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Short review

Surface science perspective of carbon dioxide chemistry—Adsorption kinetics and dynamics of CO_2 on selected model surfaces

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ABSTRACT

The adsorption or formation of CO_2 on surfaces is important in a variety of industrial and environmental applications such as methanol synthesis, exhaust cleaning, CO_2 capturing/sequestering, fuel cell poisoning, fuel synthesis, etc. For most of these processes, a deeper understanding of the kinetics and dynamics of CO_2 adsorption on surfaces could help to optimize the performance of catalysts. Historically, most surface science studies have focused on CO rather than CO_2 as the probe molecule, i.e., fundamental knowledge about CO_2 adsorption is still needed. This paper will focus on summarizing a few fundamental properties of CO_2 adsorption on a number of selected model systems recently studied in our group. In particular, metals (Cu, Cr) and metal oxide (ZnO, TiO_2, CaO) single crystals as well as so-called model catalysts (Cu-on-ZnO, Zn-on-Cu) and nanocatalysts will be considered. The similarities and differences between metals and metal oxides will be highlighted as well as the effect of surface defects. An attempt to tie the different systems together by proposing structure–activity relationships rules will be made. Kinetics experiments and molecular beam scattering data are summarized, some of which have been modeled by Monte Carlo simulations and density function theory.

1. Introduction

What motivates a physicist, trained in traditional experimental surface science, to study CO_2 chemistry? Historically [1], surface science focused on metal single-crystal surfaces using CO as the probe molecule to gain a deeper understanding of the electronic, vibration, kinetic, and dynamic properties of surfaces. Well, CO_2 may be the next more complicated probe molecule. In addition to this pragmatic view (gaining better knowhow through the collection of larger data sets), there are numerous important applications that could stem from a deeper mechanistic understanding of the interaction of CO_2 with various surfaces. (1) Disregarding an initial controversy, the main source of carbon in the synthesis of methanol (MeOH) from syngas is CO_2 [2,3]. Thus, the adsorption of CO_2 on the catalyst surface is the first elementary reaction step in the sequence of hydrogenation reactions that lead finally to the formation of MeOH (Fig. 1). MeOH, obtained by utilizing CO_2, is an important feedstock in the chemical industry and can also be directly used as a fuel in direct liquid fuel cells. Recycling the greenhouse gas CO_2 from the atmosphere to build an economy based on MeOH has been proposed [4]. As a realistic model system for MeOH synthesis, the adsorption of CO_2 has been studied on clean ZnO single-crystal surfaces [5,6] as well as on Cu nanoparticles deposited on ZnO (Cu-on-ZnO) [7,8] by a variety of groups since industrially (among other systems) ternary ZnO-Al_2O_3-Cu powder catalysts are used. Our results (mostly kinetics and molecular beam scattering experiments) [5] are summarized in Section 4.2. Studying the effect of hydrogen and CO_2 coadsorption is the next logical step [9,10] (see Section 4.2.2). A related model system is bimetallic surfaces. Thus, Section 3 will discuss the work done on copper single crystals, and Section 5 considers ZnCu surface alloys using CO_2 as the probe molecule [11–13]. Alloy sites have been considered as the active sites in the synthesis of methanol. (2) Closely related to the venue of this conference is the geological sequestration of CO_2 as well as its capture in the exhaust gas of power plants (Fig. 2). Ca is used for the latter; and an interesting class of minerals, perhaps suitable for CO_2 sequestration, consists of Ca compounds [14]. Section 4.3 will summarize our studies of CO_2 adsorption on CaO(1 0 0) surfaces [15]. Regarding metal oxides, the effect of surface defects (oxygen vacancy sites) as well as the formation of surface carbonates are interesting mechanistic details. CaO is an excellent model system in this regard. A variety of further applications for CaO are known, including catalytic gasification of Ca-containing coal [16,17], NO storage catalysts used for operating combustion engines at lean (oxygen-rich) conditions with alkaline-earth oxides as promising catalysts, the capture of SO_2 by CaO [16], the dimerization of, for example, methane [18], the reduction of NO by CO [19], and the

