1.Voc的概述和危害

Volatile organic compounds are organic chemicals that have a high vapor pressure at room temperature. VOCs are numerous, varied and ubiquitous. Among them aromatic compounds are widely distributed in the environment and have been found to be a significant cancer risk factor, and to be implicated in neurological problems in urban children. If inhaled or contacted, toluene can cause dermatitis (dry, red, cracked skin) and damage the nervous system and kidneys. Therefore, toluene emission control has become more stringent.

Volatile organic compounds are one of major air contaminants, which generally have a high vapor pressure (>0.1 mmHg) or low boiling point (<=250 ℃)(EUR-lex. Access to European law, 2004). Some VOCs are toxic at low concentration levels and cause adverse effects on human health (Rumchevet al., 2007). Moreover, VOCs can also react with nitrogen oxides (NOx) in atmosphere to form ozone (O3) and peroxyacetyl nitrate (PAN) with solar irradiation (Roberts, 1990; Ivanova et al., 2013), leading to environmental hazards. Besides, parts of VOCs are regarded as important odor-causing substances. Thus, how to effectively reduce VOCs emission has become an important issue. The effect of VOCs on the atmosphere depends on the nature of VOCs, their concentration, and emission sources. However, they have been identified as been responsible for stratospheric ozone depletion, tropospheric ozone formation, ground level smog formation, climate change, sick building syndrome, decay of plants, toxicity of the atmosphere, and carcinogenic effects in humans. As most countries have imposed strict conditions to limit VOCs in the environment, there are numerous research initiatives around the world developing efficient technologies to meet the stringent environment regulations.

VOCs are regarded as critical precursors for the potential formation of tropospheric ozone and photochemical smog.

Volatile organic compounds are those organic compounds with a Reid vapor pressure of over 10.3 Pa at normal temperature (293.15 K ) and pressure (101.325 kPa). The VOCs are a large group of carbon-based chemicals that easily evaporate at room temperature. VOCs are classified as major contributors to air pollution. They contribute both indirectly as ozone/smog precursors and directly as substances toxic to the environment.

Volatile organic compounds consist of a group of substances characterized by high vapor pressure at low temperatures. The definition covers a wide range of substances, from simple alkanes to polycyclic aromatic hydrocarbons, of which many are hazardous to the environment or human health due to their toxicity or cancero-/mutagenic properties.

Due to lot of industries, transports and residential area, the atmosphere is polluted every day with volatile organic compounds that are emitted. Although, the VOCs are present in very low concentrations, they have very serious health-related issues and bad environmental impacts because of their high vapor pressure, odor and toxicity.

Volatile organic compounds emitted from industrial processes are recognized as great contributors to air pollution and dangerous to human health.

Volatile organic compounds, as a large group of low boiling-point organic chemicals, are emitted from a great variety of sources, such as industrial processes, transports, house-hold activities and so on. Recently, the U.S. Environmental Protection Agency has recognized over 300 chemicals as VOCs which make major contributors to air pollution. Among them, the aromatic VOCs, including BTX, chlorobenzene and others, with high toxicity to human health and ‘carcinogenic-teratogenic’ effect, mainly come from industrial source. Thus, there is more increasingly strict legislation for stringent emission of industrial VOCs, causing the control technologies as a very important topic of research.

2.voc的来源

Natural sources of toluene are forest fires (incomplete combustion plants), volcanic eruptions and emissions from vegetation. These sources are minor compared with anthropogenic emissions from various oil conversion processes. Toluene emission results from the transformation of fossil fuels (oil, gas and coal). It is produced in combination with other substances (benzene, xylenes, etc.) as a result of various petrochemical processes such as catalytic reforming, steam cracking and dealkylation. Following petrochemical operations, the richest in toluene fractions will be distilled and purified to obtain pure trading toluene at 99%. Toluene is a constituent of unleaded gasoline and replaced tetramethyl lead in order to improve the octane rating. As a result toluene is emitted during the vaporization of gasoline (petrol, station, fuel transport and storage, etc.) and is present in vehicle exhaust gases (unburned products). Toluene is also found in industrial exhaust when used as a solvent or produced in the incineration processes.

