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Catalysis Today 81 (2003) 547–559

CATALYSIS TODAY

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Deactivation of metal catalysts in liquid phase organic reactions

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Abstract

The paper gives a general survey of the factors contributing to the deactivation of metal catalysts employed in liquid phase reactions for the synthesis of fine or intermediate chemicals. The main causes of catalyst deactivation are particle sintering, metal and support leaching, deposition of inactive metal layers or polymeric species, and poisoning by strongly adsorbed species. Weakly adsorbed species, poisons at low surface coverage and solvents, may act as selectivity promoters or modifiers. Three examples of long term stability studies carried out in trickle-bed reactor (glucose to sorbitol hydrogenation on Ru/C catalysts, hydroxypropanal to 1,3-propanediol hydrogenation on Ru/TiO_2 catalysts, and wet air oxidation of paper pulp effluents on Ru/TiO_2) are discussed.

Keywords: Deactivation; Ru/TiO_2; Trickle-bed reactor

1. Introduction

Activity and selectivity decay of catalysts employed in liquid phase reactions is a major concern for catalyst users and manufacturers. The latter have certainly an undisclosed expertise on ageing and regeneration of catalysts used in organic reactions but in the open literature this is not a well documented research area and keywords such as deactivation, ageing, poisoning, regeneration are not indexed in organic reaction treatises. Several reasons account for this apparent lack of interest. Catalyst deactivation is often of minor concern in fine chemistry where selectivity is the main objective. Catalysts are often employed in comparatively large amounts with respect to substrate and only for a few runs before being returned to the catalyst manufacturer. Since most liquid phase reactions are carried out in batch reactors, deactivation studies require cumbersome catalyst recycling procedures associated with a high risk of additional deactivation due to the accidental loss of catalyst or detrimental exposure to air. Accelerated decay procedures used in gas phase reactions consisting of running reactions at higher temperatures are usually not possible in liquid phase because of limitations associated with boiling point of solvents, stability of molecules, and secondary reactions changing the selectivity. Also, deactivation studies are made difficult because of the high number of factors potentially involved: sintering or leaching of active components, poisoning of active sites by heteroatom-containing molecules, inactive metal or metal oxide deposition, impurities in solvents and reagents, oligomeric or polymeric by-products. Because of the many factors involved in activity and selectivity decay and because different catalyst lots may not be identical, there is also a high probability of irreproducible results.

In this paper we will make a general survey of the various causes of activity and selectivity decay in liquid phase reactions on metal catalysts as well as on

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doi:10.1016/S0920-5861(03)00153-6

possible regeneration procedures. Then, we will describe briefly the results obtained in our laboratory on three studies of catalyst stability during hydrogenation and oxidation reactions in continuous reactors.

2. Survey of deactivation mechanism in liquid phase reactions

2.1. Sintering of metal particles and coalescence of colloids

Sintering of metal particles resulting in loss of active surface area is an irreversible cause of catalyst deactivation. Sintering can be easily followed by XRD and TEM particle size measurements and by H_2 or CO chemisorption [1]. As far as supported metal catalysts are concerned, sintering due to temperature driven migration and coalescence of metal particles on supports is unlikely because most liquid phase reactions are carried out at comparatively low temperatures. In contrast, unsupported metal particles can easily sinter even at temperatures lower than 100 °C. Thus, the TEM view given in Fig. 1 shows that Pt-particles of unsupported Adams catalyst become much larger and facetted after cinnamaldehyde hydrogenation at 100 °C compared to 60 °C [2]. Industrial Raney nickel catalysts recycled several times in the glucose hydrogenation reaction at 130 °C experienced a partial sintering of nickel micro-crystallites shown by TEM (Fig. 2) and also evidenced by the loss of BET area and amount of chemisorbed hydrogen [3].

Colloidal metal particles suspended in aqueous or organic media are prepared by reduction of aqueous solutions of metal salts in the presence of surfactants or polymers which limit their state of aggregation. Colloidal metal particles are active catalysts, e.g. in hydrogenation reactions [4] provided the stabilising ligands are not too strongly bonded to prevent reactant adsorption on the surface. However, weaker ligands may make the preparation of metal colloids not reproducible because of easier coalescence. The deposition of colloidal particles on carriers, e.g. by filtration [4,5], prevents the coalescence of metal particles and results in egg-shell catalysts where particles are located on the external surface of carriers rather than in pores.

Sintering of supported metal particles may well occur close to room temperature, because of atomic migration process (Ostwald ripening) involving the extraction and transport of surface metal atoms by chelating molecules such as polyhydroxylic molecules. Thus, platinum particle size increased from 2.2 to 3.2 nm after methyl-α-D-glucoside oxidation on Pt/C catalyst [6]. Restructuring of large platinum particles during L-sorbose oxidation was detected by STM [7].

2.2. Leaching of active phases and supports

Leaching of catalyst in the reaction medium is the main cause of deactivation in liquid phase reactions.

