

DIRECT OXIDATION OF ALKYL AROMATICS IN BENZYLIC POSITION TO CORRESPONDING KETONES OVER MICROPOROUS MnS-1

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ABSTRACT

Porous silicates are used as catalytic supports in chemical reactions. Incorporation of transition metals into their framework generates catalytically active sites. In recent years manganese (III)-containing porous catalysts have received considerable attention as catalysts for the selective oxidation of hydrocarbons using molecular oxygen (air) as the oxidant. Here, we report, for the first time, on the successful direct oxidation of alkyl aromatics in benzylic position to the corresponding aromatic ketones by molecular oxygen in the presence of microporous Mn silicalite-1 (MnS-1). The presence of isolated Mn³⁺-species in a hydrophobic environment on the catalyst surface favours high conversion rates.

Keywords: Manganese silicalite-1, catalysis, solvent-free, oxidation.

INTRODUCTION

Porous silicates are used as catalytic supports in chemical reactions [1,2]. Incorporation of transition metals into their framework generates catalytically active sites. In recent years, manganese (III)-containing porous catalysts have received considerable attention as catalysts for the selective oxidation of hydrocarbons using molecular oxygen (air) as the oxidant [2,3]. It is important to obtain environmentally benign catalyst, together with the use mild and solvent-free conditions in the liquid phase. Among the attractive conversions is the selective oxidation of alkyl aromatics in benzylic position to the corresponding aromatic ketones. The synthesis of these ketones via Friedel–Crafts acylation of aromatics or conversion of aromatics with stoichiometric oxidants like KMnO₄ leads to the formation of hazardous waste in large amounts. Therefore, the use of solid catalysts which are selective, use molecular oxygen as the terminal oxidant and allow application of solvent-free conditions would provide an environment friendly and economically attractive alternative. Here, we report, for the first time, on the successful direct oxidation of alkyl aromatics in benzylic position to the corresponding aromatic ketones by molecular oxygen in the presence of microporous Mn silicalite-1 (MnS-1).

EXPERIMENTAL

Highly crystalline MnS-1 (crystals with 1 μm in size, Figure 1) was prepared by hydrothermal synthesis as described in the literature [4] using tetrapropylammonium hydroxide instead of tetraethylammonium hydroxide as a template. The local environment of Mn was characterized using X-ray absorption spectroscopy (EXAFS - Extended X-Ray Absorption Fine Structure and XANES - X-Ray Absorption Near Edge Structure). The catalytic experiments were carried out in the liquid phase under stirring in a stainless-steel high-pressure batch reactor (HR100, Berghof) equipped with a sampling tube with a sintered metal frit (pores < 0.5 μm) [5]. Liquid samples were collected at different reaction times (1 and 6 h) or, after cooling and depressurizing the reactor. The samples were analyzed by capillary gas chromatography using a flame ionization detector (chromatograph: Agilent 5890

Series II, column: INNOWAX (J&W), 60 m x 0.32 mm x 0.5 μm). Product identification was achieved co-injection of samples and by GC-MS.

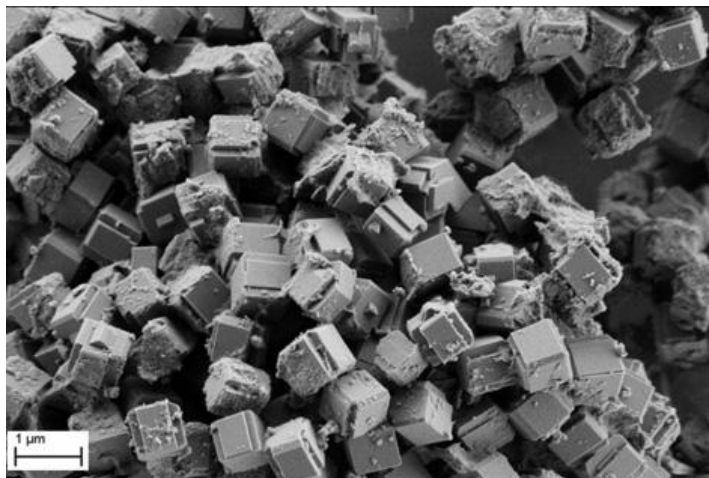


Figure 1: SEM micrograph of MnS-1.

RESULTS AND DISCUSSION

Extended X-ray Absorption Fine Structure (EXAFS) analyses of the Mn K edge absorption spectra of MnS-1 (Figure 2) revealed manganese cations coordinated to two oxygen atoms at a distance of 1.93 \AA and one oxygen atom at a longer distance of 2.15 \AA in the first coordination sphere. The short distance of 1.93 \AA is consistent with the average tetrahedral Mn^{+3} -O distance of 1.93(4) \AA as expected for an isomorphous substitution within the silicate framework. Additionally, in the second coordination sphere at the distance of 3.52 \AA a presence of Si atoms is indicated (Table 1). According to X-Ray Absorption Near Edge Structure (XANES) studies, the average oxidation number of Mn is 2.75 ± 0.05 ($n(\text{Mn}^{2+})/n(\text{Mn}^{3+}) \cong 25\%/75\%$) (Figure 3).

