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Methane Activation by Selective Oxidation

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Abstract

The selective activation of methane by oxidation is a topic that has fascinated scientists and engineers for over a century. In this paper some of the recent approaches will be described and discussed. In particular, the use of FeZSM5 as a catalyst for methane oxidation with aqueous hydrogen peroxide will be described. With this catalyst the primary product is methyl hydroperoxide which decomposes to give methanol. This catalyst is highly active at 50 ^{o}C but yields formic acid which is formed by the sequential oxidation of methanol. Addition of Cu either in solution or within the catalyst matrix switches off the sequential oxidation and methanol is obtained with very high selectivity. Comments are made concerning the prospects for the use of molecular oxygen as the terminal oxidant which is the preferred route.

1. Introduction

This paper is dedicated to the memory of Professor M. Wyn Roberts who was a leading scientist in the field of surface science. In 1986 Au and Roberts [1] showed that oxygen transients could be important in surface catalysed reactions. This discovery was very relevant to the field of methane oxidative coupling as it was considered that O^- on the surface of oxides was important in the activation of methane to give a methyl radical at elevated temperatures [2], and it was a result of this work that we met in 1988 to discuss surface oxygen species and their importance in heterogeneously catalysed oxidation reactions. Oxidative coupling of methane was first proposed by Lunsford in a landmark publication [3] in which it was shown that methane could react to form ethene and ethane over MgO at 600 ^oC with very high selectivities at low conversion. The work of Lunsford opened the floodgates for thousands of subsequent studies on the oxidative coupling of methane [4-7]. It was found that virtually all oxides could catalyse this reaction, and that this was due the reaction occurring mainly by a complex set of radical reactions in the gas phase [2].

Subsequent studies have sought to activate methane at much lower temperatures. A number of low temperature approaches have been proposed, typically involving the use of strong acids to activate methane using bipyrimadyl platinum complexes [8,9] which, cannot readily give an efficient closed process cycle as dilute acid is formed. The concept in these approaches is to use a very strong acid to form an ester with methane and then to hydrolyse the initial product to give methanol. It is the second step that means that a continuous closed catalytic cycle cannot be achieved. Iron-containing zeolites [10-12] can activate methane in the gas phase with nitrous oxide at elevated temperatures but again a closed catalytic cycle has not yet been achieved. In his case the methane reacts to form a surface methoxide species which again can only be recovered by reaction with water to give methanol. Iron phthalocyanine complexes [13,14] although promising, have low activity and stability. However, a number of enzymes are capable of activating methane selectively at low temperatures and, indeed, methane monoxygenase demonstrates that the target reaction is feasible under mild aqueous conditions but at rates not considered commercially viable [15]. Hence there is a real challenge for scientists to design a catalytic process by which methane is selectively converted to higher value products. In this paper the approaches we have taken to address this challenge will be briefly reviewed and a possible way forward identified.

2. The initial approach with AuPd catalysts

We focused our initial studies for the low temperature selective oxidation of methane using water as solvent and hydrogen peroxide (H_2O_2) as oxidant as this provided a convenient medium for both the reaction and analysis. Water was selected as the carbon containing products can be readily identified using nmr spectroscopy, with carbon containing solvents together with catalysts that give only low levels of conversion there is always the possibility of contamination or the concern that the observed materials could originate from the oxidation of the solvent. We had previously shown [16] that supported gold palladium catalysts are effective for the oxidation of alcohols with molecular oxygen as well as the direct synthesis of hydrogen peroxide from hydrogen and oxygen. It is considered that these catalysts form hydroperoxy species in these reactions. We therefore reasoned that supported AuPd nanoparticles would be a good starting point to investigate the oxidation of methane using hydrogen peroxide as oxidants. We set an initial target of matching the initial activity of methane monooxygenase which is 5 mol methanol $kg_{cat}^{-1}h^{-1}$[15]. The initial reactions showed that methane could be converted using AuPd/TiO_2 catalysts prepared by incipient wetness impregnation, deposition precipitation and sol-immobilisation [17], however, very low activities and selectivities were observed. Methanol was observed at ca. 20% selectivity at temperatures between 50-90 ^oC but the major product was CO_2. The low activity was due to the high rates of decomposition observed with these catalysts at these reaction temperatures. In view of this we investigated forming H_2O_2 in situ by reacting H_2 and O_2 with methane over the same catalysts [17]. This was found to improve the selectivity to for methanol 70%. At this stage we reasoned that the high level of H_2O_2 decomposition was hampering the observation of the underlying catalysis. In an attempt to stabilize the H_2O_2 we decided to investigate acidic supports and selected the zeolite H-ZSM-5 as a suitable support. We found that the activity of the supported AuPd catalysts increased significantly when H-ZSM-5 was used as the support. However, H-ZSM-5 in the absence of the AuPd nanoparticles was more effective (Figure 1) and gave over 98% selectivity to methanol with over 90% of the H_2O_2 remained unreacted at the end of the reaction period which was in contrast to only traces of H_2O_2 that remained when AuPd/TiO_2 was used as the catalyst. At this stage we switched our investigation to the study of zeolites as catalysts.