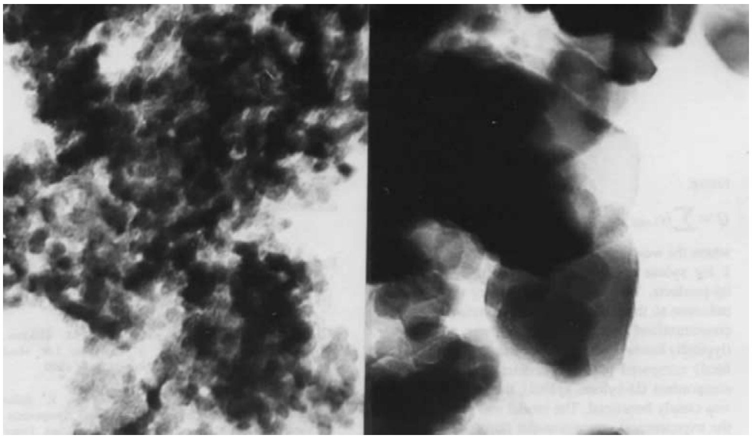


Fig. 1. TEM view of platinum Adams catalyst. Left field: after cinnamaldehyde hydrogenation at 60 °C. Right field: after hydrogenation at 100 °C.

Fig. 2. TEM view of ultramicrotome cut of industrial Raney nickel aged after several recycling in glucose hydrogenation at 130 °C. The nickel micro-crystallites have sintered in the right-hand side of Raney nickel grain (unpublished results).

In the field of supported homogeneous catalysis, the search for perfectly stable anchored metal complexes on organic or inorganic carriers is the Holy Graal quest. Oxometal species (Ti, V, Cr, Mo, Fe, Co, etc.) incorporated in the structure of molecular sieves or amorphous oxides, grafted in mesoporous materials, encapsulated by ship-in-a-bottle techniques, or ion exchanged in layered structures are also prone to leaching during liquid phase oxidation reactions. Arends and Sheldon [8] have shown that many of these catalytic systems are unstable towards leaching and that appropriate rigorous tests for heterogeneity have not been performed.

As far as metal catalysis is concerned, leaching of metal atoms depends upon the reaction medium (pH, oxidation potential, chelating properties of molecules) and upon bulk and surface metal properties. Fig. 3 shows that metal-promoted Raney nickel catalysts underwent a drastic loss of activity in glucose hydrogenation after successive recycling because of promoter leaching, particularly iron and tin [9]. In the hydrogenolysis of aqueous solutions of sorbitol on CuO–ZnO catalysts to prepare C4–C5 polyols, zinc leaching was prevented by working at basic pH [10]. Platinum-metals are much more stable to leaching and even can be used in acidic and oxidising media. Thus ruthenium catalysts sustain the harsh acidic and oxidising conditions employed in CWAO without leaching [11–14].

In a number of cases, the loss of metal from catalysts is primarily due to support leaching. Thus, leaching of palladium during oxidation of 2-methylphenoxyethanol on Pd/$CaCO_3$ [15] could be due to partial support dissolution. Both the platinum and aluminium of Pt/Al_2O_3 catalysts leached in the oxidation of aldopentose solutions [16]. Transition aluminas which are widely used as catalyst supports in hydrocarbon conversions are not well-suited in organic reactions because they dissolve in acidic and chelating medium. Aluminium atoms can be extracted by chelating molecules from aluminosilicates, even silica-rich ones, at neutral pH. Examination of Pourbaix diagrams shows that TiO_2 and ZrO_2 oxides are the most resistant to leaching, and are indeed the only ones stable enough to meet the harsh conditions of wet air oxidation [11–14]. Carbon supports are known for their very high resistance to acidic and chelating media, for this and other reasons (low cost, high surface area), they are the most used metal support in organic reactions. Still, carbon-supported catalysts cannot be regenerated

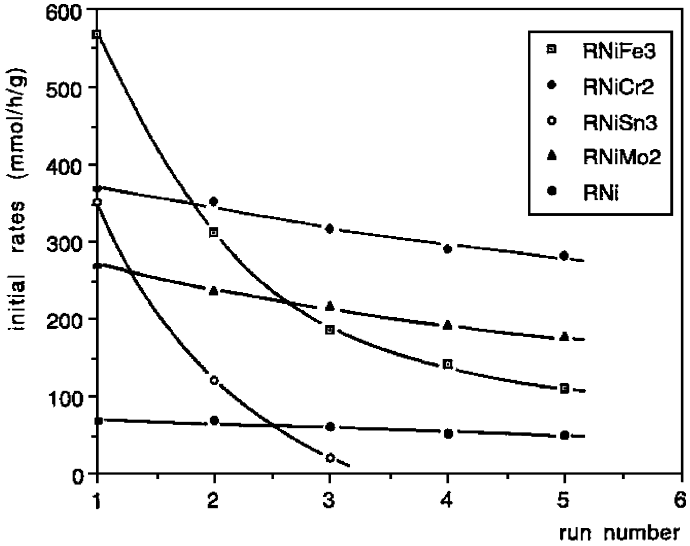
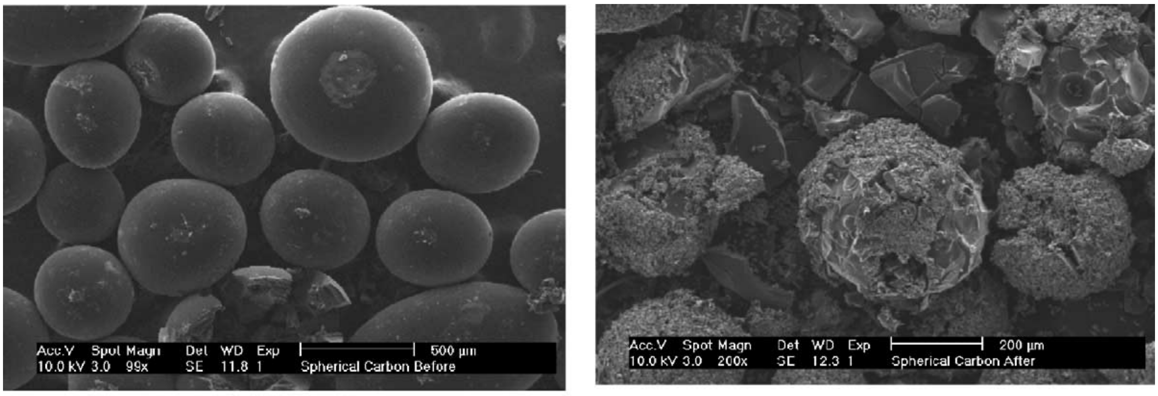


