

# A study of zeolite NaY-supported ruthenate in the oxidation of alcohols

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## Abstract

Sodium ruthenate was supported on zeolite NaY. This compound was found to be an efficient and selective catalyst, with a range of co-oxidants, for the room temperature oxidation of internal and external alcohols to their respective carbonyl products.

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## 1. Introduction

The selective oxidation of primary and secondary alcohols to their corresponding aldehydes or ketones plays a key role in synthetic organic chemistry, as it is essential for the preparation of many key synthetic intermediates [1–5]. Traditionally such transformations have been performed with inorganic oxidants, e.g. chromium(VI) compounds in stoichiometric quantities [6,7]. However, the toxic and corrosive nature of these compounds has limited their use. Whilst a number of effective homogeneous systems are known [1,6,8], issues such as product separation from the catalyst and catalyst recovery remain problematic. It is usually desirable to replace stoichiometric reagents with catalysts and to facilitate the efficient recovery of the catalyst from the reaction products, thereby reducing inorganic waste [9,10].

With ruthenium catalysts developed thus far, the oxidation of alcohols is the reaction effected with greatest efficiency [1,4,5]. Currently, the application of zeolite-supported ruthenium complexes for this transformation has been limited as indicated by the lack of literature on this topic. Some related research into the oxidation of alcohols by zeolite HZSM-5-supported chromium trioxide under microwave irradiation has been reported [11], as has iron(III) nitrate supported on HZSM-5, which was also found to oxidise alcohols to their corresponding carbonyl compounds in good yields under classical heating and microwave irradiation

[2]. Disadvantages of these systems include metal wastage as these are only stoichiometric oxidants.

We now report on sodium ruthenate supported on zeolite NaY in a series of catalytic alcohol to carbonyl oxidation reactions. NaY was chosen as support material since this particular class of zeolites has large apertures and supercages, as well as a high concentration of catalytic sites, which enhance their catalytic properties.

## 2. Experimental

### 2.1. Techniques

SEM and energy dispersive X-ray spectroscopy (EDS) analyses were carried out on a Hitachi S520. The EDS was done using a LINK ISIS energy dispersive X-ray analysis system, which was fitted to the SEM. The extent of metal loading was determined by flame emission spectroscopy (Perkin-Elmer Analyst) and conducted in triplicate. XPS data was obtained from a Physical Electronics (PHI) Quantum 2000 Scanning XPS (X-rays: Al K $\alpha$  at 15 kV beam energy and 20 W beam power; spot size: 100  $\mu$ m; pressure:  $<2 \times 10^{-8}$  Torr). IR spectra were recorded on a Nicolet 5 DX FT-spectrometer as KBr disks. DRIFT spectra and IR microscope images were recorded on a Perkin-Elmer Spectrum GX FT-IR system. Gas chromatography was carried out on Pye Unicam GCD, Fisons GC 8000 and Perkin-Elmer XL Autosystem instruments.

All catalytic and stoichiometric reactions were carried out a minimum of three times to ensure reproducibility. Catalytic reactions were carried out in the dark to prevent free radical

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oxidation reactions initiated by UV radiation and under a N<sub>2</sub> atmosphere to prevent oxidation by air.

## 2.2. Materials

*iso*-Butyl methacrylate (Acros), powdered 4 Å molecular sieves (Aldrich), cinnamyl alcohol (Acros Organics), cinnamaldehyde (Acros Organics), cinnamyl chloride (Aldrich), citral (BDH), crotyl alcohol (Aldrich), crotonaldehyde (Acros Organics), cyclobutanol (Acros Organics), cyclohexanol (BDH), cyclohexanone (Kleber), geraniol (Acros Organics), furfuryl alcohol (H & W Fine Chemicals), furfuraldehyde (BDH), 1-hexanol (Acros), hexanal (Aldrich), hexanoic acid (Aldrich), 2-hexanol (Aldrich), 2-hexanone (Aldrich), 4-nitrobenzyl alcohol (Acros), 4-nitrobenzaldehyde (Aldrich); 2,6-dichloropyridine (Acros) and iodosobenzene diacetate (Acros) were obtained commercially. Iodosylbenzene and 2,6-dichloropyridine-*N*-oxide were prepared as previously reported [12]. The other co-oxidants used, *tert*-butyl hydroperoxide (70% (m/v), Aldrich), sodium hypochlorite (15% (m/v), Associated Chemical Enterprises), hydrogen peroxide (30% (m/v), Saarchem), trimethylamine-*N*-oxide dihydrate (Aldrich), 4-methylmorpholine-*N*-oxide (Aldrich) and tetrabutylammonium periodate (Acros) were used as supplied. Zeolite NaY (Si:Al ~ 2.5, Aldrich) was dried by heating at 250 °C under nitrogen overnight before use.

