Exploration of Heterogeneous Catalyst for Molecular Hydrogen Ortho-Para Conversion

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Abstract

Molecular hydrogen ($H_2$) ortho-para conversion (O/P conversion) proceeds slowly at low temperatures accompanying a heat release. Thus, catalysts for accelerating this conversion rate are highly demanded in terms of the storage and utilization of liquid $H_2$. We experimentally screened the catalysts for this purpose by examining a broad range of materials covering magnetic, non-magnetic, metallic, and nonmetallic oxides. The primary conclusions obtained are summarized below. (1) active materials are required to be non-metallic and to bear the cations with ionic radii smaller than the bond length of $H_2$. (2) Metallic materials have almost no activity irrespective of with or without magnetism (3). The activity of materials belonging to (1) is largely enhanced when the constituting cation has a magnetic moment. In addition, there is a class of materials for which the activity is distinctly enhanced just upon substitution by the foreign ions.
Introduction

The dominant role of hydrogen in sustainable future energy, hydrogen economy, is widely accepted based on its excellent nature as an energy source for alternative fuel. However, there is a technical obstacle to overcome for industrial use of liquefied H₂. There are two isomers of molecular H₂, ortho H₂ with nuclear spin (J) of 1 and para H₂ with J = 0 -forms. In the thermal equilibrium state, ortho H₂ and para H₂ occupy the rotational ground states of J = 1 and J = 0, respectively, and the O/P ratio is 3 near the ambient temperature but this ratio becomes 0 (only para H₂ exists) at the liquefied temperature of H₂, 20 K (fig. 1). Since ortho H₂ has a non-zero moment of J = 1, it relaxes to the p-state in the condensed state where the molecular separation is 0.37 nm at low temperatures through magnetic interactions between them at a slow rate such as a time constant of ~100 h at 20 K (O/P conversion). The rotational energy released from the O/P conversion corresponding to J = 1 → 0 is 15 meV, which is larger than the evaporation energy (~12 meV) of liquefied H₂ (Fig. 1 inset). As a result, ~55% of liquefied H₂ is lost through evaporation by the O/P conversion heat when conventional H₂ gas with the O/P ratio of 3 is equilibrated at 20 K. Such an H₂ evaporation loss is called "boil-off". To avoid the boil-off, catalysis to promote the O/P conversion is needed to store liquid para H₂ with J = 0.

In 1933, E. Wigner reported a theoretical consideration on the O/P conversion and proposed this conversion is induced on the adsorbed H₂ on the magnetic materials by an inhomogeneous magnetic field arising from the electron spin magnetic dipole moment. The interaction is proportional to $\mu^2 r^6$, where $\mu$ is the magnetic moment of the magnetic ion and $r$ is the collision distance. Considering Wigner's theory, various O/P catalysts have been developed so far. Much effort has been devoted to the development of new catalysts in the 1960s. Currently, 3d-transition metal oxides such as Cr₂O₃ and hydrated iron(III) oxide (FeO₃ ∙ nH₂O) are used as a catalyst for this purpose. However, it has continued to seek more efficient catalysts as well as understanding the effective conversion mechanism until recently.

Since then, it has been believed that this conversion is not induced on the surface of diamagnetic materials. However, in the 1980s, it was found that this conversion occurs even on various nonmagnetic materials such as amorphous ice. Recently, the conversion of H₂ confined into the nano space of MOF (metal-organic framework) has gained attention. So far, fundamental research on the O/P conversion on solid surfaces has been performed employing clean materials surfaces and physical techniques. According to these
researches, the O/P conversion is induced by three origins: magnetic fields \[^{[6-8]}\], charge transfer \[^{[27-29]}\], and electric fields.\[^{[24]}\] Although each mechanism appears to be valid for the materials system examined, we think it is pivotal at the present stage for rational catalyst design to get a rough but comprehensive image of the concrete catalytic materials.

In this work, we explore the O/P conversion at 77 K for a wide range of solid materials covering magnetic/non-magnetic and metallic (no opened band gap)/semiconducting materials and classify these materials into different types depending on the conversion activity. As a consequence, the experimental results may be classified into four types and each type is featured by the mechanism except for several exceptions. The essential factor for the high catalytic activity is not magnetism but bearing the cation with small ionic radii in the non-metallic materials, to our surprise.

