On the Chemistry of Iron Oxide Supported on γ-Alumina and Silica Catalysts

Sara Mosallanejad,† Bogdan Z. Dlugogorski,‡ Eric M. Kennedy,† and Michael Stockenhuber*†‡

†School of Engineering, The University of Newcastle, Callaghan, New South Wales 2308, Australia
‡School of Engineering and Information Technology, Murdoch University, Murdoch, Western Australia 6150, Australia

ABSTRACT: Catalysts of iron oxide on γ-alumina and silica which were prepared by an incipient wetness impregnation technique have been investigated in an effort to understand how the surface chemical properties are influenced by the nature of the supports. Surprisingly, this is the first study to compare in depth the influence of the supports on physicochemical parameters such as acidity, site nuclearity, and reducibility. In this study, surface characterisation techniques including N2 physisorption at −196 °C, ammonia temperature-programmed desorption, inductively coupled plasma optical emission spectrometry, temperature-programmed reduction with hydrogen, CO-chemisorption, scanning electron microscopy, transmission electron microscopy, and NO adsorption by in situ Fourier transform infrared spectroscopy have been performed to understand the different surface reactions occurring over the two different supports. The aim of this study is to ascertain the primary differences between these two catalysts using several catalyst characterization techniques and correlate their chemical and structural differences to their catalytic activity in the conversion of 2-chlorophenol. The results disclose a higher density of acid sites, a smaller particle size of iron oxide, stabilization of Fe(II) aluminate after reduction on the alumina surface, and finally, the formation of isolated iron cations on the surface of alumina which are notably absent on the silica-supported catalyst.

INTRODUCTION

Iron exists in several oxidation states in the environment. Different phases of iron, such as hematite, magnetite, and goethite (either in their pure forms or supported on carbon, alumina, silica, and zeolite) have been used as catalysts, for a myriad of commercially significant chemical reactions. Iron oxide on various supports has gained particular attention for catalysis applications because of its use in reactions such as Fischer–Tropsch synthesis, synthesis of NH₃, and the water gas shift reaction.¹⁻⁴ However, these catalysts have also been reported to catalyze the formation of a dangerous group of pollutants: polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs, dioxins) under certain conditions where carbon, hydrogen, oxygen, and chlorine (especially a precursor molecule such as chlorophenol) are present in the reacting environment.⁵⁻⁸

In general, the type and structure of the support, method of preparation, and active site loading (e.g., iron percentage) are considered important factors that influence the catalyst’s redox properties and particle size, which in turn has a strong influence on the activity and selectivity of the supported catalysts.⁹⁻¹⁹ In addition to these variables, the support used is likely to play a vital role in the properties of the metal-supported catalyst. Thyssen et al.²⁰ reported stronger interactions of metal support with γ-alumina compared to those supported on silica and noted formation of CuO and NiO on the surface of both supports and formation of an additional species, NiAl₂O₄, on the surface of γ-alumina support; Zahaf et al.²¹ showed different abundances of Pt species on the surface of alumina and silica; Borgmann et al.¹² detected CoO₄ species on the surface of silica and CoO and CoAl₂O₄ species on the surface of γ-alumina, and finally, Tanaka et al.²² reported the tetrahedral structure of V on the γ-alumina support and square pyramidal on the silica support.

It has been established that a relationship exists between the particle size of metal oxides and the pore diameter of the support. Storsæter et al.²³ studied the particle size and dispersion of cobalt (Co⁰) and CoO₄ on different supports (γ-alumina, silica, and titania) via H₂-chemisorption and X-ray diffraction (XRD), respectively, and reported an increase in the particle size of the same order of magnitude as the average pore diameter of the supports. Similar findings were reported by Jean-Marie et al.,²⁴ who found that clusters of CoO₄ particles reduced in size formed on supports with a reduced pore diameter.

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With reference to the current available literature, there does not appear to be a comprehensive study of iron catalysts on γ-alumina and silica supports, prepared by the method of incipient wetness. Only a limited body of literature exists on the relationship between the iron oxide particle size and its dispersion on alumina and silica supports. Some studies have been undertaken to investigate the effect of the support used on the properties of oxidic iron particles. For example, Wan et al. reported for amorphous silica alumina that increasing the alumina/silica ratio enhances the size of Fe₃O₄ crystals and the nature of the Fe₂−SiO₃ interaction, with the consequence that the Fe₂O₃ to Fe₃O₄ reduction reaction shifts to higher temperatures. Braga et al. observed a reduction in the particle size of Fe₂O₃ on the surface of alumina than on the silica support. Park et al. reported a limited reduction of larger particles of Fe₂O₃ on the surface of alumina because of the smaller contact area of the metal with the support. A number of techniques have been used to characterize the size and nature of the surface sites of transition-metal-containing compounds. They include electron microscopy, XRD, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy to gain information on the size and structure (and also limited information about the chemical nature) of transition-metal sites. The chemical nature, dispersion, and some structural information can be obtained by adsorption and desorption techniques. Nitric oxide alone (or sometimes in combination with other adsorbates, particularly carbon monoxide) is widely applied as a probe molecule to study the oxidation and coordination state of surface cations. In our previous studies, we examined the catalytic conversion of 2-chlorophenol (2-CPh, a dioxin precursor) on iron oxide deposited on the surface of γ-alumina and silica. We observed that the conversion of 2-CPh to volatile organic compounds (VOCs), dioxins, and total oxidation products differs significantly on the surface of γ-alumina-supported iron oxide compared to silica-supported iron oxide. On the surface of the former catalyst, we consumed approximately 10 times more 2-CPh and were unable to detect any feed at the outlet of the reactor for the first 3 h, during which we observed CO₂, CO, HCl, and chlorobenzenes. After the first 3 h, the catalyst changed color from orange to black, and we observed the feed and chlorinated phenols in the outlet of the reactor. The yield of dioxins increased dramatically once the color change was observed. However, 2-CPh conversion on the surface of silica-supported iron oxide resulted in VOCs, dioxins, and oxidation products from the first hour with a very low concentration of the feed (50 ppm).