Fig. 3. Initial rate of glucose hydrogenation as a function of recycling run.

by high temperature oxygen treatments or used for a long period of time in oxidation reactions. Fig. 4 shows the SEM pictures of fresh and used synthetic carbons after 4 weeks on stream in cyclohexanone oxidation with air at 120 °C conducted in trickle-bed reactor. Although there was a weak loss of carbon in the used catalyst, the texture was drastically modified, which may make it prone to attrition [17]. As far as formed catalysts are concerned, e.g. extrudates manufactured by agglomeration of powder with a binder, the stability of the binder should be at least comparable to that of the powder to avoid the risk of dissolution and attrition during continuous liquid phase reaction.

2.3. *Effect of strongly adsorbed molecules: activity poisons and selectivity promoter*

The total coverage of metal surfaces by strongly adsorbed species such as sulphur compounds poisons



(a) (b)

Fig. 4. SEM views of synthetic mesoporous carbons. Left field: fresh catalyst. Right field: catalyst used in cyclohexanol oxidation at 120 °C for 4 weeks in trickle-bed reactor.

irreversibly the activity of metals under the usual conditions of liquid phase reactions. Whenever poisons are present at very low concentrations in the feedstock, deactivation increases steadily with time. Thus, Arena [18] reported that 15 ppm of sulphur present in glucose solution are adsorbed on ruthenium catalyst at a rate of 0.025 ppm g_{Ru}^{-1} g_{sol}^{-1} which produce a rapid activity loss. Passing the feed solution over a guard bed for sulphur-removal decreased deactivation. Catalytic transformations of sulphur-containing compounds are difficult to achieve on metal catalysts.

Significant deactivation may occur with organic impurities initially present in the liquid feed (reactant or solvent) or formed as by-products in the reaction. Adsorption of reaction by-products was identified as the main cause of catalyst deactivation in oxidation of alcohols. [19–21]. Deactivation of ruthenium catalyst in glucose hydrogenation was attributed to the formation of D-gluconic acid [18]. Regeneration of catalysts poisoned by strongly adsorbed acidic species may be achieved by catalyst washing in basic medium.

Partial coverage of metal surfaces by adsorbed species (molecules, adatoms, ions) can be beneficial for the selectivity of reactions. These species, which should be adsorbed strongly enough to act permanently, may act as selectivity promoters or modifiers. Thus, lead is used in Lindlar catalyst (Pd–Pb/$CaCO_3$) to inhibit C=C bond adsorption thus increasing the selectivity of C≡C to C=C [22] or to inhibit the hydrogenation of unsaturated groups in substituted nitroarene compounds to obtain a high chemoselectivity for the hydrogenation of NO_2 groups [23]. The adsorption of strong bases increases the selectivity to unsaturated alcohols in α,β-unsaturated aldehyde hydrogenation [24], and increases the diastereoselectivity in disubstituted aromatic hydrogenation [25].

2.4. Effect of solvents on catalytic activity and selectivity

Liquid phase hydrogenation reactions are frequently carried out in the presence of solvents. In most cases their adsorption is weak otherwise strong poisoning effect would occur due to high solvent concentration. Solvents play an important role in selectivity control either by their bonding with the metal surface or with the reactant molecules. Thus, in the hydrogenation of nitroaromatic compounds, the selectivity to hydroxylamine increased in the presence of pyridine or piperidine because they compete with hydroxylamine for adsorption on metal surface which favours the desorption of the latter from the surface [26]. Also a common technique for minimising secondary amine formation during the hydrogenation of nitriles to primary amines is to carry out the reaction in the presence of ammonia. The rate of pyridine hydrogenation to piperidine is slow because of the inhibition caused by the basic function, and the use of acidic solvents favours the formation of pyridinium ions which are hydrogenated more easily [27].

The decrease of activity and the formation of alkylpentylamines during the hydrogenation of valeronitrile over Raney nickel was attributed to the presence of carbonyl compounds formed by dehydrogenation of alcohol solvents (MeOH or EtOH) on the catalyst [28]. In the hydrogenation of ethyl-*p*-aminobenzoate in ethanolic phosphoric acid solutions on 5% Rh/C the rate of hydrogenation was found to decrease rapidly after repeated use because hydrogenolysis of the amino group yielded ammonium dihydrogen phosphate which poisoned the catalyst [29].

2.5. Deactivation by deposition of inactive metals

Noble metals can be deactivated by the deposition of an overlayer of a less active or totally inactive metal. This type of deactivation is little documented in the literature. A clear example of deactivation of ruthenium catalysts by iron in glucose hydrogenation conducted in trickle-bed was provided by Arena [18]. Because of their chelating properties towards iron, glucose and sorbitol molecules corroded the stainless steel reactor walls so that iron leached into the reaction medium to reach a concentration of 3 ppm Fe. Iron deposited on catalyst bed with a build-up proportional to ruthenium content. It was verified that adding $FeCl_2$ in solution poisons Ru-catalysts. Iron deposition on ruthenium surface probably occurred according to a surface oxido-reduction reaction between Fe^{2+} ions and surface metal atoms M covered with hydrogen: $2MH + Fe^{2+} \rightarrow M_2Fe + 2H^+$ as previously observed in the case of iron deposition on platinum [30]. Note that lining reactor walls with a protective polymer layer can prevent reactor corrosion.

