



## Oxidation of *n*-hexadecane with uranyl loaded/anchored microporous zeolites and ozone

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### ABSTRACT

The selective oxidation of higher *n*-alkanes at moderate temperature and pressure conditions is challenging. The scope of microporous molecular sieve materials as catalysts in the ozone initiated functionalisation of higher *n*-alkanes is investigated at  $20 \pm 1$  °C and  $\sim 1$  atm. In the ozone initiated oxidation of the higher hydrocarbons hexadecane, tetradecane or dodecane with uranyl loaded silica or zeolite-Y (Na-Y) or ZSM-5 catalysts lead to the keto-isomers as main products, where oxygen is introduced into carbonyl site of the product molecule, and small amounts of organic acids were produced. This paper emphasises the effect of microporous catalysts, the conversion, reaction products, yields and selectivity on ozonation of higher alkanes (e.g. hexadecane). A plausible mechanism for the ozonation of higher alkanes with new heterogeneous uranyl anchored zeolite catalysts is proposed. Using uranyl anchored/loaded microporous zeolite catalysts and ozone as oxidant higher normal alkanes are successfully oxidized to ketones, but with the moderate/reasonable selectivity.

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### 1. Introduction

The selective oxidation of alkanes at room temperature and pressure conditions is one of the objectives of organic chemistry. The problem in the functionalisation of saturated hydrocarbons is their components, carbon and hydrogen, do not have electron pairs, and the molecules do not have orbitals of sufficient energy that they are easily accessible [1]. Thus, very reactive reagents and/or extreme reaction conditions are typically required. Mostly the reaction products get further oxidized yielding undesired byproducts. The use of zeolites and molecular sieve based catalysts in oxidation reactions is assuming a lot of importance in recent times. Literature [2] shows that uranium oxides (uranyl ions  $\text{UO}_2^{2+}$ ) dispersed over dense oxide supports may serve as promising oxidizing catalysts because of its variable valence states and vacant *f*-orbitals. This prompted us to prepare the uranium oxide dispersed on silica and zeolitic supports (Na-Y and ZSM-5) for the oxidation of *n*-hexadecane with ozone. Uranyl ions possess instinctive excitation and emission characteristics and are strong oxidizing species [3].

Uranium (uranyl ions  $\text{UO}_2^{2+}$  or uranium oxides) with its variable valence states vis-à-vis vacant *f*-orbitals [2] may serve as promising oxidizing catalyst. Literature shows that the uranium oxides are dispersed over dense oxide supports [4] such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,

$\text{SiO}_2$ , MgO and mesoporous molecular sieves [5]. Compared to any other inorganic cations, the uranyl ions possess distinctive photo absorption, excitation, and emission characteristics [3]. The lowest excited Eigen value ( $E + 2.6$  V) of the  $\text{UO}_2^{2+}$  is a strongly oxidizing species, found to be quenched by a variety of organic substrates resulting in the abstraction of their hydrogen atoms [6,7].

Numerous studies have showed that the utilization of uranyl ions for homogeneous-phase photooxidation reactions of hydrocarbons [8,9], chlorophenols [10], and substituted phenols [11]. Suib and co-workers [12] studied the photooxidation of ethanol, isopropyl alcohol, and diethyl ether by employing uranyl-exchanged clays and zeolites, to yield the corresponding aldehydes and ketones. Dai et al. [13] reported that the photocatalytic oxidation of ethanol solution by  $\text{UO}_2^{2+}$  doped glass resulted in the formation of acetaldehyde.