In another paper, we used two techniques of Fourier transform infrared (FTIR) spectroscopy (in situ-FTIR) and XPS to further study the catalysts’ behavior in these particular reactions. In summary, we found that dioxin precursors (chlorophenolate/chlorophenoxy compounds) were formed on the surface of silica-supported iron oxide from the beginning of the experiment at very low pressures (0.01 µbar) of 2-CPh, but over alumina-supported iron oxide, we observed the formation of coke and formate species on the surface. As soon as active sites on the catalyst were masked by oxidation products, dioxin precursors were detected. XPS analysis of fresh catalysts revealed a higher surface coverage of iron on the surface of alumina compared to the silica, despite containing the same concentration of iron in the bulk of the two supports. This indicates that oxidic iron species are present in smaller clusters on the alumina surface compared to the silica support. It was also found that significantly more carbon accumulated on the surface of the spent alumina-supported iron oxide compared to the spent silica-supported iron oxide. An additional chloride species was also found on the surface of the spent alumina-supported iron oxide which can be specified as either metal chloride or a HCl bond. Finally, reduction of iron(III) is evident in all spent catalysts.

In the current study, we aimed to correlate the structural and chemical properties of iron oxide on silica and γ-alumina to their catalytic activity in the conversion of 2-CPh. To understand more about the physical and chemical properties of the iron oxide on silica and γ-alumina supports, other characterization techniques such as N₂ adsorption, ammonia temperature-programmed desorption (NH₃-TPD), inductively coupled plasma optical emission spectrometry (ICP–OES), CO-chemisorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and NO-FTIR analyses were applied.

## RESULTS AND DISCUSSION

### N₂ Adsorption

Table 1 lists the Brunauer–Emmett–Teller (BET) surface area (m² g⁻¹), average pore volume (cm³ g⁻¹), and average pore diameter (nm) obtained by N₂ adsorption/desorption isotherms presented in Figures S2–S5 of the Supporting Information. The isotherms for the samples are type IV which is indicative of either nonporous adsorbents or adsorbents having relatively large pores.

According to Table 1, it was determined that the silica and silica-supported iron oxide samples had a larger average pore diameter compared to the alumina and alumina-supported iron oxide samples. In addition, the pore volume of the silica and silica-supported iron oxide catalysts was significantly higher than that of the alumina and alumina-supported iron oxide catalysts. Similar observations have been reported for cobalt oxide supported on γ-alumina and silica.

### Acidic Properties of the Catalysts

Figure 1 presents the NH₃-TPD profiles of all catalysts. The profiles of alumina-supported and silica-supported iron oxide were already published in our previous paper and are included here to compare with the data of the alumina and silica supports. Hall et al. have expressed the total acidity of catalysts in terms of extensive and intensive factors. Extensive factors represent the total number of acid sites and intensive factors indicate the strength of the individual sites. Peak areas in the different temperature regions indicate the relative concentration of acid sites on the surface of the catalysts (extensive factor), and the maximum peak temperature signifies the relative strength of the acid site (intensive factor). The classification of the acid site...
strength is defined as follows: weak sites (150–300 °C), medium strength sites (300–500 °C), and strong acid sites (greater than 500 °C). The γ-alumina support displays a considerably higher concentration of acidic sites compared to silica, at least in terms of weak and medium acidity strength regions. However, the strength of acid sites is higher in the silica support. Ammonia desorbed at temperatures of 300 and 541 °C from the surface of silica and at temperatures of 215 and 470 °C from the surface of alumina. Further, the higher intensity of the modified alumina and silica indicates that iron oxide enhances the concentration of weak and medium acid sites. Table 2 presents the quantities of acid sites of the γ-alumina, silica, and iron oxide on γ-alumina and silica catalysts.

Table 2. Ammonia Desorption over Unmodified and Modified Catalysts

| catalyst                  | acid site density (µmol m⁻²) | acid site concentration (mmol g⁻¹) |
|--------------------------|-----------------------------|----------------------------------|
| γ-alumina                | 1.25                        | 0.24                             |
| silica                   | 0.04                        | 0.0090                           |
| iron oxide on γ-alumina  | 2.48                        | 0.42                             |
| iron oxide on silica     | 0.11                        | 0.025                            |

**Temperature-Programmed Reduction with Hydrogen.** The reduction behavior of the two silica-supported and alumina-supported iron oxide catalysts was studied by H₂-TPR. Figure 2 presents the reduction profiles of these two catalysts. In the case of the silica-supported iron oxide catalyst, we observed three distinct stages of reduction. The first reduction region contains two partially overlapping peaks. The peaks at 385 and 438 °C can be ascribed to the transformations of Fe₂O₃ → Fe₃O₄ and Fe₃O₄ → FeO, respectively. The third peak at 608 °C can be attributed to the transformation of FeO → Fe. However, for the alumina-supported iron oxide catalyst, we observed a two-stage reduction profile, a peak with a shoulder. The shoulder at 275 °C can be assigned to Fe₂O₃ → Fe₃O₄, and the peak at 370 °C can be attributed to Fe₂O₄ → FeO or Fe(II) aluminate (FeAl₂O₄). It is apparent that this structure was stabilized, and reduction of Fe(II) to Fe metal was not taking place. Reduction of Fe(III) on the silica support occurs at higher temperatures compared to the one on the alumina support. This can be due to different particle sizes of oxidic iron species and different interactions between iron oxide particles with the two supports.

**ICP–OES and CO-Chemisorption.** Table 3 compares the Fe loading, (the sum of the bulk and surface iron atoms) of the catalysts based on ICP–OES analysis and provides an estimation of the concentration of accessible iron sites (from CO-chemisorption experiments on the surface of the modified alumina and silica).

The dispersion of iron on the surface of silica (1.95%) is less than that determined for the surface of alumina (6.2%). Particle agglomeration on the surface of silica compared to the alumina and the reducibility of iron on the two supports provide possible explanations for this difference. CO chemisorbed much better on the reduced form of iron. The catalysts were reduced under a flow of H₂ at 450 °C prior to CO-chemisorption experiments. The color of reduced alumina-supported iron oxide changed to greenish, which most likely represents the transformation of the Fe⁵⁺ to Fe⁴⁺ species. However, a black color observed for silica-supported iron oxide appears to represent a combination of Fe³⁺ and Fe²⁺ species on the catalyst.

