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An Efficient Method for Chemoselective Acetylation of Activated Alcohols Using Nano ZnFe_2O_4 as Catalyst

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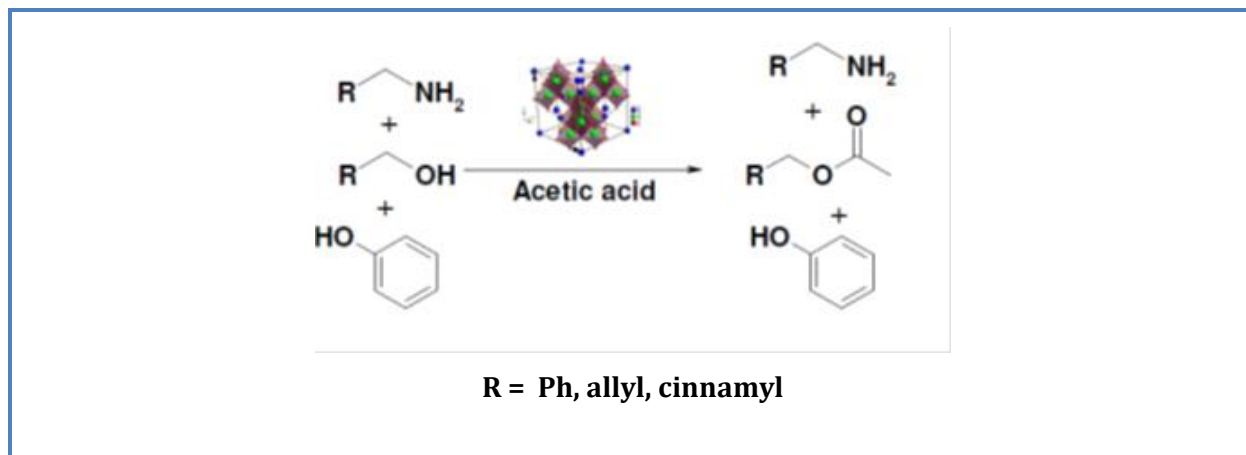
ABSTRACT

The spinels of AB_2O_4 type display very interesting catalytic properties and have been shown to possess potential industrial applications. Especially spinels have been shown to be selective and active catalysts. Nano ZnFe_2O_4 ferrite synthesized by sol-gel auto-combustion method was found to be an efficient catalyst for acetylation of activated alcohols using acetic acid as reagent. A variety of activated alcohols undergo acetylation under the reaction conditions to afford the corresponding acetates in good yield. The salient features of this protocol include selectivity towards activated alcohols, use of cheap catalyst and environmentally benign protocol. The chemoselectivity of the protocol for activated systems making amines, phenols and other nucleophiles inert to the present reaction conditions makes this approach synthetically attractive and would supplement the many other protocols that are available.

Graphical Abstract

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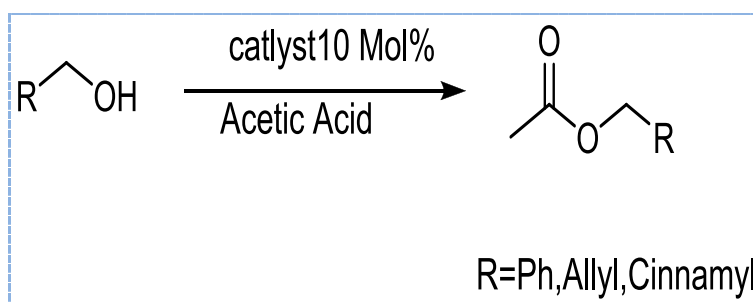
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Introduction

