

STUDY OF MANGANESE (II) SUPPORTED TITANIUM TUNGSTATE AS CATALYST FOR EPOXIDATION OF CYCLOHEXENE WITH DRY TBHP

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ABSTRACT

Manganese supported titanium tungstate {TiMn(II)W} was synthesized by ion-exchange method and characterized by DSC and FTIR techniques. Its catalytic activity for epoxidation of cyclohexene using dry *tert*-butylhydroperoxide (TBHP) as an oxidant was studied. In the epoxidation reaction, under optimized condition cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone. A maximum 67.49% selectivity for epoxidation of cyclohexene was observed for Ti Mn(II)W/dryTBHP system after 6 hours of reaction when concentrations of the catalyst and the substrate were 0.20 mmole and 20 mmole respectively.

Key Words : Epoxidation, Cyclohexene, Titanium tungstate, *tert*-butylhydroperoxide, Catalyst

INTRODUCTION

The catalytic functionalization of hydrocarbon is of chemical and biochemical significance. Within such functionalization epoxidation of olefins, using a metal catalyzed system poses a synthetic and theoretical challenge¹. In this line of research, manganese porphyrin and non-porphyrin metal complexes are extensively studied as homogenous catalysts using various oxidants²⁻⁴. Chiral Mn(II) and Mn(III) Salen systems are vigorously studied for the enantiomeric epoxidation of the unfunctionalised olefins⁵. Catalytic activity of hydrogenised Mn-porphyrin, Mn(Salen) and its analogues using supports of clays, microporous zeolites, MCM-41 and polymers⁶⁻⁸ are reported. The immobilization of transition metals and transition metal complexes on solid supports have provided

catalysts that are easier to handle and exhibit improved activities and selectivity's induced by the support⁹. The ion-exchange method of catalyst immobilization on layered compounds is simpler compared to the procedures required for attachment of complexes to polymers¹⁰. Based on cation exchange, polymer-supported catalysts are also developed¹¹, however the thermo-oxidative instability of the polymer under reaction conditions and the poor mechanical properties of the organic support are the main drawbacks of these systems¹². Recently we have reported epoxidation of cyclohexene catalysed by Mn(II) supported on α -titanium arsenate as catalyst with dry TBHP¹³. In continuation our work, in present paper, we are reporting our results on the synthesis and catalytic behaviour of Mn(II) supported titanium tungstate (TiMn(II)W) for the

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epoxidation of cyclohexene using dry *tert*-butylhydroperoxide (TBHP) as an oxidant.

MATERIAL AND METHODS

Sodium tungstate (E. Merck), 15% w/v titanate chloride solution (BDH) and manganese acetate (E. Merck) were of reagent grade. Cyclohexene (E. Merck) was checked by gas chromatography (G.C.) to ensure that no oxidation products were present in the substrate. The solution of dry TBHP in benzene was obtained by careful azeotropic distillation of the aqueous 70% commercial solution (E. Merck) according to the procedure described by Sharpless et al.¹⁴. The strength of dry TBHP was estimated by a known procedure¹⁴. The reference sample of epoxide was prepared by the standard procedure¹⁵.

Analytical gas chromatography was carried out on a Shimadzu Gas Chromatograph GC-14B with dual flame ionization detector (FID) and attached with Shimadzu printer. Differential scanning calorimetry (DSC) studies of hydrogen form of titanium tungstate (TiH_2W) and Mn(II) supported on titanium tungstate $\{TiMn(II)W\}$ were done on a differential scanning calorimeter at a heating rate of 10 °C/ min. Infrared spectra were taken in a Perkin Elmer model 1750 FTIR.

