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Zirconium Doped Tunnel Structure Manganese Oxide OMS-2 Catalysts

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Abstract

Zirconium doped tunnel structure manganese oxide (OMS-2) materials were synthesized by reflux and impregnation methods by adopting suitable synthetic conditions. XRD and TGA analyses were used to characterize the crystal structure and thermal stability of as synthesized zirconium doped manganese oxide OMS-2 catalysts. FT-IR and BET analyses were used to interpret the stretching frequency of corresponding functional group present in the catalysts and surface area of as synthesized catalysts. Fibrous structure and the aggregated particle morphology of zirconium doped manganese oxide OMS-2 catalysts were confirmed by TEM analyses. The synthesized catalysts were tested for liquid phase oxidation of side chain aromatic compounds such as ethyl benzene and benzyl alcohol, TBHP (tert-butyl hydrogen peroxide) as the chemical oxidant. Liquid phase oxidation ethyl benzene over zirconium doped tunnel structure manganese oxide OMS-2 catalysts show the higher substrate conversion compared to that of benzyl alcohol oxidation on as synthesized zirconium doped manganese oxide OMS-2 catalysts.

Introduction

Manganese oxide octahedral molecular sieve (OMS) are a class of tunnel structure materials similar to the naturally occurring minerals todorokite, cryptomelane and hollandite type manganese oxide minerals. The basic structural unit of OMS material is MnO_6 octahedron arranged in tunnel-like microstructures. The presence of one-dimensional tunnel structure allows them to be utilized in a manner similar to that of molecular sieves. Cryptomelane is one of the major manganese oxide minerals found in the deep-sea manganese nodules and in soil sediments [1]. The tunnels of cryptomelane consist of (2×2) matrix of edge-shared MnO_6 octahedral chains that are corner shared to form a one-dimensional tunnel structure. Manganese oxide OMS type materials are widely used in many chemical processes because of their porous structure, mild surface acid-base properties and ion-exchange abilities. Especially, the divalent and trivalent transition metal ions doped cryptomelane type manganese oxide (OMS-2 type) materials, with specific pore sizes of 4.6 Å, have been developed recently as promising catalysts for the oxidation of alcohols and compounds containing side chain [2]. Hydrophobic property of cryptomelane type manganese oxide OMS-2 material has also been tested for total oxidation of volatile organic compounds [3] (Fig. 1).

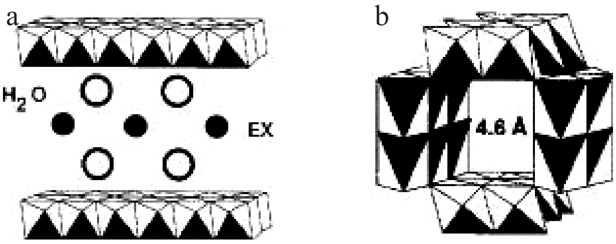

Fig. 1. (a) – Potassium birnessite (Ex = K); (b) – Cryptomelane type K-OMS-2 structure.

Doping of higher valent transition metal ion into the tunnel structure of OMS-2 material, by adopting a suitable synthetic methodology, can provide potential catalytic activity for oxidation reactions. Recently, stability and reactivity of Cu^{2+} and Ni^{2+} ion doped synthetic OMS-2 catalysts have been studied by using TPR (temperature programmed reduction) and TPD (temperature programmed desorption) techniques [4-5]. Recently, zirconium doped manganese oxide composite type catalysts and coprecipitated Mn-Zr oxides and their behavior for catalytic oxidation of isopropyl alcohol and phenanthrene have also been investigated [6]. Radu *et al.* have studied the