The spinels of AB_2O_4 type display very interesting catalytic properties and have been shown to possess potential industrial applications [1-3]. Especially spinels have been shown to be selective and active catalysts [4]. In particular, spinel ferrites have been reported to catalyze oxidation of hydrocarbon [5] and hydrogenation processes [6] in a facile manner. The catalyst surface is heterogeneous due to the possibility that metal ions can exist in different geometrical environment. $ZnFe_2O_4$ has a normal spinel structure with Zn^{2+} ions in tetrahedral (A) and Fe^{3+} in octahedral [B] sites. It is a commercially important material and widely used as catalyst [7], and photo-catalyst [8]. Protection of alcohols as acetates is one of the most fundamental and important transformation with extensive applications in organic synthesis [8]. Also, acetates find applications as intermediates in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, and chiral auxiliaries. The most commonly used methods employ acetyl chloride/acetic anhydride (both are corrosive and lachrymator) as reagent in the presence of acidic / basic catalyst [9] or tertiary amines such as triethylamine, pyridine and DMAP. Several metal triflates such as $In(OTf)_3$ [10], $Cu(OTf)_2$ [11], $Bi(OTf)_3$ [12], $ZrO(OTf)_2$ [13], $Ce(OTf)_4$ [14], $Gd(OTf)_3$ [15] and $Sc(OTf)_3$ [16–20], as well as Me_3SiOTf [21, 22] have been reported as excellent catalyst for efficient acetylation of various types of structurally diverse alcohols with acetic anhydride. Different metal salts such as $TiCl_4-AgClO_4$ [23], $LiClO_4$ [24], $CoCl_2$ [25] and $Mg(ClO_4)_2$ [26] and Iodine [27] are also known to effect influence the acetylation with acetic anhydride. However, only few catalytic methods employ use acetic acid as reagent for effective acetate protection of alcohols [28-35]. Although most of these reported methods work well, they suffer in terms of use of expensive hazardous reagents, longer reaction time and tedious work up procedure and there is

still a great need for development of simple, mild, less toxic and easy-to-handle catalytic protocols to prepare acetates. Solid super acids by virtue of its Bronsted and Lewis acid sites are known to dehydrate alcohols and facilitate generation of stable carbocations that could be manipulated to get the desired products. Along these lines, we explored the use of zinc ferrites to generate stable carbocation from the activated alcohols which could be trapped with acetic acid to afford the acetates. As, Nano catalysts display distinct advantages over conventional heterogenous catalysts they have been widely explored for different transformations. We explored zinc nanoferrite for acetylation of activated alcohols and as envisaged, the reaction proceeded well to afford the acetate in good yield (scheme 1).



Scheme 1

2 Experimental

2.1 Preparation and characterization of catalyst

Nano Zinc zinc ferrite (ZnFe_2O_4) was prepared by sol-gel auto-combination method. The A.R. Grade citric acid, ferric nitrate and Zinc zinc nitrate were used as starting materials. The preparation was carried out in the presence of air and inert conditions were not required.

The molar ratio of metal nitrates to citric acid was taken as 1:3. The metal nitrates were dissolved together in a minimum amount of double distilled water to get a clear solution. To the mixed solution of citric acid and metal nitrates in water, The ammonia solution was added slowly to the solution of citric acid and metal nitrates till the pH became was 7. Then the solution was heated on hot plate at up to 800 C with stirring and removal of water results in formation of viscous gel leading to frothing at the end . At this stage, in few minutes the gel gets autoignited which burnt with glowing flints. The decomposition continued till all the citrate complex was consumed. The auto ignition continued for a minute and yielded a brown colored ash the precursor, which was

calcined at 700o C for 4 h for transformationto transform into the spinel phase. Phase identification of the prepared sample was carried out using X-ray diffractometer with CuK α ($\lambda = 1.5406^{\circ}\text{A}$) as the source. The average crystallite size(D), and lattice parameter (a), were calculated from X-ray diffractogramthe XRD results. The particle size, distribution of nanoparticles, and surface morphology were confirmed evaluated by using Philips Model CM 200 Transmission transmission Electron electron Microscopemicroscope (Philips model CM 200).

Results and Discussion

3.1 Structural characteristics

The spinel nature of ZnFe_2O_4 synthesised by sol-gel auto-combustion method can be explained as follows. Dried gels first generate metal oxides ZnO and Fe_3O_4 in the beginning of the combustion process and during the combustion process lot of heat is released and the following reaction takes place.