**SEM and TEM.** SEM and energy-dispersive X-ray (EDX) served to study the morphology and elemental distribution of iron on each of the supports. Figures S6 and S7 in the Supporting Information offer a typical SEM micrograph and an example of EDX elemental mapping. From the SEM image, it is evident that particles of iron oxide supported on the silica are on average larger in diameter when compared to those on the alumina support. The alumina support consists of various agglomerated, relatively small diameter particles of a nearly spherical shape. Moreover, alumina contains smaller pores compared to the silica catalyst. EDX analysis was employed to determine the chemical compositions of silica-supported and alumina-supported iron oxide (Figures S5 and S6, part c). TEM images and the particle size distributions are shown in Figure 3. The lighter regions in the images are composed primarily of the support, while the darker regions are iron particles. The majority of iron oxide particles on alumina and silica supports are in the range of 0.4–2 and 6–8 nm, respectively, as estimated statistically from the TEM data. TEM also confirmed agglomerated and larger particle sizes of iron oxide on the surface of the silica support. The size of iron oxide particles on the surface can be explained by considering the point of zero
charge (PZC) of the two supports and the pH of the impregnating solution. The PZC of silica and γ-alumina are well-established in the literature, and these values range between 1.7 to 4.5 and 7 to 9, respectively. This is consistent with the published PZC and NH3-TPD profiles of the supports (see Figure 1); PZC is related to the extensive factor of catalyst acidity, and higher density of acid sites was measured on the surface of alumina compared to the silica support. We used an iron(III) nitrate solution with a pH of 1.0 ± 0.2 for preparing the silica-supported and alumina-supported iron oxide by the incipient wetness method. Because the pH of the solution was lower than PZC of the two supports, the surface of the two adsorbents was positively charged. However, the surface of alumina is more positive and enhanced by the electrostatic repulsive force, suppresses the agglomeration, and subsequently reduces hydrodynamic size of clusters. This explanation is in good agreement with the smaller clusters measured, and even isolated cations on the surface of alumina.

Figure 3. TEM images of (a) alumina-supported iron oxide and (b) silica-supported iron oxide and (c) histogram plot of particle size distribution for silica-supported and alumina-supported iron oxide.

Figure 4. (a) IR spectra of adsorbed NO on the surface of vacuum-treated alumina at 30 °C, (b) IR spectra in the range of 1200–1700 cm⁻¹, the numbers correspond to NO adsorption at low coverage on the surface, and (c) IR spectra in the range of 3200–3800 cm⁻¹.
presents the possible conformation of NO₃ species during adsorption of NO on alumina. Nitrite species are formed at low NO gas coverages, and nitrate species increase in concentration as the pressure of NO increases. The reaction of labile surface oxygen originating from alumina has been postulated as a reason for the formation of nitrate species. The nitrate species were suggested to be formed from NO₂. It is also possible that, as depicted in reactions 1 and 2, NO₂ and N₂O arise in the gas phase at elevated pressures of NO gas because of disproportionation. The formation of the absorption bands on the catalyst suggests that the reactions 3 and 4 occur on the surface of the catalyst.

\[3\text{NO}(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{NO}_2(g)\]  
(1)

\[4\text{NO}(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{N}_2\text{O}_3(g)\]  
(2)

\[2\text{NO}_2(g) + \text{O}^2-(surf) \rightarrow \text{N}_2\text{O}_3(\text{ads}) + \text{NO}_2^-(\text{ads})\]  
(3)

\[2\text{NO}_3(g) \equiv \text{N}_2\text{O}_5(g) \equiv \text{NO}^+(\text{ads}) + \text{NO}_3^-(\text{ads})\]  
(4)

According to the published literature, the band at 2234 cm⁻¹ can be assigned to an N≡N stretching mode of N₂O. Adsorbed N₂O exhibits a blue shift in comparison with the infrared spectra of gaseous N₂O. As presented in Figure 4, the intensity of the absorption band at 1961 cm⁻¹ increased with the increasing NO coverage. This band can be assigned to an adsorbed N₂O₃ species. The IR frequencies of N₂O₃ are widely documented with characteristic absorption bands at approximately 1500, 1300, and 1570 cm⁻¹. The two bands at 1300 and 1570 cm⁻¹ are a combination of N₂O₃ stretching vibration bands overlapping the bands of adsorbed nitrate species.

Absorption bands of a nitrosonium (NO⁺) on the surface of alumina are characterized by the appearance of the absorption bands at 2264 cm⁻¹.

The appearance of negative bands within the 3650–3800 cm⁻¹ region indicates the interaction of isolated hydroxyl groups on the surface of alumina with NO. Five different bands at 3690, 3733, 3757, 3773, and 3791 cm⁻¹ can be assigned to five different hydroxyl groups with different coordination geometries. The most prominent band at 3733 cm⁻¹ is attributed to hydroxyls groups which are bound to two octahedrally coordinated Al³⁺ sites, present in a bridging configuration. The shoulder around 3690 cm⁻¹ and the band at 3791 cm⁻¹ are associated with hydroxyl groups bound to three and a single Al³⁺ sites with octahedral coordination, respectively. The two remaining features at 3773 and 3757 cm⁻¹ are assigned to the terminal hydroxyl groups adsorbed on a single Al³⁺ site with a tetrahedral coordination that can exist on two different crystallographic orientations [i.e., (111) and (110)] of the surface of δ-Al₂O₃.

**Scheme 1. Structure of Various NO₃ Species on Alumina**

![Scheme 1](image-url)
The appearances of negative bands in 3743 cm$^{-1}$ indicate the interaction of isolated hydroxyl groups on the surface of silica with NO$_x$.

**NO Adsorption on Alumina-Supported Iron Oxide Catalysts.** The IR spectra of NO adsorbed on supports (alumina and silica) are recorded, in an effort to differentiate bands that are formed because of the chemisorption of NO on the oxidic iron species (see Figures 6 and 7). Intense bands at 1816 and 1823 cm$^{-1}$ are evident, and the spectral region between 1800 and 1860 cm$^{-1}$ is attributed to the formation of adsorbed nitrosyl species on reduced Fe sites.