![Equilibrium ratio of ortho/para H\(_2\) concentration. Inset shows the energy diagram for molecular hydrogen.](image)

**Fig. 1** Equilibrium ratio of ortho/para H\(_2\) concentration. Inset shows the energy diagram for molecular hydrogen.

**Experimental**

**Catalyst materials**

We investigated a wide range of solid materials covering magnetic/non-magnetic and metallic (no opened band gap)/semiconducting materials. These powder samples were purchased from the manufacturers (Sigma-Aldrich, Alfa Aesar, Kishida Chemical, Kojundo Chemical Laboratory, Fruuchi Chemical, or Furuya Metal.) or made by ourselves by gas atomizing or gas reduction of precursors. The particle size of most of the catalysts was in a range of 1 through 10 \(\mu\)m, except for some nanoparticulate catalysts including SnO, Sn\(_3\)O\(_4\), NiO, CuO and Pr-doped CeO\(_2\), of which particle size was smaller than 100 nm. See figure S1 and S2 for powder X-ray (\(p\)XRD) characterization data for the catalysts.
Fig. 2 Experimental setup for the catalytic O/P conversion measurement.

The O/P conversion activity of various catalyst materials was evaluated at 77 K using a batch reactor equipped with a plunger pump and a gas-tight cell respectively for gas circulation and Raman spectroscopy (fig. 2). H₂ gas (99.9 %) was used as purchased without further purification. An aliquot of 100 mg of catalyst particles (particle size < 10 μm) was loaded in a glass-made sample tube with an inner diameter of 6 mm. The sample tube was attached to the batch reactor, evacuated down to 10 Pa, and backfilled with H₂ gas up to 80 kPa. The H₂ gas was repeatedly passed through the catalyst layer and the gas cell in sequence, being monitored with a Raman spectrometer (JASCO RMP-510) on the population of ortho- and para H₂.

Fig. 3 Time evolution of Raman spectra for the O/P conversion over Fe₂O₃ catalysts.
Figure 3 shows a series of Raman spectra acquired at 77 K at different duration times after the circulating H\(_2\) gas was subjected to an iron oxide (Fe\(_2\)O\(_3\)) catalyst. The volume fraction of para H\(_2\) was calculated as 29±1.0 % from the intensity ratio of the major Raman peaks at 354.4 cm\(^{-1}\) and 588.4 cm\(^{-1}\) that corresponds to the \(J = 0\) to \(J = 2\) and \(J = 1\) to \(J = 3\) transitions (see the inset of fig. 1), respectively.\(^{[30]}\) The evaluated fraction was close to 25 %, which is theoretically expected at room temperature from the Boltzmann statistics. The para H\(_2\) fraction increased to reach 39±1.0 %, 4 hrs after the catalysis was started by immersing the sample tube into liquid nitrogen. By contrast, the O/P conversion was hardly promoted when aluminum oxide (Al\(_2\)O\(_3\)) was used as the catalyst. The para H\(_2\) fraction remained around 25 % even 5 hrs after the catalysis was started, showing that the O/P conversion activity of Al\(_2\)O\(_3\) is negligibly low compared to that of Fe\(_2\)O\(_3\) in this catalysis condition.

Results

Fig. 4 Trends of the O/P conversion at 77 K over different catalysts. The black, green, blue, and red curves are assigned to the materials of groups 1, 2, 3, and 4, respectively. Red-filled circles and open squares correspond to Mn\(_3\)O\(_4\) and CoO, respectively. Blue-filled circles, open squares, and filled triangles correspond to SnO\(_2\), Ho\(_2\)O\(_3\), and Sn\(_3\)O\(_4\), respectively. Green-filled circles, open squares, and filled triangles correspond to Sb\(_2\)O\(_5\), V\(_2\)O\(_5\), and Ta\(_2\)O\(_5\), respectively. Black-filled circles and open squares correspond to FeO and metallic Gd\(_5\)Si\(_3\),
respectively. The error bars were calculated as a standard deviation of the background spectrum acquired by filling the sample tube with no catalyst.