Toluene is one of the important volatile organic compounds which are commonly applied in chemical processes. In addition to its wide application, toluene has high toxicity at a low concentration.

Volatile organic compounds are important environmental pollutants produced from refineries, fuel storage and loading operations, motor vehicles, solvent cleaning, printing and painting operations.

Rapid urbanization and industrialization contribute to the growing emissions of VOCs into the environment. Emission of VOCs can be from a wide range of outdoor and indoor sources. Outdoor sources include but are not limited to chemical industries, paper production, food processing, paint drying, transportation, petroleum refineries, automobile manufacturers, metal degreasing, textile manufacturers, electronic component plants, solvents, and cleaning products. Indoor sources include household products, office supplies, printers, heat-exchanger systems, insulating materials, pressed woods, wood stoves, and leaks from piping.

Human life is dependent upon different energy sources, among which carbonaceous fuels that still play a crucial role for the transportation and energy sectors. The fuels are combusted to …

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3. VOC的处理方法

Generally, the best way to reduce VOC emissions is to replace VOCs or to limit their use in industrial processes. If VOC substitution is not possible, it is necessary to control their emission in air using non-destructive or destructive methods. The first group includes adsorption, absorption and condensation. Absorption and condensation are very useful in recovering expensive solvents and operating at a large capacity, but they require high capital and operating costs. Adsorption is a reliable alternative to eliminate organic compounds from industrial waste gases because of the flexibility of the system, low energy requirements and low operation costs. The second group includes thermal and catalytic oxidation. Thermal oxidation, which requires high capital and operating costs, is the simplest method but it has to be carried out at high temperature typically over 1000 ℃. Also this method can generate harmful by-products such as dioxin and nitrogen oxides. In the case of toluene, control of its emission is often accomplished by catalytic oxidation or adsorption. Toluene removal by adsorption is the traditional method for cleaning air contaminants. However, the use of adsorbents just transfers pollutants from the gaseous phase to the solid phase and causes a disposal and regeneration problem. Catalytic oxidation is an attractive technique to selectively destroy this compound in CO2 and H2O. catalytic oxidation of toluene can be carried out at temperatures 200-600 ℃ lower than that for thermal oxidation and has high selectivity for the formation of harmless reaction products such as H2O and CO2.

Thermal catalysis is regarded as an effective way for VOCs removal because it provides oxidation route to successfully convert VOCs into carbon dioxide and water. Compared with other technologies such as adsorption, incineration, and absorption, thermal catalysis not only consumes less energy for maintaining high performance but also reveals high durability.

Catalytic oxidation seems to be a very promising VOCs control around technology. It is environmentally friendly as low temperatures (generally 250-500 ℃) are required, and is associated with less NOx formation compared to conventional thermal oxidation, which operates at much higher temperatures (650-1100 ℃).

The emission of VOCs can be controlled using methods based on recovery and destruction. The techniques based on recovery include absorption, adsorption, membrane separation, and condensation…. In the methods based on destruction, the VOCs are converted into carbon dioxide and water. The destruction processes can be thermal, catalytic, or biological oxidation. Thermal oxidation or thermal incineration is suitable for removing VOCs from flue gas streams with a high flow rate and a high concentration of VOCs. More than 99% of the VOCs can be burned by thermal oxidation, typically at high temperatures (>1000 ℃), which requires additional fuel and temperature resistant materials. Incomplete thermal combustion produces undesirable byproducts such as dioxins and carbon monoxide in the incinerator flue gas… Catalytic oxidation is one of the most effective and economically feasible techniques for the oxidation of VOCs into CO2, water, and other relatively less harmful compounds. The catalytic oxidation targets the complete destruction of VOCs rather than transferring it to another phase as in other techniques, such as in condensation and adsorption. In this approach, the VOCs are oxidized in presence of a suitable catalyst at much lower temperatures (250-500 ℃) than thermal oxidation processes. Catalytic combustion is a more thermally efficient process than the other non-catalytic thermal oxidation processes and can be used for dilute effluent stream of VOCs (< 1%). Furthermore, it can be more energy efficient if used in the recuperative mode, coupling with a heat exchanger after the catalytic combustion chamber…As catalytic oxidation is the most suitable for effluent streams with low concentration of VOCs, it is highly suitable for end-of-pipe VOCs pollution control. One of the main challenges of catalytic destruction of VOCs is the selection of the proper catalysts from the large number of available catalysts. Due to their wide variety and nature of the range of mixtures of VOCs, it is most often difficult to identify the best possible catalysts.

