Research Paper

A structure sensitivity approach to temperature programmed desorption

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ARTICLE INFO

ABSTRACT

A novel approach for explaining the effect of the metal cluster size on Temperature Programmed Desorption (TPD) from supported catalysts is described. Based on the assumption that metal clusters have regular cuboctahedral geometry, it was possible to develop a model that describes how three dimensional aspects of the metal clusters may affect the TPD profiles. Depending on the way that the metal clusters are assumed to be arranged in the surface, two different approaches are described to account for desorption. The first one, named Monocluster Model, considers a surface with a narrow cluster size distribution in which an average cluster diameter reasonably well describes the cluster population. A more complete approach, named Multicluster Model, explains desorption based on the cluster size distribution of the metal sites. TPD curves of ammonia from different platinum supported carbon materials were numerically treated and compared with the geometrical information obtained from Transition Electron Microscopy. The results displayed a reasonable agreement, indicating that TPD curves should be interpreted taking into account the metal cluster size.

1. Introduction

Structure sensitivity is an area within catalysis that investigates the effects of size and shape of supported metal clusters in the reaction rate, selectivity and deactivation of catalytic processes [1–5]. Since the early 1970′s, certain reactions involving hydrocarbons were found to be structure sensitivity while others were coined structure insensitive [6]. Advances in the characterization methods and especially widespread utilization of TEM in 1990–2000 s revived an interest for such intriguing phenomena.

An interesting aspect of structure sensitivity often overlooked is related to quantitative description of temperature programmed techniques applied for catalyst characterization. In such methods a certain process (e.g. desorption of pre-adsorbed species or their chemical reactions, reduction of a catalyst, oxidation of accumulated coke) is followed while temperature is increased linearly [7]. Temperature programmed desorption in particular (TPD) involves heating a sample with raising temperature and simultaneously detecting the released gas using a suitable device (e.g. mass spectrometer). At low T when the coverage is high and on the contrary the desorption rate constant is low, overall the desorption rate is low. With the temperature increase, the rate constant is increasing while the coverage is decreasing. At intermediate temperatures a maximum (or even maxima) in TPD curves is observed because both the coverage and the rate constant are high and thus the desorption rate is high as well. At higher T the coverage is virtually zero and the desorption rate is virtually zero despite a very high desorption

constant. The temperature of the peak maximum provides information on the binding energy. Quantitative analysis of TPD, namely determination of activation energy of desorption, is done [7] by conducting experiments at different heating rates followed by a theoretical treatment, which basis will be discussed below.

In the present work, TPD curves of ammonia over different platinum supported materials reported in [8] were evaluated conserving influence of structure sensitivity. The TPD signals were measured in terms of molar fraction of ammonia in the gas leaving the heating chamber. A more detailed description of the equipment, experimental procedure and materials can be found in [8].

In order to geometrically describe platinum nanoclusters, it is assumed that the metal atoms agglomerate in the form of regular cuboctahedral structures. According to van Santen and Neurock [9], FCC metals tend to acquire the cuboctahedron shape [10] allowing the minimum in energy. Since platinum is an FCC metal it will be considered below that all platinum is organized as cuboctahedrons even if in reality, a mixture of different structural patterns can be present on the surface (tetrahedral, cubes, rods, etc.) [11].

Cluster size dependence or structure sensitivity in heterogeneous catalysis namely turnover frequency (activity per exposed catalyst site) variations with the active phase dispersion were discussed by considering intrinsic differences in reactivity on edges, terraces and corners as responsible for the cluster size effect [12–14]. For a certain cluster geometry the ratio between different active sites changes with dispersion or cluster size allowing to incorporate the cluster dimension

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a	Lowest cluster order	n	Number of clusters used in the cluster size distribution [moles]
A	Pre-exponential factor [1/s]	$n^{(a)}$	Total number of clusters of ath order [moles]
β	Heating rate [K/s]	$\dot{n}_A$	Molar flow rate of A [moles/seconds]
Ea_i	Activation energy of desorption site of type i [J/mol]	$\dot{n}_T^G$	Molar flow rate of inert gas [moles/seconds]
$f^{(m)}$	Fraction of cluster of order m	n_T	Total number of clusters in the sample [moles]
θ_i	Coverage of site i	n_B	Total number of metal atoms B in the sample [moles]
k_i	Desorption rate consant of site of type i [s^{-1}]	p	Highest cluster order
MM_B	Molecular weight of metal B [g/mol]	P_0	Total pressure [Pa]
m_B	Mass of metal B in the catalyst sample [g]	Q	Objective function
m_{cat}	Mass of catalyst sample [g]	R	Ideal gas constant [8.314 J/mol/K]
N_A	Avogadro's constant [$6.022 \cdot 10^{23}$ molecules/mol]	R^2	Degree of explanation
$N_i^{(m)}$	Number of sites of type i in a cluster of order m [moles]	T	Absolute temperature [K]
$N_T^{(m)}$	Total number of atoms in a cluster of order m [moles]	T_0	Initial temperature of TPD experiment [K]
N_A^{ads}	Total moles of A adsorbed [moles]	t	Time [s]
$N_{A,i}^{ads}$	Moles of A adsorbed in site of type i [moles]	wt_B	Metal loading in the catalyst sample
N_A^G	Moles of A in the gas phase [moles]	x_A	Mole fraction of a in the gas phase
$N_{i,T}$	Total number of sites of type i in the sample [moles]	x_A^{exp}	Experimental mole fraction of a in the gas phase
		$\dot{V}$	Volumetric flow rate [m^3/s]

directly into the rate equations.