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*corresponding author. E-mail: bviswanathan@hotmail.com structure and redox properties of MnO_x supported yttrium stabilized zirconia catalysts for CO and CH_4 oxidation [7]. In classical synthetic laboratory procedures, permanganate or dichromate has been used preferably as stoichiometric oxidant for oxidation reaction. Normally, titanium substituted silicates are usually thought to catalyze ring hydroxylation of arenes, and substitution of vanadium [8-12], tin [13-16], chromium [17–19] into zeolite and aluminophosphate structures favor side chain oxidation. Most notably, chromium substituted aluminophosphate, Cr-APO-5, catalyzes the formation of ketones from alkyl arenes with TBHP as oxidant in moderate yields with good selectivity greater than 90% [19-20]. Cobalt containing silicate xerogels have been used as catalysts for the oxidation of side chain aromatic compound by using 3M TBHP in isooctane as the oxidant with good selectivity [21]. Studies on zirconium doping in to ordered phase of porous manganese oxide materials are not well established and hence in the present study an attempt has been made to synthesize zirconium doped ordered porous manganese oxide such as OMS-2 type tunneled manganese oxide materials by adopting suitable synthetic strategies. As synthesized zirconium doped OMS-2 catalysts were tested for oxidation of side chain alkyl aromatic compounds by using cleaner peroxide oxidant. In the present study as synthesized zirconium doped tunneled manganese oxide OMS-2 type catalysts were tested for oxidation of side chain aromatic compounds such as ethyl benzene, benzyl alcohol using 70% aqueous solution of TBHP. Effect of mole ratio between substrate to oxidant for side chain oxidation, has also been studied.

Experimental

Materials and Physical measurements

All the chemicals purchased from E-merck and SRL (India) are reagent grade and the catalysts prepared were characterized by powder X-ray diffraction method using Philips Diffractometer (Philips Generator, Holland, Model PW 1140) provided with an online recorder. The diffraction patterns were recorded using Fe K_α ($\lambda = 1.97$ Å) radiation at a scanning speed of 2°/min. Thermal stability and phase transitions were analyzed by using Perkin Elmer Delta Series DSC 7 instrument, at 10 degree/min scanning rate. FT-IR Shimadzu 8400 series was used for IR studies in the range of 400 cm^{-1} to 4000 cm^{-1}. Transmission electron micrographs (TEM) were recorded using Philips CM12/STEM, Scientific and Analytical Equipment. TEM sampling grids were prepared by placing 2 μL of the solution on a carbon-coated grid and the solution was evaporated at room temperature, surface area values of as synthesized materials were obtained by BET (Brunauer-Emmett-Teller) method using Carlo-Erba sorptometer (Model 1800). The products of the catalytic reactions were analyzed using gas chromatography (Nucon 5600, FID, SE 30 column).

Syntheses of zirconium incorporated tunneled OMS-2 catalysts

Potassium containing OMS-2 type manganese oxide materials were synthesized by refluxing 30 mL of 1.75 M solution of manganese (II) sulphate with 95 mL of 0.4 M potassium permanganate in the presence of concentrated nitric acid (6.8 mL). An appropriate amount of aqueous solution of zirconyl (IV) nitrate was added to the above solution mixture. Molar ratio between potassium permanganate and manganese sulphate was maintained at 0.72 and molar ratio of Zr^{4+}/Mn^{2+} at 0.20 for one sample and 0.25 for the second sample. pH of the reflux solution was maintained between 2-3 by adding required amount of concentrated nitric acid. Refluxing was continued upto 24 h and the product was filtered, washed several times with distilled deionized water and dried at 390 K overnight. As synthesized samples were designated as Zr-K-OMS-2 (0.20) and Zr-K-OMS-2 (0.25).

Syntheses of zirconium modified tunneled OMS-2 catalysts

Another two types of zirconium-modified catalysts were synthesized from potassium birnessite and cryptomelane type manganese oxide materials. Potassium birnessite was synthesized by the oxidation of O.5 M solution of manganese (II) acetate in strong alkaline medium. Hydrous Mn $(OH)_2$ suspension was obtained by the drop wise addition of 5.0 M KOH solution. As synthesized manganese oxide suspension was then oxidized by potassium permanganate solution (0.10 M) followed by ageing the precipitated suspension for 4-5 days. Molar ratio between MnO_4^-/Mn^{2+} was maintained at 0.36. After 4-5 days, the suspension was filtered, washed several times with double distilled water and dried at room temperature. As synthesized potassium birnessite was then used to prepare zirconium modified OMS-2 type catalyst. An appropriate amount (0.40 g) of zirconyl nitrate was dissolved in methanol and the solution was stirred with 1.6 g of potassium birnessite material for 24 h, followed by evaporation of the solvent. As synthesized material was subjected to heat treatment at 730 K in air for 20 h, which resulted in the formation of tunneled structure manganese oxide OMS-2 catalyst, designated as Zr-K-OMS-2 (Bir).

