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# Alumina-supported FeCl$_3$, MnCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$ as catalysts for the benzylation of benzene by benzyl chloride

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## Abstract

Benzylation of benzene in liquid phase by benzyl chloride to diphenylmethane over FeCl$_3$, MnCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$ supported on acidic alumina (at 80 °C) has been investigated. The redox property of alumina-supported transition metal chloride seems to play a very important role in the benzene benzylation process. Among the catalyst, the FeCl$_3$/Al$_2$O$_3$ showed both high conversation and high selectivity for the benzylation of benzene. These catalysts can also be reused in the benzylation of benzene for several times. A plausible reaction mechanism for the benzene benzylation over the alumina-supported metal chloride catalysts is proposed.
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*Keywords:* Benzylation of benzene; Diphenylmethane; FeCl$_3$ and MCl$_2$ (M = Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Zn$^{2+}$) supported on alumina

## 1. Introduction

The benzylation of aromatic compounds has been studied extensively in the past using various Lewis acid catalysts (e.g. AlCl$_3$, BF$_3$, TiCl$_4$, FeCl$_3$, etc.) and protonic acid (e.g. H$_2$SO$_4$, HF, HNO$_3$, etc.) [1–3]. These benzylation are carried out industrially, using conventional homogeneous acid catalysts, such as anhydrous AlCl$_3$. These processes generate a high volume of waste material and with the current drive towards "green chemistry", it is recognised that there is a need to replace the conventional Lewis acid catalysts with reusable, environment friendly catalysts that generate minimal waste by-products. Further, the homogeneous acid catalysts are difficult to separate from the reaction mixture; require additional processing stages, stochiometric amount of the catalyst with respect to the benzylating agent, disposal of spent catalysts, corrosion, high toxicity, etc.

In order to overcome the difficulties of the homogeneous systems, the development and utilisation of solid catalyst is important to replace homogenous acid catalysts. Development of reusable heterogenous catalysts having high activity and selectivity with little or no moisture sensitivity for the liquid phase Friedel-Grafts type reactions is

therefore of great practical importance. Hence, efforts are made to replace the homogeneous catalysts by heterogenous solid acid catalysts, such as Fe-modified ZSM-5 and H-β zeolites; Fe$_2$O$_3$ or FeCl$_3$ deposited on micro-, meso- and macro-porous [4] Ga- and Mg-oxides and/or chlorides derived from Ga–Mg-hydrotalicite [5]; InCl$_3$, GaCl$_3$, FeCl$_3$ and ZnCl$_2$ supported on clays and Si-MCM-41 [6]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [7]; MCM-supported AlCl$_3$ and other Lewis acid [8]; supported thallium oxide catalysts [9]; Sb supporting K10 [10]; solid superacid and silica-supported polytrifluoro-methanesulfosil oxane [11]; Si-MCM-41-supported Ga$_2$O$_3$ and In$_2$O$_3$ [12]; H$_2$SO$_4$, HNO$_3$ and HClO$_4$/metakaolinite [12]; Fe-containing mesoporous molecular sieves materials [13]; alkali metal salts and ammonium salts of keggin-type heteropolyacids [14]; ion-exchanged clays [15]; clayzic [16]; solid superacids based on sulfated ZrO$_2$ [17], HY [18], H-ZSM5 [19] and Fe/MCM-41 [20] for the benzylation of benzene and other aromatic compounds. Such catalysts are interesting and efficient for organic synthesis because the catalyst is easily separated from the product and the organic reactions occur in the uniform of alumina, and hence the reactivity and selectivity may be different from those in homogeneous solutions.

The aim of the present work is to develop a new catalytic method for the selective benzylation of benzene to diphenyl-methane using alumina-supported metal chloride (FeCl$_3$,

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$MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$) as the catalyst and benzyl chloride as the benzylating agent. We also report the results of the effect of time and solvents of reaction, effect of benzene/benzyl chloride molar ratio and reaction temperature. The simple preparation, low cost and easy handling of this catalyst prompted us to study its application for benzylation, an important reaction for the diphenylmethane synthesis.