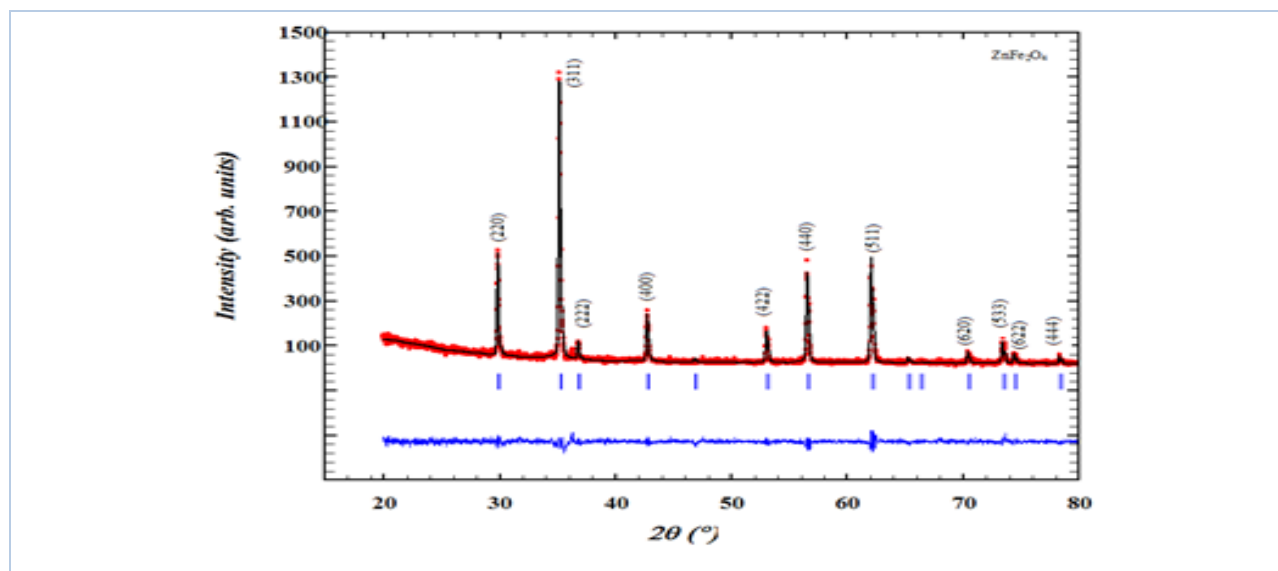
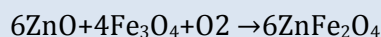


Fig.1 The Reitveld refined x-ray diffraction pattern of ZnFe_2O_4

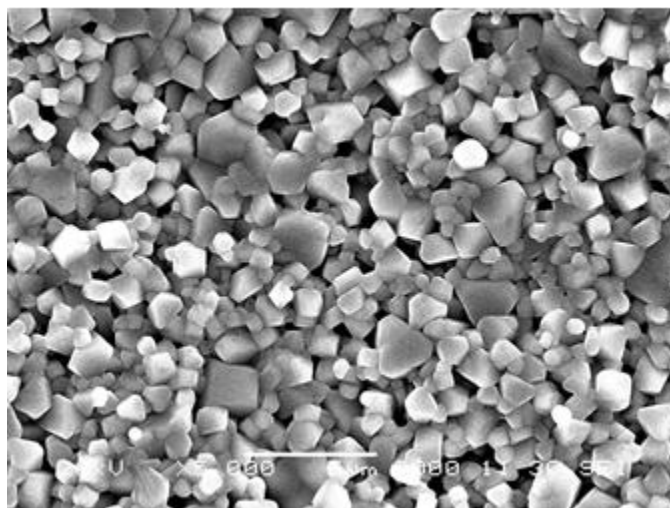


Fig. 2 The TEM photograph of the nanocrystalline ZnFe_2O_4 with particle size of ~ 25 nm

The pattern shows the formation of single phase cubic structure without any secondary phase. The data values of discrepancy factor $R_{wp} = 13.4$, expected value $R_{exp} = 13.6$, goodness of fit index $\chi^2 = 1.68$ and lattice constant $a = 8.410 \text{ \AA}$, were found to be in good agreement with the reported values [20]. Fig 2 indicates that the compound is in single-phase with no unreacted oxides present, and the distribution of the grain is homogenous, consisting of well formed crystalline grains.

