"Total oxidation of chlorinated VOCs on supported oxide catalysts"

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ABSTRACT

Biomass-fed cogeneration units and waste incinerators have the advantages of producing efficiently heat and power and of reducing the amount of CO2 emitted per produced energy. However, they produce toxic polychlorinated VOCs (dioxins), CO and NOx. This thesis aims at developing a catalytic system for the total oxidation of chlorinated VOCs that: i) convert efficiently chlorinated VOCs below 250 °C and ii) resist to the exhaust co-pollutants (H2O, CO, NOx). Moreover, this thesis aims at having a complete understanding of the catalytic mechanism. Part I demonstrated that VOx/TiO2 based catalysts are very efficient in the total oxidation of chlorobenzene (taken as a model molecule). In particular, they proved to be highly resistant against deactivation. Moreover, Part I established that the addition of secondary phases producing VOx-WOx/TiO2 or VOx-MoOx/TiO2 induces a synergetic effect that improves the performances. Furthermore, the replacement of a classical TiO2 by a sulfated one i...

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The small-scale biomass-fed cogeneration units have the huge advantages of producing more efficiently heat and power and of reducing the amount of CO$_2$ emitted per produced energy. However, the biomass-fed cogeneration units are well known as huge producers of toxic polychlorinated VOCs. Moreover, the involved process of combustion produces simultaneously, beside dioxins, CO and NO$_x$.

The aim of this thesis is to find a catalytic system for the total oxidation of chlorinated VOCs. The catalytic system must respect precise requirements: i) it must be the best catalytic formulation for the total oxidation of chlorinated VOCs and convert them efficiently below 250 °C and ii) it must resist to the co-pollutants present in the exhaust gases (H$_2$O, CO, NO$_x$). Moreover, this thesis aims at having a complete understanding of the catalytic mechanism. In order to achieve these three objectives, the research has followed a step-by-step process presented in the three parts of this manuscript. Each part aims at achieving a specific objective. The first part aims at designing the best catalyst for the total oxidation of chlorinated VOCs. The second part investigates the effect brought by the co-pollutants on the best catalysts activity. And finally, the third part revisits all the catalytic results and characterizations in order to build a clear picture of the combustion mechanism of the chlorinated VOCs.

Part I demonstrated that VO$_x$/TiO$_2$ based catalysts are very efficient in the total oxidation abatement of chlorobenzene (taken as a model molecule for dioxins) from combustion exhaust gases. In particular, they proved to be
General conclusion

highly resistant against deactivation which proceeds on other elements than V through the chlorination of the active phase or the blocking of the active sites. Moreover, Part I established that the addition of secondary phases producing VOₓ-WOₓ/TiO₂ or VOₓ-MoOₓ/TiO₂ formulations induces a synergetic effect. This effect leads to a high improvement of the catalyst performances. Furthermore, the replacement of a classical TiO₂ by a sulfated TiO₂ improves the catalytic performances of the formulations.

In Part II, the deep investigation of the influence of co-pollutants (H₂O, CO and NOₓ) on the catalysts ability to destruct chlorinated VOCs demonstrated their quite good resistance. Indeed, the presence of CO does not induce any deactivation of the catalysts while NOₓ induces a huge improvement of the catalysts ability to destruct chlorinated VOCs. The beneficial effect of NO is explained by the in situ production of a strong oxidant (NO₂) that speeds up the reoxidation of the reduced VOₓ sites. Nevertheless, H₂O vapor can affect negatively the catalyst activity when present in a high concentration in the gaseous stream.

Part III aims at drawing a clear picture of the mechanism of the total oxidation of chlorinated VOCs on VOₓ/TiO₂ based catalysts by bringing together and by revisiting catalytic and characterization results exposed in Part I and II. This investigation demonstrated that the mechanism through which the total oxidation of chlorinated VOCs proceeds can be described in four steps: i) adsorption of chlorinated VOCs on medium-strong Brønsted sites, mainly located at the surface of the secondary phases, ii) VOₓ redox sites give some of their lattice oxygen atoms to oxidize step-by-step the aromatic ring producing H₂O and COₓ, iii) reoxidation of the VOₓ reduced sites thanks to the oxidant present in the gas stream (O₂) and iv) retrieving of the chlorine from the surface thanks to its reaction with water producing HCl easily desorbed. The second and third steps compose a classical Mars and van Krevelen mechanism. The third step, namely the reoxidation of the reduced VOₓ site, is identified as the rate limiting step of the mechanism. Our work thus shows that the catalytic performances can be improved by
tuning the redox properties of the VO_x phases: i) improvement of the reducibility of the VO_x phase and ii) stabilization of the vanadium oxidation level above a limit value, estimated in the case of the TsVW catalyst around 4.87.
ANNEXES

