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Ozone Initiated Oxidation of Hexadecane with Metal Loaded γ-Al_2O_3 Catalysts

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Abstract The scope of metal loaded γ-Al_2O_3 materials as catalysts in the ozone initiated functionalisation of higher *n*-alkanes is investigated at moderate conditions (20 ± 1 °C and ~1 atm). In the ozone initiated oxidation of the higher hydrocarbon, *n*-hexadecane with 0.5% Pd or Ni or V loaded γ-Al_2O_3 catalysts lead to the keto-isomers as main products, and organic acids as minor products. This paper emphasises the effect of γ-Al_2O_3 catalysts on the conversion, selectivity and reaction products during ozonation of *n*-hexadecane.

Keywords Oxidation · Ozone · Metal loaded γ-Al_2O_3 · *n*-Hexadecane · 4-Hexadecanone

1 Introduction

The selective oxidation of alkanes at room temperature and pressure conditions is one of the challenges of organic chemistry. The problem in the functionalisation of saturated hydrocarbons is that their components, carbon and hydrogen, do not have electron pairs, and the molecules do not have orbitals of sufficient energy that are easily accessible [1]. Thus, very reactive reagents and/or extreme reaction conditions are typically necessary. Mostly the reaction products get further oxidized yielding undesired byproducts. The use of molecular sieve based catalysts in oxidation reactions is assuming a lot of importance in recent times.

Literature survey shows that considerable attention is paid in the recent past to the application of ozone in the absence and presence of catalysts [2, 3]. Ozone is a strong oxidizing agent and is commonly used for effective oxidative degradation of organic and inorganic species which produce environmentally acceptable products, and for disinfection of drinking water [4–6], in waste water [7] and effluent treatment [8]. Ozone has also been drawing attention as an alternative oxidant, due to its strong oxidizing capability even at low reaction temperatures [9, 10]. 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 solvents and under severe reaction conditions of high temperature, high pressure and high concentration of ozone and the organics [4]. Ozone is generally found to be efficient 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.

Even though ozone is a powerful oxidant, it reacts slowly with some organic compounds such as inactivated aromatics. In many cases, the oxidation of organic compounds (e.g. natural organic matter, NOM), which results in the formation of biodegradable organic matter (carboxylic acids, carbonyl compounds). In order to optimise the ozonation process efficacy, new methods of advanced oxidation have been investigated. Advanced oxidation process (AOP) such as catalytic ozonation involve the generation of hydroxyl radicals, which are active oxidative species.

Several researchers have explored the possibility of the application of parent alumina or alumina supported with

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metals or metal oxides as catalysts of the ozonation process [11]. γ-Alumina was found to be an effective catalyst for refractory organic compounds such as oxalic, acetic, salicylic and succinic acid ozonation in water [12]. The main reasons for the wide usage in several applications of alumina as an adsorbent and as catalyst are its acid-base properties, high surface area, mechanical strength and thermal stability [5, 12, 13].

Reactions of saturated organic compounds with ozone are at the focus of current research [14]. 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 [15], there is no or little information reported on the ozonation of higher aliphatic hydrocarbons with γ-alumina materials as catalysts. The present report contains the results of oxidation of higher hydrocarbons with metal (Pd, V and Ni) loaded γ-alumina and ozone.

This paper gives an overview of the scope of γ-alumina as the heterogeneous catalyst in the catalytic oxidation of higher hydrocarbons using ozone. No literature is available on this topic and this is the first report on the catalytic ozonation of higher *n*-alkanes using metal loaded γ-Al_2O_3 at normal temperature and pressure conditions.

2 Experimental

The Ni [Nickel sulfate ($NiSO_4{\cdot}6H_2O$), Aldrich-99%], V [Vanadyl sulfate ($VOSO_4{\cdot}3H_2O$), Aldrich-99%] and Pd [Palladium chloride ($PdCl_2$), Aldrich-99%] metal (0.5%) impregnated γ-Al_2O_3 (Sarabhai Chemicals, 99%) catalyst samples were obtained as follows. Firstly, prior to impregnation, the γ-Al_2O_3 was activated at 393 K for 2 h. Aqueous metal precursor solutions were added drop wise to each 1.0 g of the host γ-Al_2O_3 and were kept under mild stirring for 1–2 h. The solutions were then allowed to stand overnight to ensure maximum loading. The resulting products were then heated gently ($\sim$80 °C) on a hotplate to evaporate the water until the catalyst becomes dry, followed by heating at 353 K for 6 h in an oven. The metal impregnated γ-Al_2O_3 samples were calcined in a temperature programmed tubular furnace under flowing air or nitrogen atmosphere (50.0 mL min^{-1}) at 823 K for 5–6 h, heating rate of 1 K min^{-1} and are designated as Ni/γ-Al_2O_3, V/γ-Al_2O_3 and Pd/γ-Al_2O_3, Ni/γ-Al_2O_3 N_2 calcined, V/γ-Al_2O_3 N_2 calcined, Pd/γ-Al_2O_3 N_2 calcined. The catalysts were characterized with powder X-ray diffraction, diffuse reflectance UV-spectroscopy and SEM techniques.