3. Methane conversion with zeolite catalysts

The oxidation of methane with hydrogen peroxide with H-ZSM-5 at 50 ^oC was found to be very selective to oxygenates (Figure 2) [18,19] but the major product was formic acid rather than methanol. However, detailed time-on-line studies showed that the primary product for this reaction is methyl hydroperoxide and that methanol and formic acid were formed in sequential reactions (Figure 3). Detailed EPR studies showed that there were no carbon based radicals formed during the reaction and only oxygen-based radicals were observed [18,19]. The reaction proceeds so that methane is oxidised giving methyl hydroperoxide as the primary product, which subsequently reacts to form methanol which then is sequentially oxidised to formic acid and finally CO_2.

We investigated a range of zeolites and zeotypes (Figure 2) and found that H-ZSM-5 was the preferred catalyst as other materials were ineffective under our mild reaction conditions. Zeotypes that were isostructural with H-ZSM-5, namely silicalite and TS-1, were inactive indicating that confinement effects within the pores was not the crucial design feature with these catalysts. Other zeolites with wider pores, namely Ferreirite and zeolite β showed some activity but it was negligible compared with H-ZSM-5 [19]. We examined the role of impurities and focussed on the potential role of iron although there was no correlation observed between catalyst activity and the total iron content (Figure 2). The catalyst activity can be promoted by the addition of iron either by impregnation, ion exchange, solid state ion exchange or vapour impregnation methods.

The nature of the Fe-species present in the catalysts was investigated and in this respect we concentrated on the commercial ZSM-5 and Fe-silicalite-1 since these displayed the highest intrinsic activity of catalysts we investigated. TEM analysis showed that the Fe was dispersed throughout the interior structure; no nano-crystalline iron oxide was observed, and this was further confirmed by XPS analysis since Fe was not detected. For Fe-silicalite-1, IR spectroscopy revealed that Fe was present in tetrahedral framework sites [20] but that it migrates to octahedral extra-framework sites upon heat pre-treatment, which correlates with the observed activity as the activity increases with the heat treatment. EXAFS also demonstrated that ZSM-5 catalysts show an increase of octahedral Fe^{3+} with high temperature treatments, leading to the most active catalysts being formed. Hence, we postulated that catalytic activity depends upon the formation of dispersed Brønsted acid sites within the nanoporous environment that facilitate the formation of active octahedral Fe^{3+} species.