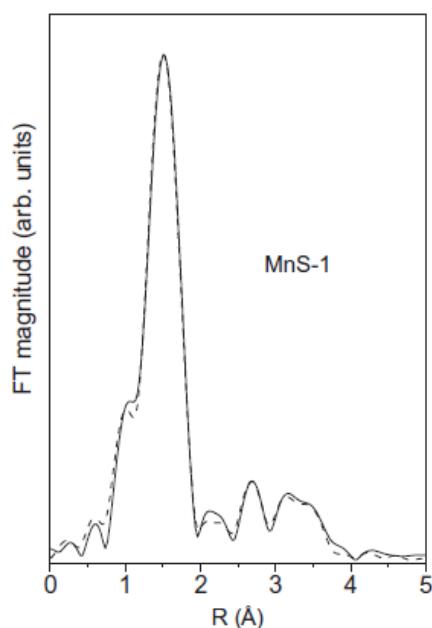


Figure 2: Fourier transform magnitude of the k^3 -weighted Mn EXAFS spectra of the MnS-1 (solid line – experiment, dashed line – EXAFS model).

Table 1: Structural parameters of the nearest coordination shells around Mn atom in calcined MnS-1: type of neighbor atom, average number N, distance R, and Debye–Waller factor σ^2 . The amplitude reduction factor ($S^2_0 = 0.8$) was determined on MnO and kept fixed during the fit. Uncertainties in the last digit are given in the parentheses.

Neighbor	N	R(Å)	$\sigma^2(\text{Å}^2)$
<i>MnS-1 (microporous, Mn²⁺/Mn³⁺ = 10%/90%)</i>			
O	2.2(2)	1.89(1)	0.005(2)
O	0.5(2)	2.26(3)	0.005(2)
O	4(1)	2.98(2)	0.010(5)
O	2(1)	3.65(2)	0.010(5)
Si	4(3)	3.95(2)	0.021(9)
<i>MnMCM-41 (Mesoporous, hexagonal, Mn²⁺/Mn³⁺ = 10%/90%)</i>			
O	2.7(5)	1.89(1)	0.006(1)
O	1.3(5)	2.21(1)	0.006(1)
O	3(1)	2.97(5)	0.02(1)
Si	3(1)	3.34(5)	0.02(1)
<i>MnMCM-48 (Mesoporous, cubic, Mn³⁺ = 100%)</i>			
O	2.8(5)	1.90(1)	0.006(1)
O	0.7(5)	2.23(1)	0.006(1)
O	3(1)	2.98(5)	0.013(5)
Si	1.0(5)	3.48(5)	0.011(5)

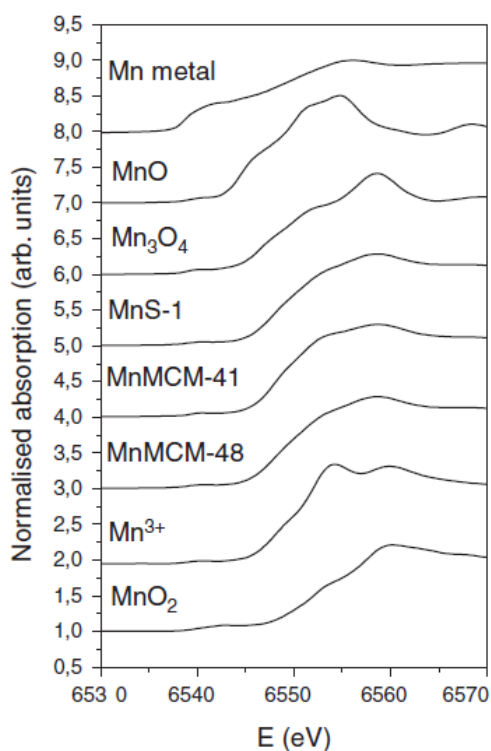


Figure 3: Normalized Mn K-edge XANES spectra of sample MnS-1 and Mn reference samples Mn metal, Mn²⁺O, Mn^{2.7+}₃O₄, K₃[Mn³⁺(C₂O₄)₃] \cdot 3H₂O, and Mn⁴⁺O₂. The energy scale is relative to the Mn Kedge in Mn metal (6539.0 eV). The spectra are displaced vertically for clarity.

Ethylbenzene, 4-methylethylbenzene and diphenylmethane were converted with very high to excellent selectivity for the corresponding aromatic ketone over the manganese-containing nanoporous silica catalyst MnS-1. With diphenylmethane as the substrate the conversion is much lower probably due to the larger molecular diameter of diphenylmethane. (Table 2).

Table 2. Results of the selective oxidation of alkyl aromatics with molecular oxygen over [Mn]S-1.^a

Substrate	Catalyst	Conv ./%	TOF/ h ⁻¹	Product selectivity/mol%	
				Ketone	Others ^b
Ethylbenzene	MnS-1	33	106	87	13
4-Methylethylbenzene	MnS-1	54	173	87	13
Diphenylmethane	MnS-1	4	12	100	-

^a Reaction conditions: $n(\text{substrate}) = 50$ mmol, $n(1,4\text{-dichlorobenzene}) = 5.0$ mmol (0.74 g, internal standard), $m(\text{catalyst}) = 0.25$ g; $p_{\text{O}_2} = 10$ bar; $T = 110$ °C; $t = 6$ h. ^b Mixture of 1-(R)ethanol and R-carboxylic acid [R = phenyl and 4-methylphenyl].

CONCLUSION

In summary, the oxidation of various alkyl aromatics in benzylic position to the corresponding aromatic ketones can be successfully achieved in high selectivity over the microporous Mn-containing silicalite-1 using molecular oxygen as the terminal and single oxidant under mild, solvent-free liquid-phase conditions. The presence of isolated Mn³⁺-species in a hydrophobic environment on the catalyst surface favours high conversion rates.

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