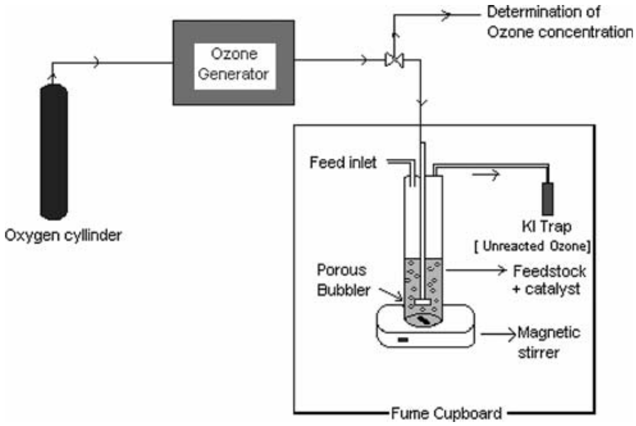

Fig. 1 Schematic diagram of catalytic ozonation reaction setup

Ozonation experiments with substrate sample (*n*-hexadecane, Aldrich, 99%) of 25.0 mL were carried out at normal temperature and pressure conditions with the metal (Ni, V and Pd) loaded γ-Al_2O_3 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 ± 1 °C. Ozone was produced from pure compressed oxygen (Afrox, 99%) by an ozone generator (Ozonox) at a concentration of 20.41 mg L^{-1}. The ozone gas was introduced at the bottom of the column through a sintered diffuser of porosity 2 with O_2 flow rate of 1 LPM. The rotameter was used to regulate the feed gas (O_2) flow (Fig. 1). All the experiments were carried out in replicate.

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 (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 mg min^{-1} was used. The products were characterized by GC-MS, FT-IR, ^{1}H NMR, melting point and boiling point techniques.[1]

3 Results and Discussion

3.1 Catalyst Characterization

Loading of catalysts with the various metals used in this study does not lead to loss in crystallinity. Diffuse reflectance spectroscopy results showed the symmetry and the

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[1] Product and catalyst characterization is attached as supplementary material.

valence of the supported Ni-, V- and Pd-loaded catalysts as shown in Fig. 2a–c. The DR UV baseline function corrected spectra for nickel-loaded γ-Al_2O_3 are represented in Fig. 2a. The baseline corrected figures distinctly shows the presence of bands at 400 nm. The band at 270–290 nm is the characteristic of the catalysts. The DR UV spectra of Ni/γ-Al_2O_3 catalyst displayed a major band at 400 nm as illustrated in Fig. 2a, which may be due to Ni^{2+}-O charge-transfer transitions [16]. The absorption in the UV region located at 275 nm for V/γ-Al_2O_3 is an intense and broad band and is due to the CT transition [17] of the support γ-Al_2O_3. A high intensity charge transfer band in the 300–450 nm region is observed for all V loaded samples. The bands located at 320 and 420 nm show that the deposited vanadates maintain the valence and the environment of the initial solution species (Fig. 2b). The absorption band at 400–480 nm is characteristic of V^{5+} in octahedral environment, while band at 270–300 nm (Fig. 2b) is considered to be the due to V^{5+} in a highly isolated tetrahedral environment [18–20]. DR UV-visible spectroscopy for all calcined samples, vanadium retains the oxidation +5 after calcination. However, the band shift towards 400 nm indicates an evolution of the vanadium superficial state to a mixture of tetrahedral and octahedral environments [21]. The presence of Pd^{2+} cations in the support is confirmed by an adsorption at approximately 250–290 nm in the DR UV spectra (Fig. 2c), which agrees with the earlier literature data [22]. The support contains isolated Pd^{2+} cations coordinated to lattice sites, as indicated by absorption at ~477 nm in the DR UV spectrum [22–24].

SEM images (Fig. 3a–d) summarize the main features of the metal loaded γ-Al_2O_3 reflecting morphologies of very crystalline materials. Magnification in micrographs ranges from 1800× to 3500× with working distance of ~15 and