3.2. Catalytic activity

Different nano ferrites were prepared and tested for catalytic activity in acetylation of alcohol using acetic acid as shown in Table 1. Among different catalysts studied, zinc ferrite showed good activity with 10 mol % concentration and further increase in concentration did not make any difference in yield.

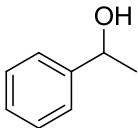
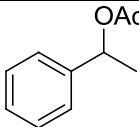
Table 1 Effect of different nano catalysts on acetylation of benzyl alcohol in acetic acid

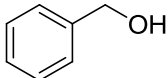
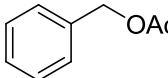
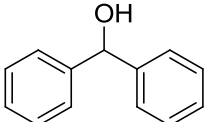
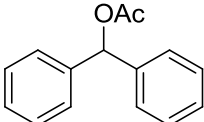
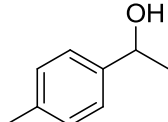
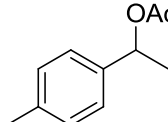
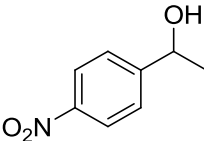
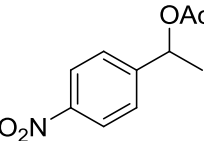
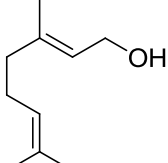
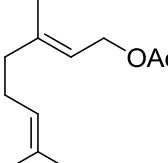
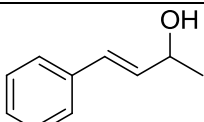
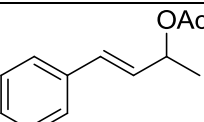
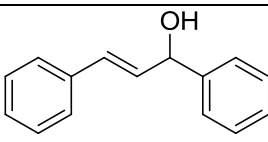
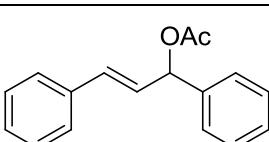
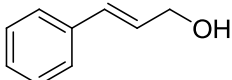
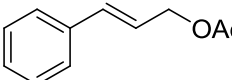
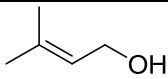
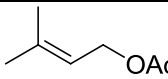
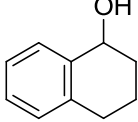
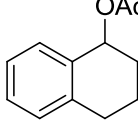
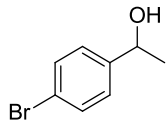
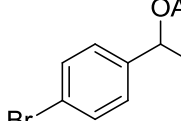
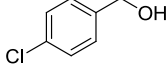
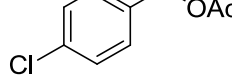
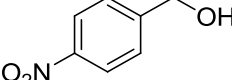
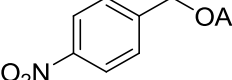
Entry	Catalyst (%mol)	Condition	Yield
1	No Catalyst	Reflux, 24h	0%
2	ZnO	Reflux, 24h	0%