## 2.3. Catalyst preparation

### 2.3.1. Preparation of RuO<sub>4</sub>

RuO<sub>4</sub> was prepared as previously reported [13]. Thus RuCl<sub>3</sub>·3H<sub>2</sub>O (1.54 g, 5.88 mmol) and NaIO<sub>4</sub> (5.50 g, 25.7 mmol) in de-ionised water (40 mL) were stirred overnight in a round-bottomed flask with a Teflon stopper (It is important avoid any contact between RuO<sub>4</sub> and grease). The RuO<sub>4</sub> formed was extracted into CCl<sub>4</sub> (40 mL) and stored under an aqueous NaIO<sub>4</sub> solution (1.00 g NaIO<sub>4</sub> in 30 mL water).

### 2.3.2. Preparation of zeolite NaY-supported sodium ruthenate

A solution of sodium ruthenate was prepared by stirring 7.8 mL of a 1 M NaOH solution with an equivolume of the RuO<sub>4</sub> in CCl<sub>4</sub> from the above (approximately 0.05 M) stock solution under N<sub>2</sub> for 24 h. Zeolite NaY (1 g) was then added to this ruthenate solution and the mixture stirred for a further 6 h. It was observed that the colour of the off-white solid changed to orange, which was suspended in a now colourless liquid. The loaded zeolite was dried under vacuum and stored under N<sub>2</sub>.

## 2.4. Oxidation reactions

### 2.4.1. Typical catalytic oxidation procedure of alcohols using the zeolite-supported oxidant

Activated 4 Å powdered molecular sieves (180 mg) and 6 mL solvent (CH<sub>2</sub>Cl<sub>2</sub> or toluene) were added to a nitrogen filled Schlenk tube. The alcohol (0.478 mmol) and isobutyl-

methacrylate (80 μL, 0.5 mmol) as the internal standard were then added. A 1.5-fold excess, relative to the substrate (0.717 mmol), of the appropriate co-oxidant and the catalyst (200 mg) was added and the mixture stirred at room temperature under N<sub>2</sub>. Aliquots were sampled at the start of the reaction, after 3, 24 and 48 h. The aliquots were dried with anhydrous magnesium sulphate and filtered through cotton wool. The filtrate was then immediately analysed by gas-chromatography.

### 2.4.2. Typical isolation of reaction products (e.g. cinnamaldehyde)

The reaction mixture, as described above, was stirred for 24 h. Thereafter, the molecular sieves and catalyst were filtered off and the solvent eluted through a silica column in order to remove the co-oxidant (TBAP) and any possible traces of leached ruthenium. The product was then isolated by fractional distillation and quantified gravimetrically (95%). TLC and NMR were used to further confirm the identity of the product.

### 2.4.3. Procedure for recycling the loaded zeolite

After the oxidation reaction mixture was stirred for 48 h, the mixture was filtered through a sintered glass crucible to separate the catalyst from the reaction products. The supported catalyst was then added to a new Schlenk tube prepared as above. The recycling procedure was repeated five times with a minimal mechanical loss of catalyst.

### 2.4.4. Typical stoichiometric oxidation procedure of alcohols using the zeolite-supported oxidant

This procedure was identical to the procedure using the zeolite-supported catalysts with the only difference being that no co-oxidant was added.