Figure 4 shows the trend of the O/P conversion catalysis at 77 K for different materials including metal and simple metal oxides (AO\textsubscript{x}), which are categorized into four groups. The first is a group of materials that exhibit no finite activity toward the O/P conversion (group 1, black curves in Fig. 4). This group involves all of the metallic materials and most of the oxides containing low-valence metal cations. The para H\textsubscript{2} fraction stayed around the initial value of 25 % over hours even though H\textsubscript{2} gas repeatedly passed through the metal catalysts including bismuth (Bi), gold (Au), platinum (Pt), or intermetallic compounds such as ErAl\textsubscript{2}, GdAl\textsubscript{2} or HoB\textsubscript{2}. The metal oxides containing hollow or filled d-orbitals such as Cu\textsubscript{2}O or ZnO were as inert as the metal catalysts. None of the low-valence metal oxides such as Mn\textsuperscript{2+}O, Fe\textsuperscript{2+}O, Ni\textsuperscript{2+}O, Sn\textsuperscript{2+}O, Pb\textsuperscript{2+}O, V\textsuperscript{3+}O\textsubscript{3}, In\textsuperscript{3+}O\textsubscript{3} or Bi\textsuperscript{3+}O\textsubscript{3} efficiently promoted the O/P conversion.

The second group consists of metal oxides that contain high-valence cations such as V\textsuperscript{5+}O\textsubscript{5}, Mn\textsuperscript{4+}O\textsubscript{2}, Ta\textsuperscript{5+}O\textsubscript{5}, and Sb\textsuperscript{5+}O\textsubscript{5} (group 2, green curves in Fig. 4). The group 2 materials exhibited finite O/P conversion activity: the para H\textsubscript{2} fraction monotonously increased from 25 % showing a tendency to saturate toward 50 %. Most of the group 2 oxides comprise non-magnetic metal ions without d-electrons (V\textsuperscript{5+}, Y\textsuperscript{3+}, Ta\textsuperscript{5+}, Sb\textsuperscript{5+}).

The third group involves metal oxides comprising high-valence metal ions such as Mn\textsuperscript{3+}O\textsubscript{3}, Cu\textsuperscript{2+}O, Zr\textsuperscript{4+}O\textsubscript{2}, Sn\textsuperscript{4+}Sn\textsuperscript{2+}O\textsubscript{4}, Sn\textsuperscript{4+}O\textsubscript{2}, Ho\textsuperscript{3+}O\textsubscript{3} and Gd\textsuperscript{3+}O\textsubscript{3} (group 3, blue curves in Fig. 4). The group 3 materials are similar in the ionic- and catalytic nature to the group 2 materials yet showed superior catalytic activity. The last group involves some of the metal oxides and hydroxides that consist of magnetic metal cations (group 5, red curves in Fig. 4). Mn\textsuperscript{3+}Mn\textsuperscript{3+}O\textsubscript{4} and Co\textsuperscript{2+}O showed much higher catalytic activity than any other materials belonging to group 1, 2 or 3. The O/P conversion over Mn\textsubscript{3}O\textsubscript{4} and/or CoO was so fast that the para H\textsubscript{2} fraction reached the theoretical maximum of 50 %, within a half hour. Cerium dioxide (CeO\textsubscript{2}) exhibited higher activity even than Mn\textsubscript{3}O\textsubscript{4} or CoO. Mn\textsubscript{3}O\textsubscript{4} and CoO have been known as semiconductors having a bandgap of 2.8 and 2.1 eV, respectively.\textsuperscript{32, 33} Moreover, the inherent activity of CeO\textsubscript{2} was significantly improved when the tetravalent Ce\textsuperscript{4+} was partially substituted with trivalent Gd\textsuperscript{3+} as gadolinium-doped ceria (Gd: CeO\textsubscript{2}).
Fig. 5 Rate constants of the O/P conversion over representative catalyst materials. The rate constants were obtained by numerical fitting to the experimental data using an exponential function (see Fig. S3 and the caption for details on the numerical fitting).

Discussion

First, we discuss the effect of an electric field which works in nonmagnetic ionic compounds categorized into group 3. H₂ molecules are modulated in nuclear spins through an interaction with the electrons of ions constituting the surface when weakly adsorbed on the catalyst surface retaining the H-H bond (physisorption). It is acknowledged that quantum transition in the total spin momentum of H₂ nuclei from \( J = 0 \) to \( J = 1 \), namely the O/P conversion, can be promoted especially when the physisorbed H₂ molecules are subjected to localized electric fields with high intensity and spatial anisotropy. The effect has been considered to be key to realizing the conversion on MOF or amorphous ice. Such anisotropic electric fields are scarcely formed over the metal surface, where the local charge is evenly screened and smoothened by itinerant electrons. The screened, isotropic electric fields can hardly promote the nuclear spin transition, resulting in the much low O/P conversion activity of metallic materials (fig. 5).
Fig. 6 Relation between the O/P conversion activity of single metal oxides and the radius of the constituent metal ions.