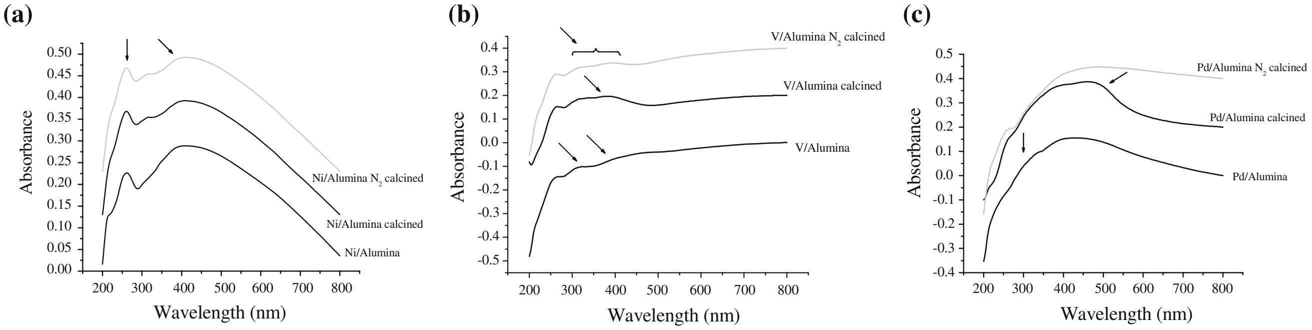


Fig. 2 DR UV spectra of (**a**) Ni loaded γ-Al_2O_3 (**b**) V loaded γ-Al_2O_3 (**c**) Pd loaded γ-Al_2O_3 catalysts

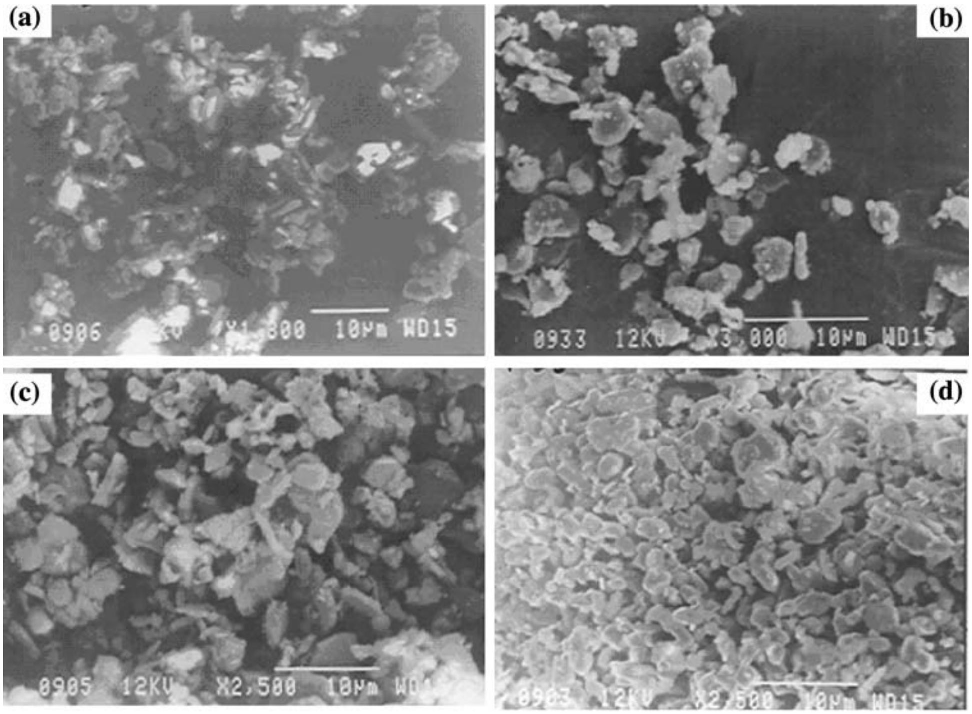


Fig. 3 SEM image of (**a**) γ-Al_2O_3 support (**b**) Ni/γ-Al_2O_3 N_2 calcined. (**c**) Pd/γ-Al_2O_3 N_2 calcined (**d**) V/γ-Al_2O_3 N_2 calcined catalysts

12 KV. Metals with γ-Al_2O_3 support calcined under N_2 flow conditions showed regular shapes. SEM images further reveal a uniform particle size of the sample with a regular shape. From the micrograph the aggregation of the metal particles (Ni, Pd and V) with support particles is also seen.

3.2 Product Analysis: Gas Chromatography Analysis of Product Mixture

The chromatograms of the *n*-hexadecane before and after ozonation are shown in the Fig. 4a–b. The peak at retention time 10.8 refers to the unreacted *n*-hexadecane and group of peaks at the retention time 11.7–12.0 refers to the isomer compounds of hexadecanone, i.e. 4-hexadecanone, 3-hexadecanone and 2-hexadecanone products. Further, the unreacted *n*-hexadecane from the chromatogram is confirmed by injecting the substrate, which elutes at the retention time 10.8 ± 0.2. The small peaks from 4.4 to 10.0 retention time refer to the different carboxylic acid compounds formed due to the further oxidation of the main products of the reaction, hexadecanone isomers.