## 3. Results and discussion

### 3.1. Catalyst preparation and characterisation

Sodium ruthenate was prepared by the reduction of ruthenium tetroxide with NaOH. The ruthenate was loaded on dried zeolite NaY following an incipient wet impregnation technique (see Section 2.3). The 3.4% (by weight) ruthenium loaded zeolite (RuNaY) was then dried under vacuum and stored under N<sub>2</sub>. The ruthenium loading was determined by flame emission spectroscopy (FES).

IR data for the ruthenium loaded zeolite NaY are shown in Table 1. The IR spectrum of the ruthenium loaded zeolite showed the characteristic band positions at 830 and 867 cm<sup>-1</sup> which could be assigned to the asymmetric stretch of the trans O=Ru=O species, thereby confirming the presence of the ruthenium compound. The weak intensities of these bands could be attributed to the low metal loading on the support. Similar framework band positions and intensities as in the unloaded zeolite were observed for the loaded NaY zeolite. Weak peaks at 820 and 833 cm<sup>-1</sup> in the diffuse reflectance infra-red Fourier-transform (DRIFT) spectra were assigned to an asymmetric Ru=O stretch. This could imply that a certain proportion of sodium ruthenate was surface-supported on the zeolite.

Table 1  
Assignment of selected infra-red bands for RuNaY

Complex	Infra-red spectra—selected bands (cm <sup>-1</sup> )
NaY (unloaded)	459 m (ring and cage vibrations)
	576 w (ring and cage vibrations)
	791 w (ring and cage vibrations)
	1018 vs (ring and cage vibrations)
	3447 s (bridged hydroxyl group)
RuNaY (loaded)	830 w ( $\nu_{\text{asym}}$ ) (O=Ru=O)
	867 w ( $\nu_{\text{asym}}$ ) (Ru=O)
	820 m ( $\nu_{\text{asym}}$ ) (O=Ru=O) (DRIFT) <sup>a</sup>
	833 w ( $\nu_{\text{asym}}$ ) (O=Ru=O) (DRIFT) <sup>a</sup>

<sup>a</sup> DRIFT—diffuse reflectance infra-red Fourier-transform.

X-ray photoelectron spectroscopy (XPS) on the loaded zeolite gave an electron binding energy of 282.01 eV, which is characteristic of a Ru(VI) species [14], and further supports our proposal that ruthenate is the supported species. The proposed catalytic site is shown in Fig. 1. A similar mode of attachment was determined for Te<sup>2-</sup> on zeolite NaX [15,16].

Scanning electron microscopy (SEM) images of the loaded zeolites did not provide any valuable information regarding their surface morphology. Images of the ruthenium loaded zeolite showed that a small degree of detectable surface deposition of the sodium ruthenate did occur. A ruthenium peak in the energy dispersive X-ray spectroscopy (EDS) further confirmed the presence of a supported ruthenium moiety.

### 3.2. Oxidation reactions

The supported ruthenium compound was investigated as a catalyst for the oxidation of 1- and 2-hexanol with various co-oxidants (Table 2). It was observed that 1-hexanol underwent rapid oxidation to hexanal with the zeolite-supported sodium ruthenate using either iodosyl benzene (PhIO), tetrabutyl ammonium periodate (TBAP), trimethylamine-*N*-oxide (Me<sub>3</sub>NO) and *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidants in dichloromethane, with the first three being the most efficient. The fastest rate of oxidation of 1-hexanol was with the RuNaY–TBAP system, but this may also be partially attributed to the high activity of TBAP as primary oxidant (i.e. in the absence of catalyst) for this transformation [17]. However, the selectivity of the zeolite-supported ruthenate was not maintained when leaving the reaction mixture over the catalyst for long time periods as the over-oxidation product, hexanoic acid,

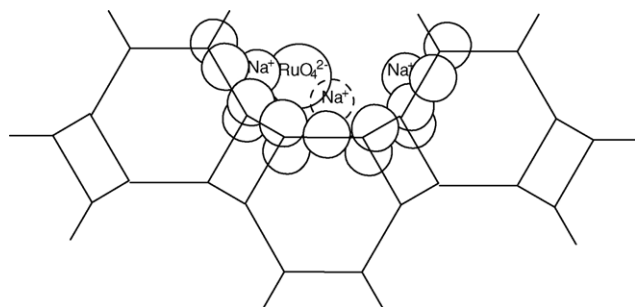


Fig. 1.

