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Review

Nature of active species in copper-based catalysts and their chemistry of transformation of nitrogen oxides

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Abstract

Copper-based catalysts are active in a wide range reactions of transformation of nitrogen oxides and represent an useful model system to better understand the fundamental aspects of the chemistry and mechanism of reaction of catalytic transformation of these pollutants. After an introduction on the reactivity of copper-based catalysts (supported and unsupported copper oxide, Cu-zeolites, cuprates and other copper compounds) in various reactions of conversion of nitrogen oxides, four main sub-topics are discussed in detail: (i) nature of copper species, (ii) chemisorption and surface transformations of NO, (iii) relationship between copper species and activity in the conversion of nitrogen oxides and (iv) mechanism of reduction of nitrogen oxides to N_2. Five reactions of transformation of nitrogen oxides are discussed in detail: (i) decomposition of NO, (ii) reduction of NO with ammonia in the presence or not of oxygen, (iii) reduction of NO with hydrocarbons in the presence of oxygen, (iv) reduction of NO with CO and (v) decomposition of N_2O. The mechanism of reduction of nitrite and N_2O by copper enzymes is also discussed, with a view to provide some useful insights on the chemistry of transformation. In this review particular attention is directed towards controversial points in the literature, underestimated questions, and hypothesis and theories which do not allow interpretation of all sets of experimental data. Discussion is also focused on the presence of multiple and competitive pathways of transformation, the relative roles of which depend on reaction conditions.

Keywords: Nitrogen oxides; NO_x; N_2O; NO reduction; Copper-based catalysts; Cu-zeolites; Cu/ZSM-5; Reaction mechanism; Chemisorption

Contents

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1. Introduction

The general term nitrogen oxides indicates the class of compounds of nitrogen and oxygen which includes N_2O, NO/N_2O_2, NO_2/N_2O_4, N_2O_3, N_2O_5 and NO_3 (unstable), where the/symbol shows compounds in reversible equilibrium. NO emissions in the lower atmosphere are caused principally by combustion processes in stationary or mobile sources. Especially in industrialized countries, the latter is responsible for up to 60% of global atmospheric NO emissions. In contact with air and light, NO readily transforms to NO_2. Both nitrogen oxides then give rise to a series of complex chemical/photochemical reactions in the upper atmosphere which result in the formation on the one hand of nitric/nitrous acid, which significantly contributes to *acid rain*, and on the other hand in the formation of *photo-*

chemical smog. NO itself is not an irritant, but can react with haemoglobin to form methaemoglobin [1]. In respect to its toxicity, the TLV-TWA value for NO is 25 ppm. NO_2, on the contrary, is an irritant gas and causes pulmonary edema and exudative inflammation [1]. Chronic exposure to low doses results in coughing, headache and gastrointestinal disorder. The TLV-TWA value for NO_2 is 3 ppm.

N_2O forms mainly via microbial action in soil, but significantly high N_2O emissions occur in several chemical processes (for example, up to 30–50% in adipic acid production) [2]. N_2O does not play a significant role in the troposphere, but contributes substantially to ozone depletion in the stratosphere as well as to the greenhouse effect [2–4]. N_2O does not irritate the mucous membrane and has a powerful analgesic action; however chronic exposure may cause polyneuropathy and myelopathy [1]. The TLV-TWA value for N_2O is 50 ppm.

Several approaches are possible to reduce nitrogen oxides emissions into the atmosphere from stationary or mobile sources, but the catalytic approach is the most effective to meet current and future requirements. An early patent on this topic goes back to 1924 by Fauser, but it is from the beginning of the 1960's that a great deal of research interest has been centred on the problem of the catalytic removal of nitrogen oxides. Current commercial catalytic systems are principally noble-metal based three-way catalysts for the purification of car emissions (gasoline engines) and vanadium-on-titania based catalysts for the control of stationary-source NO emissions by selective catalytic reduction (SCR) in the presence of ammonia [5–7].

In recent years, a great deal of research has also been centred on the study of copper-based catalysts for the conversion of nitrogen oxides, principally for the possibility of developing new technologies of direct decomposition of NO to $N_2 + O_2$ or of selective NO reduction with hydrocarbons in an oxygen-rich atmosphere [8–12]. Copper-containing catalysts (zeolite- and oxide-based samples) are active in a wider range of reactions of transformation of nitrogen oxides with respect to other catalytic systems. Copper is also the key component in the enzymes involved in the nitrogen cycle. Copper-based catalysts are thus an ideal model to understand the mechanism of transformation of nitrogen oxides because they give the opportunity to approach the problem from a multiplicity of points of view and to verify the validity of hypotheses and theories on analogous reactions and/or catalysts.

The scope of this review is to discuss and analyze critically the literature data on (i) the nature of copper species in supported copper oxides and copper ion-exchanged zeolites and (ii) the mechanistic aspects of the chemistry of interaction and transformation of nitrogen oxides over these catalysts. A comparison with the mechanism of action of copper-based enzymes in the transformations of nitrogen oxides is also given to evidence the several analogies between these enzymes and solid catalysts. Scope of the review is not to compare the reactivity of the various catalysts to indicate which samples show superior performances, but instead to discuss the properties of all copper-based catalysts in the transformation of nitrogen

oxides. In fact, a significative limit of several of the hypotheses present in literature is that they cannot be generalized to explain the behaviour of other samples. The possibility offered by copper-based catalysts to analyze the chemistry of transformation of nitrogen oxides from various perspectives (different, but homogeneous series of samples; reactions involving different nitrogen oxides or reducing agents; reactivity in the presence or not oxygen; comparison with the behaviour of analogous enzymes) is thus unique and may be very fruitful for the fundamental aim of a better understanding of the relationship between surface properties, reactivity and reaction mechanism.