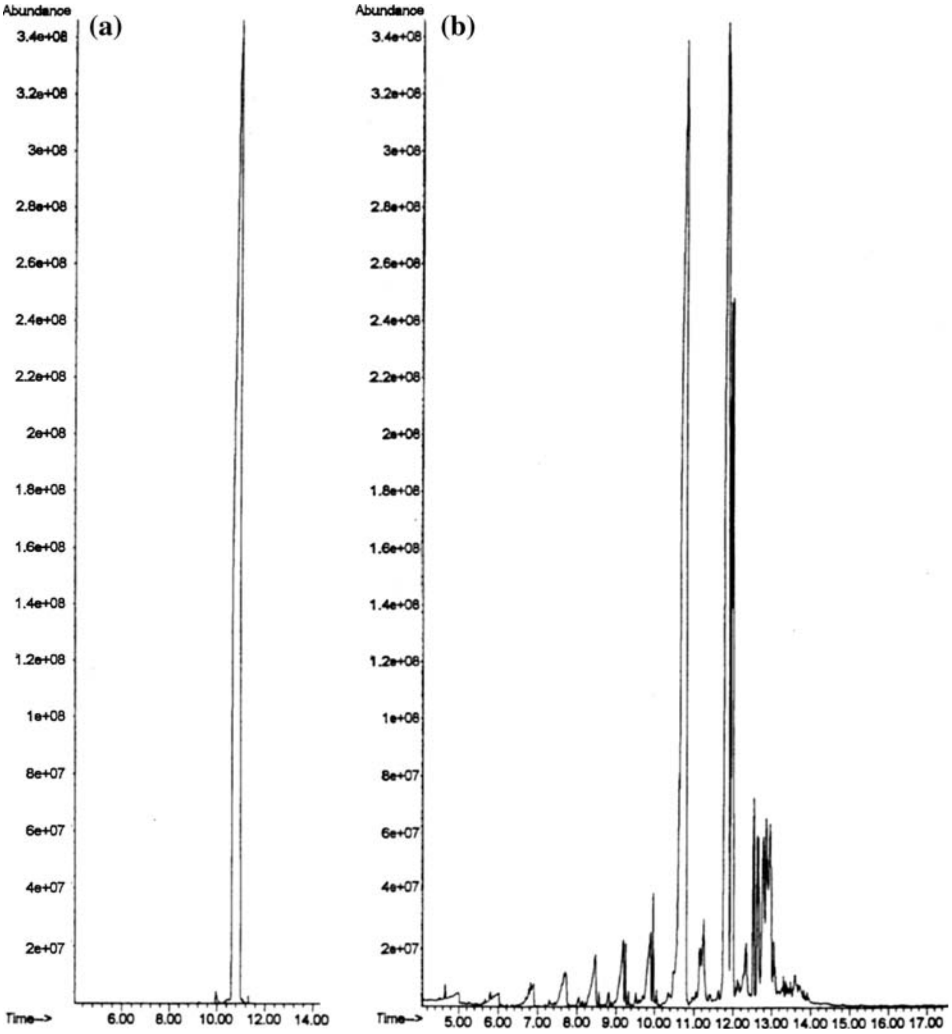
3.3 Mass Spectrometry of 4-Hexadecanone Product

The base peak at $m/z = 71$ refers to the radical $CH_3CH_2CH_2C{=}O$. The molecular ion at m/z-240 represents the $M^{+\cdot}$ of 4-hexadecanone. The series of ions detected that corresponds to the molecular ion, M^+ fragments (43, 58, 71, 85, 99, 114, 127, 141, 155, 169, 183, 197 and 211) that differ by ~14 mass units, formed by the cleavage of $-CH_2-$ units (Fig. 5). This mass pattern represents the peak at retention time 11.70 min on the GC-MS total ion chromatogram shown in Fig. 4b. The mass pattern for 4-hexadecanone was compared with that of the literature [25].

3.4 FT-IR Analysis of the Isolated 4-Hexadecanone

The FT-IR spectra of the compounds isolated from the column chromatography, the peak at 1,704 cm^{-1} refers to

Fig. 4 Chromatogram of *n*-hexadecane (**a**) before ozonation (**b**) after ozonation



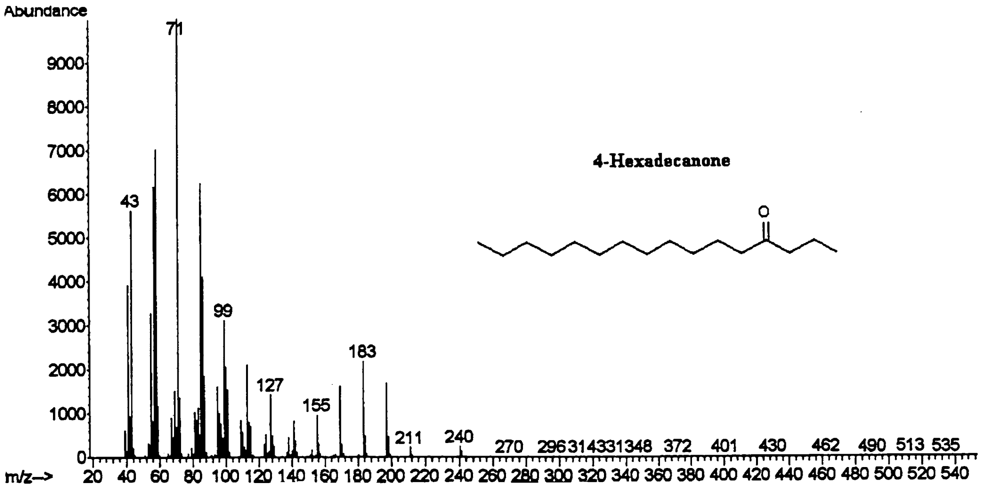


Fig. 5 MS of 4-hexadecanone product

the carbonyl group of a keto compound (Rajasekhar Pullabhotla et al., unpublished work) [26].