Table 2  
Oxidation of 1-hexanol to hexanal and 2-hexanol to 2-hexanone, using the loaded zeolite

Co-oxidant	Time (h)	1-Hexanol Yield (%)	2-Hexanol Yield (%) <sup>a</sup>
None (stoichiometric)	0.1	10 <sup>b</sup>	20 <sup>c</sup>
	3	18	22
	24	22	
	48		26
			34
NaOCl	0.1	39	46
	3	46	49
	24		51
	48		23
			25
H <sub>2</sub> O <sub>2</sub>	0.1	22	23
	3	23	25
	24		34
	48		35
			38
<i>t</i> -BuOOH	0.1	39	34
	3	39	35
	24		38
	48		48
			73
NMO	0.1	7	38
	3	20	48
	24	35	73
	48	69 (7) <sup>d</sup>	83
			100 <sup>d</sup>
Me <sub>3</sub> NO	0.1	69	23
	3	41 (28) <sup>d</sup>	32
	24	39 (30) <sup>d</sup>	59
	48		70
			85 <sup>d</sup>
PhIO	0.1	53	70
	3	56	74
	24	58	75
	48		81
			93
PhIO (50 °C)	0.1	79	93
	3	89	100
	24		
	48	90	
			90 <sup>c</sup> (10) <sup>d</sup>
TBAP	0.1	70	37
	3	76	53
	24	85 <sup>b</sup> (15) <sup>d</sup>	69
	72		82 <sup>e</sup>
O <sub>2</sub>	0.1	10	20
	24	18	21

<sup>a</sup> These values are also the conversion, since only 2-hexanone is formed.

<sup>b</sup> Aldehyde (hexanal).

<sup>c</sup> Ketone (2-hexanone).

<sup>d</sup> Hexanoic acid.

<sup>e</sup> Excess co-oxidant added.

was detected when PhIO (at 50 °C), NMO, Me<sub>3</sub>NO and TBAP were used as co-oxidants. With the exception of the system using Me<sub>3</sub>NO as co-oxidant, the over-oxidation product was only observed after more than 3 h. Since, with the exception of the RuNaY–NMO system, a maximum yield of hexanal was obtained within 3 h, the reaction could be stopped at that point to prevent any over-oxidation.

It is known that an aldehyde hydrate is necessary for carboxylic acid formation [18]. Whilst molecular sieves were added to the reaction mixture to remove water that is formed during the reaction and the zeolites were rigorously dried before loading with sodium ruthenate, there may still have been water of crystallisation co-ordinated to the aluminosilicate framework of the zeolite, thereby facilitating the formation of the aldehyde hydrate. More importantly, perhaps, zeolite NaY is hydrophilic and will therefore have a strong affinity for polar molecules

(H<sub>2</sub>O), which are formed during the course of the reaction. These molecules are small and can therefore easily move within the zeolite pores. This would facilitate the formation of the carboxylic acid via the aldehyde hydrate, thereby indicating that the reaction pathway to hexanoic acid could occur within the zeolite supercages. The co-oxidants Me<sub>3</sub>NO and NMO are also very hygroscopic, thereby possibly facilitating the formation of the aldehyde hydrate intermediate, if the molecular sieves do not effectively remove the water molecules.