Figure 6 shows the adsorption of NO gas on the surface of alumina-supported iron oxide. Importantly, it is well-documented that NO does not adsorb strongly on Fe$^{3+}$ sites; thus, the peak around 1816 cm$^{-1}$ reflects bond formation between Fe$^{2+}$ and NO. The formation of an Fe$^{2+}$ cation originates from auto-reduction of the iron species; a similar phenomenon has been reported elsewhere. At very low concentrations of NO, a new spectral feature at approximately 1816 cm$^{-1}$ is observed. Increasing the pressure of NO to a level greater than 1 mbar caused an apparent shift of this band to higher wavenumbers. Concomitant with this blue shift, we
observe the appearance of nitrate (1250–1620 cm$^{-1}$) and N$_2$O$_3$ bands (1959 cm$^{-1}$).

**NO Adsorption on Silica-Supported Iron Oxide Catalysts.** The IR spectra of NO adsorption on the surface of silica-supported iron oxide are illustrated in Figure 7. The adsorption of NO on Fe$^{2+}$ species appears at higher wavenumbers and at a notably decreased intensity compared to alumina-supported catalysts. At low coverage of NO, a band at 1823 cm$^{-1}$ appeared and, similar to NO adsorption on oxidic iron on alumina, increasing NO coverage resulted in a blue shift of the band to a higher wavenumber (1852 cm$^{-1}$).

At low coverages, NO adsors on highly reactive, coordinatively unsaturated Fe$^{2+}$ species. However, increasing NO coverage results in the formation and co-existence of NO and NO$_2$ surface species. Kayhan et al. reported the decomposition of NO$_2$ gas on Fe$^{2+}$/Fe$(3-x)^{+}$ sites, producing a surface oxygen atom and oxidizing the reduced iron in the vicinity of the oxygen species. Thus, by increasing NO coverage, the band indicative of reduced Fe sites decreases in intensity and shifts to higher wavenumbers. To understand the nature of these differences, we selected the spectrum obtained at 10 μbar pressure to perform peak deconvolution of distinct surface species assuming a Gaussian peak shape, in the range 1750 and 1900 cm$^{-1}$. Four species for the alumina-supported iron oxide (with maxima at 1783, 1807, 1825, and 1841 cm$^{-1}$) and three for the silica-supported iron oxide (with maxima at 1790, 1805, and 1825 cm$^{-1}$) were fitted. The results are presented in Table 4.

**Table 4. Wavenumber of Each Peak for Both Catalysts**

|                | peak 1, Fe$^{2+}$(NO) (cm$^{-1}$) | peak 2, Fe$^{2+}$(NO)$_2$ (cm$^{-1}$) | peak 3, Fe$^{2+}$(NO) (cm$^{-1}$) | peak 4, Fe$^{2+}$(NO) (cm$^{-1}$) |
|----------------|---------------------------------|-------------------------------------|---------------------------------|---------------------------------|
| iron oxide     | 1783                            | 1807                                | 1825                            | 1841                            |
| on γ-alumina   |                                 |                                     |                                 |                                 |
| iron oxide     | 1790                            | 1805                                | 1825                            |                                 |
| on silica      |                                 |                                     |                                 |                                 |

*Low-coordination Fe. *High-coordination Fe. Isolated Fe.

Figure 8 illustrates the IR spectra for both silica- and alumina-supported iron oxide between 1750 and 1900 cm$^{-1}$.

On the basis of the curve-fitting analysis, alumina induces an increased number of Fe$^{2+}$ sites available to NO adsorption compared to silica, most likely because of the existence of isolated Fe$^{2+}$ species on the alumina-supported catalyst and the larger dispersion of the adsorption sites (iron) on the alumina-supported surface compared to the silica-supported catalyst.

Indeed, this conclusion is consistent with the results of the investigation by Chen et al. who studied the dispersion of Fe$_2$O$_3$ on the surface of different metal oxides by Mössbauer spectroscopy and XRD analysis. They reported that the form and extent of dispersion of iron oxide on the surface of the support depends on the number and availability of vacant sites on the catalysts. They concluded that iron oxide forms crystalline α-Fe$_2$O$_3$ on the surface of silica because of the lack of vacant sites on the surface. This is in contrast to other metal oxides studied, such as γ-alumina, ceria, titania, and zirconia, which possess vacant surface sites, and where the Fe$^{3+}$ first incorporates in these sites and only once these sites are saturated with Fe$^{3+}$ in its crystalline α-Fe$_2$O$_3$ form. In another studies, Popova et al. and Rangus et al. showed that the iron concentration in KIL-2 silica, prepared through direct synthesis, influences the nature of metal species in the matrix. They reported the presence of mostly isolated Fe$^{3+}$ species in samples with the low concentration of iron, Fe/Si ≤ 0.01, while the formation of oligonuclear iron complex (Fe$_2$O$_3$) in samples with higher iron content, F/Si > 0.01. In addition, Nechita et al. surmised the formation of different types of iron species on an alumina surface compared to a silica surface.

Yuen et al. investigated the NO adsorption on silica-supported iron oxide, attributed the bands at 1810 and 1750 cm$^{-1}$ to the formation of dinitrosyl and mononitrosyl species on low-coordination tetrahedral Fe$^{2+}$/Fe$(3-x)^{+}$ sites, respectively, and the band at 1830 cm$^{-1}$ to the formation of mononitrosyl at high-coordination octahedral Fe$^{2+}$/Fe$(3-x)^{+}$ sites. They reported the low-coordination and high-coordination Fe cations as strongly interacting with the support and small particles of iron oxide on the surface, respectively. Mössbauer spectroscopy disclosed the presence of both outer and inner doublets in various catalysts with different proportions. The outer doublet is associated with the iron atoms on the surface (high-coordination), while the inner doublet arises because of iron atoms in the interior of crystallite (low-coordination). According to Figure 7, the ratio of iron as small particles of oxide on the surface to species, which strongly interact with the support in the interior portion of the catalyst, is greater for the silica-supported catalyst compared to alumina. The absorption band at a wavenumber of 1841 cm$^{-1}$ is assigned to NO adsorbed on isolated Fe$^{2+}$ cations. No isolated Fe$^{2+}$ was observed on the surface of silica.

The overall intensity of the IR absorption bands in the wavenumber region of 1800–1860 cm$^{-1}$ is higher for alumina-supported iron oxide compared to silica-supported iron oxide. The reasons for this could be either (i) stabilization of Fe$^{2+}$ as
FeAl$_2$O$_4$ during the formation of the catalyst in the interaction of Fe$_2$O$_3$ with Al$_2$O$_3$ or (ii) improvement in the redox property of Fe$^{3+}$ due to a strong interaction between iron oxide and alumina. The interaction inhibits iron particle agglomeration, and as a result, the particle size distribution is relatively narrow on the alumina support, but a significantly broader particle size distribution is reported for iron nanoparticles on the silica support. Moreover, the interaction of iron oxide with the silica support is reported to be weaker than that observed with alumina as a support.