Catalysts preparation

The catalyst was prepared in two steps. In the first step, TiH_2W , $\{Ti(HWO_4)_2 \cdot H_2O\}$, was synthesized by a known procedure¹⁶. In the second step, hydrogen of TiH_2W was substituted by a Mn(II) to synthesize $\{TiMn(II)W\}$. For preparation of $TiMn(II)W$, stock solution of manganese acetate (0.1N) was prepared and initial pH of the solution was measured on a digital pH meter. Then 100 ml of the solution was vigorously stirred with 1.0 g of TiH_2W by a magnetic-stirrer for one hour. During stirring, the pH of the solution was measured at an interval of every ten minutes to monitor change in the pH value. The uptake of Mn(II) ion is determined from the change in pH value and constancy of pH is an indication of attainment of equilibrium. After attainment

of equilibrium, the solution was filtered. The filtered solid was added to a fresh solution (100 ml) of manganese acetate and the process was repeated again and again until there was no further change in pH of the solution. The cation exchanger, so obtained, was filtered and washed with distilled water. Finally, it was dried in an oven at 40 °C.

Catalytic epoxidation of cyclohexene

Epoxidation of cyclohexene was carried out in a three-necked round bottom flask (100 ml) under nitrogen atmosphere. Nitrogen was flushed for 10 minutes through the flask, which was loaded with benzene (10 ml), cyclohexene (20 mmole), catalyst $\{TiMn(II)W\}$, 0.2 mmole and dodecane (an internal standard, 0.1 ml). After nitrogen flushing, TBHP (4 mmole) was added and the contents of the flask were heated at 80 °C on a magnetic hot plate for 6 hours with continuous stirring. After completion of the reaction, the contents of the flask were cooled in an ice-bath and the catalyst was filtered out. In the filtrate, 10 ml of freshly prepared 10% solution of sodium sulfite was added drop by drop under constant stirring to destroy unreacted TBHP. The products were extracted with ether and then dried using anhydrous magnesium sulphate. These products were analyzed by gas chromatography using XE-60 as column at 120 °C.

The effect of catalyst concentration on the epoxidation of cyclohexene was studied by changing the concentration of the catalyst $\{TiMn(II)W\}$ from 0.1 to 0.5 mmole. The effect of cyclohexene concentration was studied by taking catalyst ($TiMn(II)W$, 0.2 mmole), TBHP (4 mmole), dodecane (0.1 ml) and six different concentrations of cyclohexene (1, 5, 10, 15, 20 and 25 mmol) in benzene (10 ml) under nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of the catalysts

The catalyst, $TiMnW$, was prepared by exchanging surface protons (hydrogen ions) from TiH_2W with Mn(II) ion. The total number of released hydrogen ions $[H^+]$ in the exchange

reaction determined the total uptake of Mn(II) ions on the surface of TiH_2W . The number of hydrogen ions $[\text{H}^+]$ released in the exchange reaction in each trial was calculated from pH value of the metal solution at equilibrium¹⁷. The process of attaining equilibrium was repeated until the subsequent pH change was negligible and the total uptake of Mn(II) ions is determined from the total change in the pH value in all trials.

The initial pH of the of 0.1 M solution of $(\text{CH}_3\text{COO})_2\text{Mn}$ was 7.14, however when this solution was used for uploading of Mn(II) on TiH_2W , the total uptake of Mn(II) ions was not significant equal to 0.00097 m eq./gm in three trials. To increase the uptake of Mn(II) ions on TiH_2W , the pH of the 0.1 M solution of $(\text{CH}_3\text{COO})_2\text{Mn}$ was adjusted up to 4.11 by adding CH_3COOH (pH = 4.11) because an increase in uptake of Mn(II) on TiH_2W is reported when the pH of the of the solution was below 4.0¹⁸. By using this solutions, the final pH value of $(\text{CH}_3\text{OO})_2\text{Mn}4\text{H}_2\text{O}$ solution in the 1st trial, was 4.06; thus $[\text{H}^+] = 8.709 \times 10^{-5} \text{ M/L} = 4.354 \times 10^{-6} \text{ moles per 50 ml}$. Converting this to meq/g, when the weight of the sample (TiH_2W) was 1.0 g, thus $4.354 \times 10^{-3} \text{ moles per 50ml}$ is equal to 0.004 meq./g. Three such trials were required after which change in pH was negligible. The total uptake of Mn(II) ions on TiH_2W , obtained by summing uptakes of Mn(II) ions in all trials, was 0.012 meq./g (0.004, 0.004, 0.004 and 0 at pH 4.06-4.08). Thus by changing the pH of the solution from 7.14 to 4.11 increases the uploading of Mn(II) ions on TiH_2W .