## 2. Experimental

### 2.1. Materials

All solvents used for synthesis and benzylation reaction were purchased from Merck (pro analysi) and were dried with molecular sieves (Linde 4 Å). Benzene and benzyl chloride were purified by standard procedures, and distilled under nitrogen stored over molecular sieves (4 Å) before use. Acidic alumina was purchased from Merck (Art. No. 1078, aluminium oxide 90 active acidic, 0.063–0.200 mm). It was activated at 500 °C for 8 h before use. $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ were obtained from Merck. Diphenylmethane were identified by comparisons of their retention times with those of pure compounds (obtained from Merck).

### 2.2. Physical measurements

The products were analyzed by GC-mass, using a Philips Pu 4400 Chromatograph (capillary column: DB5MS, 30 m), Varian 3400 Chromatograph (15 m capillary column of HP-5; FID) coupled with a QP Finnigan MAT INCOF 50, 70 eV. The manganese, iron, cobalt, nickel, copper and zinc contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100-1319) using a flame approach, after acid (HF) dissolution of known amount of the alumina material in Parr digest pump.

### 2.3. Preparation of heterogenous catalyst

Alumina-supported transition metal chloride ($FeCl_3/Al_2O_3$, $MnCl_2/Al_2O_3$, $CoCl_2/Al_2O_3$, $NiCl_2/Al_2O_3$, $CuCl_2/Al_2O_3$, and $ZnCl_2/Al_2O_3$) were prepared by impregnating acidic alumina with anhydrous metal chloride (purity 99.99% Aldrich) from their acetonitrile solution by incipient wetness technique and evaporating the solvent in vacuum oven at 120 °C for 10 h (loading of metal chloride = 1.2 mmol g$^{-1}$). All the catalysts were stored in dessicator.

### 2.4. Benzylation of benzene, general procedure

The liquid phase benzylation reactions over the supported transition metal chloride catalysts were carried out in a magnetically stirred glass reactor (50 cm³) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture at the following reaction conditions by the procedure given earlier [21], reaction mixture = 13 ml of moisture-free benzene mixes with 11.5 ml of moisture-free solvent + 1.0 ml of benzyl chloride, amount of catalyst = 0.4 g. The reaction was started by injecting benzyl chloride in the reaction mixture, containing catalyst at the reaction temperature (at 80 °C) with or without solvent. Measuring quantitatively the HCl evolved in the reaction by acid–base titration followed the course of the reaction. The experimental procedure and product analysis are given earlier [21–23]. The polybenzyl chloride (which is formed by the condensation of benzyl chloride) was isolated from the reaction mixture by the procedure given elsewhere [22]. In all the cases, the major product formed was mainly mono-benzylated compound along with polybenzyl chloride as side product depending upon the condition used.

## 3. Results and discussion

### 3.1. Comparison of the alumina-supported metal chloride

The $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ supported metal chloride catalysts are compared for their performance in the benzylation of benzene (at 80 °C) in Table 1. From comparison of results in Tables 1–3 and Figs. 1 and 2, the following important observations can be made:

- The alumina support itself shows very little activity in the benzylation of benzene; however, its catalytic activity is increased drastically because of the impregnation of transition metal chloride (Table 1).
- Among the supported metal chloride catalysts, the $FeCl_3/Al_2O_3$ showed both high conversion and high selectivity in the benzylation. The conversion for the

Table 1
Results of the benzene benzylation by benzyl chloride over different transition metal chloride supported on alumina catalysts at 80 °C