Literature survey shows in the recent past, considerable work on the application of ozone in the presence and absence of catalysts has been done [14,15]. Ozone, a strong oxidizing agent with environmentally acceptable products, is commonly used for effective oxidative degradation of organic and inorganic species, and for disinfection of drinking water [16–18] in waste water [19] and effluent treatment [20]. Ozone has also been attracting attention as an alternative oxidant, due to its strong oxidizing ability even at low reaction temperatures [21,22]. It has been reported that ozone exhibits variations in its reactivity with different classes of compounds, when reaction takes place in aqueous and/or non-aqueous

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solvents and under severe reaction conditions of high temperature, high pressure and high concentration of ozone and the organics [16]. Ozone is generally found to be effective at enhancing the conversion of volatile organics, especially at low temperatures due to its stability and high reactivity. The oxidation potential (2.07 V) of ozone is higher than that of chlorine (1.36 V), which facilitates oxidation of most of the organic compounds.

Reactions of saturated organic compounds with ozone are at the focus of current research [23]. Among the various less explored topics of research in utilization of ozone are the reactions of saturated higher hydrocarbons with ozone. Although, the oxidation of both lower aliphatic and aromatic hydrocarbons has been extensively studied [24], there is no or little information reported on the ozonation of higher aliphatic hydrocarbons with microporous materials as catalysts. The present report contains the results of oxidation of higher hydrocarbons with microporous materials and ozone.

## 2. Experimental

The uranyl impregnated silica, Na-Y and ZSM-5 zeolite catalyst samples were obtained as follows. Firstly, prior to impregnation, the as-synthesized silica (Aldrich, 99%), Na-Y and ZSM-5 (Süd Chemie, India) samples were activated at 393 K for 2 h. Aqueous uranyl nitrate (Merck, 99%) solution was added drop wise to 1.0 g of the host and was kept under mild stirring for 1–2 h. The solution was then allowed to stand overnight to ensure maximum loading. The resulting products were then heated gently ( $\sim 80^\circ\text{C}$ ) on a hot-plate to evaporate the water until the catalyst becomes dry, followed by heating at 353 K for 6 h in an oven. The uranyl impregnated zeolite samples were calcined at 823 K for 5–6 h, heating rate of  $1\text{ K min}^{-1}$  and are designated as U/Na-Y and U/ZSM-5. The catalyst materials were characterized using XRD, FT-IR, SEM and BET surface area techniques.

### 2.1. Powder X-ray diffraction (XRD)

In the powder diffraction characterisation of materials, the diffraction pattern is the fingerprint of any crystalline phase and powder diffraction is used extensively to identify the mixture of phases which generally constitutes a catalyst. The dry catalyst samples after calcination were grounded with the help of mortar and pestle. The fine powder of catalysts was packed on the surface of a sample holder. Powder XRD patterns were recorded for all the samples in order to verify the formation and structure of various microporous materials. The diffraction patterns measurements were recorded in the high angle  $2\theta$  range of  $2\text{--}80^\circ$  using a Rigaku miniflex X-ray diffractometer, equipped with nickel filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ ). The scan speed and step size were  $0.5^\circ\text{ min}^{-1}$  and  $0.02^\circ$ , respectively.

#### 2.1.1. FT-IR

FT-IR spectra of various catalyst samples were recorded on a Nicolet Impact 400 equipment and Nicolet Impact Model-420 spectrometer with a  $4\text{ cm}^{-1}$  resolution and 128 scans in the mid IR ( $400\text{--}4000\text{ cm}^{-1}$ ) region using the KBr pellet technique. About 100.0 mg of dry KBr was mixed with a little amount (10.0 mg) of the sample and was ground for homogenisation. During the mixing an IR lamp was used for drying. The mixture was then pressed into a transparent, thin pellet at  $10\text{ tons cm}^{-2}$ . These pellets were used for the IR spectral measurements.

#### 2.1.2. SEM

The SEM measurements were carried out using a JEOL JSM-6100 microscope equipped with an energy-dispersive X-ray analyzer (EDX). The images were taken with an emission current =  $100\text{ }\mu\text{A}$

by a Tungsten (W) filament and an accelerator voltage = 12 kV. The catalysts were secured onto brass stubs with carbon conductive tape, sputter coated with gold and viewed in JEOL JSM-6100 microscope. The pre-treatment of the samples consisted of coating with an evaporated Au film in a Polaron SC 500 Sputter Coater metallizator to increase the catalyst electric conductivity.