2.6. *Deactivation due metal oxidation*

Transition metals of the first row are easily oxidised by exposure to air at ambient temperature. They should be reduced ex situ and kept protected from air exposure before use in reactions. Thus, Raney nickel catalysts are kept in basic water solution and fatty compounds protect nickel catalysts employed for amines or triglycerides hydrogenation. On platinum-group metals only the surface layer is oxidised upon contact with air; oxide overlayers have to be reduced in situ before reaction particularly in the case of rhodium.

Deactivation of metal catalysts employed in oxidation of alcohols and aldehydes with oxygen as oxidising agent has been reviewed in detail [31,32]. The mechanism involves a dehydrogenation of alcohol functions on metal surface followed by the elimination of hydrogen by reaction with adsorbed oxygen. As the oxygen coverage on the metal surface increases, alcohol adsorption is progressively suppressed and conversion attains a plateau. The deactivation of catalysts by over-oxidation depends primarily on the composition, structure, and texture of catalysts. Metals of high reduction potentials such as platinum and palladium [33], and particularly gold [34] are less prone to oxidation. Small metal particles (<2 nm) deactivate more readily because of their stronger affinity to oxygen. Deactivation also depends on the reducing potential of the substrate, e.g. the deactivation is much lower for aldehyde than for alcohols. Thus, platinum catalysts in glyoxal oxidation did not deactivate by over-oxidation because the di-aldehyde behaves as a strong reducing agent for the surface [33]. Over-oxidation can be decreased by operating at lower concentration of dissolved oxygen in the liquid phase, e.g. by regulating the flow rate of oxygen supply, diluting with N_2, or conducting the reaction under oxygen mass transfer control.

The behaviour of palladium catalysts during oxidation of glucose to gluconic acid provides an example of deactivation by over-oxidation. Fig. 5 shows that the activity of Pd/C catalysts decreased progressively particularly on sample prepared with 1–2.5 nm particles [35]. The discovery that addition of p-electron metals such as lead and bismuth to platinum or palladium catalysts improved the rate and selectivity of reactions was a great breakthrough [36,37]. To avoid the deactivation of palladium in glucose oxidation, a Pd–Bi/C catalyst was prepared by adding controlled amounts of bismuth subnitrate to a suspension of Pd/C catalyst in glucose solution [38]. Fig. 6 shows that the activity of Pd–Bi/C catalyst with $Bi/Pd_s = 1$ is much higher than that of the parent Pd/C. The beneficial effect of bismuth was interpreted by the mechanism described in Fig. 7 where bismuth acts as co-catalyst preventing the over-oxidation of palladium.

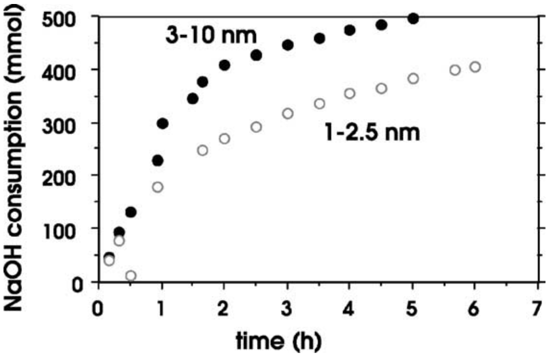


Fig. 5. Oxidation of glucose to gluconic acid on Pd/C catalysts with different palladium particle sizes (air, pH = 9).

2.7. *Deactivation by oligomeric/polymeric species*

Polymeric or oligomeric species formed in liquid phase as a result of secondary reactions on reactant

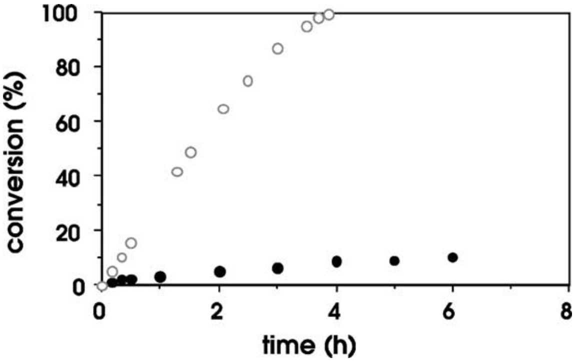


Fig. 6. Oxidation of glucose to gluconic acid (pH = 9, 40 °C, air flow rate $1.5\,l\,min^{-1}$ air, concentration $1.7\,mol\,l^{-1}$, molar ratio glucose/palladium 3150). Open circle: Pd–Bi/C catalyst ($Bi/Pd_s = 1$). Full circle: Pd/C.