3.5 ^{1}H NMR Analysis of 4-Hexadecanone Products

Signal at 0.8–0.9 δ refers to the 6 protons of methyl ($-CH_3$) groups, a multiplet. 1.2–1.3 δ represents a signal for 18 protons of methylene ($-CH_2-$) groups. The signal at 1.48–1.58 δ refers to the 4 protons of methylene ($-CH_2-$) groups, a multiplet. The deshielded 4 protons of $-CH_2COCH_2-$ group can be observed at chemical shift 2.3–2.4 δ, which is a multiplet, refers to 4-hexadecanone [26].

3.6 Ozonation of *n*-Hexadecane with 0.5% Metal (Pd, Ni and V) Loaded on γ-Alumina Catalysts: Comparison of Conversion and Selectivities

In the ozonation of *n*-hexadecane, different catalysts viz. 0.5% of Ni, Pd and V metal loaded γ-Al_2O_3 were employed for the oxidation conversion and selectivity studies. The comparative conversion results on the activity of different metals loaded on γ-Al_2O_3 catalysts and uncatalysed were shown in Fig. 6 and Table 1. The ozonation results with pure γ-Al_2O_3 showed poor activity. The comparative study on different catalysts activity in the ozonation of *n*-hexadecane, Pd/γ-Al_2O_3 N_2 calcined and V/γ-Al_2O_3 N_2 calcined were noticed to be the best catalysts after 3 h ozonation, during 6 h Pd/γ-Al_2O_3 N_2 calcined catalyst yielded higher conversion as shown in Fig. 6. Pd/γ-Al_2O_3 N_2 calcined was found to be the best catalysts for 12 h ozonation as represented in Table 1. Pd/γ-Al_2O_3 N_2 calcined and Pd/γ-Al_2O_3 catalysts conferred higher conversions after 18 and 24 h ozonation (Fig. 6). It was observed that the activity of the Pd loaded γ-Al_2O_3 catalyst was more than Ni and V metals impregnated on γ-Al_2O_3 catalysts. According to Lin et al. [27] the average rate of decomposition of ozone on different metals (Ru, Rh, Pd, Ag, Ni, Pt) loaded γ-Al_2O_3, Pd/γ-Al_2O_3 showed more activity than the others. The conversion of *n*-hexadecane was increased with time due to the longer exposure to ozone.

Table 2 summarises the percentage selectivity for the main product, 4-hexadecanone with different 0.5% metal loaded γ-Al_2O_3 catalysts and in uncatalysed oxidation. In the selective ozonation of *n*-hexadecane, uncatalysed reaction showed poor results. The selectivity towards 4-hexadecanone in the initial stages of ozonation (3 h) was high with Pd/γ-Al_2O_3 and V/γ-Al_2O_3 catalysts, 55%. V/γ-Al_2O_3 and Ni/γ-Al_2O_3 N_2 calcined catalysts yielded higher activity in the selectivities, 59% and 58%, respectively during 6 h ozonation. V/γ-Al_2O_3 showed more activity (58%) and V/γ-Al_2O_3 N_2 calcined also showed selectivity of 55% during 12 h ozonation. The selectivity upon 18 h ozonation was marginal (49–51%) with all the catalysts, Ni/γ-Al_2O_3 N_2 calcined (51%) and V/γ-Al_2O_3 N_2 calcined (50%) as shown in Table 2. SEM results indicates that the aggregation of the metal particles on the γ-Al_2O_3 support

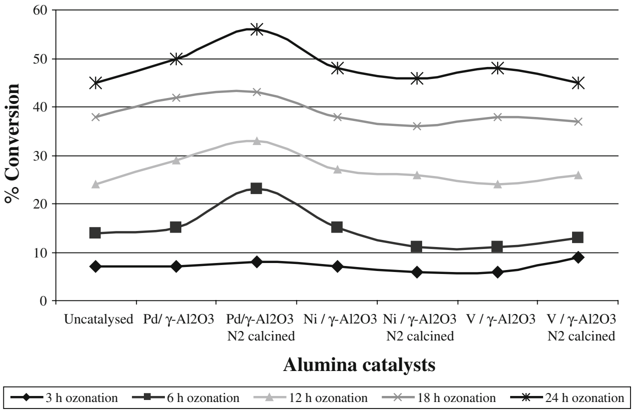


Fig. 6 Conversion with different 0.5% metal loaded γ-Al_2O_3 catalysts in the ozonation of *n*-hexadecane

