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# Mixed oxides as catalysts for the selective reduction of nitrobenzene

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The catalytic behaviour of the PbO–$Mn_3O_4$ and the $Bi_2O_3$–$MoO_3$ systems was investigated in the selective reduction of nitrobenzene to nitrosobenzene. Lead compounds appeared to be good catalysts, and co-catalysts when used with $Mn_3O_4$. Different from oxidations by di-oxygen, $Bi_2O_3$ alone is a good catalyst and formation of mixed Bi–Mo–O compounds does not enhance the catalytic activity. It is suggested that the difference between these catalysts in the mentioned reaction is related to the way in which the oxygen vacancy is represented by the oxygen donor.

**Keywords:** PbO–$Mn_3O_4$; $Bi_2O_3$–$MoO_3$; nitrobenzene reduction

## 1. Introduction

The mechanism of selective oxidation reactions over oxidic catalysts is described by Mars and Van Krevelen [1] as follows: lattice oxygen is used to oxidise the reacting molecule, whereafter the created oxygen vacancy is replenished by di-oxygen. A possible modification of this "redox" mechanism is a version in which oxygen enters and leaves the catalyst through different sites. For example, $Bi_2O_3/MoO_3$ is a good catalyst for the selective oxidation of propene and in this case, propene is dehydrogenated on the Bi sites, but the admixed $MoO_x$ serves as a site on which oxidation occurs by di-oxygen. Migration of oxygen atoms should occur from the $MoO_x$ site to the Bi site [2].

Different from selective oxidations, not much attention has been paid up to now to selective reduction reactions. To fill up this gap, the selective reduction of nitrobenzene to nitrosobenzene has been chosen here as a model reaction. This reaction has also some industrial importance: nitrosobenzene is used as an intermediate in synthesis of antioxidants. Without a catalyst, the batch-wise synthesis

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of nitrosobenzene needs two steps: reduction with Zn/HCl to phenyl hydroxylamine, followed by oxidation with potassium chromate to the desired product. Patents claim that a combination of lead oxide and manganese oxide is a good catalyst for the selective gas phase continuous reduction of nitrobenzene and that lead oxide itself is inactive [3,4]. Our preliminary experiments showed that also pure manganese oxide is active in the form of $Mn_3O_4$ [5]. In this work, the influence of lead oxide on $Mn_3O_4$ is investigated and the catalysts based on manganese are compared with the catalyst $Bi_2O_3/MoO_3$, which is known to be a good catalyst for the commercial (amm-)oxidation of propene.

## 2. Experimental

### 2.1. PREPARATION OF THE CATALYSTS

$Mn_3O_4$, PbO, $Pb_3O_4$ and $PbO_2$ were prepared from the corresponding metal hydroxides, obtained by precipitation of the corresponding nitrates with $NH_4OH$ at pH = 9. $Mn(OH)_2$ was decomposed in air at 400 K for 20 h to obtain $Mn_3O_4$. $Pb(OH)_2$ was heated at 473 K in flowing air to obtain yellow PbO (orthorhombic, mineral name: massicot), at 748 K in flowing nitrogen to obtain red PbO (tetragonal, mineral name: litharge) and at 773 K in flowing air to obtain $Pb_3O_4$. $PbO_2$ was a commercial sample (Janssen Chimica). The $PbO/Mn_3O_4$ catalysts were obtained by impregnation (incipient wetness) of $Mn_3O_4$ with lead(II) acetate, followed by drying in air at 400 K and decomposition of the acetates in flowing nitrogen at 623 K. The loading of $PbO_x$ on $Mn_3O_4$ varied from 1 to 33%; the loading being expressed as the atomic ratio of lead with respect to manganese times one hundred. The 3% $PbO/Mn_3O_4$ catalyst was also prepared in a slightly different way, by impregnation of $Mn_3O_4$ with lead(II) nitrate, followed by drying in air at 400 K. Furthermore, a physical mixture of 3% $PbO/Mn_3O_4$ was made by mechanically mixing of the two oxides.