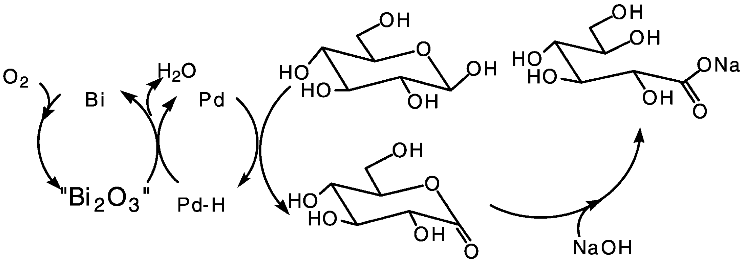


Fig. 7. Scheme of reaction mechanism of glucose oxidation on bismuth-promoted Pd-catalyst.

or impurities tend to deposit on the surface of heterogeneous catalysts and restrict the reactant access and product desorption. Even small molecular weight oligomers are able to block pore entrance or restrict considerably the reactant diffusion towards metal particles. Deactivation of platinum catalysts in 1-methoxy-2-propanol oxidation was attributed to polymeric species formed by aldol-dimerization and detected by chromatographic and spectroscopic methods [39]. Whereas catalysts poisoned by carbonaceous deposit in gas phase reactions are regenerated by oxidation at high temperatures, catalysts used in liquid phase reaction particularly those deposited on carbons and polymers cannot be regenerated likewise. Washing with solvents may be used to dissolve organic overlayers covering the catalyst surface. To cope with this type of deactivation, porosity of catalysts should be tailored, e.g. by using macroporous carriers, as shown in Section 3.2 dealing with the oxidation of 3-hydroxypropanal [10].

3. Catalyst stability studies in liquid phase hydrogenation and oxidation

During the past few years hydrogenation and oxidation reactions have been conducted in our laboratory to study the stability of metal-supported catalysts as a function of reaction conditions and time on stream in trickle-bed reactor. Continuous fixed-bed operation is well-suited to study activity or selectivity decay because they are easily monitored as a function of time on stream, reaction conditions and feedstock impurities without detrimental manipulations of catalysts.

3.1. Activity and selectivity of ruthenium-based catalysts in glucose hydrogenation

Glucose hydrogenation is employed to prepare sorbitol a commodity product used in food, pharmaceutical and chemical industries as well as an additive in many end-products. Most of the industrial production is still conducted batch-wise on Raney nickel catalysts, but, because of the risk of nickel or metallic promoter leaching they tend to be replaced by carbon-supported ruthenium catalysts. Conversion of 100% and selectivity approaching 99% are required. The main by-products are gluconic acid formed by the Cannizaro reaction and mannitol formed by sorbitol epimerisation (Fig. 8). In a previous study [40], it has been shown that 1.8% Ru/C catalyst prepared by cationic exchange or anionic adsorption on Norit extrudates provided up to 99.5% yield in sorbitol for an extended period of time on stream (596 h) in trickle-bed reactor. The activity at low conversion (initial activity) was 1080 mmol h^{-1} g_{Ru}^{-1} compared to 50 mmol h^{-1} g_{Ni}^{-1} on 48% Ni/kieselguhr catalyst.

In a subsequent investigation [41] the deactivation of a commercial 1.2% Ru/C catalyst was compared to that of a bimetallic catalyst 1.6% Ru–0.2% Pt/C ($Ru_{94}Pt_6$) prepared by co-exchange of $Ru(NH_3)_6{}^{3+}$ and $Pt(NH_3)_4{}^{2+}$ on Norit extrudates. It was verified by high resolution analytical microscopy that the particles are bimetallic. Fig. 9 shows that the bimetallic catalyst exhibits a much more stable activity with time. According to Arena [18] ruthenium may deactivate because of poisoning by gluconic acid formed by oxidation of glucose with traces of oxygen present in the liquid feed. If it were the case, the presence of platinum would have a beneficial role by preventing

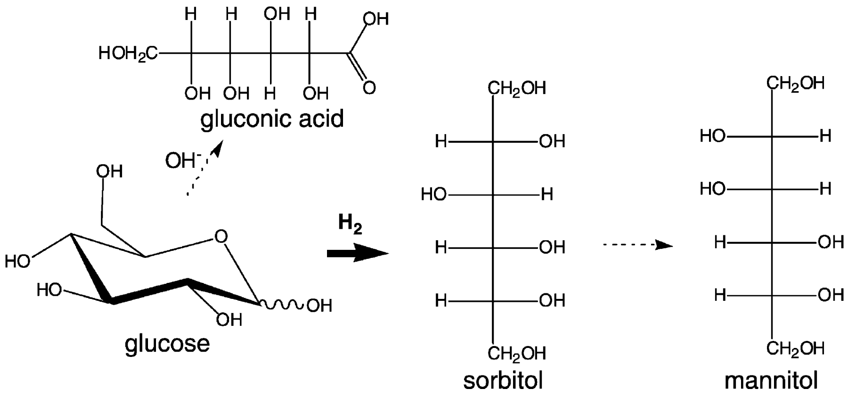


Fig. 8. Scheme of glucose hydrogenation.

any superficial oxidation of ruthenium. Platinum may also prevent the formation of other impurities including oligomeric or cracking products and also prevent any oxidation of ruthenium.

3.2. Catalyst stability in the hydrogenation of 3-hydroxypropanal to 1,3-propanediol

The market of 1,3-propanediol is expected to increase sharply because of its use in the synthesis of poly-trimethylene terephthalate, a polyester with excellent stretch and recovery properties. It is produced by hydrogenation of 3-hydroxypropanal obtained by hydroformylation of ethylene oxide (Shell process) or by hydration of acrolein (Degussa/DuPont process). The hydrogenation of 3-hydroxypropanal in the Degussa process can be carried out on Ni/SiO_2 catalysts, but, beside the risk of nickel leaching, these catalysts deactivate because of fouling by high molecular weight oligomeric impurities formed by successive condensation of unreacted acrolein with 3-hydroxypropanal as shown in the reaction scheme given in Fig. 10. The objective of the work was to obtain a higher stability of the hydrogenation catalyst in trickle-bed operation by substituting nickel by ruthenium and silica by titanium dioxide [42].