EXAFS analysis showed that in samples containing the lowest Fe concentrations, the Fe-Fe co-ordination number is low, and consistent with diiron species that have been suggested in previous studies [21-25] DFT calculations were employed to simulate model diiron species which could be compared to the EXAFS data. Of the several possible alternatives a close match was obtained for a diiron complex containing two octahedral Fe^{3+} centres: $[Fe_2(\mu_2\text{-}OH)_2(OH)_2(H_2O)_2]^{2+}$. This structure is the resting state of the catalytic sites in both the ZSM-5 with iron impurities and Fe-ZSM-5, where the additional iron has been added by a range of methods. This can then be activated by H_2O_2 to produce a centre capable of oxidising methane to give the methyl hydroperoxide intermediate and water in a closed catalytic cycle. Identifying the active site as an extra-framework cation accounts for the observation that the presence of cation exchange sites is crucial in order to obtain the specific geometrical aspects of the active diiron species. We considered that the active sites consists of a species containing a high valent ferryl ion (Fe^{4+}=O), which provides a strong driving force for the reductive cleavage of the C-H bond of methane. Methyl hydroperoxide can subsequently undergo a surface catalysed conversion to methanol *via* the hydrolysis of surface-bound methoxy species. The formation of the methoxy species relies upon the cleavage of the RO-OH bond, and results in the release of HO· radicals into solution which can react with methanol to form formic acid. Indeed, the generation of hydroxyl radicals could be a major limitation to the catalyst selectivity due to their role in non-selective chemistry. However, we have found that the addition of Cu^{2+} to the catalyst, either as a heterogeneous component of the catalyst or as a heterogeneous or homogeneous additive to the reactor, avoids unselective over-oxidation processes. This is shown in Figure 4 for the addition of Cu^{2+} to Fe-ZSM-5 where the copper is added by impregnation. However, with these ZSM-5 based catalysts we still observe high H_2O_2 decomposition which is switched off by using silicalite as the framework. If catalysts based on silicalite are used in place of ZSM-5 the decomposition of H_2O_2 is minimized; although Fe-silicalite gives formic acid as the major product. However, when Cu-silicalite is added to the reaction mixture, a material that exhibits very low activity, the formation of formic acid is switched of and now we can observe 93% selectivity to methanol at 9.5% methane conversion. With this catalyst we observe a rate of 35 mol methanol kg_{cat}^{-1} h^{-1} which is considerably higher than that of methane monooxygenase under comparable conditions [15]. All these studies have been carried out on a small scale in stirred batch reactors and as such are not ideal on which to base any assumptions concerning the potential feasibility of the catalysts at a larger scale. For this experiments are required in flow reactors and this is the topic of our current studies.

4. Possible future strategy for alkane activation

In the previous section we have described the design of a methane activation catalyst in which methane is oxidised with hydrogen peroxide to give methanol with high selectivity (>90%) at 10% conversion at 50 ^oC in aqueous media. While we consider this is a significant advance in methane activation catalysis, there are, however, some problems that preclude this discovery from reaching commercialisation. First, hydrogen peroxide is typically more expensive than methanol and so there is no cost incentive for this chemistry. Second, the reaction is an exothermic oxidation and for the recovery of this energy it would be more efficient if the reaction was carried out at 150 – 200 ^oC. Third, recovery of methanol from a dilute aqueous solution would be problematic. Hence it would be better if the reaction used molecular oxygen as the terminal oxidant at 150 – 200 ^oC in a solvent that permitted higher concentrations of dissolved methane. We have yet to achieve this with methane oxidation but we have successfully oxidised the methyl group of toluene under solvent-free conditions with O_2 at 160^{o}C using a supported AuPd catalyst [26] (Figure 5). A very high yield of benzyl benzoate are obtained (96%) as a consequence of the reaction mechanism (Figure 6). Toluene is initially oxidised to benzyl alcohol, which forms benzaldehyde. These two then react to form a hemiacetyl that is oxidised to benzyl benzoate. Interestingly, the oxidation to benzoic acid is not observed and this is because the aldehyde is stabilised if the alcohol is present [27]. We consider that this approach might be feasible for selective methane oxidation if a sufficiently active catalyst can be designed. However, it should be noted that although we have observed this catalysis for toluene it is a highly activated molecule and to date our attempts have not been successful but we will continue to try.