Table 1 Percentage conversion in *n*-hexadecane ozonation with 0.5% metal loaded γ-Al2O3 catalysts

Ozonation Time, h	Uncatalysed reaction	Pd/γ-Al_2O_3	Pd/γ-Al_2O_3 N_2 calcined	Ni/γ-Al_2O_3	Ni/γ-Al_2O_3 N_2 calcined	V/γ-Al_2O_3	V/γ-Al_2O_3 N_2 calcined
3	7	7	8	7	6	6	9
6	14	15	23	15	11	11	13
12	24	29	33	27	26	24	26
18	38	42	43	38	36	38	37
24	45	50	56	48	46	48	45

Table 2 Percentage selectivity for the main product, 4-hexadecanone with different 0.5% metal loaded γ-Al2O3 catalysts

Ozonation Time, h	Uncatalysed reaction	Pd/γ-Al_2O_3	Pd/γ-Al_2O_3 N_2 calcined	Ni/γ-Al_2O_3	Ni/γ-Al_2O_3 N_2 calcined	V/γ-Al_2O_3	V/γ-Al_2O_3 N_2 calcined
3	45	55	54	53	54	55	48
6	47	56	53	55	58	59	57
12	46	52	51	53	52	58	55
18	40	49	48	49	51	49	50
24	38	46	44	48	47	46	49

particles, this possibly is the reason for the lower conversions of Ni/γ-Al_2O_3 N_2 calcined, V/γ-Al_2O_3 during 6 h and V/γ-Al_2O_3 N_2 calcined during 24 h ozonation. The distribution of thick metal particles on the γ-Al_2O_3 support may have contributed to the less activity and less conversion of the catalysts compared to the uncatalysed reaction. Even though in few catalysed cases, conversions were similar to the uncatalysed, higher selectivity towards the main product, 4-hexadecanone is evidently noticeable in catalysed reactions. In the uncatalysed reactions the formation of the carboxylic acids is more compared to that of the catalytic reactions. In the overall reaction after 24 h V/γ-Al_2O_3 N_2 calcined yielded higher activity towards the selectivity for 4-hexadecanone as illustrated in Fig. 7. The selectivity of the 4-hexadecanone is lowered due to the further oxidation of the products, probably due to the carboxylic acids formation during 12–24 h exposure to ozone. Pd/γ-Al_2O_3 N_2 calcined catalyst which showed the highest conversion, yielded moderate selectivity in favour of 4-hexadecanone during the 3, 6, 12, 18 and 24 h ozonation, respectively as represented in Fig. 3. The catalytic activity order of metal supported on Al_2O_3 was found to be Pd > Ni. The metals examined such as Pd, Ni and also V were found effective in ozone decomposition and in good accordance with Legube and Karpel Vel Leitner [5]. One can observe the percentage conversion and selectivity are more with the catalysts calcined under N_2 flow conditions. The objective of attaining the high selectivities and optimum conversions is achieved with different metal loaded γ-Al_2O_3 catalysts.

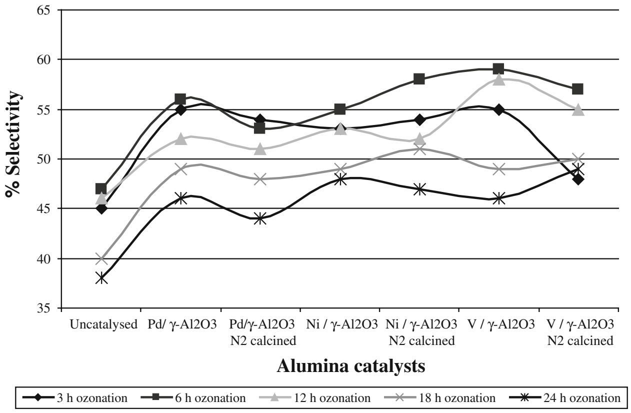
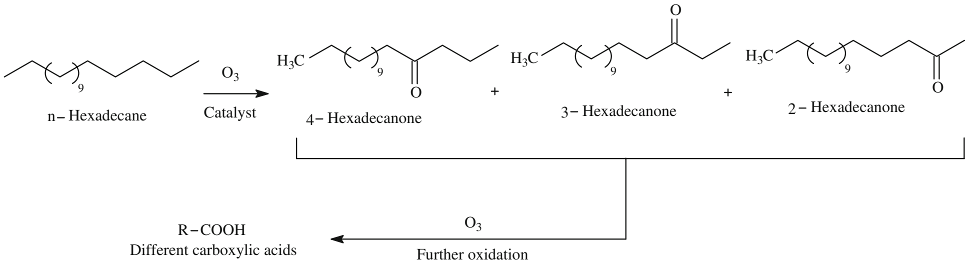