Table 1 gives the characteristics of three supporting materials, which were impregnated with $RuCl_3$

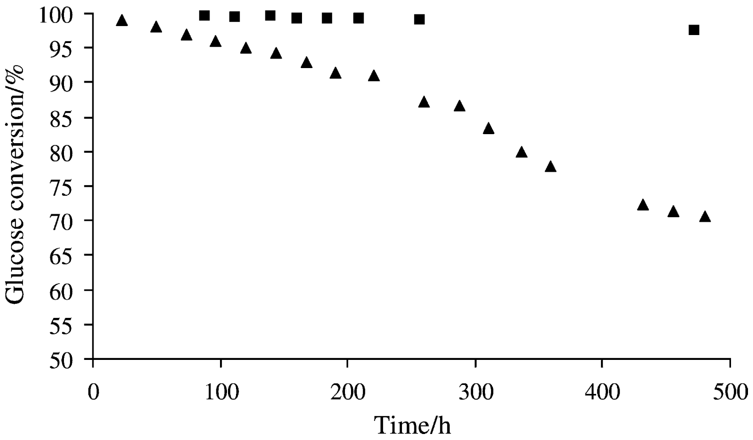


Fig. 9. Glucose hydrogenation vs. time on stream in trickle-bed reactor (40 wt.% aqueous glucose solution 100 °C, 80 bar of H_2, 20 NL h^{-1} of H_2). Square: 1.6% Ru–0.2% Pt/C catalyst. Triangle: commercial 1.2% Ru/C catalyst.

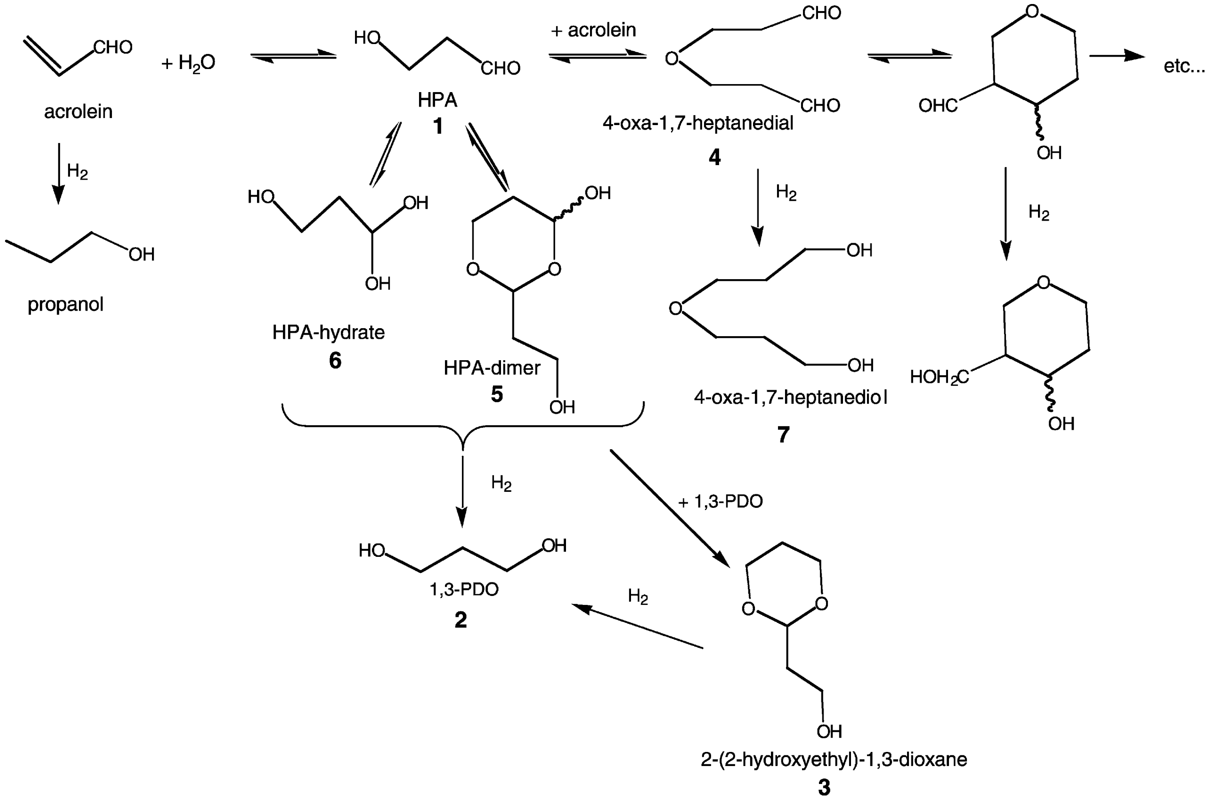


Fig. 10. Reactions involved in the synthesis of 1,3-propanediol from 3-hydroxypropanal.