NO Adsorption on Oxidized Alumina- and Silica-Supported Iron Oxide Catalyst. Figure 9 illustrates the IR spectra of NO adsorption on the oxidized alumina-supported iron oxide catalyst. Although the intensity of the peak associated with NO adsorbed on Fe$^{2+}$ decreases, it highlights the presence of Fe$^{2+}$ in the catalyst (oxygen-treated). The remaining Fe$^{3+}$ cations on the surface in the oxidized state have been reported as stabilized compounds, such as FeAl$_2$O$_4$. The presence of this structure has been confirmed by the H$_2$-TPR experiment in the alumina-supported iron oxide catalyst.

Figure 9. IR spectra of adsorbed NO on the surface of oxygen-treated alumina-supported iron oxide at 30 °C.

Figure 10. IR difference spectra of the NO adsorption region for oxygen-treated iron oxide/alumina after adsorbing (a) NO at 1 μbar pressure and (b) N$_2$O at 1 μbar pressure.

Figure 11. IR spectra of adsorbed NO on the surface of oxygen-treated silica-supported iron oxide at 30 °C.
The presence of Fe$^{2+}$ on the surface of the oxygen-treated alumina-supported iron oxide catalyst was confirmed by studying the adsorption of N$_2$O on the catalyst surfaces. Grubert et al.\textsuperscript{95} reported conversion of N$_2$O to NO on the surface of Fe-ZSM-5 and Fe-MCM-41-PS in which iron cations are in their reduced form and iron is present exclusively in the form of Fe$^{2+}$ species. Figure 10 presents the IR spectra of the surface of Fe-ZSM-5 and Fe-MCM-41-PS in which iron cations of Fe$^{2+}$ species to Fe$^{3+}$.

Surface acidities as well as the isolated cationic iron species of Fe$^{2+}$ cations on the surface of alumina support. It is also established that isolated iron cations, significantly higher compared to that of the alumina. In addition, reducibility of transition metals plays a significant role in the formation of dioxins from precursors.\textsuperscript{99} According to the TPR results, formation of FeAl$_2$O$_4$ species prevents the reduction of iron oxide on the alumina support. It is also established that isolated iron cations, tetrahedrally coordinated FeO$_6$ exhibited higher catalytic activity compared to iron oxide clusters and particles,\textsuperscript{100,101} and we propose that the presence of isolated iron cations on the alumina support could be responsible for significant decomposition of 2-CPh and accumulation of a large quantity of carbon on the surface of the alumina-supported iron oxide catalyst.

## CONCLUSIONS

The type of supports and catalysts’ preparation techniques have a notable influence on the nature, acidity, dispersion, and reducibility of the formed metal oxide species as well as on their catalytic activity. Characterization and in situ FTIR analysis of catalysts confirms the existence of significant differences between the two catalysts. Having a larger pore diameter on the surface of silica enhanced agglomeration of the iron oxide particle on that surface and the enhanced interaction and vacant sites for iron on the $\delta$-alumina results in formation of isolated iron (Fe$^{2+}$) species on this support. Moreover, on the basis of the TPD analysis, the acidity of alumina-supported iron oxide is significantly higher compared to that of the silica-supported catalyst. Also, based on CO-chemisorption, the dispersion of iron on the surface of alumina is greater than that determined for the surface of silica. Finally, the reducibility of the two catalysts of silica- and alumina-supported iron oxide is very different. The former catalyst can reduce to Fe metal under reductant atmosphere; however, the FeAl$_2$O$_4$ structure stabilized in the latter catalyst and prevents further reduction of iron particles. All these differentiation in chemistry between silica-supported and alumina-supported iron oxide can explain the different observed behaviors of 2-CPh conversion on the surface of these catalysts.

### METHODOLOGY

**Catalyst Preparation.** γ-Alumina-supported and silica-supported iron oxide samples were prepared by adopting the method of incipient wetness. A solution of iron(III) nitrate nonahydrate (Chem-Supply) was mixed with alumina (Catal International Ltd) and, in a separate preparation, the silica gel (Davisil grade 645) support, in proportions designed to produce an approximately 3 wt% loading of iron (with respect to the mass of the support) on the surface of each of the supports. The solution was added to the supports drop-wise, while mixing continuously until the mixture assumed paste-like consistency. The sample was then dried at 110 °C and finally, calcined in air at 450 °C for 5 h. The 3% loading of iron on the supports is representative of the concentration of iron in most combustion systems.\textsuperscript{102} In addition, we use this specific iron concentration to compare our catalyst relative reactivities with the same concentration of iron on the silica support studied by Nganai et al.\textsuperscript{5}

**Catalyst Characterization.** N$_2$ Adsorption. The BET surface area (m$^2$ g$^{-1}$), average pore volume (cm$^3$ g$^{-1}$), and pore diameter (nm) of the samples were determined by nitrogen adsorption at $-196$ °C using a Micromeritics TriStar 3000 surface area analyser. Prior to any measurement, the samples were degassed overnight at 150 °C using Micrometrics VacPrep 061. The BET theory yielded the surface area of the samples, and the Barrett–Joyner–Halenda (BJH) method served to estimate the pore-volume and pore-size distribution.

**Acidic Properties of the Catalysts.** NH$_3$-TPD experiments were performed in a stainless steel apparatus, as described previously.\textsuperscript{103} Desorption of gaseous species during controlled heating of the sample was recorded by a Pfeiffer Prisma quadrupole mass spectrometer, using the m/z signal at 16 for quantification of ammonia desorbing from the catalyst during heating. In the TPD measurements, 0.1 g samples were activated in situ, in the desorption tube at 450 °C for half an hour. Following activation, ammonia gas adsorbed onto the catalyst surface at 150 °C. Finally, the ammonia desorption experiments proceeded with the sample being heated between 30 and 750 °C at a heating rate of 5 °C min$^{-1}$. Figure S1 represents the three primary m/z (17, 16 and 15) ions of ammonia desorbed from the surface of alumina-supported iron oxide. As presented, the m/z = 17 ion current was affected by water vapor at temperatures greater than 450 °C. Thus, the signal of m/z = 16 best reflects the desorption of ammonia (NH$_3$), as this mass to charge ratio is least contaminated with ions originating from water. For quantitative analysis, ZSM-5 with Si/Al = 15 was used.