1. TOF-SIMS [174]

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) uses a pulsed primary ion beam to desorb and ionize species from a sample surface. The resulting secondary ions are accelerated into a mass spectrometer, where they are mass analyzed by measuring their time-of-flight from the sample surface to the detector. An image is generated by rastering a finely focused beam across the sample surface. Due to the parallel detection nature of TOF-SIMS, the entire mass spectrum is acquired from every pixel in the image. The mass spectrum and the secondary ion images are then used to determine the composition and distribution of sample surface constituents. TOF-SIMS provides spectroscopy for characterization of chemical composition, imaging for determining the distribution of chemical species, and depth profiling for thin film characterization.
In the spectroscopy and imaging modes, only the outermost (1-2) atomic layers of the sample are analyzed. To ensure that the analyzed secondary ions originate from the outer surface of the sample, a primary ion dose of less than $10^{12}$ ions/cm$^2$ is employed. Below this "static limit," roughly less than one in one thousand surface atoms or molecules are struck by a primary ion. The actual desorption of material from the surface is caused by a "collision cascade" which is initiated by the primary ion impacting the surface. The emitted secondary ions are extracted into the TOF analyzer by applying a potential between the sample surface and the mass analyzer. TOF-SIMS spectra are generated using a pulsed primary ion source (very short pulses of <1 ns). Secondary ions travel through the TOF analyzer with different velocities, depending on their mass to charge ratio ($ke=\frac{1}{2}mv^2$). For each primary ion pulse, a full mass spectrum is obtained by measuring the arrival times of the secondary ions at the detector and performing a simple time to mass conversion.

2. EPR

EPR is a spectroscopic technique which detects chemical species that have unpaired electrons. A great number of materials contain such paramagnetic entities, which may occur either as electrons in unfilled conduction bands, electrons trapped in radiation damaged sites, or as free radicals, various transition ions, bi-radicals, triplet states, impurities in semi-conductors, as well as other types.

One of the fundamental roles of any spectroscopic technique is the identification of the chemical species being studied. In cases where two or more paramagnetic species co-exist, the spectral EPR lines arising from each can be simultaneously observed. The definitive identification of the individual species is often realized solely from the analysis of the EPR spectrum. Furthermore, EPR spectroscopy is capable of providing molecular structural details inaccessible by any other analytical tool.
These capabilities of EPR are a result of the unpaired electron’s spin magnetic moment being very sensitive to local magnetic fields within the sample. These fields often arise from the nuclear magnetic moments of various nuclei that may be present within the bulk medium. Examples of such nuclei are interstitial atoms (or ions) within a crystal or glass matrix, nuclei (such as nitrogen) within the molecular structure that also contains the unpaired electron, and so on. Thus EPR provides a unique means of studying internal structures in great detail.

EPR has been successfully applied in such diverse disciplines as biology, physics, geology, chemistry, medical science, material science, anthropology, to name but a few. Solids, liquids and gases are all accessible through EPR. By utilizing a variety of specialized techniques (such as spin-trapping, spin-labeling, ESEEM and ENDOR) in conjunction with EPR, researchers are capable of obtaining detailed information about many topics of scientific interest. For example, chemical kinetics, electron exchange, electrochemical processes, crystalline structure, fundamental quantum theory, catalysis, and polymerization reactions have all been studied with great success.

