CATALYTIC AND ELECTROCATALYTIC OXIDATION OF ANILINE TO NITROBENZENE OVER VANADIUM SILICATE MOLECULAR SIEVES: VS-1 USING t-BUTYL HYDROPEROXIDE (TBHP) AS OXIDANT

T. Selvam*, M. P. Vinodb and K. Vijayamohananb

*Catalysis Division and bPhysical Chemistry Division
National Chemical Laboratory, Pune -411 008, India

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Abstract
A comparison of the results of catalytic and electrocatalytic oxidation of aniline using VS-1 in the presence of H2O2 and TBHP indicates remarkable differences in conversion and selectivity. VS-1 catalyzes the oxidation of aniline selectively to nitrobenzene (73%) in the presence of t-butyl hydroperoxide (TBHP), while azoxybenzene (95.2%) is formed selectively when H2O2 is used. Cyclic voltammetric studies show a three-step oxidation of aniline to nitrobenzene in H2O2 but in the presence of TBHP only one step is observed. Electrocatalytic oxidation of aniline to nitrobenzene occurs at a potential 700 mV less than that corresponding to H2O2 as oxidant along with a selectivity of 91.8%. The enhancement of electrocatalytic rate is attributed to the stabilization of electron deficient transition state.

Keywords: Aniline oxidation with VS-1, catalytic and electrocatalytic oxidation of aniline

INTRODUCTION
The transformation of organic compounds over metallosilicate molecular sieves has been of great interest in recent years. More specifically, from the synthetic point of view, the oxidation of amines has drawn considerable attention because of their greater utility in synthetic and pharmaceutical industry [1]. For
example, vanadium oxyacetylacetonate [2], sodium perborate [3], ozone [4] and peracetic acid [5] have been reported to be good reagents for the oxidation of anilines to nitrobenzenes. In addition, oxidation of various primary amines to the corresponding oximes and imines over vanadium silicate molecular sieves, VS-1 has also been reported [6]. Further, detailed studies regarding the oxidation of aniline to azoxybenzene over TS-1 using both H₂O₂ and TBHP have recently demonstrated several important mechanistic features [7]. Since vanadium oxyacetylacetonate [2] and TBHP are reported to convert anilines to nitrobenzenes in homogeneous condition, it is important to correlate the common features associated with the same process using vanadium silicate molecular sieves (VS-1), albeit under heterogeneous conditions. Although, the conversion of aniline to nitrobenzene has no immediate practical utility because aniline itself is prepared by reduction of nitrobenzene, an understanding of the mechanism of conversion of aniline to nitrobenzene using VS-1 will be important to decide the role of vanadium redox transformations especially in restricted environments.

Zeolite Modified Electrodes (ZME) are one new class of rapidly developing electrodes with their unique size and shape selective properties leading to unusual product selectivity [8]. Transition metal incorporated zeolites are particularly interesting due to the possibility of using their inherent catalytic properties in electrocatalysis. In this study we report such a comparative investigation of catalytic and electrocatalytic oxidation of aniline over VS-1. Further, the effect of change in oxidant from H₂O₂ to TBHP is also analyzed to illustrate the importance of steric effect in controlling both catalytic and electrocatalytic selectivity.

**EXPERIMENTAL**

The catalyst used in this study, VS-1, was synthesized according to published procedures [9] and the catalytic runs were carried out in batch reactors; in a typical reaction, aqueous TBHP (Aldrich, 70%, 54 mmol) was added to a mixture of aniline (E. Merck, 99%, 54 mmol) and the catalyst (0.25 g VS-1) in acetonitrile (10 mL). The reaction was carried out at 353 K for 5 h with stirring and after completion of the reaction, the products were analyzed in a capillary gas chromatograph (HP 5880), fitted with a 50 m long cross-linked methyl silicone gum capillary column. The identity of the products were established by GC-MS (Shimadzu, Q 2000 a).

Cyclic voltammetric (CV) studies were carried out in a three-compartment, single electrode cell with zeolite modified working electrode as prepared according to the published procedures [8]. In brief, 100 mg VS-1, 100 mg graphite and 10 mg polystyrene were mixed in 2 mL of THF and the paste was