$Bi_2O_3$ and $MoO_3$ were synthesised by the decomposition of respectively bismuth(III) nitrate and $(NH_4)_6Mo_7O_{24}$ at 873 K in air, for 17 h (hereafter called $MoO_3$(a)). Another $MoO_3$ was prepared at 900 K, for 40 h (hereafter called $MoO_3$(b). The $Bi_2Mo_3O_{12}$-unsupported catalyst was a commercial sample, kindly supplied by Akzo Research Centre, Amsterdam. The catalysts were analysed by X-ray powder diffraction (XRD). Total surface area measurements were carried out on a Quantasorb, supplied by Quantachrome.

### 2.2. CATALYTIC DATA: MEASUREMENTS AND EVALUATION

Catalytic measurements were carried out in an open flow system with fixed bed reactor. Products were analysed with a GC. The reaction conditions were the following: the standard temperature of the reaction was 573 K, the carrier gas was helium, the pressure of nitrobenzene was 70 Pa (total pressure was 1 bar) and the flow rate was 25 ml/min. The reaction was performed either as "autoredox" (i.e. a part of the nitrobenzene molecules is used to reduce the catalyst and create the oxygen vacancies) or an external reductor, methane, was used (He : $CH_4$ ratio = 6 : 1). Analysis was performed on-line by a GC, using an automatically driven sampling valve.

## 3. Results

According to the X-ray powder diffraction data, pure $Mn_3O_4$, $Pb_3O_4$, $MoO_3$ and $Bi_2O_3$ have been formed. The red modification of PbO could be prepared as pure, but the yellow PbO contained a considerable amount of red PbO. The X-ray diffraction pattern of 1% PbO/$Mn_3O_4$ and 3% PbO/$Mn_3O_4$, which has been prepared from nitrates, are identical with the diffraction pattern of $Mn_3O_4$. The physical mixture of PbO and $Mn_3O_4$ does not contain other phases than PbO and $Mn_3O_4$. There is no difference in most XRD patterns between the fresh and the spent catalysts. Only $PbO_2$ is partially converted into $Pb_3O_4$, during the reaction.

The XRD patterns of catalysts loaded with 3.3 and 10% PbO (prepared from acetates) showed the presence of both $Mn_3O_4$ and red PbO. The XRD pattern of the 33% PbO/$Mn_3O_4$ catalyst showed the presence of three phases: $Mn_3O_4$, red PbO and yellow PbO. Moreover, the $Mn_3O_4$ diffraction lines were considerably broadened when the loading by PbO was high. The XRD profiles of the spent catalyst revealed a further decrease in crystallinity with respect to the fresh catalyst.

IR spectroscopy on the fresh PbO/$Mn_3O_4$ catalysts confirmed the absence of acetate after thermal composition of the catalyst precursors. The BET surface area of the 33% PbO/$Mn_3O_4$ catalyst was similar to that of unloaded $Mn_3O_4$, while it was larger with a factor 2 to 4 for catalysts loaded with 1–10% PbO. The surface area of the 3% PbO/$Mn_3O_4$ catalyst prepared from nitrates did not increase upon impregnation.

The catalytic activity has been defined as the formation rate of nitrosobenzene. The selectivity has been arbitrarily defined as the concentration of nitrosobenzene divided by the sum of nitrosobenzene and aniline, the latter being the most abundant side product. Not only $Mn_3O_4$ is active in the selective reduction of nitrobenzene, the lead oxide PbO alone is also active. Its activity is lower than that of $Mn_3O_4$, when no external reducer has been used (see fig. 1). However, the activity of PbO (yellow and red modification) is about equal to that of $Mn_3O_4$ when methane has been added to the gas flow. This difference in activity is not necessarily due to the use of methane, but can also be caused by a difference in surface structure, because two different samples were used.

There is a difference between the yellow and the red modification: yellow PbO is already active from the beginning of the reaction, whereas red PbO has an induction period of about four hours.