The EPR works by application of a strong magnetic field B to material containing paramagnetic species, the individual magnetic moment arising via the electron “spin” of the unpaired electron can be oriented either parallel or anti-parallel to the applied field. This creates distinct energy levels for the unpaired electrons, making it possible for net absorption of electromagnetic radiation (in the form of microwaves) to occur. The situation referred to as the resonance condition takes place when the magnetic field and the microwave frequency are “just right” (i.e., when the energy of the microwaves corresponds to the energy difference ΔE of the pair of involved spin states).
2.1. EPR theory

2.1.1. Units and constants

A magnetic Field is described by some constants and units:

- Magnetic induction \( \vec{B} \) in tesla (T)
- Magnetic flux density \( \vec{H} \) in amperes per metre (A/m)
- \( \vec{B} \) and \( \vec{H} \) relationship:

\[
\vec{B} = \mu_0 \vec{H}
\]

- The CGS unit for magnetic induction is the gauss (G) which is equivalent to \( 10^{-4} \) T

Furthermore, in describing EPR, following units are very important:

- Planck's constant \( h = 6.63 \times 10^{-34} \text{ J s} \)
- Boltzmann constant \( k = 1.38 \times 10^{-23} \text{ J K}^{-1} \)
- Bohr magneton \( \mu_B = 9.27 \times 10^{-24} \text{ J T}^{-1} \)

2.1.2. Basics

EPR is based on the Zeeman effect, which depends on the splitting of the electronic energy levels of paramagnetic molecules within a magnetic field.

A molecule with a magnetic moment \( \mu \) in a magnetic field \( \vec{B} \) has an energy \( E \) according to:

\[
E = -\mu \cdot \vec{B}
\]
For an atom with an angular momentum $\vec{J}$, the dipole magnetic moment is

$$\vec{\mu} = -g\beta \vec{J}$$

where $g$ is the spectroscopic splitting factor, and $\beta$ the Bohr magneton. Placed in a magnetic field, the atom gains energy:

$$E_J = g\beta \vec{J} \cdot \vec{B}$$

The $\vec{J}$ vector of any atom can possess only some allowed orientations determined by $M_J$ quantum number values collection. It is the reason why energy linked with orientation of atom is limited to $M_J$ dependent collection.

$$E_J = gM_J\beta B_\perp$$

where: $M_J=J, J-1, J-2, ..., -J$.

In an external magnetic field the splitting (fission) of single $J$ level for $2J+1$ sublevels occurs; this phenomenon is called Zeeman splitting. When constant magnetic field $\vec{B}$ is added to variable magnetic field $\vec{B}_1$ with $\nu$ frequency, a movement between Zeeman levels can occur. This movement depends on:

- $\vec{E}_1 \perp \vec{B}$
- $\Delta M_J = 1$ movement between neighbouring levels is most probable.
• $h\nu = g\beta B$ condition of energetic fitting.

In practice, single paramagnetic probe never occurs, but only population of probes with many paramagnetic centers. If this configuration of probes is in thermodynamic equilibrium, statistical distribution is described by Boltzmann distribution.

2.1.3. Boltzmann distribution

$$\frac{n_{M_J+1}}{n_{M_J}} = \exp \left( -\frac{E_{M_J+1} - E_{M_J}}{kT} \right) = \exp \left( -\frac{\Delta E}{kT} \right)$$

where $n_{M_J+1}$ - number of probes on $n_{M_J}$ level

$k$ - Boltzmann constant

$T$ - temperature in Kelvin.

For X-band radiation ($\nu = 10 \text{ GHz}$) and at room temperature, $n_{M_J} = 0.998$. Because the lower level has more electrons than the higher one, transitions from the lower to the higher level are more probable. The fundamental equation in EPR theory is:

$$h\nu = g \times \beta \times B$$
EPR signals can be generated by resonant energy absorption measurements made at different electromagnetic radiation frequencies $\nu$ in a constant external magnetic field. Conversely, measurements can be provided by changing the magnetic field $B$ and using a constant frequency radiation; due to technical considerations, this second way is more common. In the case of clear spin magnetism ($g = 2.0$) and $\nu$ frequency, energy absorption occurs in magnetic field induction:

$$B = \frac{\nu[H_2]}{2.8 \times 10^{10}[T]}$$

For radiation at the commonly used frequency of 9.5 GHz (known as X-band microwave radiation, and thus giving rise to X-band spectra), resonance occurs at a magnetic field of about 0.34 Tesla (3400 Gauss).
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