| Catalyst | Conversion (%) | Product selectivity (%) | |
|---|---|---|---|
| | | Diphenylmethane | Polybenzyl chloride |
| $FeCl_3/Al_2O_3$ | 98.4 | 97.6 | 2.2 |
| $CuCl_2/Al_2O_3$ | 87.6 | 91.4 | 6.5 |
| $ZnCl_2/Al_2O_3$ | 80.7 | 88.4 | 9.3 |
| $NiCl_2/Al_2O_3$ | 51.1 | 100 | – |
| $MnCl_2/Al_2O_3$ | 45.6 | 100 | – |
| $CoCl_2/Al_2O_3$ | 41.6 | 83.2 | 11.3 |
| $FeCl_3$ | 68.4 | 47.4 | 51.6 |
| $CuCl_2$ | 64.6 | 39.6 | 30.7 |
| $ZnCl_2$ | 63.2 | 56.4 | 34.5 |
| $NiCl_2$ | 37.4 | 51.2 | 42.4 |
| $MnCl_2$ | 32.6 | 37.6 | 39.6 |
| $CoCl_2$ | 30.4 | 30.2 | 46.2 |
| $Al_2O_3$ | 5.1 | – | – |

Reaction mixture is 0.4 g catalyst + 13 ml of moisture-free benzene + 1 ml benzyl chloride; time = 180 min.

Table 2
Benzylation of benzene with benzyl chloride at different FeCl$_3$/Al$_2$O$_3$ concentration

| Catalyst (g) | Conversion (%) | Product selectivity (%) | |
| --- | --- | --- | --- |
| | | Diphenylmethane | Polybenzyl chloride |
| 0.2 | 84.6 | 100 | – |
| 0.4 | 98.4 | 97.6 | 2.2 |
| 0.7 | 100 | 76.1 | 23.3 |
| 0.9 | 100 | 53.2 | 47.4 |

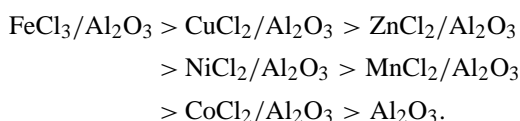Conditions: benzene = 13 ml, benzyl chloride = 1 ml, time = 180 min, temperature = 80 °C.

Table 3
Benzylation of benzene with benzyl chloride at different temperatures over FeCl$_3$/Al$_2$O$_3$ catalyst

| Temperature (°C) | Conversion (%) | Product selectivity (%) | |
| --- | --- | --- | --- |
| | | Diphenylmethane | Polybenzyl chloride |
| 50 | 56.1 | 94.3 | 5.7 |
| 80 | 98.4 | 97.6 | 2.2 |
| 90 | 99.2 | 73.2 | 14.6 |
| 100 | 100 | 54.4 | 37.9 |
| 120 | 100 | 40.3 | 56.3 |

Conditions: benzene = 13 ml, benzyl chloride = 1 ml, time = 180 min, catalyst = 0.4 g.

alumina-supported transition metal chloride catalyst is much higher than that for the transition metal chloride without any support (Table 1).

- The benzylation activity of the alumina-supported transition metal chloride catalysts is in the following order:

$$FeCl_3/Al_2O_3 > CuCl_2/Al_2O_3 > ZnCl_2/Al_2O_3$$
$$> NiCl_2/Al_2O_3 > MnCl_2/Al_2O_3$$
$$> CoCl_2/Al_2O_3 > Al_2O_3.$$

- It is interesting to note that this order for the conversion of benzylation of benzene is quite similar to that of the redox potential of the metal in the supported metal chloride

catalysts. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal chlorides.

- At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with solvent and reused under similar conditions. Although the analysis of the recovered catalysts by Atomic Absorption Spectroscopy showed no reduction in the amount of metal ions, they showed a slightly lower catalytic activity. These catalysts can also be reused for the benzylation several times (Fig. 1). However, there is an appreciable loss in the activity in the reuse of these catalysts. This is expected mostly because of the leaching of the active catalyst component (i.e. iron) during the benzylation reaction. Further work is necessary to strongly bind the active component on the support.