Cryptomelane type tunneled manganese oxide OMS-2 catalyst was synthesized as follows [14]. 113 mL of 0.4 M solution of potassium permanganate was added to a 500 mL round-bottom flask containing a mixture of manganese sulfate hydrate solution (33 mL of 1.75 M) and concentrated nitric acid (3.4 mL). As synthesized manganese oxide tunneled OMS-2 material (cryptomelane structure) was dried at 383 K for 24 h. Appropriate amount (0.40 g) of zirconayl nitrate was dissolved in methanol and stirred with 1.60 g of as synthesized OMS-2 type cryptomelane material for 24 h, followed by evaporation of the solvent. As synthesized material was then heat treated at 500 K for 3 h in air. As synthesized zirconium modified cryptomelane type OMS-2 catalyst is designated as Zr-K-OMS-2 (Cry).

Oxidation of ethylbenzene and benzyl alcohols: general procedure

A mixture containing 100 mg catalyst, 15 mL of solvent (acetonitrile) and suitable amount of organic substrate was stirred in a round bottom flask equipped with a condenser. Then appropriate amount of TBHP (tert-butylhydroperoxide) was used as an oxidant. The resulting mixture was then refluxed for 8 h at 340 K. After completion of reaction, the catalyst was removed by filtration and the filtrate was subjected to GC analysis.

Results and Discussion

X-ray Diffraction Results

The X-ray diffraction patterns of the four types of zirconium modified tunneled manganese oxide OMS-2 catalysts such as Zr-K-OMS-2 (0.20), Zr-K-OMS-2 (0.25), Zr-K-OMS-2 (Bir) and Zr-K-OMS-2 (Cry) are shown in Fig. 2. The d-spacing values of as synthesized zirconium modified OMS-2 materials are compared with JCPDS data of cryptomelane (JCPDS = 34-168) type manganese oxide mineral, which has the OMS-2 type tunnel structure with composition of KMn_8O_{16}.

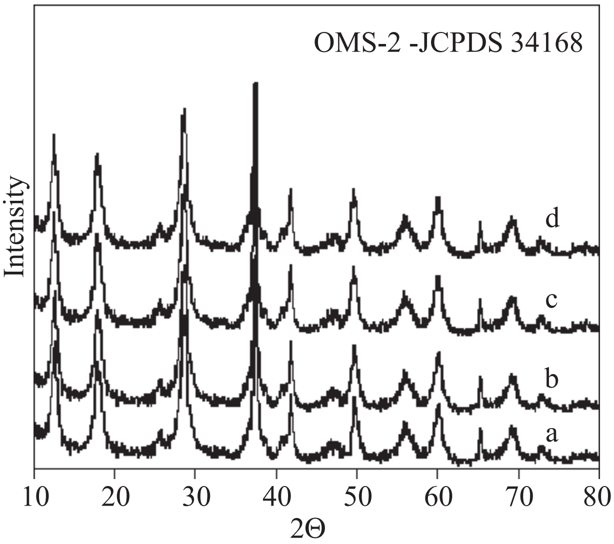

Fig. 2. XRD patterns of zirconium modified OMS-2 catalysts (a) Zr-K-OMS-2 (0.20), (b) Zr-K-OMS-2 (0.25), (c) Zr-K-OMS-2 (Bir), (d) Zr-K-OMS-2 (Cry).

Thermal and FT-IR analyses

Figure 3 shows the TGA (thermo gravimetric analysis) of the four-types of zirconium modified tunneled OMS-2 catalysts. All the four samples are thermally stable upto 580°C. All the four samples show a major weight loss in the range between 550°C –750°C. Zirconium framework substituted OMS-2 type catalysts [(Zr-K-OMS-2 (0.20), Zr-K-OMS-2 (0.25)] show higher weight loss due to the transformation of OMS-2 type tunnel structure into more stable bixbyite type phase (Mn_2O_3). In the case of zirconium doped OMS-2 catalysts [Zr-K-OMS-2 (Bir), Zr-K-OMS-2 (Cry)], the lower weight loss value is due to removal of dispersed zirconia in the manganese oxide surface. FT-IR spectra of zirconium modified OMS-2 catalysts [Zr-K-OMS-2 (Bir), Zr-K-OMS-2 (Cry)] are shown in Fig. 4. The band in the range 3400-3420 cm^{-1} is due to the presence of OH group in the manganese oxide surface and the bands at 1638 cm^{-1}, 1384 cm^{-1}, 1020 cm^{-1} and 582 cm^{-1} are due to the presence of MnO_x species [22]. The samples Zr-K-OMS-2 (Bir), Zr-K-OMS-2 (Cry) shows a band at 721 cm^{-1}, which corresponds to the monoclinic ZrO_2 [23].