**Inductively Coupled Plasma Optical Emission Spectrometry.** The elemental composition of the catalysts was measured using ICP–OES (Varian 715 ES spectrometer ICP–OES). Prior to analysis, samples were dissolved in a solution containing 4.5 mL of HNO$_3$ (65%), 4.5 mL of HCl (37%), and
3 mL of HBF_4 (50%). Thulium (600 μL, 1000 ppmv) was added as an internal standard. To ensure complete sample dissolution, the samples were digested in a Milestone Start D microwave unit for a minimum of 2 h.

**Temperature-Programmed Reduction with Hydrogen.** The temperature-programmed reduction of the samples was performed using 10% H_2 mixed with argon (Ar) with a flow rate of 32 cm³ min⁻¹ as a reductant. A sample (600 mg) was charged in a quartz tube, treated in a flow of Ar at 400 °C for 1 h, and then cooled to room temperature. Finally, the sample was heated to 800 °C with a ramp rate of 10 °C min⁻¹ under the reductant mixture. A thermal conductivity detector (Micromeritics AutoChem II 2920) was used to measure the hydrogen consumption.

**CO Chemisorption.** A static volumetric method allowed measurement of the extent of metal dispersion and an estimation of the active particle size of the metal on the surface of the support using CO as the probe gas. Approximately 0.5 g of the sample was charged into a sample holder placed in a temperature-controlled furnace. The temperature of the sample was increased slowly to 450 °C under a flow of He with a ramp rate of 5 °C min⁻¹; the sample was then treated in the flow of H_2 (50 mL min⁻¹) at 450 °C for 16 h, following purging with He for 20 min. CO chemisorption was performed at 50 °C in the pressure range between 30 and 90 mbar. Pfeiffer 362-TPG 261 Baratron and an acquisition program developed in LabVIEW version 7.1.1 software were used. The program facilitated vacuum measurements and data logging. Estimation of the dispersion involved an assumption of one atom of CO molecule adsorbing onto two iron surface atoms (Fe₅), thus the stoichiometric factor used was CO/Fe⁻¹ = 0.5. The Supporting Information presents the formula for estimating dispersion of the active particle size (eq S1).

**Scanning and Transmission Electron Microscopy.** Zeiss SIGMA VP FESEM was used for the collection of SEM images of the catalysts and supports. Images of the samples were taken by a secondary electron and back-scattered electron detector at 15 kV. An EDX spectroscopy detector enabled elemental analysis using Link Isis software. A JEOL 2100 transmission electron microscope was used for TEM imaging of supported catalysts. We measured the particle size by using Gatan DigitalMicrograph software.

**NO Adsorption Followed by in Situ FTIR Spectroscopy.** All transmission spectra were recorded on a TENSOR 27 spectrometer at a spectral resolution of 4 cm⁻¹. The sample powders were transformed into thin, self-supporting wafers, and transferred into an in situ cell as described in a previous manuscript. Before the adsorption measurements at 30 °C, samples were activated for 30 min at 450 °C under vacuum (vacuum-treated), followed by 30 min in oxygen (oxygen-treated). Subsequent to these treatment processes, NO absorption spectra were obtained over the pressure range of 0.1 μbar to 10 mbar. Finally, difference spectra are reported where the clean activated catalyst is subtracted from the spectrum of the catalyst in contact with the probe molecule. All spectra were recorded at the same temperature (30 °C).

**ASSOCIATED CONTENT**

- Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00201.

Three major m/z ratios of ammonia after desorbing from alumina-supported iron oxide; nitrogen adsorption/desorption isotherm for four samples of γ-alumina, silica, γ-alumina-supported iron oxide, and silica-supported iron oxide; active site dispersion formula; and SEM and EDX (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*
E-mail: michael.stockenhuber@newcastle.edu.au.

**ORCID**
Bogdan Z. Dlugogorski: 0000-0001-8909-029X
Michael Stockenhuber: 0000-0001-5026-2218

Notes
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**REFERENCES**

(1) Dong, H.; Xie, M.; Xu, J.; Li, M.; Peng, L.; Guo, X.; Ding, W. Iron Oxide and Alumina Nanocomposites Applied to Fischer-Tropsch Synthesis. *Chem. Commun.* 2011, 47, 4019−4021.
(2) Davis, B. H. Fischer−Tropsch Synthesis: Reaction Mechanisms for Iron Catalysts. *Catal. Today* 2009, 141, 25−33.
(3) Bouarab, B.; Bennici, S.; Mirodatos, C.; Auroux, A. Hydrogen Production from the Water-Gas Shift Reaction on Iron Oxide Catalysts. *J. Catal.* 2014, 2014, 1.
(4) Torres Galvis, H. M.; Bitter, J. H.; Khare, C. B.; Ruitenbeek, M.; Dugulan, A. I.; de Jong, K. P.Supported Iron Nanoparticles as Catalysts for Sustainable Production of Lower Olefins. *Science* 2012, 335, 835−838.
(5) Ngai, S.; Lomnicki, S.; Dellinger, B. Ferric Oxide Mediated Formation of PCDD/Fs from 2-Monochlorophenol. *Environ. Sci. Technol.* 2009, 43, 368−373.
(6) Mosallanejad, S.; Dlugogorski, B. Z.; Kennedy, E. M.; Stockenhuber, M.; Altarawneh, M. Decomposition of Dibenzo-P-Dioxins and DibenzoFuran in Oxidation of 2-Chlorophenol over Iron Oxide/Silica Surface. *Organohalogen Compd.* 2013, 75, 919−923.
(7) Mosallanejad, S.; Dlugogorski, B. Z.; Altarawneh, M.; Kennedy, E. M.; Yokota, M.; Nakano, T.; Stockenhuber, M. Decomposition of 2-Chlorophenol on Surface of Neat Alumina and Alumina-Supported Iron (III) Oxide Catalyst. *Organohalogen Compd.* 2014, 76, 396−399.
(8) Jansson, B.; Sundström, G.; Ahling, B. Formation of Polychlorinated Dibenzo-p-Dioxins During Combustion of Chlorophenol Formulations. *Sci. Total Environ.* 1978, 10, 209−217.
(9) Pecci, G.; Reyes, P.; Villasenor, J. Fe-Supported Catalysts Prepared by the Sol-Gel Method. Characterization and Evaluation in Phenol Abatement. *J. Sol-Gel Sci. Technol.* 2003, 26, 865−867.
(10) Mustard, D. G.; Bartholomew, C. H. Determination of Metal Crystalite Size and Morphology in Supported Nickel Catalysts. *J. Catal.* 1981, 67, 186−206.
(11) Park, J.-Y.; Lee, Y.-J.; Khanna, P. K.; Jun, K.-W.; Bae, J. W.; Kim, Y. H. Alumina-Supported Iron Oxide Nanoparticles as Fischer−Tropsch Catalysts: Effect of Particle Size of Iron Oxide. *J. Mol. Catal. A: Chem.* 2010, 323, 84−90.
(12) Voß, M.; Borgmann, D.; Wedler, G. Characterization of Alumina, Silica, and Titania Supported Cobalt Catalysts. *J. Catal.* 2002, 212, 10−21.
Kostova, N.; Tsoncheva, T. Toluene Oxidation on Titanium- and Iron-Supported on γ-Al₂O₃ and SiO₂ Assessed in Glycerol Steam Reforming Reaction. Method for HC-SCR Denox Application. ACS Omega, 2018, 3, 5362−5374.