Many different procedures for VOC’s removal have been used, for example, combustion, adsorption, biotechnology, membrane separation, condensation and oxidation. From oxidation method, the catalytic oxidation is one of the most actively studied techniques, in this very technique, considerably high removal efficiencies can be obtained at room temperatures giving relatively high environmental and cost benefits in contrast to the traditional methods. Some traditional techniques cannot work at lower concentrations of VOCs, while catalytic oxidation proves to be more efficient for the lower levels of VOCs pollution (<1000 ppm).

Among those techniques, catalytic oxidation is regarded as the most promising method for VOC removal due to its higher efficiency, lower operating temperature, and generation of less secondary pollution.

Nowadays, several abatement technologies (adsorption, thermal oxidation, wet scrubbing, photocatalysis, catalytic oxidation, plasma oxidation and so forth) have been used to control the release of VOCs into environment. Among all the applied control technologies, catalytic oxidation is considered as the most efficient and economical way with harmless products (CO2 and H2O) and in relatively moderate conditions (at temperatures between 250 and 550 ℃) for a wide range of pollutants. Because of the dependence of the catalytic oxidation on catalysts, the search for catalytic materials with high activity, low cost and high tolerability is attracting much effort.

4.催化剂概述

Supported noble metal (pt, pd, rh) materials have been intensively examined in VOC catalytic combustion, but their limited availability and high price have encouraged their replacement by other active phases. Transition metal oxides have been found to be very active and present advantages over noble metals associated with their lower cost, high thermal stability and greater resistance to poisoning. The most active and selective transition metal-containing catalysts for VOC total oxidation are based on copper oxides.

Metal oxides including MnOx, CuO, Co3O4 and Fe2O3 have been applied as catalysts for removal of VOCs. However, they need to be operated at a high temperature (>350 ℃) for good performance in removing aromatic VOCs.

Metal oxides and supported noble metals have been examined as heterogeneous catalysts for VOCs oxidation. Common oxide carriers include alumina, titania, zirconia, zeolites and carbon based materials. Noble metal-based catalysts are very efficient, due to their high activity at low temperatures, in conjunction with their adequate stability. Platinum and palladium are also been investigated. Nevertheless, their high cost and low resistance to halogens, have turned the research interest toward the development of NM-free catalytic systems. Usual metal oxide based catalysts for oxidation reactions are: manganese oxides, copper oxide, nickel oxide, iron oxide, and cobalt oxide, among others. Although these metal oxides are more resistant to poisoning phenomena, they are, in general, less active for the oxidation of VOC containing streams than the supported precious metals. **However, mixed oxides, perovskites and cryptomelane type materials demonstrate adequate activity in VOCs oxidation processes. In particular, Cu-based oxides, such as CuO-CeO2 and CuO-Co3O4 exhibit excellent catalytic performance. This is mainly attributed to the synergistic interactions between the different counterparts toward enhancing the reactivity of surface oxygen species (catalyst reducibility). The latter is considered as one of the most important factors influencing VOC oxidation activity.** In addition, the lower cost of Cu, when compared to noble metals and commonly employed transition metals (such as Co and Ni) is of particular importance towards the development of low cost catalytic systems for practical applications. Despite the wide application range of Cu-based catalysts, there is no systematic study on the influence of the support nature on the redox properties and VOC oxidation performance….