2. Overview of the reactions of transformation of nitrogen oxides in which copper-based catalysts are active

2.1. Reduction of NO with or without reducing agents: background and overview

Interest in the activity of copper-based catalysts for the conversion of NO began around the end of the sixties [13–17]. At that time attention was focused on investigating possible alternative catalytic systems to those based on the use of noble metals for the purification of exhaust gas from gasoline engines. Supported copper oxides were found to have the highest activity among the tested transition metal oxides for the reduction of NO in the presence of CO [14]. Later, copper-exchanged zeolites (Y and X types) were also shown to have high activity in this reaction [18,19]. Several studies have been reported on the characterization of these copper-exchanged zeolite catalysts [18–31], but these studies were focused especially on the investigation of the redox changes in the reaction with CO, hydrocarbons, ammonia and H_2 and not on the activity in the conversion of NO.

The high activity of copper oxide in the reduction of NO with NH_3 in the presence of O_2 was also recognized early [32]. Later, copper-zeolites were also found to be highly active in this reaction. Partially Cu^{II}-exchanged Y-type zeolites [$Cu^{II}NaY$], in particular, were shown to exhibit excellent as well as unique catalytic activities [33–39]. The key feature of these catalysts is the presence of a reversible maximum in the activity at very low temperature (about 110°C) due to a reversible change in oxidation state of the copper. The low-temperature activity of this catalyst in the reduction of NO with NH_3 in the presence of O_2 is comparable to that of Pt-based catalysts [40], but for practical applications V_2O_5/TiO_2-based catalysts are preferable for the treatment of emissions from stationary sources due to their reduced sensitivity to poisoning and higher stability [7], albeit they are active at higher temperatures (usually in the 300–400°C range). It should be noted, however, that zeolite catalysts are commercialized for the reduction of NO with NH_3/O_2 [40,41] for particular high-temperature applications (above 400–450°C). Centi et al. [42] showed that Cu/ZSM-5 has a distinct advantage over V_2O_5/TiO_2 catalysts in terms of a reduced rate of the side reaction of ammonia oxidation.

The interest in copper-zeolites and especially Cu/ZSM-5 increased considerably as a result of the finding of Iwamoto et al. [43,44] of the superior activity of Cu/ZSM-5 in the direct decomposition of NO to $N_2 + O_2$ [43–48] in comparison with other copper ion-exchanged zeolites [49,50] or catalysts. Cu/ZSM-5 was found to be sensitive to poisoning by SO_2, H_2O and oxygen, decreasing the prospects for possible application. However, soon was discovered that the addition of hydrocarbons to the oxygen-rich feed leads to a drastic increase in the rate of the selective reduction of NO to N_2 [48,51,52]. This discovery opened the field of applications for these catalysts to the treatment of oxygen-rich exhaust gas from mobile sources such as those deriving from two-stroke or lean-burn gasoline engines or diesel engines. The presence of excess oxygen in these emissions limits the efficiency of current three-way noble-metal catalysts for the reduction of NO to N_2. Alternative catalytic systems thus appear to be attractive [8,9]. Noble metal-based, in fact, are active in the selective reduction of NO in the presence of excess oxygen [53–55], but show a very sharp maximum in the conversion of NO increasing the reaction temperature. Indeed, several unresolved problems limit the outlook for successful use of zeolites in automotive converters: (i) hydrothermal stability, (ii) sensitivity to poisoning, (iii) possibility of manufacturing suitable shapes with sufficient mechanical resistance to thermal stress and vibrations, (iv) high light-off temperature and limited temperature window, (v) possible formation of harmful byproducts, and (vi) necessity of post-engine hydrocarbon additions to reach the optimum hydrocarbon/NO ratio required to meet current and future legislative regulations on NO emissions. A low hydrothermal stability, in particular, is the more critical weakness of copper-containing zeolites.

Interesting possibilities are also offered by a combination of noble metals and copper. Pd–Cu have been shown to be able to combine both advantages [56], eliminating the necessity for the use of Rh in automotive converters. Copper-based catalysts were proposed for automotive exhaust purification [57], when a low level of sulphur in gasoline is present. Recent developments from the Toyota research group [58,59] have also indicated the fruitful combination of a nitrogen oxide storage component to a noble metal component ('NO_x storage–reduction catalysts'). These catalysts store NO_x under oxidized conditions and then reduce the stored NO_x to nitrogen under stoichiometric and reduced conditions. The new catalyst is claimed to have higher NO_x reduction activity in a wide temperature range. The NO_x storage capacity of alumina may be promoted by a component such as copper which forms stable nitrates and enhances their rate of formation. Pt/Cu on alumina catalysts thus are potential catalysts for this application. A Pt/Cu catalyst also was found to have superior activity at room temperature in the reduction of NO with CO in an aqueous acid solution [60], even though the practical relevance is questionable.

Various other metal-exchanged zeolites have been found to be active in the NO selective reduction by hydrocarbons/O_2 such as Ga/ZSM-5 [61,62], Co/ZSM-5 [63], Ce/ZSM-5 [64], Ga/ferrierite [65], Co/ferrierite [66] as well as the zeolite

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