DSC studies of TiH_2W showed two endotherms at 131.32 and 222.90 °C, which are in consistent with the earlier observation¹⁶. Endotherm at 131.32°C was due to loss of external water molecules while endotherm at 222.90 °C was due to loss of structural water molecule in TiH_2W . In case of TiMnW , only one endotherm at 137.92°C was observed. The absence of the endotherm at 222.90°C indicated absence of any replaceable H^+ ion.

These results confirm that hydrogen form of titanium tungstate is converted into manganese supported titanium tungstate

FT-IR spectra of TiH_2W and TiMn(II)W are shown in **Fig. 1**. FT-IR spectra of TiH_2W show a broad band in the region 3500, 3300-3350, and 3150 cm^{-1} attributed to asymmetric and symmetric hydroxo -OH and aquo -OH stretches¹⁹. The absorption band at 2350 cm^{-1} is assigned to acidic OH group due to strong hydrogen bonding. A sharp medium band at 1620 cm^{-1} is attributed to the bending mode of interstitial water. The absorption bands at 1384, 1031 cm^{-1} are attributed to symmetric and asymmetric stretching modes of W-O bonds in the H_2WO_4 or HWO_4 groups. The band at 527-420 cm^{-1} is assigned to the stretching vibration of Ti-O bond. It was observed that in FTIR spectra of TiMn(II)W the band of W-O bond is almost disappeared and the band Ti-O was shifted to higher frequency indicating the presence of Mn-O interaction in TiMn(II)W .

Catalytic epoxidation of cyclohexene

The epoxidation of cyclohexene using TiMn(II)W /dryTBHP system was studied under atmospheric air as well as under nitrogen. It was observed that cyclohexene was oxidized to cyclohexene oxide, cyclohexenol and cyclohexenone in the epoxidation reaction. The yield of epoxide was more in the epoxidation reaction under nitrogen compared to that under atmospheric air. Similar observation is reported in the epoxidation reaction with CrO_3 /TBHP system²⁰. The epoxidation reaction is inhibited by water while accelerated by nondonar polar solvents²¹ and azeotropically dried solution of TBHP in benzene is very stable to storage²². Thus instead of commercial TBHP (70% in water), dry TBHP in benzene was used as the oxidant in the epoxidation of cyclohexene. The yields of the products were based on the internal standard (dodecane) and the consumption of TBHP was determined iodometrically.