Fig. 7 Selectivity towards 4-hexadecanone with different 0.5% metal loaded γ-Al_2O_3 catalysts

A schematic diagram of the starting material and its positively identified major and minor products is illustrated (Scheme 1). Several explanations on the reaction mechanisms of the heterogeneous catalysed reaction with ozone exist. The proper description of the reaction mechanism is either ozone attacks the organic compounds directly or indirectly via the radical mechanism in the presence of the heterogeneous catalyst. The adsorption of organics as well as ozone on the material surface certainly plays an important role. As a result, ozone may decompose on active metal sites of the catalyst's surface or because of the morphological structure of its support. The decomposition of ozone on the catalyst's surface or due to the support's morphological structure is proposed by Cooper and Burch [28, 29]. A majority of researchers [30] reported that as a result of this decomposition the acceleration of the indirect radical chain starts, but the ideas of how the initiation takes place differ from one another. Some consider the possible enhancement of direct ozonation with heterogeneous catalysis. Ozonation researchers are taking efforts to design a well conceived mechanism for catalytic oxidation with ozone.

The higher the activity of the metal impregnated catalysts can be seen for ozone decomposition when compared

Scheme 1 Products formed in the ozonation of *n*-hexadecane in presence of catalyst



to the supports itself. This probably results from an increase of electron transfer and furthermore, an increase in the rate of redox reaction that takes place in the case of metal on support catalysts, which accelerates the catalytic reactions [5].

It has been reported that noble metals (Pt, Ru, Rh, and Pd) on support were efficient catalysts for the decomposition of gaseous ozone [31]. Besides noble metals, Ni aslo reportedly showed high activities in the decomposition of ozone [32]. Noble metals (Ru, Rh, Pd, Os, Ir and Pt) are efficient redox catalysts [33]. A redox catalyst can decompose ozone and the bond between metal and oxygen species is appropriately strong and the other bond is weak enough for oxidant species to react with other reactant. Lin et al. [27] have suggested that the higher activity is due to the factors like interaction of a metal with a catalyst support, and adsorption abilities of catalyst supports could affect the activity of a catalyst. In the current ozonation of n-hexadecane the appropriate interaction of Pd with γ-Al_2O_3, and also the property of γ-Al_2O_3 of more easily adsorbing O_3 contribute to the high activity of Pd/γ-Al_2O_3.

3.7 Mechanism

The mechanisms of the heterogeneous catalysed ozonation reactions are still to be well understood. In the catalytic ozonation process gaseous, liquid and solid phases are involved. The four possible mechanisms of the heterogeneous catalysis are (i) adsorption of ozone on the catalyst surface leading to the formation of active species which react with non-chemisorbed *n*-alkane molecule (n-$C_{16}H_{34}$), (ii) adsorption of both ozone and *n*-alkane substrate molecules and the subsequent interaction between chemisorbed species [34, 35], (iii) adsorption of substrate *n*-alkane molecules on the catalytic surface and its further reaction with ozone and (iv) molecular ozone reactions with the *n*-alkane are also possible.

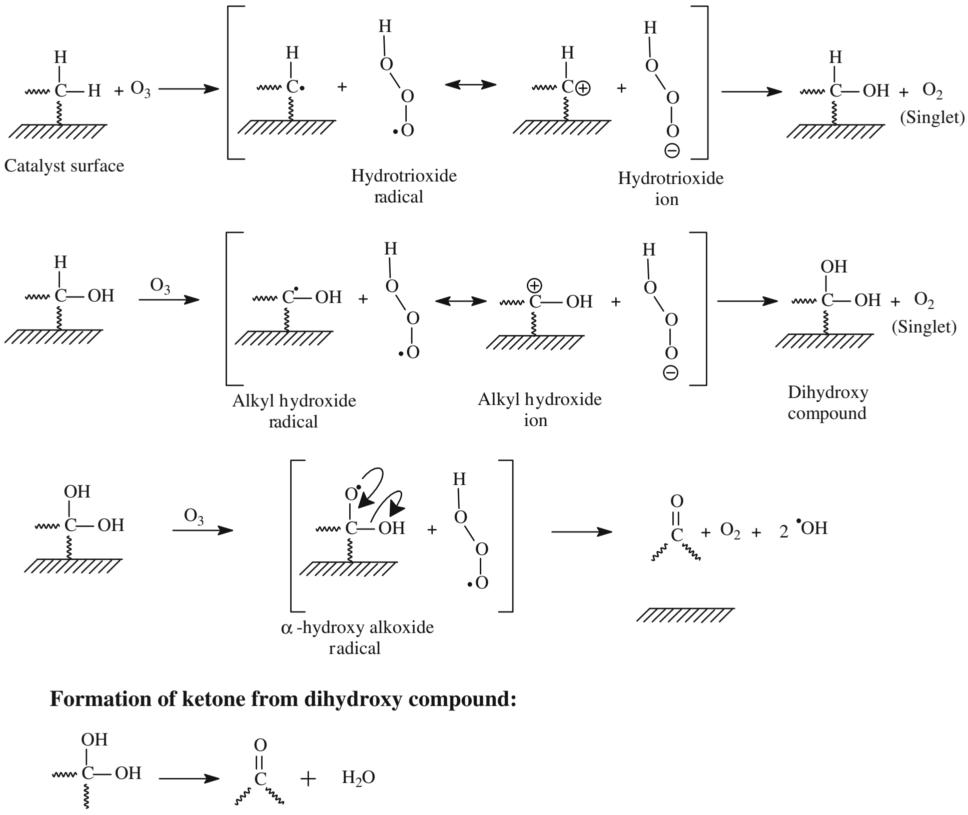
The plausible schematic mechanism for oxidation of higher *n*-alkane is shown in Scheme 2, assuming the adsorption of alkane on the surface of the catalyst and the further reaction with ozone. In the catalytic ozonation of *n*-hexadecane, the hydrocarbon is adsorbed on the catalyst surface, ozone seems to abstract the hydrogen atom from the 4- (or 3- or 2-) positions of the alkane resulting in the formation of alkyl radical/carbocation with hydrotrioxide radical/ion. The hydrotrioxide formed is highly unstable radical/ion, and dissociates into O_2 and hydroxide radical/ion, which reacts with alkyl radical/carbocation to produce alcohol.