BET and TEM analyses

BET surface area values of all the four samples

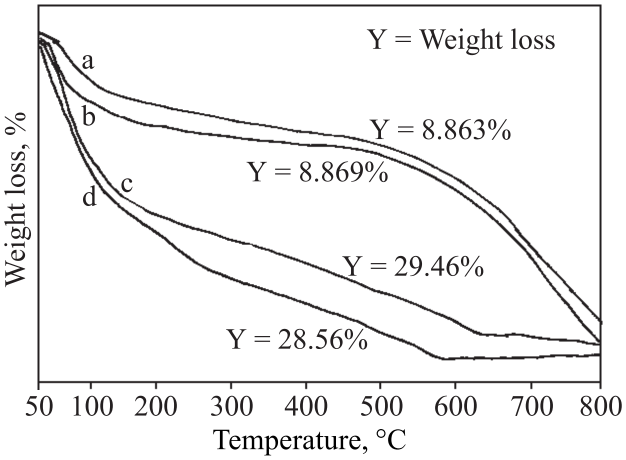

Fig. 3. TGA of zirconium modified OMS-2 catalysts (a) Zr-K-OMS-2 (0.20), (b) Zr-K-OMS-2 (0.25), (c) Zr-K-OMS-2 (Bir), (d) Zr-K-OMS-2 (Cry).

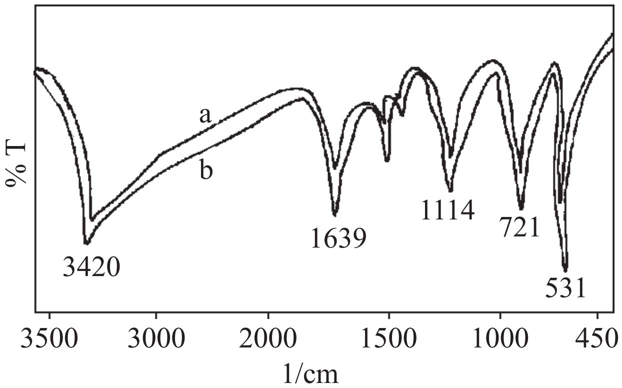

Fig. 4. Ft-IR spectra of zirconium modified OMS-2 catalysts (a) Zr-K-OMS-2 (Bir), (b) Zr-K-OMS-2 (Cry).

are given in Table 1. They show higher surface area values compared to the conventionally synthesized tunneled manganese oxide (K-OMS-2) catalysts [3]. TEM micrographs of zirconium modified catalysts [Zr-K-OMS-2 (Bir), Zr-K-OMS-2 (Cry)] are shown in Fig 5. Zirconia dispersion on the fibrous structure of OMS-2 catalyst [Zr-K-OMS-2 (Bir)] is shown in the Figs. 5a and 5b. TEM pictures of Zr-K-OMS-2 (Cry) (Figs. 5c and 5d) catalyst also indicate the zirconium deposition on fibrous morphology of OMS-2 material.

Table1

Surface area values of zirconium modified OMS-2 catalysts

Catalyst	Surface area, (m^2/g)
Zr-K-OMS-2 (0.20)	564
Zr-K-OMS-2 (0.25)	721
Zr-K-OMS-2 (Bir)	380
Zr-K-OMS-2 (Cry)	246
K-OMS-2*	97

*Literature reported

Catalytic activity of zirconium modified OMS-2 materials

Oxidation of side chain aromatic and arene compounds into their corresponding ketones are industrially important processes. In the present study as synthesized zirconium modified tunneled manganese oxide OMS-2 catalysts were tested for liquid phase oxidation of ethyl benzene and benzyl alcohol using TBHP as the chemical oxidant. Tables 2 and 3 show the conversion of ethyl benzene on zirconium modified manganese oxide OMS-2 catalyst with different amounts of TBHP and the corresponding bar diagram is shown in Fig. 6. The bar diagram (Fig. 7) show the comparison of conversion of ethylbenzene (Table 3) and benzyl alcohol conversion (Table 4) for the same amount of TBHP.