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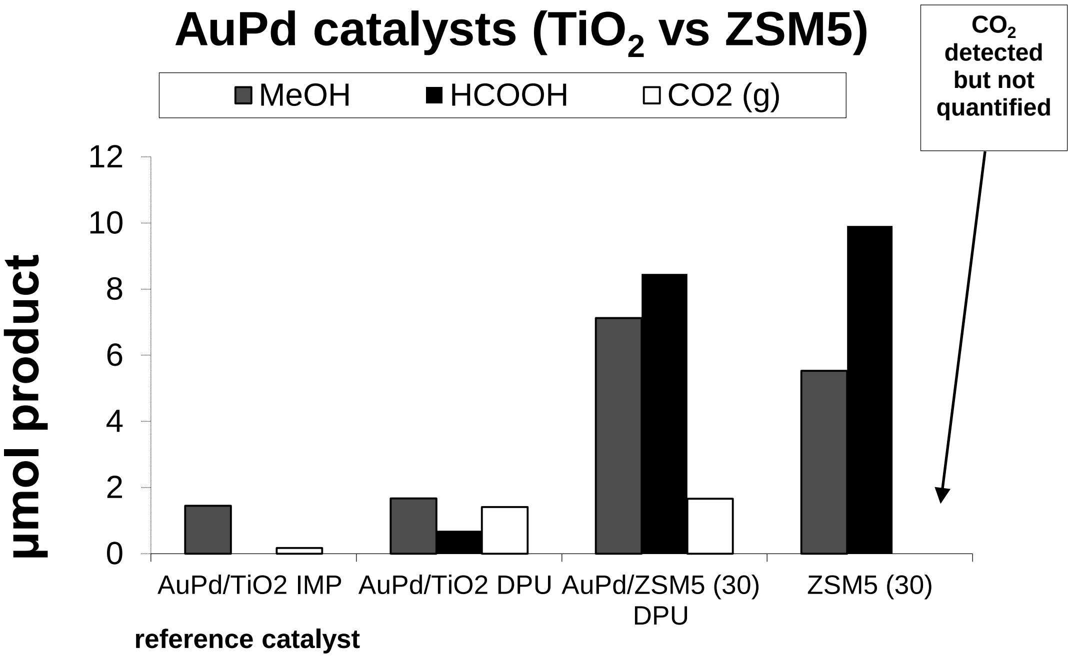

Figure 1 Comparison of the activity and selectivity of AuPd nanoparticles supported on TiO_2 and H-ZSM-5. Reaction conditions: autoclave reactor, H_2O_2: 5000 μmol, 50°C, 30 min reaction, $p(CH_4)$ = 440 psi, mass of catalyst 27 mg.

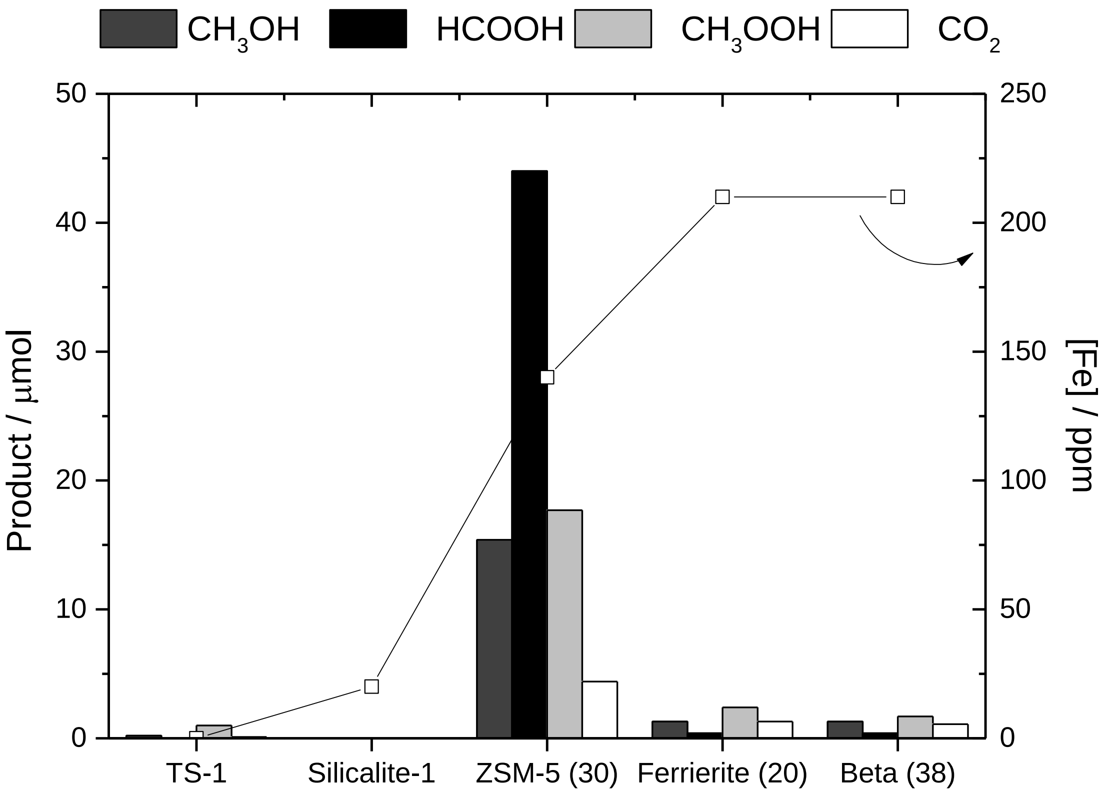

Figure 2 Oxidation of methane using zeolites and zeotypes with hydrogen peroxide. Reaction conditions: catalyst 27 mg, 50 °C, water 10 ml, [H_2O_2] = 0.5 M, P (CH_4) = 30.5 bar, 0.5 h, 1500 rpm