Amenitsch, H.; Kauc; Thyssen, V. V.; Maia, T. A.; Assaf, E. M. Cu and Ni Catalysts for Fischer–Tropsch Synthesis. J. Nat. Gas Chem. 2007, 16, 130−138.

Novak Tůnár, N.; Ristić, A.; Cezowskī, S.; Arčon, I.; Lázár, K.; Arens, H.; Káučík, V. Local Environment of Isolated Iron in Mesoporous Silicate Catalyst FeTUD-1. Microporous Mesoporous Mater. 2007, 104, 289−295.

Szegedi, Á.; Popova, M.; Dimitrova, A.; Cherkezova-Zheleva, Z.; Mitov, I. Effect of the Pretreatment Conditions on the Physico-Chemical and Catalytic Properties of Cobalt- and Iron-Containing Ti-MCM-41 Materials. Microporous Mesoporous Mater. 2010, 136, 106−114.

Szegedi, Á.; Popova, M.; Lázár, K.; Klébert, S.; Drotár, E. Impact of Silica Structure of Copper and Iron-Containing SBA-15 and SBA-16 Materials on Toluene Oxidation. Microporous Mesoporous Mater. 2013, 177, 97−104.

Popova, M.; Szegedi, Á.; Lázár, K.; Károlyi, Z. The Physico-Chemical and Catalytic Properties of Ferrite-Containing MCM-41 and SBA-15 Materials. Microporous Mesoporous Mater. 2012, 151, 180−187.

Popova, M.; Szegedi, Á.; Cherkezova-Zheleva, Z.; Mitov, I.; Kostova, N.; Tsoncheva, T. Toluene Oxidation on Titanium- and Iron-Modified MCM-41 Materials. J. Hazard. Mater. 2009, 168, 226−232.

Thyssen, V. V.; Maia, T. A.; Assaf, E. M. Cu and Ni Catalysts Supported on g-Al₂O₃ and SiO₂ Assessed in Glycerol Steam Reforming Reaction. J. Braz. Chem. Soc. 2015, 26, 22−31.

Zahaf, R.; Jung, J. W.; Coker, Z.; Kim, S.; Choi, T.-Y.; Lee, D. Pt Catalyst over SiO₂ and Al₂O₃ Supports Synthesized by Aerosol Method for HC-SCR Denox Application. Aerosol Air Qual. Res. 2015, 15, 2409−2421.

Tanaka, T.; Yamashita, H.; Tsuchitani, R.;Funabuki, T.; Yoshida, S. X-Ray Absorption (EXAFS/XANES) Study of Supported Vanadium Oxide Catalysts. Structure of Surface Vanadium Oxide Species on Silica and [Gamma]-Alumina at a Low Level of Vanadium Loading. J. Chem. Soc., Faraday Trans. 1 1998, 84, 2987−2999.

Storsæter, S.; Tøtdal, B.; Walmsley, J. C.; Tanem, B. S.; Holmen, A. Characterization of Alumina-, Silica-, and Titania-Supported Cobalt Fischer–Tropsch Catalysts. J. Catal. 2005, 236, 139−152.

Jean-Marie, A; Griboval-Constant, A; Khodakov, A. Y.; Diehl, F. Cobalt Supported on Alumina and Silica-Doped Alumina: Catalyst Structure and Catalytic Performance in Fischer–Tropsch Synthesis. C. R. Chim. 2009, 12, 660−667.

Wan, H.; Wu, B.; Zhang, C.; Teng, B.; Tao, Z.; Yang, Y.; Zhu, Y.; Xiang, H.; Li, Y. Effect of Al₂O₃/SiO₂ Ratio on Iron-Based Catalysts for Fischer–Tropsch Synthesis. Fuel 2006, 85, 1371−1377.

Braga, T. P.; Pinheiro, A. N.; Herrera, W. T.; Xing, Y. T.; Baggio-Saitovitch, E.; Valentiní, A. Synthesis and Characterization of Iron Oxide Nanoparticles Dispersed in Mesoporous Aluminum Oxide. R. Chim. 2011, 49, 481−491.

Lombardo, E. A.; Sill, G. A.; Hall, W. K. The Assay of Acid Sites on Zeolites as Measured by Ammonia Poisioning. J. Catal. 1989, 119, 426−440.

Umansky, B.; Engelhardt, J.; Hall, W. K. On the Strength of Solid Acids. J. Catal. 1991, 127, 128−140.

Umansky, B. S.; Hall, W. K. A Spectrophotometric Study of the Acidity of Some Solid Acids. J. Catal. 1990, 124, 97−108.