Here, we attempt to compare the size-matching between H₂ and the catalyst surface. The ionic radius proposed by Shannon [34] is utilized as a measure. The ionic radii for Bi³⁺ (96 pm), Y³⁺ (90 pm), and In³⁺ (80 pm) are larger than the bond length of H₂: 74.1 pm (fig. 6). The ionic radius of Pb⁴⁺ in PbO₂, 78 pm, is also larger than 74.1 pm. As already addressed in the experimental section, the low-valence metal oxides such as Bi₂O₃, Y₂O₃, MnO, In₂O₃, and FeO show much low O/P conversion activity. The activity for PbO₂ is as low as the other low-valence metal oxides. The large-sized metal ions are not favorable to offer sufficiently strong electric fields to the H₂ molecules, which results in low O/P conversion activity. Unlike the metal oxides comprising large metal ions, the metal oxides composed of small metal ions (ionic radii < 74.1 nm) exhibit high O/P conversion activity (fig. 6).

The H₂ molecules physisorbed on the small metal ions are strongly polarized to interact with the anisotropic electric field, resulting in promoted O/P conversions. Over the surface of the metal oxides belonging to group 1, such as Mn²⁺O²⁻, Fe²⁺ O²⁻, Sn²⁺ O²⁻, and Pb²⁺ O²⁻, there are distributed local extrema of electric potentials at each of the surface ions. The electric potential abruptly changes the polarity at the ion boundary to develop an electric field with high anisotropy (fig. 7). However, low-valence metal ions are large: the ionic radii of Fe²⁺ (HS: 78 pm), Mn²⁺ (HS: 83 pm), Sn²⁺ (122 pm), and Pb²⁺ (119 pm) are larger than the bond length of the H₂ molecule, 74.1 pm [34]. The H₂ molecules adsorbed on such large ions are subjected to a weak electric field, which may lead to a sluggish O/P conversion as similarly occurring over the metal catalysts. The radii of the high-valence metal ions are generally smaller than those of the low-valence ions. Indeed, V⁵⁺ (ionic radius: 54 pm), Sb⁵⁺ (ionic radius: 60 pm), and Ta⁶⁺ (ionic radius: 64 pm) are smaller than the corresponding low-valence
ions, V\(^{3+}\) (ionic radius: 64 pm), Sb\(^{3+}\) (ionic radius: 76 pm) and Ta\(^{3+}\) (ionic radius: 72 pm), respectively. The polarization of \(\text{H}_2\) molecules on the high-valence metal surface is large when the molecules are adsorbed pointing the side to the surface (side-on adsorption), subjected to a strong, anisotropic electric field. High-valence metal oxides such as V\(^{5+}\)\(\text{O}_5\), Sb\(^{5+}\)\(\text{O}_5\), Ta\(^{5+}\)\(\text{O}_5\), and Zr\(^{4+}\)\(\text{O}_2\) exhibit prominent O/P conversion activity due to the promoted nuclear spin transition by the electric field.

Second, we discuss the character of group 4 where the magnetic field plays a crucial role. The nuclei of \(\text{H}_2\) molecules are affected not only by electric fields but also by magnetic interactions with the local moments that are distributed over the catalyst surface.\(^{[6,24]}\) Indeed, the O/P conversion of hydrogen nuclei is promoted by a magnetic dipole-dipole coupling with the electrons of hydrogen molecules in direct contact with electrically non-polar matter such as oxygen molecules.\(^{[35]}\) However, the present experimental results show none of the magnetically metallic materials exhibits finite O/P activity although some of the metals such as Fe (Co, Ni) show inherently magnetism. Thus, magnetic interactions appear less predominant than electric interactions judging as a whole. Prominent O/P conversions are realized only if both the electric- and magnetic interactions are constructively applied to the \(\text{H}_2\) molecules, \(i.e.,\) in the case of group 4 materials including Mn\(_2\)O\(_4\). Mn\(_3\)O\(_4\) crystallizes in the normal Spinel structure (fig. 8(a)).\(^{[36]}\) The Mn\(^{3+}\) cation is coordinated by six oxygen atoms to form a MnO\(_6\) octahedron. The octahedrally coordinated Mn\(^{3+}\) cation is so small in ionic radius that it is likely able to apply an anisotropic electric field to the \(\text{H}_2\) molecule and provide an opportunity for magnetic exchanges between the \(\text{H}_2\) nuclei and metal \(d\)-electrons to accelerate the O/P conversion.