When the ZnCl$_2$/Al$_2$O$_3$ catalyst was thermally activated at 300 °C and cooled in air, the resulting catalyst showed only a small improvement in the benzylation of benzene. The conversion of the FeCl$_3$/Al$_2$O$_3$ catalyst (Table 1) is much higher than that of ZnCl$_2$/Al$_2$O$_3$ even after its thermal activation. Earlier studies [24,25] showed that a clayzic catalyst (which is a thermally activated ZnCl$_2$/Mont.-K10 at 280 °C) shows high benzene benzylation activity. However, the clayzic catalyst is less selective (∼80% selectivity for diphenylmethane) [24] and moreover, it is highly hygroscopic in nature, it rapidly loses its activity when exposed to air [25]. The above results of the ZnCl$_2$/Mont.-K10 are consistent with this work; the high hygroscopic nature of clayzic catalyst puts a severe restriction on its use strictly under moisture-free conditions.

### 3.2. Effect of solvent

To understand the role of solvent in benzylation of benzene by alumina-supported transition metal chloride with benzyl chloride, the reaction was carried out with different solvents, such as dichloroethane, *n*-heptane, acetonitrile and nitrobenzene. The reaction conditions and the results of benzene benzylation with FeCl$_3$/Al$_2$O$_3$ catalyst are
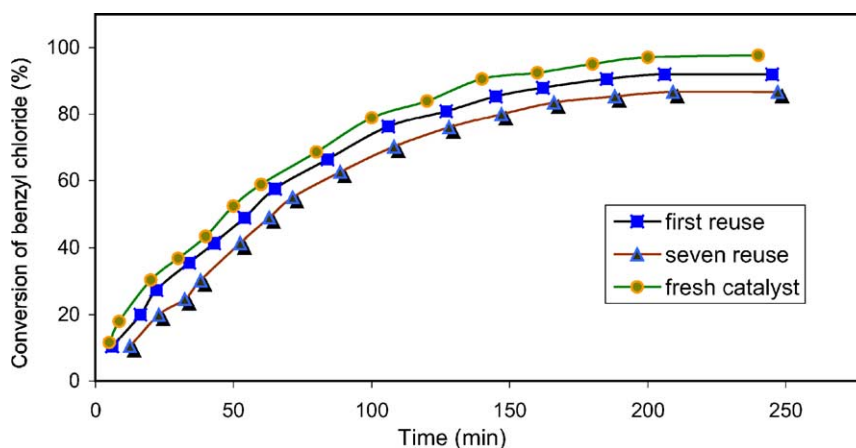


Fig. 1. Reusability of FeCl$_3$/Al$_2$O$_3$ catalyst in the benzylation of benzene by benzyl chloride at 80 °C.
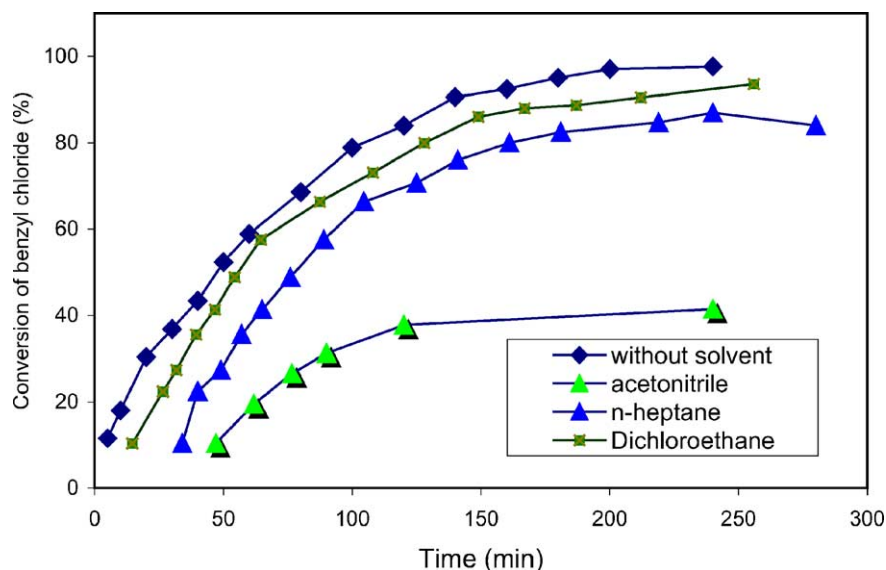
Fig. 2. Effect of solvent on the conversion of benzyl chloride at 80 °C in the benzylation of benzene over FeCl$_3$/Al$_2$O$_3$.