solutions followed by hydrogen reduction at 200 °C. It was checked by TEM that the metal particles are homogeneously distributed in the formed catalyst. Early hydrogenation experiments, with unfiltered 3-hydroxypropanal feedstock deactivated rapidly. The beneficial effect of filtering on a carbon cartridge was clearly shown in the case of Ru/TiO_2(P25) catalyst (Fig. 11). The conversions of HPA on the catalysts after 24 and 100 h on stream are given in Table 1. Although, Ru/SiO_2 showed a high activity at 24 h, subsequent deactivation was rapid. Catalyst Ru/TiO_2(P25) also deactivated during the period 24–100 h. In contrast, the activity of catalyst Ru/TiO_2(XT90045) was stable. It was verified that there was no leaching of ruthenium or TiO_2. Differences in catalyst stability can be accounted by the texture of the supporting materials: microporous, and even mesoporous supports, are subject to fouling by heavy molecular weight species which restrict the access of reactants to metal particles, while the large pores of Ru/TiO_2(XT90045)

Table 1
Activity and stability with time of ruthenium catalysts supported on different supports[a]

Support	Ru (wt.%)	Source	S_{BET} ($m^2 g^{-1}$)	Phase	Conversion (%)	
TiO_2 XT 90045 (0.8–2 mm granules)	1.0	Norton	1 macroporous	Rutile	45.0 (24 h)	47.9 (100 h)
TiO_2 P25 (1.7 mm extrudates)	1.2	Degussa	52 mesoporous	Rutile + anatase	56.8 (24 h)	40.6 (100 h)
SiO_2 V432 (0.8–1.2 mm granules)	3.7	Grace	340 microporous	Silica gel	98.5 (24 h)	76.2 (100 h)

[a] Operating conditions: temperature 40 °C, H_2 pressure 40 bar, feed 10% HPA, catalyst volume 36 ml, LHSV 2 h^{-1}.

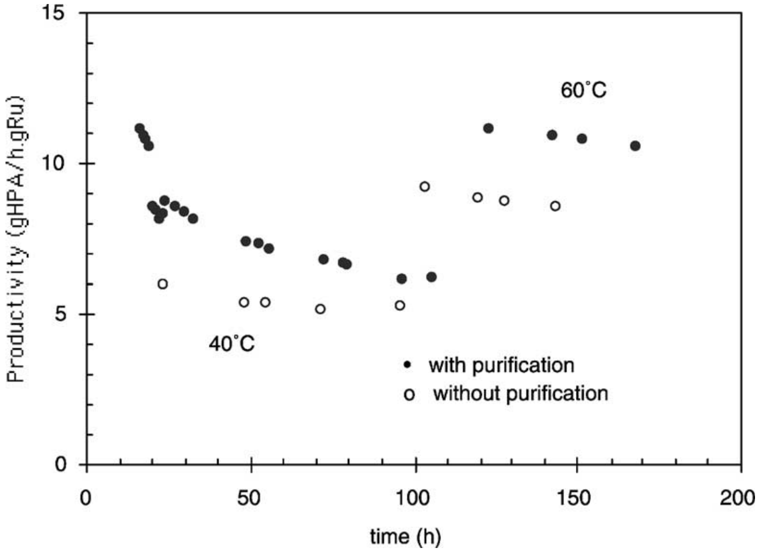


Fig. 11. Effect of purification of 3-hydroxypropanal feedstock on the activity of 1.2% Ru/TiO_2 (P25). Operating conditions: temperature 40 °C, H_2 pressure 40 bar, feed 10% HPA, catalyst volume 36 ml, LHSV $2\,h^{-1}$.

remain unplugged. The deposition of oligomeric species poisoning catalyst surface was confirmed by total organic carbon measurements made on catalysts after 100 h on stream: 3370 and 210 ppm of organic carbon were measured on catalysts Ru/TiO_2(P25) and Ru/TiO_2(XT90045), respectively.

3.3. Stability of catalysts in wet air oxidation

Catalytic wet air oxidation (CWAO) is an emerging technology for the treatment of organic wastes in industrial water particularly for concentrated and/or abiotic effluents and for the treatment of sewage sludges [43]. The process consists of total oxidation to CO_2 or partial degradation of pollutants, which makes further conventional biotreatments more amenable. Although homogeneous catalysts, e.g. dissolved copper salts, are efficient their use implies an additional recovery step. One of the main challenge of CWAO is to find heterogeneous catalysts active and stable to leaching in the very corrosive acidic and oxidising reaction medium at temperatures greater than 150 °C. Many attempts (see [44]) have been made to use transition metals from the first row (e.g. Mn, Fe, Cu) under the form of oxides or encapsulated species (zeolite, clays). However, the laws of thermodynamics, and more specifically potential–pH diagrams rule that these elements must leach albeit at different rates depending upon their coordination in the structure of the catalyst. In contrast we have used catalysts based on platinum-group metals supported on TiO_2 or ZrO_2 which are all resistant to corrosion to oxidising carboxylic acid solutions or effluents from the paper-pulp industry in batch or trickle-bed reactors [11–14].

Standard operating conditions in batch reactor were the followings: 0.15 l of $5\,g\,l^{-1}$ solution, 1 g of 2.8 wt.% Ru/TiO_2, 190 °C, 5 MPa total pressure (i.e. 0.72 MPa of O_2). Succinic acid was totally converted within 150 min; the only reaction products detected were CO_2, acetic acid, and acrylic acid. The initial rate of reaction was $16\,mol_{acid}\,h^{-1}\,mol_{Ru}^{-1}$ or $43\,mol_{C}\,h^{-1}\,mol_{Ru}^{-1}$, and the TOC abatement was 97.6% after a period of 4 h. Only traces of acetic acid remained. The catalyst was recycled without any loss of activity after the second recycling. Since most industrial effluents contain inorganic salts, particularly chlorides, succinic oxidation was also conducted in the presence of $6.7\,g\,l^{-1}$ of NaCl. Under the same conditions TOC abatement was still 92.3%. No leaching of ruthenium or titanium was detected.