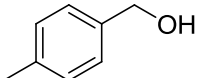
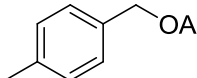
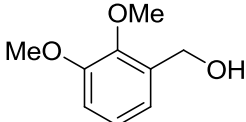
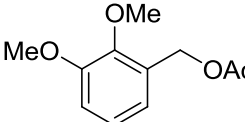
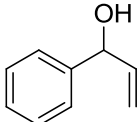
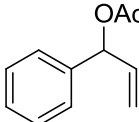
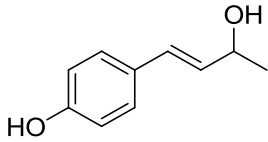
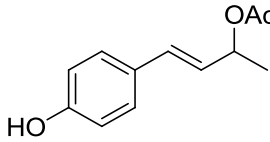
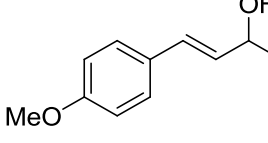
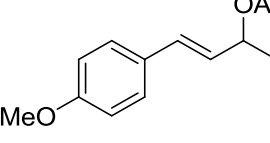
3	Nano ZnO ₂	Reflux, 24h	0%
4	Nano CuFe ₂ O ₄	Reflux, 24h	30%
5	Nano Fe ₃ O ₄	Reflux, 24h	10%
6	Nano CoFe ₂ O ₄	Reflux, 24h	50%
7	Nano ZnFe ₂ O ₄ (10%)	RT, 24h	10%
8	Nano ZnFe ₂ O ₄ (5 mol%)	Reflux, 5h	60%
9	Nano ZnFe ₂ O ₄ (10 mol%)	Reflux, 2h	95%
10	Nano ZnFe ₂ O ₄ (20 mol%)	Reflux, 2h	95%

To evaluate the scope and limitations of the current procedure, a wide array of structurally diverse alcohols were prepared and subjected to the present reaction conditions. and the The results are summarised in Table 2. As is obvious from the shown in table Table 2, the reaction proceeds well to afford the corresponding acetates in good to excellent yield. As expected aromatic moieties bearing electron withdrawing groups required more time and afford the acetates in moderate yield (entry 14). The reaction with secondary alcohols proceed faster as compared to primary alcohols. Also, Cinnamyl systems undergo facile acetylation in good yield in short time while unactivated alcohols are inert under the reaction conditions. Further, The nucleophiles such as amines and phenols do not undergo acetylation under the reaction conditions and remain inert. These observations suggest formation of carbocation from alcohols which is trapped by acetic acid to yield acetate but we do not observe products arising from delocalisation of carbocation in allylic systems. Also no dehydration was observed in tetralin system and the acetate was obtained in good yield.

Table 2: Nano ZnFe₂O₄ catalysed acylation of alcohols

Entry	Substrate	Product	Time (hr)	Yield %
1			1	85

2			1	82
3			1.5	80
4			1	80
5			2	70
6			2.5	82
7			1	85
8			1	90
9			1	85
10			1	85
11			2	93
12			1	95
13			1	80
14			2	75

15			1.5	70
16			2.5	90
17			1.5	75
18			1	85
19			2	85

4. Experimental

General procedure for acetylation. To a stirred A solution consists of alcohol (1 mmol), in acetic acid (3 mL), and ZnFe₂₀₄ (10 mol%) was mixed added and heated at up to 80 o C for appropriate time (TLC). After completion, the The reaction mixture was allowed to cool to room temperature and diluted with ether (30 mL). The reaction mixture was filtered through celite pad and the filtrate was washed with brine (3 × 20 mL). The organic phase was dried (Na₂SO₄) and concentrated under reduced pressure to give corresponding acetate (95% yield).

Spectral data:

benzhydryl acetate : ¹H NMR (400 MHz, CDCl₃) : δ 2.20 (s, 3H), 6.39 (s, 1H), 7.36-7.41 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): 21.29, 74.97, 126.22, 126.81 127.38, 127.70 128.77, 129.17, 137.88, 138.13, 170.54; MS: m/z (rel.abund.%) 227 (M+1).

1,2,3,4-tetrahydronaphthalen-1-yl acetate :

¹H NMR (300 MHz, CDCl₃): δ 1.67-2.05 (m, 4H), 2.19 (s, 3H), 2.60-2.71 (m, 2H), 5.39-5.45 (t J=5.4 Hz, 1H), 7.09-7.16 (m, 1H), 7.21 - 7.30 (m, 2H), 7.43 - 7.48 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 18.21,

20.98, 29.89, 31.37, 71.04, 124.83, 126.51, 127.66, 127.96, 135.49, 139.93, 170.84; EI MS: m/z 191 (M^{+1})

1-phenylethyl acetate : Colorless liquid; ^1H NMR (400 MHz, CDCl_3) : δ 1.54 (d, J = 6.6 Hz, 3H), 2.07 (s, 3H), 5.88 (q, J = 6.7 Hz, 1H), 7.36-7.31 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 20.78, 22.29, 73.98, 126.15, 128.21, 129.77, 142.08, 170.46; MS: m/z 165 (M^{+1}).