An alternative approach to treat structure sensitivity was utilized in [15] when turnover frequency (TOF) dependence on the cluster size was presented as a sum over contributions of TOF of terraces, steps and corners with the corresponding fractions of them varying with the cluster size.

The aim of the current work is to develop a deterministic model that explains the structure sensitivity by means of a detailed geometric description of the metal clusters, as an attempt to model the complexity of the surface statistics and its effect on the observed behaviour in TPD experiments. This in the future can be expanded for other structure sensitivity related phenomena such as calorimetry, catalyst deactivation, temperature programmed reactions, etc.

2. Geometrical considerations

Metal nanoclusters have a variety of geometries, depending on a number of factors, including the metal species, the oxidation state, the preparation method and temperature. The ability to control and fine-tune the clusters geometrical arrangements have been extensively investigated by a number of research groups [16,17]. Even though a high degree of organization is observed in certain metal clusters, in general the entire cluster population does not follow an exactly the same geometrical pattern. Therefore, in the considerations below for the sake of simplicity the cluster population was limited to regular cuboctahedrons.

According to Semagina and Kiwi-Minsker [16], transition metal nanonspheres tend to form cuboctahedrons clusters, with their surfaces being constituted by a mixture of (100) and (111) facets, as shown in Fig. 1.

Five different types of atomic arrangements are distinguished in the surface of a regular cuboctahedron, according to local differences in the number and orientation of their nearest neighbour atoms. Generally, one could classify these five different atomic arrangements in three types: corner, edge and terrace atoms, as summarized in Table 1.

Corner and edge atoms are commonly referred to as defect atoms because they are situated at the boundaries of plane regular regions, which are constituted of terrace atoms. Structure sensitivity is often related to different reactivity of corner, edge and terrace atoms [12–15]. The number of different surface atoms in a metal cluster can be related to the cluster order m, or the number of atoms lying on an equivalent edge, including corner atoms, following [18]:

$$N_1^{(m)} = 24 \tag{1}$$

$$N_2^{(m)} = 12(m-2) \tag{2}$$

$$N_3^{(m)} = 24(m-2) \tag{3}$$

$$N_4^{(m)} = 6(m-2)^2 \tag{4}$$

$$N_5^{(m)} = 8(3m^2 - 9m + 7) \tag{5}$$

where $N_i^{(m)}$ indicates the number of atoms of type i (Table 1) in a cluster of order m. According to Eqs. (1)–(5), the cluster order can only assume integer values equal or higher than 2 [16,18]. In addition, the total number of atoms in a cubo-octahedral cluster of order m is

$$N_T^{(m)} = 16m^3 - 33m^2 + 24m - 6 \tag{6}$$

The cluster diameter/size can be estimated from $N_T^{(m)}$ by the following relation [16]:

$$d_{sph} = d_M \cdot 1.105(N_T^{(m)})^{1/3} \tag{7}$$

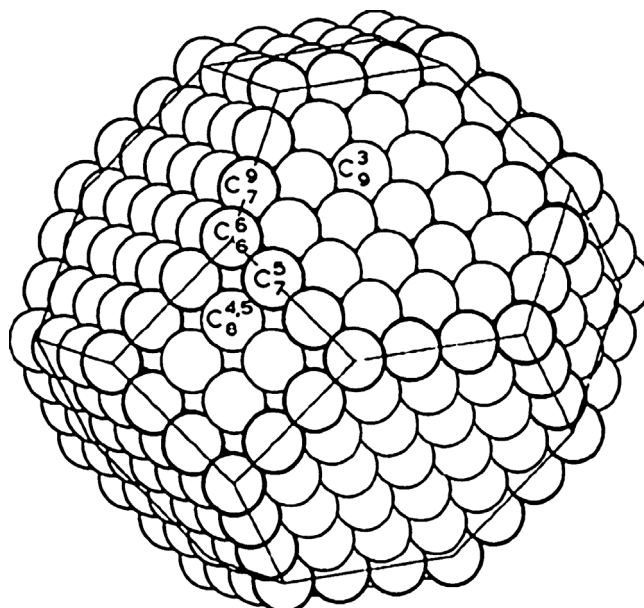where d_M is the metal atomic distance. Alternatively, the cluster

Fig. 1. Cuboctahedral structure with its 5 different atomic arrangements indicated [16,18]. Reproduced with permission.