presented in Fig. 2. The conversion of the catalyst decreased considerably in presence of aprotic solvent due to the interaction of negative charge or the electron lone pair of solvent with acidic sites of the catalyst. The conversion is highest in the absence of any solvent. It is decreased when the solvent (via dichloroethane and *n*-heptane) is used, the decrease is quite large when *n*-heptane is used as a solvent but it is small for dichloroethane as a solvent. The observed solvent effect on the conversion is expected because of the competitive adsorption of both the reactants and the solvent on the catalyst. The results show that between the two solvents, dichloroethane is a better solvent for the benzylation reaction. The decrease of the polymerised product in the present of dichloromethane could also be due to a faster desorption of the primary product according to the competitive adsorption of solvent on the catalyst surface. However, in presence of solvent formation of polymerised product was less due to dilution effect and this was considered as an advantage of solvent in the above reaction.

### 3.3. Effect of catalyst concentration

The reaction profile using different amount of FeCl$_3$/Al$_2$O$_3$ catalyst revealed that selectivity to diphenylmethane was higher at a lower concentration (Table 2). At the higher concentration of the FeCl$_3$/Al$_2$O$_3$, the conversion of benzene increased to an optimum value and formation of polymerised product also increased simultaneously. Hence, an optimum of 0.4 g of catalyst in the reaction mixture was ideal for achieving better conversion (98.4%) and selectivity for diphenylmethane (97.6%).

### 3.4. Effect of temperature

The results of the temperature studies are shown in Table 3. Reactions were carried out using FeCl$_3$/Al$_2$O$_3$ in

the temperature range of 50–120 °C. It was found that conversion were very poor at lower temperature of 50 °C. A temperature of at least 80 °C is required for appreciable conversion and diphenylmethane to product. On increasing the temperature from 80 to 120 °C, the formation of diphenylmethane decreased as expected. High reaction temperatures (120 °C) do not favour the formation of polymerised product.

### 3.5. Effect of benzene/benzyl chloride

The selectivity towards diphenylmethane over FeCl$_3$/Al$_2$O$_3$ can be improved at higher dilutions of the benzyl chloride (Fig. 3). At benzene:benzyl chloride molar ratio of 16:1, a selectivity of 97.6% can be achieved. However, such a high molar ratio of benzene to benzyl chloride is impractical for industrial use, since the unreacted benzene has to be recovered and recycled. At more reasonable benzene:benzyl chloride ratio of 5:1, the selectivity is 83.4%.