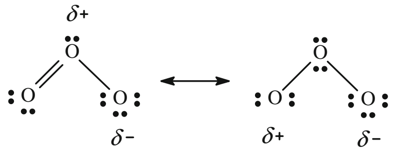
The ozone again attacks the carbon atom at which the hydroxide attached and abstracts the remained hydrogen atom, to form alkyl hydroxide radical/ion. Further the hydrotrioxide, which is unstable gives out oxygen and a hydroxyl radical/ion and combines with alkyl hydroxide to form a dihydroxy compound. The dihydroxy compound can possibly follow two paths. (1) The highly unstable dihydroxy compound can give out water molecule and readily form a ketone with the same number of carbon atoms as the starting material or (2) Ozone abstracts the hydrogen atom from one of the hydroxyl group present and forms the α-hydroxy alkoxide radical. The hydrotrioxide will split into O_2 and hydroxide radical/ion, which further combines with the hydroxide on the carbon atom to form ketone and $^{\cdot}OH$. The ketone products will get desorbed from the catalyst surface. The hydroxyl radical generated can further react with *n*-hexadecane and can produce the ketones.

We earlier reported a plausible mechanism for the direct uncatalysed ozonation of *n*-hexadecane [26]. A modified mechanism for the catalytic ozonation of the *n*-alkane is proposed which involves the adsorption of substrate on the catalyst surface and ozone attacking the substrate leading to the keto isomers as products. The carboxylic acids are formed by the further oxidation of the ketones in the reaction. The carboxylic acid formation follows the mechanism involving ester as an intermediate, followed by the scission of –COOC– bond with >C=O on each fragment [26, 36].

Ozone, due to its resonance, can act as either an electrophile or a nucleophile (Scheme 3). Thus, ozone can attack either the electron rich or deficient carbon centres of the *n*-hexadecane. The adsorbed *n*-hexadecane is expected to have latent polarity $\delta+$ and $\delta-$ in sequence on each subsequent carbon atoms, due to the electron-cloud distribution resulting from the hydrocarbon–catalyst interactions. The ability of ozone to react with both the $\delta+$ and $\delta-$ sites of the alkane is a consequence of its resonance structure.

Scheme 2 Plausible mechanism of the ozonation of *n*-hexadecane in presence of catalyst





Scheme 3 Resonance structures of ozone

A probable explanation for the selective formation of 4-hexadecanone during the reaction is that positions 2- and 3- of the hydrocarbon adsorbed on the catalyst may be more hindered due to their vicinity to the catalyst surface than the 4-position.

4 Conclusions

The ozone-initiated oxidation of *n*-hexadecane with different metal loaded γ-Al_2O_3 is accomplished at moderate conditions. The products formed are mainly mixture of ketones and small amounts of acids. The % conversion increased with time. The ketone isomers are the preferred products of oxidation. With longer exposure to the ozone, further oxidation of the isomers of ketones is observed producing corresponding carboxylic acids. Ozone attacks the saturated hydrocarbon at 4, 3 and 2 positions, resulting in higher ketones namely 4-, 3- and 2-hexadecanones. From the ozonation of higher *n*-alkanes with γ-Al_2O_3 catalysts, it is clear that Pd/γ-Al_2O_3 N_2 calcined catalyst has good conversion activity 56% and V/γ-Al_2O_3 N_2 calcined catalyst showed higher selectivity towards the main product 4-hexadecanone.

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