	Sulfated zirconia	15.15%	4	94	[28]
4	PS-PEG-SO ₃ H	0.3 g	10	80	[21]
5	ZrOCl _{2.} 8H ₂ O	10 mol%	2	56	[29]
6	Silica-sulfuric acid	35%	6	91	[19]
7	$H_3PMo_{12}O_{40}$	11%	5	80	[30]
8	Zeolite [HY(Si/Al = 2.43, $H_{56}(SiO_2)_{136}(AlO_2)_{56}]$	15%	12	80	[31]
9	Bentonite/PS-SO ₃ H	0.1 g	0.5	89	[32]
10	Fe ₃ O ₄ @Silica sulfuric acid	0.05	0.6	92	[33]

Table 4 Comparison of the efficacy of RHA@[SiPrImBuSO₃H]Cl catalyst with some of those reported in the literature

4. Theoretical Section

4.1. ¹H and ¹³C NMR Study

In this section, the ¹H and ¹³C NMR chemical shifts of the considered compound is simulated and compared with the experimental results. For this purpose, the product of the reaction between 4-chlorobenzaldehyde (1 mmol), acetyl acetone (1 mmol) and urea (2 mmol) (entry19 in Table 3) is chosen to assign each peak to the corresponding atom. The full geometry optimization of the corresponding product is carried out at B3LYP/6-311++G(d,p) level of theory [34]. The obtained optimized structure is displayed in Fig. 7. The minimum nature is examined by frequency analysis at the same computational level. Since the experimental chemical shifts are achieved in DMSO solvent, the chemical shielding of the titled compound, and tetramethylsilane (TMS) are calculated through the GIAO formalism [35], in DMSO solvent using IEFPCM model at B3LYP /6-311++G(d,p) level of theory. All calculations are accomplished using Gaussian 03 program revision A.02 [36]. The values of

31.882 (¹H) and 182.465 (¹³C) ppm in DMSO solvent are applied to scale the ¹H and ¹³C NMR chemical shifts to the TMS. Both experimental and theoretical ¹H and ¹³C NMR spectra are depicted in Fig. 8 for the studied compounds. The calculated chemical shifts are also listed in Table 5, which reveals that all of the calculated ¹H/¹³C chemical shifts with respect to TMS are in the range of 1.63-7.90/22-200.20 ppm; whereas the experimental values are observed at 2.13-7.40/19.43-194.62 ppm. The result shows a significant correlation (R² = 0.98) between the experimental and calculated ¹H/¹³C chemical shifts (Fig. 9). Note that the estimated slopes for both graphs are close to unity (0.937 and 0.924 for ¹H and ¹³C spectra, respectively) showing the similarity between the experimental and the corresponding theoretical spectra. It is noteworthy that the hydrogen atoms positions in NH group (24-H and 23-H in Fig. 7) are sensitive and influenced by different experimental conditions [37, 38].



Figure 7 The optimized geometry of entry 19 in Table 3.

Table 5 The calculated (δ_{Calc}) and experimental (δ_{Exp}) chemical shift values of ¹H NMR and ¹³C NMR for the entry 19 in Table 3 (all in ppm).

Atom	δ Calc.	δ Exp.	Atom	δ Calc.	δ Exp.
21-Н	7.90	7.242-7.409(7.32)	13-C	200.20	194.62
20-Н	7.37		7-C	185.08	152.53
31-H	7.34		10-C	157.16	148.98
22-Н	5.67	5.26	16-C	150.85	143.64
25-Н	2.58	2.13	1-C	146.12	132.30
29-Н	2.56	2.50	4-C	134.30	128.94
27-Н	2.49	2.13	2-C	133.41	128.77
30-Н	2.31	2.50	3-C	132.98	128.77
28-H	2.04	2.50	17-C	130.82	128.94
26-H	1.63	2.13	6-C	118.52	109.96
			5-C	57.09	53.49
			15-C	33.06	30.91
			12-C	22.00	19.43



200 180 160 140 120 100 80 60 40 20 0 ppm



Figure 8 The obtained experimental (a) ¹H NMR and (b) ¹³C NMR spectra together with theoretical (c) ¹H NMR and (d) ¹³C NMR spectra simulated at B3LYP/6-311++G** in DMSO for the entry 19 in Table 3(see Fig. 7).



Figure 9 The correlations between the experimental and calculated (a) ¹H NMR together with (b) ¹³C NMR chemical shifts of the entry 19 in Table 3.

4.2. Structural Study

The optimized geometry of the product of the reaction between 4-chlorobenzaldehyde (1 mmol), acetyl acetone (1 mmol) and thiourea (2 mmol) (entry 20 in Table3) at B3LYP/6-311++G(d,p) level of theory is shown in Fig.10. In order to check the reliability of the optimized structure, it is attempted to find the correlation between the obtained bond lengths from this calculation and those which are reported in the X-ray data [39]. The calculated

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values for some selected bond lengths and the corresponding experimental data are listed in Table 6; and the correlation between these bonds lengths are shown in Fig. 11. The closeness of the calculated slope to unity (0.955) and the negligible intercept (0.076) verify significant correlation between the optimized structure and the reported experimental data.



Figure 10 The optimized geometry of entry 20 in Table 3.

Table 6 Some of optimized (B3LYP/6-311++G**) and experimental bond lengt	ths of the
entry 20 in Table 3 (see Fig.10).	

Bond	R _{Exp} .	R _{Calc.}	Bond	R _{Exp.}	R _{Calc} .
1C-2C	1.343	1.390	10C-8N	1.359	1.384
1C-3C	1.370	1.391	6C-7C	1.353	1.363
3C-4C	1.392	1.392	10C-11S	1.686	1.671
4C-16C	1.386	1.400	7C-12C	1.498	1.507
2C-17C	1.397	1.393	6C-13C	1.469	1.477
16C-5C	1.525	1.533	13C-15C	1.501	1.519
5C-9N	1.461	1.468	13C-14O	1.211	1.227
5C-6C	1.515	1.530	1C-18CL	1.747	1.760
9N-10C	1.320	1.344	C16-C17	1.374	1.399



Figure 11 The correlation between the calculated and experimental values of some selected bond lengths in the backbone of the entry 20 in Table 3.

5. Conclusion

RH@[SiPrImBuSO₃H]Cl is successfully achieved by a multiple synthetic procedure which is confirmed with FT-IR, TGA, SEM and BET. The most interesting features of the present work include durability as well as remarkable catalytic activity for one-pot synthesis of 3,4dihydropyrimidin-2(1H)-ones/thiones via three component coupling reactions under reflux condition. This method offers several advantages including high yield, short reaction time, simple workup procedure, ease of separation and recyclability of the catalyst, as well as the ability to tolerate a wide variety of substitutions in the reagents. Moreover, the ¹H and ¹³C chemical shift and X-ray spectra values together with the structural parameters of 3,4dihydropyrimidinones have been also computed, and the scaled values have been compared with the corresponding experimental NMR and X-ray spectra. Consequently, the calculated ¹H and ¹³C chemical shift and X-ray spectra are in good agreement with the experimental results.

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Highlights

- extraction of silica nanoparticles from the rice husk followed by the modification using an acidic ionic liquid.
- Diverse 3,4-dihydropyrimidinones/thiones derivatives were produced up to excellent yields in a short period of time.
- The ¹H and ¹³C chemical shift and X-ray spectra values together with the structural parameters of 3,4-dihydropyrimidinones have been computed.
- The calculated ¹H and ¹³C chemical shift and X-ray spectra are in good agreement with the experimental results.

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