### 2.2. BET surface area analysis

The Brunauer–Emmett–Teller (BET) surface area analysis for the catalysts was done to find the surface area available, which influences the conversion and selectivity in the ozonation of *n*-hexadecane. The catalysts were pretreated by degassing under  $\text{N}_2$  flow overnight at  $250^\circ\text{C}$  in Micrometrics flow prep 060. The degassed samples were analysed in the Micrometrics Gemini 2360, fully automatic, single- or multi-point BET surface area analyzer under the liquid  $\text{N}_2$  conditions. It uses a flowing-gas technique in which the analysis gas flows into a tube containing the sample and into a balance tube at the same time and provides rapid and accurate sample analysis for solid materials.

Ozonation experiments with substrate sample (*n*-hexadecane, Aldrich, 99%) of 25.0 mL were carried out at normal temperature and pressure conditions with the uranyl loaded Silica or Zeolite-Y (Na-Y) or ZSM-5 catalysts. The schematic illustration of the long column reactor setup is shown in Fig. 1. The catalyst (5% w/v charged) in the fine powder form was dispersed in the reaction medium, i.e., *n*-hexadecane by means of a magnetic stirrer (Hanna Instruments HI 190 M magnetic stirrer). The reaction mixture was kept at a constant room temperature of  $20 \pm 1^\circ\text{C}$ . Ozone was produced from pure compressed oxygen (Afrox, 99%) by an ozone generator (Ozonox) at a concentration of  $20.41\text{ mg L}^{-1}$ . The ozone gas was introduced at the bottom of the column through a sintered diffuser of porosity 2 with  $\text{O}_2$  flow rate of 1 LPM. The rotameter was used to regulate the feed gas ( $\text{O}_2$ ) flow (Fig. 1).

Samples of liquid were drawn off using a pasteur pipette from time to time for GC-MS analysis and ozone concentrations were measured. Two 250.0 mL volume of gas washing bottles containing 200.0 mL of 2% potassium iodide (KI, Merck, 99%) solution were connected in series to the reactor for collecting all unreacted ozone passing through the reactor. All parts of experimental setup were made of stainless steel, glass or Teflon. Teflon tubing was used for the ozone gas lines. The entire setup was kept in a fume hood for safety, and all connections were reinforced with Teflon tape. Ozone concentration  $20.41\text{ mg min}^{-1}$  was used. The products were characterized using GC-MS, FT-IR,  $^1\text{H}$  NMR spectral data, melting point and boiling point techniques.

#### 2.2.1. GC-MS

For analysis of compounds, Agilent 6890 gas chromatograph equipped with a quadruple Agilent 5973n mass selective detector was used. Column specifications: J & W DB5MS, 30 m length,  $250\text{ }\mu\text{m}$  diameter and  $0.25\text{ }\mu\text{m}$  film thickness. The GC-MS analysis was carried out in EI mode and the spectra were recorded in the interval 35–500 amu. The temperature program used during the GC-MS analysis was ramped as follows:  $50^\circ\text{C}$  (2 min),  $20^\circ\text{C min}^{-1}$  until  $300^\circ\text{C}$  (10 min). The sample was carried out with a 1.50 min. splitless time at  $250^\circ\text{C}$ . The carrier used was helium.

#### 2.2.2. FT-IR

FT-IR spectra of product samples were also recorded on the same instrument with a  $4\text{ cm}^{-1}$  resolution and 128 scans in the mid IR ( $400\text{--}4000\text{ cm}^{-1}$ ) region.

#### 2.2.3. $^1\text{H}$ NMR

Isolated pure products (in  $\text{CDCl}_3$ )  $^1\text{H}$  NMR analyses were run with Varian Gemini 300 MHz at ambient temperature.

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