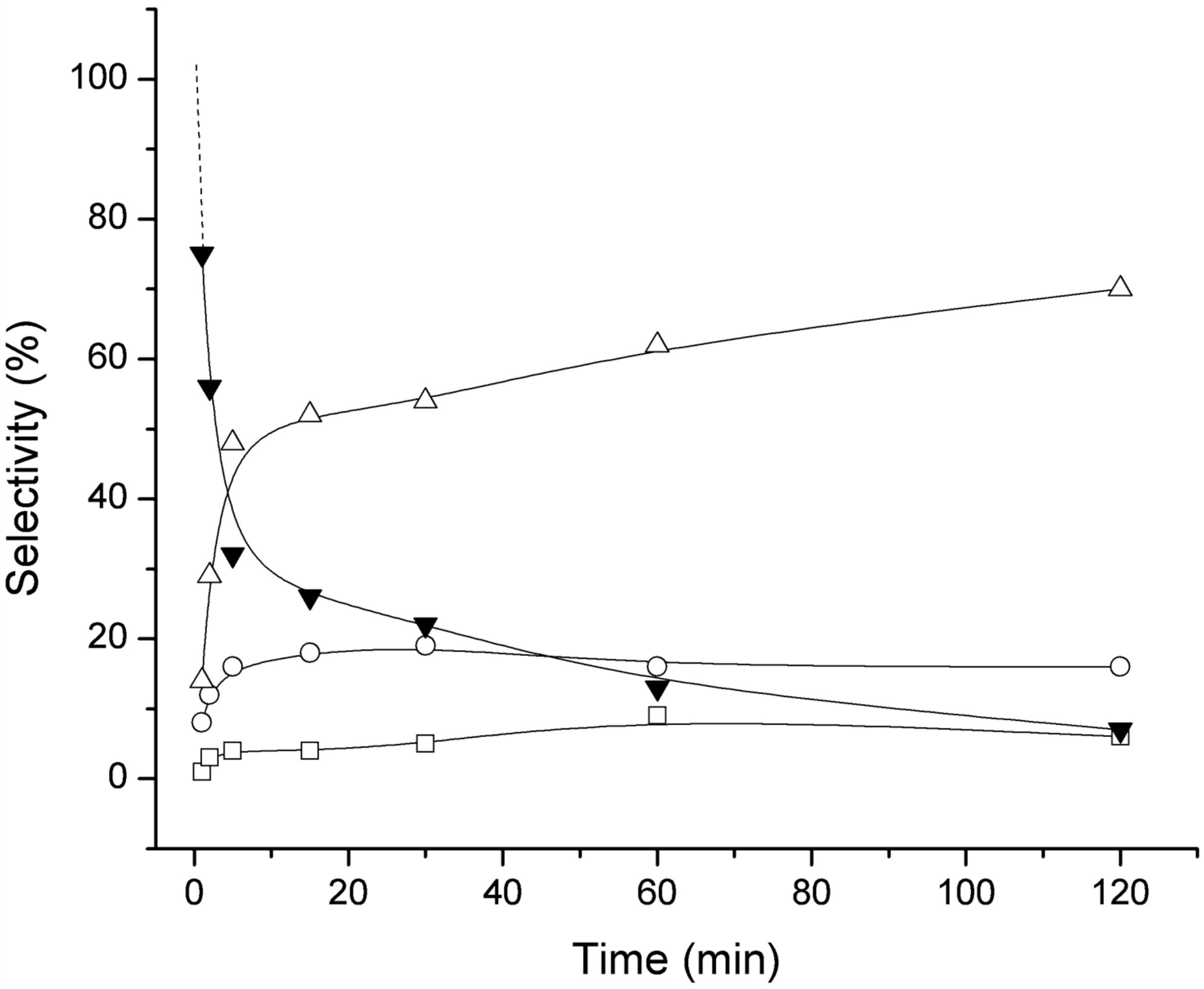

Figure 3 Effect of time on line for the selective oxidation of methane with hydrogen peroxide using Fe-ZSM-5 showing that methyl hyroperoxide is the primary product. Reaction conditions: catalyst 27 mg, 50 °C, water 10 ml, [H_2O_2]= 0.5 M, P (CH_4) = 30.5 bar, 1500 rpm.