1-(2-hydroxyphenyl)ethyl acetate : Colorless liquid; ^1H NMR (400 MHz, CDCl_3) : δ 1.55 (d, J = 6.6 Hz, 3H), 2.10 (s, 3H), 5.77- 5.88 (m, 2H), 7.36-7.31 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): 20.78, 22.29, 73.98, 126.15, 129.77, 142.08, 155.09, 170.46; MS: m/z 181 (M^{+1}).

1-(3,4,5-trimethoxyphenyl)ethyl acetate : Colorless liquid; ^1H NMR (400 MHz, CDCl_3) : δ 1.54 (d, J = 6.6 Hz, 3H), 2.09 (s, 3H), 3.89 (s, 9H), 5.88 (q, J = 6.7 Hz, 1H), 6.88-6.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): 20.78, 22.29, 58.3, 62.4, 73.98, 102.15, 128.21, 129.77, 140.08, 170.46; MS: m/z 255 (M^{+1}).

benzyl acetate :

^1H NMR (400 MHz, CDCl_3) : δ 2.17 (s, 3H), 5.37 (s, 2H), 7.36-7.41 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): 20.69, 65.97, 126.22, 127.38, 128.77, 135.88, 170.27; MS: m/z 151 (M^{+1})

4-methoxybenzyl acetate : ^1H NMR (400 MHz, CDCl_3) : δ 2.17 (s, 3H), 3.80 (s, 3H), 5.38 (s, 2H), 7.36-7.41 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): 20.69, 56.34, 65.97, 120.22, 127.38, 128.77, 135.88, 157.70, 170.27; MS: m/z 181 (M^{+1})

cinnamyl acetate : ^1H NMR (400 MHz, CDCl_3) : δ 2.09 (s, 3H), 5.53 (qu, 1H, J = 6.6 Hz), 6.17 (dd, 1H, J = 6.8 Hz, 16.0 Hz), 6.58 (d, 1H, J = 15.6 Hz), 7.25 (d, 1H, J = 7.2 Hz), 7.25-7.30 (m, 2H), 7.38 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 21.93, 65.05, 120.98, 124.77, 126.09, 127.37, 132.11, 136.04, 170.43; EI MS: 177 (M^{+1})

(E)-4-phenylbut-3-en-2-yl acetate :

^1H NMR (400 MHz, CDCl_3): δ 1.42 (d, 3H, 6.8 Hz), 2.11 (s, 3H), 5.50 (qu, 1H, J = 6.8 Hz), 6.21 (dd, 1H, J = 6.8 Hz, 16.0 Hz), 6.63 (d, 1H, J = 15.6 Hz), 7.21 (d, 1H, J = 7.2 Hz), 7.30-7.34 (m, 2H), 7.40 (d, 2H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 20.03, 22.07, 71.83, 123.98, 124.91, 126.79, 127.77, 133.09, 136.65, 170.31; EI MS: 191 (M^{+1})

(E)-1,3-diphenylallyl acetate :

^1H NMR (400 MHz, CDCl_3): δ 2.11 (s, 3H), 5.47 (qu, 1H, $J = 6.8$ Hz), 6.17 (dd, 1H, $J = 6.8$ Hz, 16.0 Hz), 6.61 (d, 1H, $J = 15.6$ Hz), 7.17-7.24 (m, 2H), 7.30-7.48 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.03, 22.07, 71.83, 123.98, 124.91, 126.79, 127.77, 133.09, 136.65, 170.31; EI MS: m/z 253 (M^+).

5. Conclusion

The present paper study describes a facile eco friendly approach for acetylation of alcohols using acetic acid. The chemoselectivity of the protocol for activated systems making amines, phenols and other nucleophiles inert to the present reaction conditions makes this approach synthetically attractive and would supplement the many other protocols that are available.

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