The oxidation of 2-hexanol by the zeolite-supported oxidant showed similar trends as observed for the oxidation of 1-hexanol, with TBAP, Me<sub>3</sub>NO and PhIO being the co-oxidants which were most effective (Table 2). Total conversion was achieved when an excess of NMO was added after 48 h, as well as when PhIO was used as a co-oxidant at an elevated reaction temperature of 50 °C. The gentle heating probably facilitates a greater interaction between the substrate and the active site of the RuNaY. The increase in conversion after addition of an excess of co-oxidant (NMO, TBAP, Me<sub>3</sub>NO) implied that 1.5 equivalents of co-oxidant (relative to the substrate) was insufficient for the continuous regeneration of the catalyst, as an enhancement occurred when more co-oxidant was added after the conversions began to plateau. It is unlikely that this enhancement in activity has occurred due to the additional co-oxidant reacting stoichiometrically with the substrate, as these co-oxidants were only slightly reactive (with regard to the oxidation of the alcohol) in the absence of primary oxidant. A turnover number of 2 (calculated on the assumption that all the ruthenium present was involved in the catalysis) was obtained for the stoichiometric oxidation of 2-hexanol, suggesting a degree of autocatalysis in these reactions.

It was seen that the oxidation of the primary alcohol occurred more rapidly than the secondary alcohol with the majority of co-oxidants. This could be ascribed to steric factors in both the substrates and the catalyst.

Conversions obtained with O<sub>2</sub> as co-oxidant for the oxidation of 1- and 2-hexanol by RuNaY were almost identical to those obtained for the stoichiometric oxidations of the same substrates, indicating that molecular oxygen was ineffective in regenerating the primary oxidant.

The catalyst, with PhIO and TBAP as co-oxidants was further investigated with a wide range of alcohols. The results are shown in Table 3. Thus cinnamyl alcohol was selectively oxidised to cinnamaldehyde in good yields, with no attack on the carbon–carbon double bond observed. The catalyst with TBAP gave essentially quantitative conversion of the alcohol to the aldehyde. Whilst the system with PhIO showed a faster initial reaction rate, this may partly be due to the direct reaction of PhIO with the alcohol as PhIO shows some activity as a stoichiometric oxidant. TBAP, in the absence of RuNaY, is inactive. Unsupported sodium ruthenate, in contrast to the above results, gives a mixture of products with cinnamyl alcohol and thus shows much lower selectivity than RuNaY [19]. In a reaction carried out on a preparative scale using RuNaY, cinnamyl alcohol was isolated in almost quantitative yield, emphasising the advantage of a selective heterogeneous system, namely easy catalyst removal and product isolation.

Table 3  
The oxidation of alcohols using the Ru-loaded zeolite

Substrate	Solvent	Co-oxidant	Time (h)	Yield <sup>a</sup> (%)
Cinnamyl alcohol	Toluene	PhIO	0.1	57
			24	77
Cinnamyl alcohol	Toluene	TBAP	0.1	15
			24	100
Cinnamyl chloride	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	0
			48	0
Cinnamyl chloride	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	0
			24	0
Furfuryl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	51
			24	83
Furfuryl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	65
			24	70
4-Nitrobenzyl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	58
			24	96
4-Nitrobenzyl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	36
			24	58
Cyclobutanol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	91
			3	100
Cyclobutanol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	83
			24	84
Cyclohexanol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	86
			24	100
Cyclohexanol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	81
			24	100
Geraniol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	48
			24	74
Geraniol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	40
			24	56
Crotyl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	TBAP	0.1	23
			24	50
Crotyl alcohol	CH <sub>2</sub> Cl <sub>2</sub>	PhIO	0.1	20
			24	59

<sup>a</sup> These values are also the conversion, since no other products are formed.

Selective oxidations were also carried out on substrates containing heteroatoms and furfuryl alcohol and 4-nitrobenzyl alcohol were converted into furfural and 4-nitrobenzaldehyde, respectively, in good yield. Both co-oxidants show low activity in the absence of catalyst. The absence of any oxidation products of cinnamyl chloride indicated that the zeolite oxidant was selective as the double bond and halogen atom were not subjected to oxidative attack. Oxidations of the cyclic alcohols cyclobutanol and cyclohexanol were also selectively accomplished in excellent yields by the RuNaY–TBAP and PhIO systems. The complete conversion of cyclobutanol to its corresponding ketone suggests that RuNaY is a two-electron oxidant [20]. PhIO on its own shows some oxidative activity, whilst TBAP does not. Both RuNaY systems are more efficient than unsupported sodium ruthenate [21].