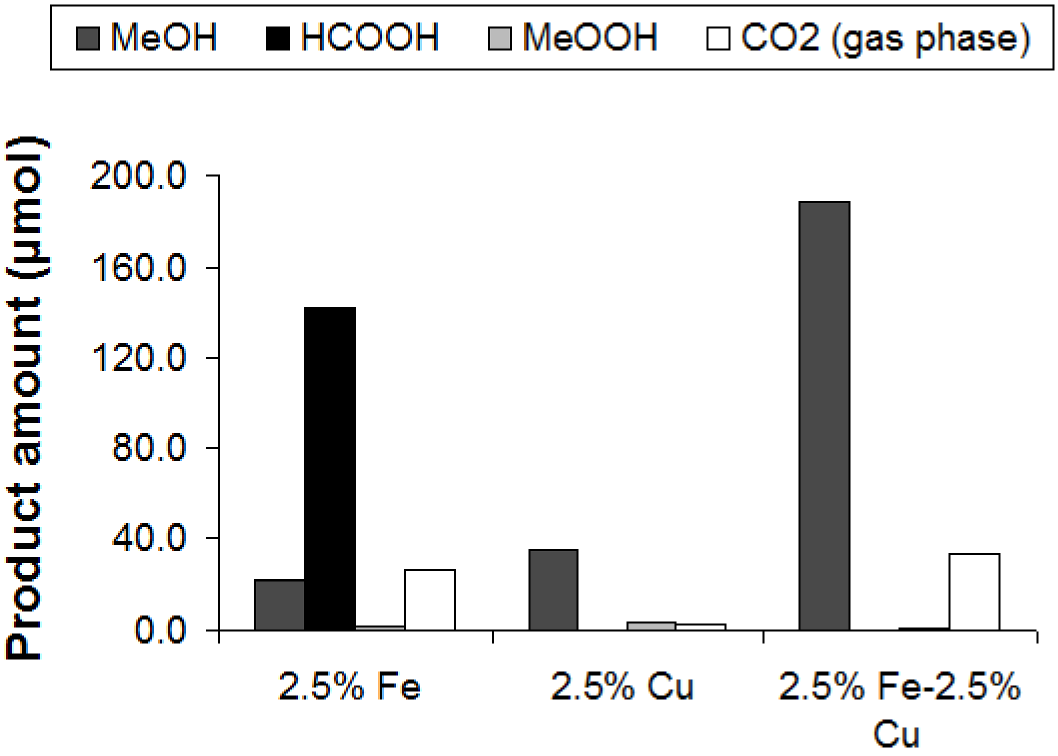

Figure 4 Methane oxidation with hydrogen peroxide at 50 °C using Fe-ZSM5, Cu-ZSM-5 and Fe-Cu-ZSM5. Reaction conditions: autoclave reactor, H_2O_2: 5000 µmol, 50°C, 30 min reaction, p(CH_4) = 440 psi, mass of catalyst 27 mg.