### 3.6. Reaction mechanism

The mechanism of benzylation of benzene catalyzed by alumina-supported transition metal chloride such as FeCl$_3$/Al$_2$O$_3$ under liquid phase conditions is shown in Scheme 1. The alumina-supported transition metal chloride species have redox properties, which are expected to play important role in the benzylation reaction. The following probable redox mechanism for the activation of both benzyl chloride and benzene by the transition metal chloride species leading to the benzylation reaction is proposed. The redox mechanism is similar to that proposed earlier for the benzene benzylation [26] and alkylation or acylation reactions [27–29]. This mechanism is quite consistent with the observations, the order for the benzene
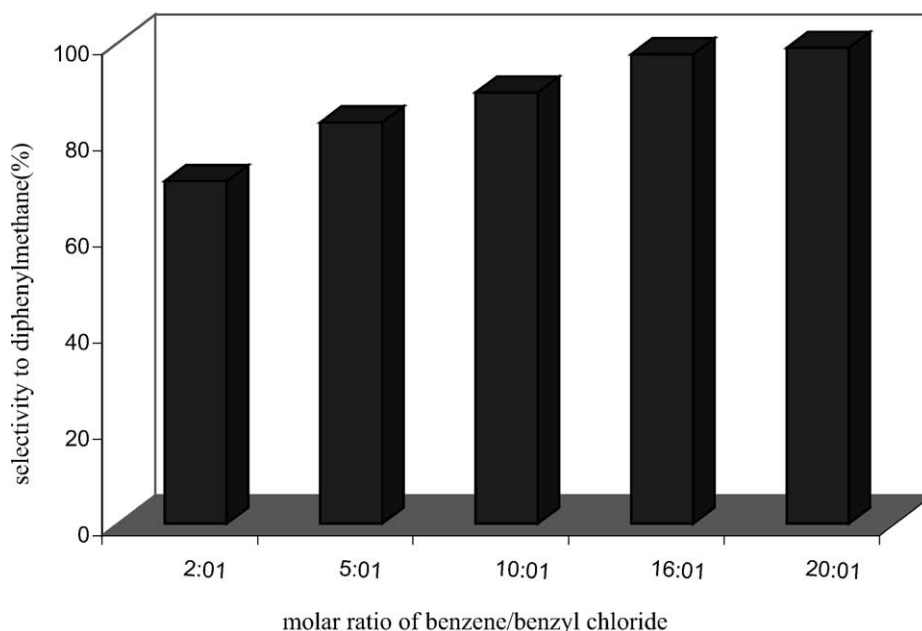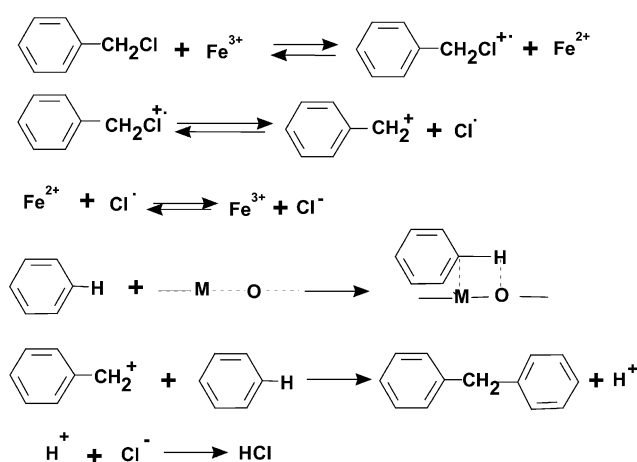
Fig. 3. Selectivity towards diphenylmethane FeCl$_3$/alumina as a function of molar ratio of benzene/benzyl chloride.



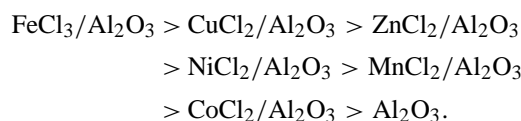Scheme 1. Mechanism of benzene benzylation.

benzylation conversion of the alumina-supported transition metal chloride (FeCl$_3$/Al$_2$O$_3$, CuCl$_2$/Al$_2$O$_3$, ZnCl$_2$/Al$_2$O$_3$, NiCl$_2$/Al$_2$O$_3$, MnCl$_2$/Al$_2$O$_3$, and CoCl$_2$/Al$_2$O$_3$) catalysts is almost same as that for the redox potential of the metal present in the catalysts.

## 4. Conclusion

The benzylation of benzene with benzyl chloride using alumina supported and unsupported (FeCl$_3$, MnCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$) catalysts has been investigated. Comparing unsupported and alumina-supported transition metal chloride as catalyst shows that alumina-supported catalysts gave higher conversion than their corresponding un-supported catalysts. The following points may be noted:

- The major product of benzylation of benzene with benzyl chloride is diphenyl methane.
- The FeCl$_3$/Al$_2$O$_3$ is highly active catalyst for the benzylation of benzene with benzyl chloride.
- The alumina-supported complexes did not undergo any colour change during the reaction and could be easily separated and reused many times.
- The alumina alone in the absence of transition metal chloride was little catalytically active. The activity of benzene benzylation decreases in the series:

$$FeCl_3/Al_2O_3 > CuCl_2/Al_2O_3 > ZnCl_2/Al_2O_3$$
$$> NiCl_2/Al_2O_3 > MnCl_2/Al_2O_3$$
$$> CoCl_2/Al_2O_3 > Al_2O_3.$$

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