All zirconium modified manganese oxide OMS-2 catalysts shows moderate conversion to ethylbenzene with good selectivity towards acetophenone (Table 2 and 3).

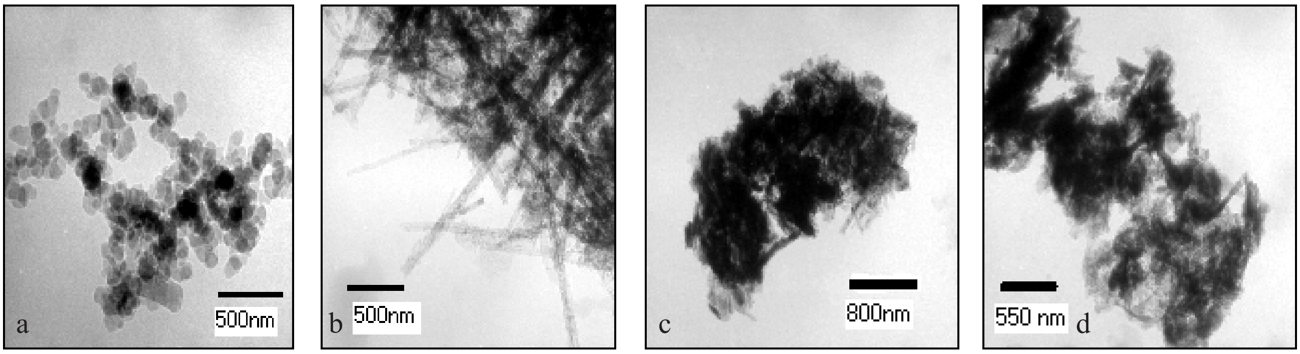

Fig. 5. TEM pictures of Zr-K-OMS-2 (Bir) (5a and 5b) and Zr-K-OMS-2 (Cry) (5c and 5d).

Table 2

Oxidation of ethylbenzene with TBHP in CH_3CN

Catalyst	Conversion, (%)	Selectivity, (%) (acetophenone)
Zr-K-OMS-2 (0.20)	26.2	98
Zr-K-OMS-2 (0.25)	20.4	98
Zr-K-OMS-2 (Bir)	34.8	98
Zr-K-OMS-2 (Cry)	37.4	98

Reaction condition: solvent (acetonitrile) = 15mL, substrate (ethylbenzene) = 94 mmol, TBHP = 70 mmol; weight of the catalyst = 100 mg; T = 340 K; duration = 10 h

Table 3

Oxidation of ethylbenzene with TBHP in CH_3CN

Catalyst	Conversion, (%)	Selectivity, (%) (acetophenone)
Zr-K-OMS-2 (0.20)	31.2	98
Zr-K-OMS-2 (0.25)	25.4	98
Zr-K-OMS-2 (Bir)	36.6	94
Zr-K-OMS-2 (Cry)	62.4	98

Reaction condition: solvent (acetonitrile) = 15mL, substrate (ethylbenzene) = 94 mmol, TBHP = 70 mmol; weight of the catalyst = 100 mg; T = 340 K; duration = 10 h

Table 4

Oxidation of benzyl alcohol with TBHP in CH_3CN

Catalyst	Conversion, (%)	Selectivity, (%) (benzaldehyde)
Zr-K-OMS-2 (0.20)	24.2	100
Zr-K-OMS-2 (0.25)	18.4	100
Zr-K-OMS-2 (Bir)	39.7	100
Zr-K-OMS-2 (Cry)	48.4	100

Reaction condition: solvent (acetonitrile) = 15mL, substrate (benzyl alcohol) =360 mmol, TBHP = 140 mmol; weight of the catalyst = 150 mg; T = 340 K; duration = 8 h