Yori, J. C.; Grau, J. M.; Benítez, V. M.; Sepúlveda, J. Hydroisomerization-Cracking of N-Octane on Heteropolyacid H₃PW₁₂O₄₀ Supported on ZrO₂, SiO₂ and Carbon: Effect of Pt Incorporation on Catalyst Performance. Appl. Catal., A 2005, 286, 71−78.

Yu, W.; Wu, B.; Xu, J.; Tao, Z.; Xiang, H.; Li, Y. Effect of Pt Impregnation on a Precipitated Iron-Based Fischer–Tropsch Synthesis Catalyst. Catal. Lett. 2008, 125, 116−122.

Nasir, N. A. M.; Zubair, S. N. A. M.; Kait, C. F. Synthesis and Characterization of Silica-Supported Iron Nanocatalyst by Modified Colloidial Method. J. Appl. Phys. 2011, 12, 1391−1395.

Webb, P. A. Introduction to Chemical Adsorption Analytical Techniques and Their Applications to Catalysis; Micrometrics Instrument Corporation: Norcross, Georgia 30093, 2003.

Kishan, G.; Lee, M.-W.; Nam, S.-S.; Choi, M.-J.; Lee, K.-W. The Catalytic Conversion of CO₂ to Hydrocarbons over Fe−K Supported on Al₂O₃−MgO Mixed Oxides. Catal. Lett. 1998, 56, 215−219.

Liu, W.; Ismail, M.; Dunstan, M. T.; Hu, W.; Zhang, Z.; Fennell, P. S.; Scott, S. A.; Dennis, J. S. Inhibiting the Interaction between FeO−
(92) Miyata, H.; Nakagawa, Y.; Miyagawa, S.; Kubokawa, Y. Adsorption of Nitrogen Monoxide on Iron Oxides Supported on Various Supports and Its Carrier Effects. *J. Chem. Soc., Faraday Trans.* 1 1988, 84, 2129–2134.

(93) Zhang, X.; Dou, G.; Wang, Z.; Li, L.; Wang, Y.; Wang, H.; Hao, Z. Selective Catalytic Oxidation of H₂S over Iron Oxide Supported on Alumina-Intercalated Laponite Clay Catalysts. *J. Hazard. Mater.* 2013, 260, 104–111.

(94) Mattevi, C.; et al. In-Situ X-Ray Photoelectron Spectroscopy Study of Catalyst–Support Interactions and Growth of Carbon Nanotube Forests. *J. Phys. Chem. C* 2008, 112, 12207–12213.

(95) Grubert, G.; Hudson, M. J.; Joyner, R. W.; Stockenhuber, M. The Room Temperature, Stoichiometric Conversion of N₂O to Adsorbed NO by Fe-MCM-41 and Fe-ZSM-5. *J. Catal.* 2000, 196, 126–133.

(96) Hattori, H.; Ono, Y. Solid Acid Catalysis: From Fundamentals to Applications; Pan Stanford, 2015; p 530.

(97) Basheer, M. M.; Custodio, R.; Volpe, P. L. O.; Rittner, R. An Investigation of Chlorophenol Proton Affinities and Their Influence on the Biological Activity of Microorganisms. *J. Phys. Chem. A* 2006, 110, 2021–2026.

(98) Eades, R. A.; Scanlon, K.; Ellenberger, M. R.; Dixon, D. A.; Marynick, D. S. The Proton Affinity of Ammonia. A Theoretical Determination. *J. Phys. Chem.* 1980, 84, 2840–2842.

(99) Farquar, G. R.; Alderman, S. L.; Poliakoff, E. D.; Delling, B. X-Ray Spectroscopic Studies of the High Temperature Reduction of Cu(II)O by 2-Chlorophenol on a Simulated Fly Ash Surface. *Environ. Sci. Technol.* 2003, 37, 931–935.

(100) Timofeeva, M. N.; Mel’gunov, M. S.; Khodkeva, O. A.; Malyshov, M. E.; Shmakov, A. N.; Fenelonov, V. B. Full Phenol Peroxide Oxidation over Fe-MMM-2 Catalysts with Enhanced Hydrothermal Stability. *Appl. Catal., B* 2007, 75, 290–297.

(101) Wang, Y.; Zhang, Q.; Shishido, T.; Takehira, K. Characterizations of Iron-Containing MCM-41 and Its Catalytic Properties in Epoxidation of Styrene with Hydrogen Peroxide. *J. Catal.* 2002, 209, 186–196.

(102) Sarofim, A. F.; Howard, J. B.; Padia, A. S. The Physical Transformation of the Mineral Matter in Pulverized Coal under Simulated Combustion Conditions. *Combust. Sci. Technol.* 1977, 16, 187–204.

(103) Bonati, M. L. M.; Joyner, R. W.; Stockenhuber, M. A. Temperature Programmmed Desorption Study of the Interaction of Acetic Anhydride with Zeolite Beta (BEA). *Catal. Today* 2003, 81, 653–658.

(104) Pansanga, K.; Lohitharn, N.; Chien, A. C. Y.; Lotero, E.; Panpranot, J.; Praserthdam, P.; Goodwin, J. G., Jr. Copper-Modified Alumina as a Support for Iron Fischer–Tropsch Synthesis Catalysts. *Appl. Catal., A* 2007, 332, 130–137.

(105) Lohitharn, N.; Goodwin, J. G., Jr. Effect of K Promotion of Fe and FeMn Fischer–Tropsch Synthesis Catalysts: Analysis at the Site Level Using SSITKA. *J. Catal.* 2008, 260, 7–16.

(106) Venter, J.; Kaminsky, M.; Geoffroy, G. L.; Vannice, M. A. Carbon-Supported FeMn and KFeMn Clusters for the Synthesis of C₂–C₄ Olefins from Co and H₂: I. Chemisorption and Catalytic Behavior. *J. Catal.* 1987, 103, 450–465.

(107) Jung, H.-J.; Vannice, M. A.; Mulay, L. N.; Stanfield, R. M.; Delgass, W. N. The Characterization of Carbon-Supported Iron Catalysts: Chemisorption, Magnetization, and Mössbauer Spectroscopy. *J. Catal.* 1982, 76, 208–224.

(108) Mosallanejad, S.; Dlugogorski, B. Z.; Kennedy, E. M.; Stockenhuber, M. H₂ Adsorption on Copper-Modified ZSM-5: FTIR and DFT Study. *J. Phys. Chem. C* 2013, 117, 19365–19372.