Commonly used oxidation catalysts have a high content of expensive noble metals (pt, pd, rh) dispersed over oxide supports (e.g. ceria, alumina). The limited availability and fluctuating cost of these materials present a motivation to search for more earth-abundant catalytic components as substitutes. **Literature shows a wide spectrum of materials that have been tested in this regard, ranging from simple oxides, mixed oxides, and perovskites to spinels. Notably, the catalytic activity of these materials is often augmented by surface or bulk promotion with transition and alkali metals, but can also be functionalized with noble metals.**

Numerous catalysts have been developed for OVOC oxidation. Platinum and palladium catalysts display excellent catalytic performance in OVOC oxidation, whereas the drawback of high cost is an obvious limitation for their wide application. Transition metal oxides (M=Mn, Co, Cu, Fe) have also been explored, but partial oxidation byproducts are easily formed during the oxidation of OVOCs. Hence, it is still meaningful to design practical catalysts that exhibit high catalytic activity and avoid the generation of harmful byproducts. **In some reports, bimetallic catalysts have shown higher catalytic activity, selectivity, and stability than monometallic materials, due to synergistic effects. Xxx revealed the Au**-Ru synergistic effect in Au-Ru/TiO2-promoted methanol oxidation. Xxx reported Ag-M-ZSM-5-catalyzed ethyl acetate oxidation, ,where….ruthenium + copper

The catalysts based on noble metal, transition metal oxides and zeolite have been developed for oxidation of VOCs. Although noble metal catalysts show remarkable activity, the high expense and low reserves of precious metal elements can limit their widely practical application; moreover, they are always subjected to deactivation from chlorine poisoning during catalytic oxidation of chlorinated VOCs. The high activity of zeolites in removal of chlorinated VOCs is attributed to their acidic properties; however, this catalyst system would generate poly-chlorinated by-products, resulting in secondary pollution. compared to noble-metal catalysts and zeolite, the transition metal oxides have advantages in lower cost, better tolerability to poison, higher thermal stability and less secondary pollution, thereby attaching more and more attention. However, in most researches the catalysts are studied at ideal reaction conditions where exists only one kind of VOCs and the atmosphere is dry. In practice, the catalysts usually work at severe conditions containing complex mixture of gaseous contaminants and much moisture. Therefore, it is necessary to develop a robust transition-metal catalyst with high activity to remove different kinds of VOCs and high stability to resist various interferences at realistic reaction condition.

Up to now, the transition metal oxides and their composite oxides and supported noble metals have been reported to show good catalytic performance for the total oxidation of VOCs. Usually, the VOCs emitted from industrial sources contain several kinds of VOCs with different physicochemical properties, and the compositions and concentrations of VOCs depend on the emission sources. Therefore, an investigation on the catalytic removal of mixture of VOCs is more representative than that of single -component VOCs. However, few works in the literature have been addressed to the concurrent removal of mixed VOCs.

The activity of supported metal catalysts may be modified by presence of another active component. Modifiers are usually added to promote catalytic activity and enhance resistance to deactivation. At present, a lot of research on bimetallic catalysts used in VOC combustion concerns mainly Pt and Pd, and more recently Au. Over the last few years, some studies have also been focused on the catalysts with combination of a noble metal and a base metal oxides for VOCs oxidation reactions. For example, tungsten, vanadium and niobium oxides have been used and they are known to promote the activity of metal catalysts (Pd, Pt) for VOCs oxidation. It has been accepted that the positive promoting role of various modifiers for oxidation of alkanes, is generally attributed to a range of different factors, such as controlling the noble metal particle size, catalyst reducibility and metal oxidation state.

5.分子筛的概述

Usually, the active phase is supported on a porous material in order to expose their active phases in highly dispersed, easily reducible metal ions. Large pore zeolites are often chosen as supports because of their high specific surface area and acid-base properties, allowing high metal loading and generating specific interaction between the active phase and the support.

ZSM-5 modified with transition metal ions have become very interesting catalysts for a number of important applications. ZSM-5 can be used as hosts for transition metals that offer them base to act as efficient catalysts. The definite structure of ZSM-5 could limit the over growth or sintering of metal cations and keep them active. The structure, type of metal ion, and the location of metal ion in/on the structure are the major factors that control the catalytic activity. Many transition metals are under study these days, among them the cobalt showed high activity towards many applications. From the literature, it was found that the quantitative presence of cations like Na+, NH4+ along with Co possibly caused the reconstruction of Si-O-Al bonds, ultimately, affecting its acidity leading to be effective on activity. Therefore, the loading of transition metal definitely, changed the activity and stability of Co-ZSM-5.