TiMn(II)W and TiH_2W were separately

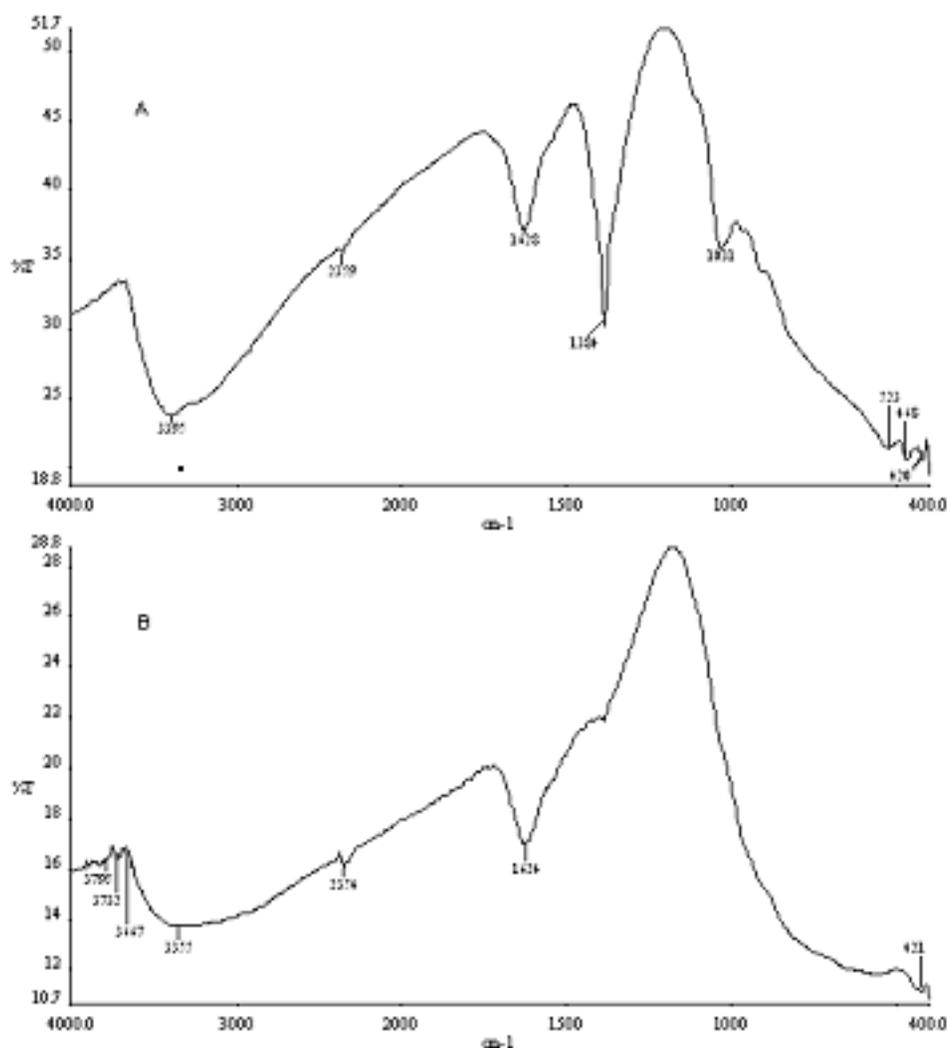
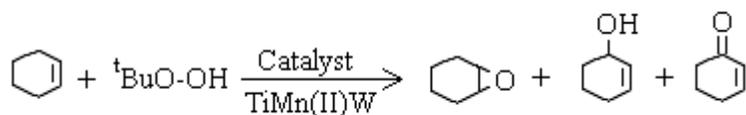


Fig. 1: FT-IR Spectrum of [A] TiH_2W and [B] TiMn(II)W

tested in similar experimental conditions for epoxidation of cyclohexene. In the study, it was found that TiMn(II)W was active for the epoxidation of cyclohexene with dry TBHP as an oxidant whereas TiH_2W was catalytically inactive. Therefore the exchange of manganese ions with hydrogen converted a non-catalyst,

TiH_2W , into active catalysts for the epoxidation of cyclohexene. The catalytic epoxidation of cyclohexene, catalyzed by TiMn(II)W /dry TBHP system can be explained by the reaction.

The formation of cyclohexenol and



cyclohexenone in the epoxidation reaction suggest that a free radical pathway is operative¹. The selectivity of the cyclohexene oxide is a measure of the reactivity of the catalyst {TiMn(II)W}. The percentage-conversion of the substrate and the percentage-selectivity of the products in the epoxidation reaction are calculated as :

$$\text{Substrate conversion (\%)} = \frac{\text{Substrate converted (Moles)}}{\text{Substrate used (Moles)}} \times 100$$

$$\text{Product selectivity (\%)} = \frac{\text{Product formed (Moles)}}{\text{Substrate converted (Moles)}} \times 100$$

The kinetics of cyclohexene epoxidation using TiMn(II)W/dryTBHP system was monitored at different time-intervals, (Fig. 2). It was observed that initial half hour was the induction period of the catalyst for epoxidation

reaction during which no product formation took place and the reaction was complete in 6 hours after which no further epoxide formation took place. The conversion of cyclohexene and the selectivity of products were estimated at different times. The percentage conversion of cyclohexene kept on increasing continuously with time. The percentage selectivity of epoxide reached a maximum (67.49%) after 6 hours and then started decreasing.