Acetic acid was oxidised at a smaller rate than C_2 carboxylic acids derived by substitution of the methyl group by Cl, NH_2, and OH groups. The difficulty of oxidation of acetic acid could be due to a low adsorption coefficient of the molecule on the metal surface or to a weak reactivity in the adsorbed state, or to a combination of both. Modelling of the kinetic data obtained in continuous fixed bed reactor supported the former interpretation [12].

In the Kraft process, paper pulp contains residual lignin, which is eliminated by bleaching with chlorine dioxide generating acidic effluents (D0), followed by alkaline extraction generating alkaline effluents (E1). The bleaching process yields recalcitrant organic compounds (lignin, organic acids, etc.) which are not easily degraded by biological waste water treatment. The present work was intended to evaluate the WAO of effluents D0 and E1 described in Table 2.

The CWAO of acidic effluent (D0) in batch reactor (6 h, 190 °C, 5.5 MPa air pressure) resulted in 80% TOC abatement on metal-free TiO_2 and 99% abatement on 3% Ru/TiO_2 catalyst [13]. The residual TOC corresponded to acetic acid while only trace amounts (0.08 mg l^{-1}) of highly toxic chlorine-containing compounds (AOX) remained in the treated water.

The CWAO of D0 and E1 bleach plant effluents carried out in a trickle-bed reactor [14] loaded with 3% Ru/TiO_2 catalyst, demonstrated that high TOC conversion can be achieved at 463 K (Fig. 12) even though large amounts of mineral impurities particularly chlorides and sulphates were present (Table 2). The deactivation can be attributed to the presence of suspended solids in effluents, which partially block the surface of catalyst particles. At sufficient residence time only trace amounts of acetic acid were found in

Table 2
Characterisation of paper pulp effluents D0 and E1

Species in solution[a]	Effluent D0	Effluent E1
Colour	Dark yellow	Dark brown
Initial pH	2.9	10.0
TOC	665	1380
COD	1660	3650
Total solids	4.0×10^3	5.6×10^3
Percentage of ash at 1073 K	2.1	2.0
Na^+	900	1300
K^+	29	10
NH_4^+	<0.2	<0.2
Ca^{2+}	91	22
Mg^{2+}	19	5
Cl^-	534	386
NO_3^-	14	21
NO_2^-	<0.02	<0.02
SO_4^{2-}	1460	681
S_{total}	547	221
PO_4^{3-}	<5	65

[a] Concentration in mg l^{-1}.

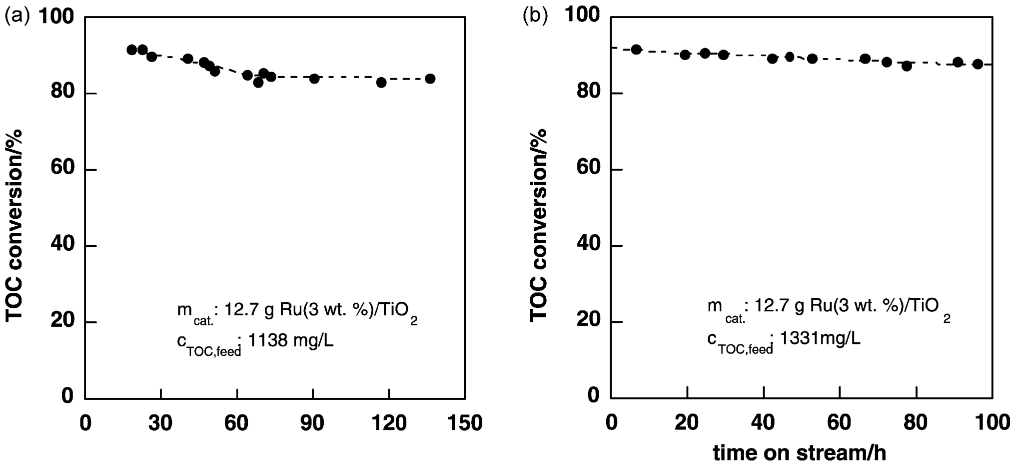


Fig. 12. Total organic carbon conversion as a function of time on stream, obtained in the trickle-bed reactor packed with 3 wt.%/TiO_2 catalyst. Feed solution: (a) D0 effluent and (b) E1 effluent. Lines show trends.

the reactor discharge. No leaching of ruthenium or titanium was detected.

4. Conclusion

Major development of academic studies on catalyst deactivation in liquid phase reactions applied to the synthesis of fine chemical is unlikely in at short term even though activity and selectivity decay is of great concern for users and catalyst manufacturers who have an undisclosed know-how in catalyst ageing. Because there is a growing trend to replace batch by continuous processes for the production of intermediates or commodity products, one can expect more deactivation studies in continuous reactors. The loss of activity or selectivity can then be easily followed as a function of time on stream, space velocity and feedstock impurities without detrimental manipulation of the catalyst.

Leaching of active phases and supports should be a permanent concern for those involved in catalytic reactions in multi-phasic media. Too many studies in the literature are worthless scientifically and practically because catalysts leached in solutions, whether or not experimenters were aware of it.

An active and promising field of research lies in the use of molecules, which may poison the activity at high doses but act as selectivity promoters at low doses. These selectivity promoters or modifiers enhance the chemo-, regio-, and enantioselectivity of many types of reactions. More studies are awaited to establish whether they react in the adsorbed state on the metal surface or if they first complex the reactant molecules, and thus modify their reactivity prior to adsorption.

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