The same scenario may be valid for the other magnetic materials belonging to group 3, where the metal ions are allowed to strongly interact with the nuclei of \(\text{H}_2\) molecules such as Co(OH)\(_2\), Cr(OH)\(_3\), Fe\(_2\)O\(_3\), or FeOOH. This effect seen in magnetic insulators obeys Wigner’s theory.\(^{[6]}\) Mn\(^{2+}\)Mn\(^{3+}\)\(\text{O}_4\) contains both Mn\(^{2+}\) (3\(d^5\) HS electronic configuration) and Mn\(^{3+}\) (3\(d^4\) HS) ions. The effective moment spin-only value, \(\mu_{\text{eff}}\) is given by \(2S(S+1)^{1/2}\), where \(S\) is the total spin of the ion. The \(\mu_{\text{eff}}\) of \(d^5\) or \(d^4\) configuration is 5.92 or 4.90 BM, respectively. Mn\(^{2+}\) ion cannot satisfy the criterion of cationic radius described above, despite the large \(\mu_{\text{eff}}\) (5.92 BM). On the other hand, the Mn\(^{3+}\) ion having a smaller ionic size contributes to the magnetic interaction through moderately large \(\mu_{\text{eff}}\) (4.90 BM), even if it undergoes Jahn-Teller distortion leading to the buildup of a large anisotropic electric field.
Fig. 7 Polarization of H₂ molecules by anisotropic electric fields between the oxygen- and metal ions. The steep gradient in the electric potential (ϕ) at the border of the metal- and oxygen ions polarizes the H₂ molecule (±δ). The atomic environment around the small metal (b) ion is more favorable than the large metal ion (a) to develop electric dipole moments (μ).

Fig. 8 Crystal structure of (a) Mn₃O₄ and (b) CeO₂. Mn₃O₄ adopts a distorted spinel-type crystal structure. The cationic distribution of Mn²⁺/Mn³⁺ obeys normal spinel type. The Mn³⁺O₆ octahedron shows Jahn-Teller distortion, inducing symmetry lowering from cubic to tetragonal cells. CeO₂ takes a fluorite-type crystal structure.
Finally, mentioned are some exceptional cases in our classification. According to the observation of Figure 5, there seems to be another group of materials in group 4. This group consists of CeO\textsubscript{2} and gadolinium oxide (Gd\textsubscript{2}O\textsubscript{3}). Figure 8(b) shows the crystal structure of CeO\textsubscript{2}. It adopts a fluorite-type crystal structure in which the Ce ion is surrounded by eight O ions (and we can see a cavity surrounded by eight O ions). They showed similar O/P conversion trends as the group 4 materials such as Mn\textsubscript{3}O\textsubscript{4}, realizing 50 % of para-H\textsubscript{2} fraction within 20 min (fig. 4). However, the ionic radii for Ce\textsuperscript{4+} and Gd\textsuperscript{3+} being 87 pm and 94 pm, respectively,\textsuperscript{[34]} are significantly larger than the bond length of H\textsubscript{2}, 74.1 pm. The H\textsubscript{2} molecules likely receive sufficiently strong electric fields from the surface of neither Ce\textsuperscript{4+} nor Gd\textsuperscript{3+} ions.

![Fig. 9 Adsorption of ortho- and/or para H\textsubscript{2} onto the metal ions (a) and oxygen vacancies (b). Black-open circles and red-closed circles denote oxygen (O\textsuperscript{2-}) and metal ions, respectively.](image)