The effect of the concentration of catalyst, TiMn(II)W, in the epoxidation of cyclohexene using dry TBHP as an oxidant was studied and the results are given in Table 1. It was observed that the selectivity's of cyclohexene oxide, cyclohexenol and cyclohexenone were different at different concentrations of the catalyst. At 0.20 mmole concentration of the catalyst, the selectivity of cyclohexene oxide was a maximum (67.49%),

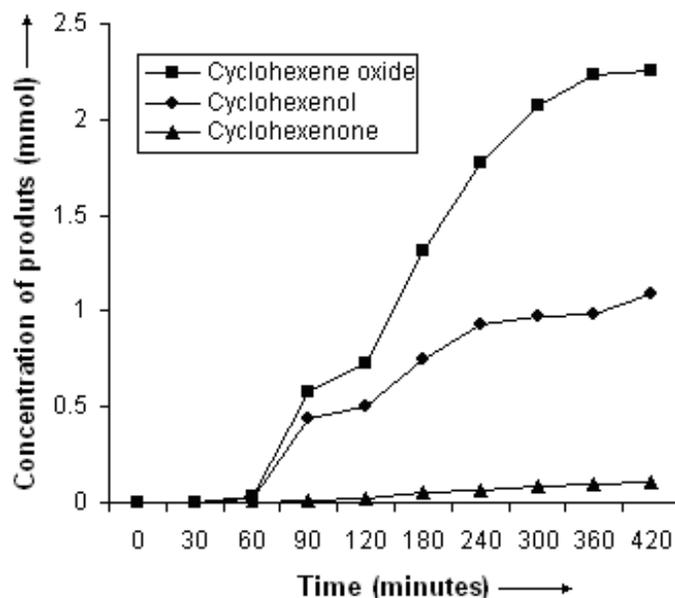


Fig. 2 : Kinetics of epoxidation of cyclohexene catalyzed by TiMn(II)W/dryTBHP system

Table 1 : Effect of concentration of catalyst on the epoxidation of cyclohexene catalyzed by TiMn(II)W/dryTBHP system

S. No.	Concentration of catalyst (mmol)	Conversion of cyclohexene (%)	Selectivity of epoxide (%)	Selectivity of cyclohexenol (%)	Selectivity of cyclohexenone (%)
1.	0.10	8.39	66.32	30.75	2.93
2.	0.20	16.55	67.49	29.76	2.75
3.	0.30	17.02	65.48	31.37	3.14
4.	0.40	17.93	63.99	32.66	3.35
5.	0.50	18.91	62.50	33.91	3.59

while selectivity of other products was a minimum (cyclohexenol = 29.76% and cyclohexenone = 2.75%). Similar observation is reported in case of α -TiRuAs/dryTBHP system⁹.

The effect of the concentration of cyclohexene (substrate) in the epoxidation reaction of cyclohexene using TiMn(II)W/dryTBHP system was studied. The results of the conversion of cyclohexene, selectivity of products for different concentrations of cyclohexene are summarized in **Table 2**. The concentration of cyclohexene was varied from 1 to 25 mmols and it was observed that the yield of all the products increased with increase

in concentration of cyclohexene. The selectivity of cyclohexene oxide reached a maximum (67.49%) for 20 mmole concentration of cyclohexene.

A similar mechanism is proposed for the epoxidation of cyclohexene using TiMn(II)W/dryTBHP system as we proposed earlier for TiRu(III)W/dryTBHP system²³. The recyclability test of the catalyst for cyclohexene epoxidation with dry TBHP was also tested for three cycles under similar reaction conditions. It was found that catalyst was stable up to three runs.

Table 2 : Effect of concentration of catalyst on the epoxidation of cyclohexene catalyzed by TiMn(II)W/dryTBHP system

S. No.	Concentration of substrate (mmol)	Conversion of cyclohexene (%)	Selectivity of epoxide (%)	Selectivity of cyclohexenol (%)	Selectivity of cyclohexenone (%)
1.	1.00	1.93	60.05	35.65	4.30
2.	5.00	3.66	62.35	34.05	3.64
3.	10.00	5.03	65.00	31.95	3.05
4.	15.00	16.70	66.89	30.25	2.86
5.	20.00	17.55	67.49	29.760	2.75
6.	25.00	19.97	65.74	31.13	3.13

CONCLUSION

Finally, it can be concluded that a recyclable catalyst TiMn(II)W was synthesized and characterized by DSC and FTIR spectroscopy. A maximum 67.49% selectivity for epoxidation of cyclohexene was observed for, TiMn(II)W/dryTBHP system after 6 hours of reaction when concentrations of catalyst, substrate and oxidant were 0.20, 20, and 4 mmol respectively.

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