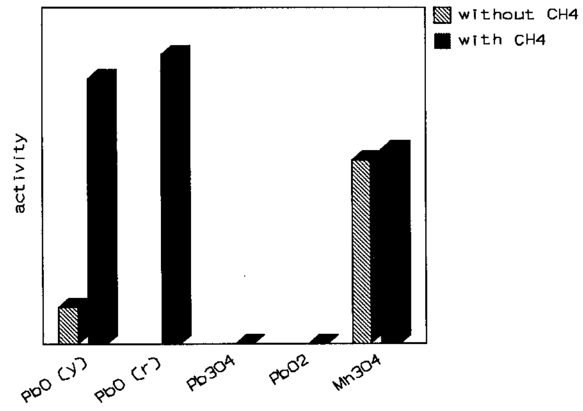

Fig. 1. The activity of $PbO_x$ and $Mn_3O_4$ catalysts, in the selective reduction of nitrobenzene, with and without methane as an external reducer.

$Pb_3O_4$ (which contains both divalent and tetravalent lead ions) and $PbO_2$ are two modifications of lead that are not active. A physical mixture of PbO and $Mn_3O_4$ has been measured as well and compared with a sample obtained by impregnation of $Mn_3O_4$ by lead nitrate. The latter sample showed a clearly higher activity. However, the $Mn_3O_4$ catalysts impregnated with lead acetate show a larger increase of the activity, except of 1% $PbO/Mn_3O_4$ (see fig. 2). There is no difference in selectivity between the different catalysts (all selectivities are between 95 and 100%).

$Bi_2O_3$ has almost the same activity as $Mn_3O_4$. $MoO_3$(a) is not active, but $MoO_3$(b) shows some activity in the selective reduction of nitrobenzene. $Bi_2Mo_3O_{12}$ shows a decrease in activity in comparison with $Bi_2O_3$ (fig. 3), in con-

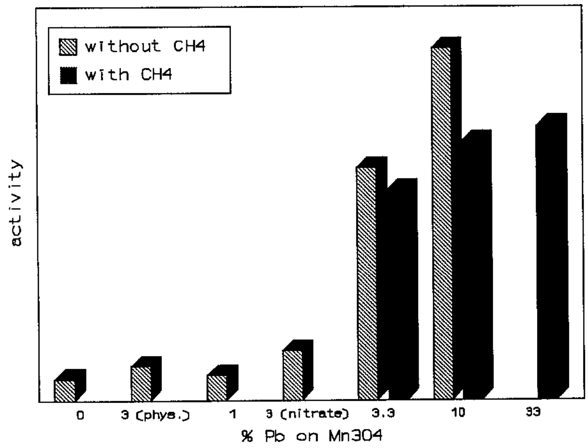

Fig. 2. The activity of $PbO/Mn_3O_4$ catalysts, in the selective reduction of nitrobenzene, with and without methane as an external reducer.

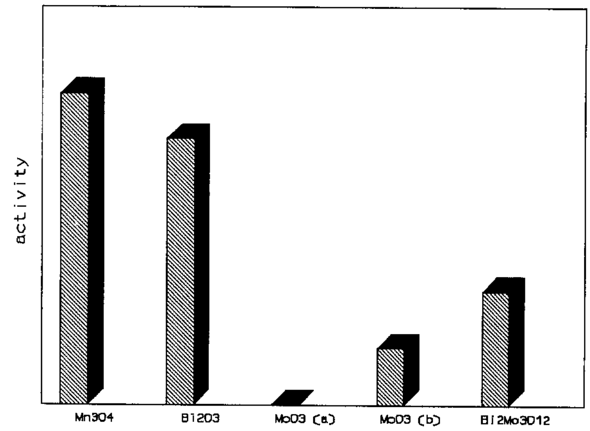

Fig. 3. The activity of $Bi_2O_3/MoO_3$ catalysts, in the selective reduction of nitrobenzene (without an external reducer).

trast to the $PbO/Mn_3O_4$ catalysts. The selectivity to nitrosobenzene is for all last mentioned catalysts equal to 100%.

## 4. Discussion

Two straightforward conclusions can be made:

(1) The claim in the patents that lead oxide itself is inactive is not correct.

(2) Lead oxide in the form of PbO is active and it increases indeed the activity of $Mn_3O_4$ in the selective reduction of nitrobenzene to nitrosobenzene.