It is acknowledged that lanthanide oxides can contain high concentrations of oxygen vacancies in the bulk and/or on the surface in particular when the lanthanide ions are capable of adopting different valence. As-synthesized CeO\textsubscript{2} materials often contain trivalent Ce\textsuperscript{3+} ions, being accompanied by equivalent oxygen vacancies. The positively charged oxygen vacancy may adsorb H\textsubscript{2} molecules in a similar way as the metal cations (fig. 9). Ortho H\textsubscript{2} molecules are efficiently converted to para H\textsubscript{2} before leaving the surface due to the anisotropic electric field at the oxygen vacancies. This scenario is supported by an experimental fact that a solid solution of CeO\textsubscript{2} and Gd\textsubscript{2}O\textsubscript{3} (Ce\textsuperscript{4+}\textsubscript{0.8}Gd\textsuperscript{3+}\textsubscript{0.2}O\textsubscript{1.9}) containing a high concentration of oxygen vacancy exhibits prominent O/P conversion activity. Artificially impregnated oxygen vacancies in Ce\textsuperscript{4+}\textsubscript{0.8}Gd\textsuperscript{3+}\textsubscript{0.2}O\textsubscript{1.9} most likely play the role of catalysis center.

**Summary**

We have screened a wide range of materials to explore effective catalysts for the O/P conversion of H\textsubscript{2} at 77 K. The primary conclusions are summarized as follows: (1) The O/P conversion catalysts are categorized into four groups. (2) The first is a group of materials that exhibit no finite activity toward the O/P conversion (group 1). This group involves all of the
metallic materials and most of the oxides containing low-valence metal cations. (3) Group 2 consists of metal oxides that contain high-valence cations such as $V^{5+}$ or $Os$. The materials exhibited finite O/P conversion activity: the para $H_2$ fraction monotonously increased from 25% showing a tendency to saturate toward 50%. Most of the group 2 oxides comprise non-magnetic metal ions without $d$-electrons ($V^{5+}$, $Y^{3+}$, $Ta^{5+}$, $Sb^{5+}$). (4) The group 3 materials such as $Mn_2O_3$ or $CuO$ are similar in the ionic- and catalytic nature to the group 2 materials yet showed superior catalytic activity. (5) Group 4 involves some of the metal oxides and hydroxides that consist of magnetic metal cations. $Mn_3O_4$ and $CoO$ showed much higher catalytic activity among the four groups. (6) Although there are various factors to influence the catalytic activity, the surface electric field in ionic compounds seems to be the most important one, which induces electric polarization of adsorbed $H_2$.

We can easily estimate this effect considering the cationic size in metal oxides: the oxides containing smaller cations (ionic radius < 75 pm) tend to show the activity empirically. This effect appears to work well for MOF materials but does not for metallic materials having itinerant electrons. (7) Magnetism induced on open-shell transition metal cations in the oxide catalysts enhances the catalytic activity through the theory proposed by Wigner. The activity of ionic oxide semiconductors including $Mn_3O_4$ and $CoO$ originates from both electric fields and magnetic interactions. (8) $CeO_2$ also shows high activity without magnetic ions. It contains a large $Ce^{4+}$ ion (the size > 75 pm) and does not satisfy the criterion about cationic size. While we cannot find the primary factor for this oxide, oxygen vacancy created as the result of the formation of $Ce^{3+}$ would give rise to induce a large and anisotropic electric field on the surface. (9) there is a class of materials for which the activity change is distinct just doping the foreign ions but cannot be understood at this stage. While further efforts are needed to solidify the scientific base, these findings obtained through materials exploration would be useful to design the optimal catalyst.

It was unexpected for us that electric field effect is more dominant than the magnetic interaction. This finding is quite consistent with inertness of metallic materials including ferromagnet. Electric field gradient over $H_2$ adsorbed on the materials surface appears to be a critical factor for effective O/P conversion catalysis. The results of the present exploratory
research imply the conversion would be controlled by enhanced spin-orbital interaction\cite{23} or nuclear quadrupole interaction.

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**References**

Supporting Information

**Figure S1.** Powder X-ray Diffraction patterns for the catalysts belonging to the group 3.

**Figure S2.** Powder X-ray Diffraction patterns for the catalysts belonging to the group 4.
**Figure S3.** Exponential fitting to the experimentally obtained data for a Mn₃O₄ catalyst material. The exponential function is defined as $W_{\text{coef}[0]} - W_{\text{coef}[1]} \times \exp(-1 \times W_{\text{coef}[2]} \times \text{Time Course})$, where $W_{\text{coef}[0]} = 50$ (constant), $W_{\text{coef}[1]} = -8.55\pm1.52$ and $W_{\text{coef}[2]} = 3.07\pm0.53$ (h⁻¹). The rate constant for a given catalyst corresponds to $W_{\text{coef}[2]}$. 