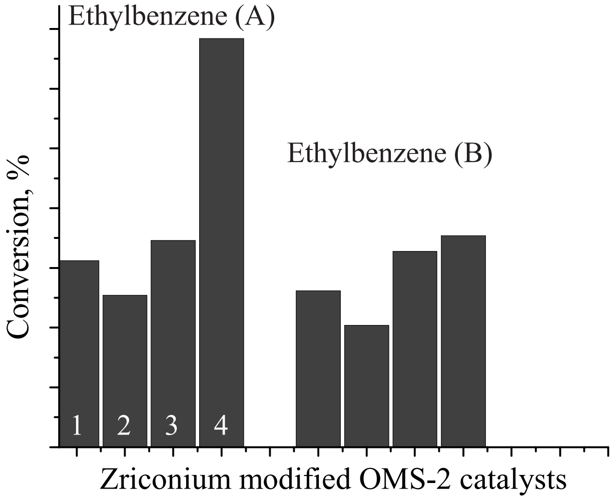

Fig. 6. Bardigram of ethylbenzen conversion (A) (70 mmol of TBHP) and ethylbenzene (B) (140 mmol of TBHP) on (1) Zr-K-OMS-2 (0.20), (2) Zr-K-OMS-2 (0.25), (3) Zr-K-OMS-2 (Bir), (4) Zr-K-OMS-2 (Cry).

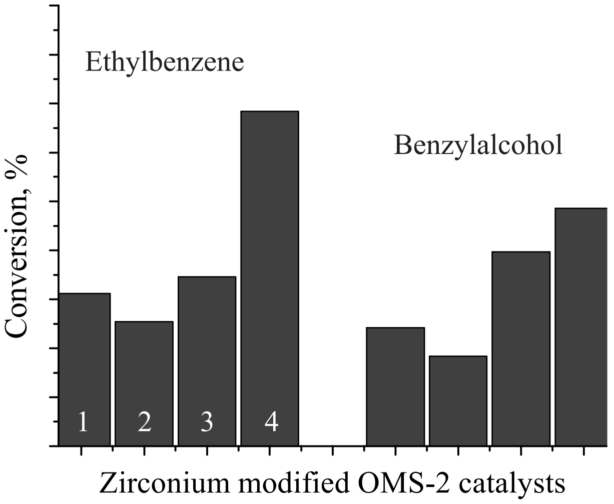

Fig. 7. Bardigram for ethyl benzene and benzyl alcohol conversion on (1) Zr-K-OMS-2 (0.20), (2) Zr-K-OMS-2 (0.25), (3) Zr-K-OMS-2 (Bir), (4) Zr-K-OMS-2 (Cry).

The zirconium modified manganese oxide catalyst [Zr-K-OMS-2 (Cry)] shows the highest conversion for ethyl benzene, compared to other zirconium modified OMS-2 catalyst (Table 3). Bennur *et al.* recently reported the ethylbenzene oxidation on macrocyclic tri and tetra copper complex encapsulated zeolite-Y catalysts using TBHP dissolved in isooctane as the chemical oxidant [22]. One of the main advantages of zirconium modified tunneled manganese oxide OMS-2 catalysts is, the simple synthetic route for catalyst preparation [23-24]. Benzyl alcohol conversion on zirconium modified manganese oxide OMS-2 catalysts is shown in Table 4. The Zr-K-OMS-2 (Cry) catalyst shows the highest conversion to benzyl alcohol oxidation (Table 4) with 100% selectivity towards benzaldehyde.

Comparison of our results with those obtained on the oxidation of benzyl alcohol and ethylbenzene with

TBHP, on mesoporous Cr-AlPO molecular sieves [25], shows that zirconium modified tunneled OMS-2 catalysts are better in terms of conversion and selectivity. In the case of mesoporous Cr-AlPO catalyst, a substrate to TBHP ratio 5:1 was used for side chain oxidation reaction, but in the case zirconium modified OMS-2 catalyst, 1:1 ratio of substrate to TBHP is sufficient for ethylbenzene oxidation.

Conclusions

Zirconium doped cryptomelane type manganese oxide OMS-2 catalysts show higher surface area values compared to potassium contain cryptomelane (K-OMS-2) material. TEM pictures confirm the zirconium dispersion on fibrous morphology of as synthesized OMS-2 materials. 20 wt.% zirconium doped OMS-2 catalyst [Zr-K-OMS-2 (Cry)] shows the higher conversion for the oxidation of ethylbenzene with good selectivity for acetophenone as well as for benzyl alcohol oxidation with 100% selectivity towards benzaldehyde.

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