The fact that $Pb_3O_4$ does not show any activity, although this modification of lead oxide also contains $Pb^{2+}$ ions like PbO, can be due to the fact that $Pb^{2+}$ ions in $Pb_3O_4$ are not present in the outmost surface layer. Another possibility is that the morphology of the lead oxide is important: PbO has a layered structure with a lone pair of electrons on the lead atoms, whereas the structure of $Pb_3O_4$ is more rigid and does not have a localised lone pair of electrons. The difference in induction period between the yellow and the red modification can be due to the fact that the red modification has been prepared in an atmosphere poor in oxygen, thus red PbO contains most likely less super-stoichiometric oxygen than the yellow modification. It is possible that during the induction period the red modification acquires additional oxygen from nitrobenzene, but formation of the two main products, nitrosobenzene and aniline, is prevented.

A physical mixture of lead oxide and manganese oxide shows only a slight promotion effect, whereas $Mn_3O_4$, impregnated with lead ions shows a much larger increase in the rate. This means that, for an increase in activity, there should be an intimate contact between the lead and manganese oxides. There are different explanations possible for the enhanced activity:

(a) PbO influences, for example, the electron transfer from the lattice of the catalyst to the oxygen of the nitro group of nitrobenzene, before this oxygen enters the lattice as $O^{2-}$. This effect is due to the non-bonding electron pair on $Pb^{2+}$ ions.

(b) The surface layer of the active lead oxide mediates a faster exchange of oxygen between (neighbouring or underlying) $Mn_3O_4$ and adsorbed nitrobenzene, for example in such a way that $Mn_3O_4$ oxidises the reducer ($CH_4$ or the phenyl ring) and its oxygen vacancies are filled by oxygen migrating from PbO, which – in its turn – acquires oxygen from nitrosobenzene.

(c) The lead ions form a mixed oxide with manganese. Such oxides, with a hollandite structure, are known.

The type of impregnation treatment seems to be very important for the enhancement of the activity, because the 3% $PbO/Mn_3O_4$, prepared from nitrates, shows a lower activity than the same catalyst, prepared from acetates. Possibly, in the latter case the contact between PbO and $Mn_3O_4$ is better.

Results obtained with $Bi_2O_3$, $MoO_3$ and Bi–Mo catalysts show several interesting points. First, the excellent propene oxidation Bi–Mo catalyst is not the best catalyst for the selective reduction of nitrobenzene, although there are strong indications [6], or even evidence [7] that in these cases the mechanism is of the Mars and Van Krevelen type [1]. Probably, the details of this mechanism are decisive: when a catalyst is being reoxidised by nitrobenzene, one oxygen atom enters the oxygen lattice; when di-oxygen is used, as upon propene oxidation, two oxygen atoms must be somehow accommodated by the oxide. The latter aspect could be that reason why in propene oxidation $MoO_3$ must be added to $Bi_2O_3$, but this is not necessary when nitrobenzene is reduced. Unlike with propene oxidation, pure $Bi_2O_3$ is a good catalyst of the nitrobenzene reduction.

Catalysts have been also prepared as Pb-hollandites (crystallographically well defined mixed Pb–Mn oxides), but these catalysts decomposed during the reaction in a mixture of oxides [7]. There is still a possibility that other Pb–Mn mixed oxides are formed [8–10] and that this leads to promotion effects, but we have not obtained any data supporting this view. On the other hand, substantial promotion effects are seen only when a separate PbO oxide structure appears in the X-ray diffractograms. Thus, the mechanism of promotion mentioned under (a) above seems to be the most likely one.

## 5. Conclusions

Bismuth oxide is a very good catalyst, showing about the same activity as $Mn_3O_4$. Promotion of $Mn_3O_4$ with lead oxide enhances the activity, whereas the catalyst $Bi_2O_3{\cdot}3MoO_3$, active in the selective oxidation of propene, is not particularly active in the reduction of nitrobenzene. The enhancement in activity, seen with the $PbO/Mn_3O_4$ catalysts, is probably due to the electronic structure of PbO.

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