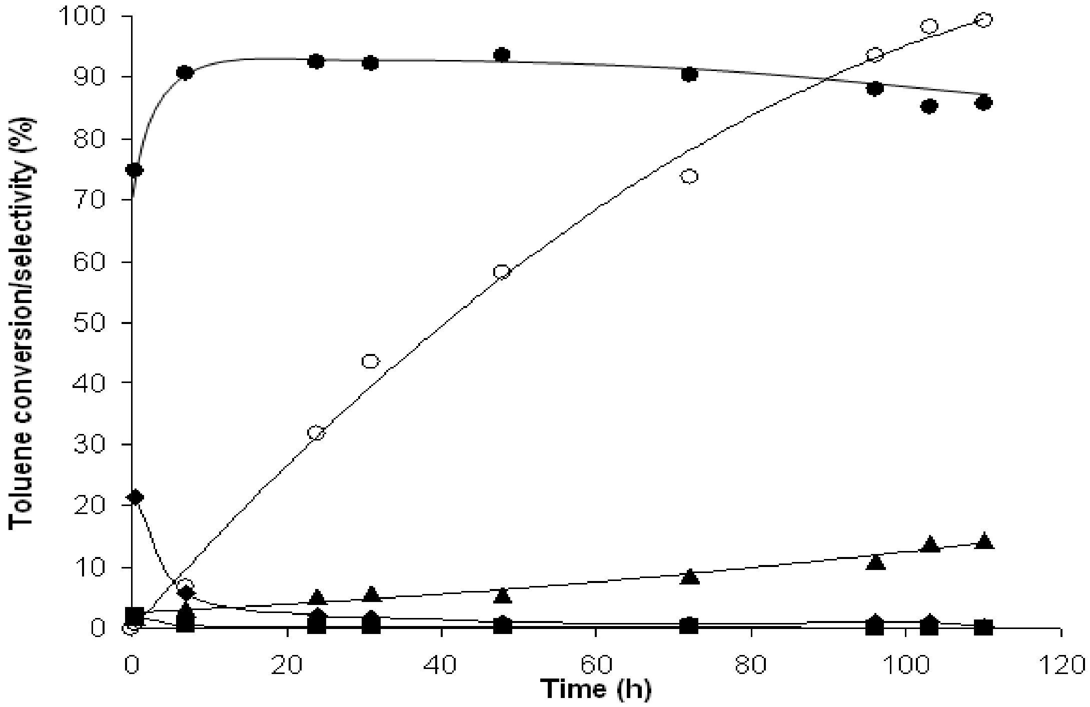

Figure 5 Oxidation of toluene with O_2 under solvent-free conditions. Reaction conditions: P_{O_2} 0.1 MPa, toluene (20 ml), of catalyst (0.8 g, 1 wt % Au-Pd/C prepared by sol immobilization), 160 °C, toluene/metal molar ratio of 3250, and reaction time, 110 h. ○ conversion, ■ selectivity to benzyl alcohol, ♦ selectivity to benzaldehyde, ▲ selectivity to benzoic acid, and ● selectivity to benzyl benzoate

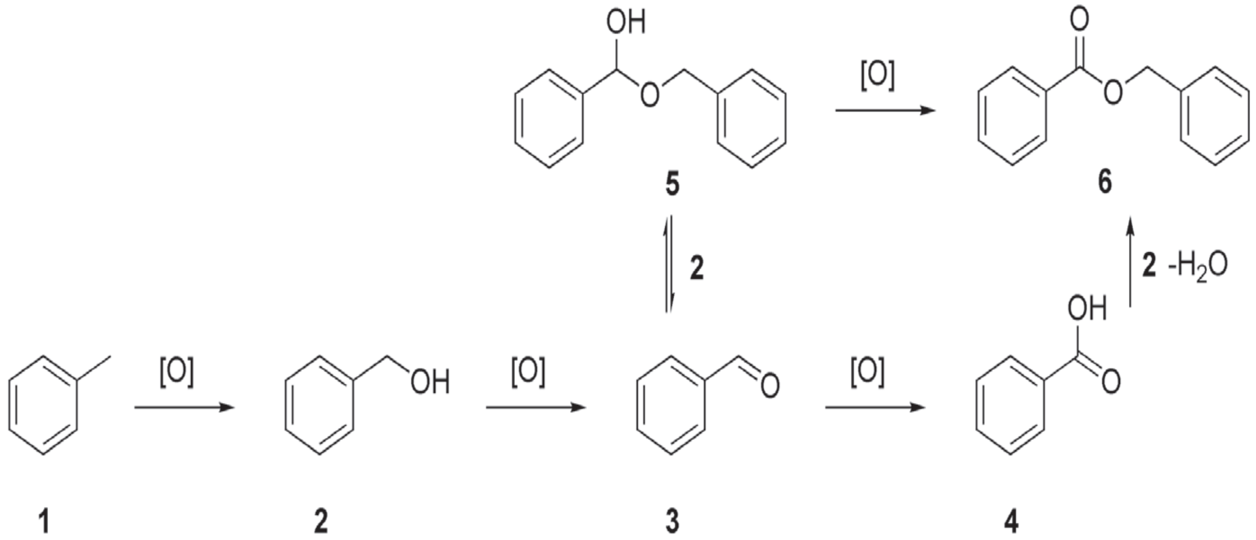

Figure 6 Reaction scheme for the oxidation of toluene to benzyl benzoate.