The RuNaY catalyst also selectively converts geraniol to geranial (citral). No isomerisation to citronellal was observed, as was reported to occur with tetrapropylammonium per-ruthenate [22]. Crotyl alcohol is also selectively converted to corresponding aldehyde by the RuNaY catalytic system. Here again the system exhibits greater selectivity than unsupported sodium ruthenate, which also gives the over-oxidation product β-methacrylic acid [21]. The enhancement in selectivity could be postulated to be due to a lower concentration of the catalyt-



Table 4  
Oxidation of 2-hexanol to 2-hexanone with a recycled Ru-loaded zeolite with PhIO as a co-oxidant

Recycle	Co-oxidant	Time (h)	Yield <sup>a</sup> (%)
Initial	PhIO	0.1	70
		3	74
		24	75
		48	81
First recycle	PhIO	0.1	30
		3	53
		24	58
		48	60
Second recycle	PhIO	1	0
		3	53
		24	67
		48	71
Third recycle	PhIO	0.1	0
		3	60
		24	62
		48	64
Fourth recycle	PhIO	0.1	0
		3	62
		24	66
		48	72
Fifth recycle	PhIO	0.1	0
		3	33
		24	54
		48	65

<sup>a</sup> These values are also the conversion, since only 2-hexanone is formed.

ically active ruthenium species being directly accessible to the substrate as compared to a homogeneous catalytic reaction.

The RuNaY–PhIO system with 2-hexanol was chosen to determine to which degree the catalyst could be recycled and it proved to be an efficient and selective system for this oxidation even after numerous recycling. A slight decrease in the initial rate of formation of 2-hexanone within the first 3 h was observed with each recycle. The very slight, but additive, mechanical loss of oxidant after each recycle may explain the decrease in yield after 3 h on the fifth recycle. The efficiency of the catalyst was, however, stable at longer reaction times as very similar conversions (yields) were obtained after 48 h for each recycle. Thus 2-hexanone yields of 81, 60, 71, 64, 72 and 65% were obtained in six successive recycle experiments (Table 4).

Two experiments to determine the degree of leaching of the ruthenium species from the catalyst were carried out. In the first test, the catalyst was filtered off after ca. 10% conversion and the reaction mixture further monitored for 48 h. No further conversion was observed. In the second experiment the catalyst was filtered off after 48 h and the degree of leached metal determined by flame emission spectroscopy. A 0.033% ruthenium contamination of the solvent was detected, which represents a loss of 0.65% of the total ruthenium on the zeolite. This, indirectly, further supports our belief that there is an interaction between the ruthenium species and the cationic sites within the zeolite, since the leaching is negligible. The leached species is either too dilute to show any detectable catalytic conversion or the species is inactive [23].

Activated powdered 4 Å molecular sieves were employed as a dehydrating agent in all the above-mentioned RuNaY catalysed

reactions. It was subsequently postulated that the entry to the zeolite pores as well as access to the catalytically active sites might be hindered by these sieves. A comparative experiment using pellet molecular sieves was consequently carried out using the RuNaY–Me<sub>3</sub>NO system on 2-hexanol. Conversions (yields) were similar after 24 h (71% versus 64%), but a larger conversion to the ketone (83% versus 65%) was obtained for the reaction using pellet molecular sieves after 48 h. This may indicate that the powdered molecular sieves do partially restrict access of the substrate to the zeolite apertures. A comparable conversion/yield (85%) was, however, obtained when more co-oxidant was added to the reaction using powdered molecular sieves.

#### 4. Conclusion

In conclusion, the zeolite NaY-supported sodium ruthenate was found to be an easily synthesised, recyclable oxidant for the efficient and selective oxidation of a wide range of alcohols to their corresponding carbonyl products at room temperature without heteroatom oxidation, double bond isomerisation or cleavage. The conversions, selectivities and yields compare very favourably with other zeolite supported oxidants [2,11,24] and are comparable to other inorganic heterogeneous ruthenium containing oxidants [25–28].

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