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Symbols and acronyms

SAR	structure–activity relationships
HAS	He atom scattering
AES	Auger electron spectroscopy
CNTs	carbon NT
DFT	density functional theory
FTIR	Fourier-transform infrared spectroscopy
HREELS	high-resolution electron energy loss spectroscopy
HOPG	highly oriented pyrolytic graphite
LEED	low-energy electron diffraction
MCS	Monte Carlo simulations
MIES	metastable impact electron spectroscopy
NEXAFS	X-ray absorption fine structure
NT	nanotubes
STM	scanning tunneling microscopy
TDS	thermal desorption spectroscopy
TiNTs	TiO_2 NT, inorganic NT
UPS	UV photoelectron spectroscopy
UHV	ultra-high vacuum
UV	ultra violet
XPS	X-ray photoelectron spectroscopy
T_s	adsorption temperature
α_i	impact angle
S_0	initial adsorption temperature
E_i	impact energy
Θ	coverage, surface particle density
$S(\Theta)$	coverage dependent adsorption probability

decomposition of chlorinated hydrocarbons [20]. For the decomposition of NO, CaO has been considered as a less expensive catalyst than systems based on noble metals [21]. Some work conducted on the prototype of a metal oxide, rutile TiO_2(1 0 0), will be summarized for completeness in Section 4.1; this discussion focuses on CO_2 adsorption [22,23]. (3) CO_2 is generated in the combustion of coal, which often includes inorganic impurities such as Ca and Fe (Fig. 3). Section 6.2 will discuss kinetics studies about CO_2 adsorption on Fe-oxide nanoparticles supported on HOPG as a model system for particulate matter that is released in the plume of coal combustion plants [24,25].

In addition to applications, as one motivation, surface science research on CO_2 aimed to address fundamental questions such as the following: (1) What are the fundamental differences in the catalysis of metal and metal oxide surfaces? How well can more complex surfaces be understood? (2) How do the adsorption kinetics and dynamics change when we go from a metal surface to a related metal oxide film [26]? (3) Is the adsorption kinetics

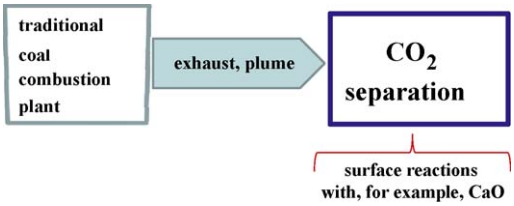

Fig. 2. CO_2 capturing.

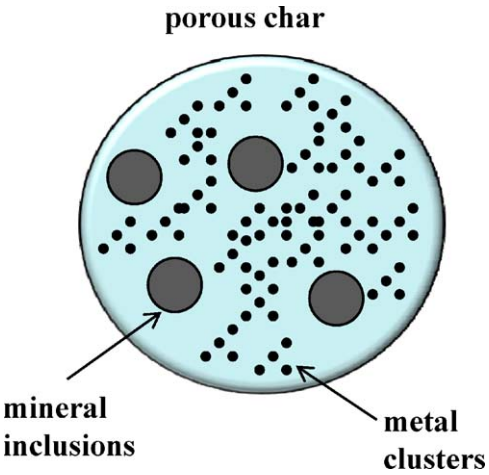

Fig. 3. Coal particle with inorganic impurities.

correlated in a simple way to the adsorption dynamics (gas-surface energy transfer processes)? For example, CO_2 binding energies on oxides are typically larger than for metal surfaces. What about adsorption probabilities governed by gas-surface energy transfer processes? (4) Oxide surfaces consist of very characteristic defects such as oxygen vacancy sites. How is the catalytic activity affected by these defects? Can we tune the reactivity of metal oxide surfaces by varying the defect density? Can these (model) defects serve to better understand powder catalysts or nanoparticles that have a large defect density? (5) How does the oxidation state of a system such as FeO_x affect the kinetics/dynamics of surface reactions? (6) How does the size (and shape) of supported metal (metal oxide) clusters relate to chemical activity? Again, a deeper understanding of the mechanism would allow for catalyst tuning, etc.

This mini review will mainly summarize the work done in 2004–09 at NDSU on CO_2 chemistry using molecular beam scattering and traditional kinetics techniques. Metal single crystals (Section 2), metal oxide films (Section 3) and single crystals (Section 4), bimetallic surfaces (Section 5), and nanostructured catalysts (Section 6) will be considered. The obtained results are discussed along with studies from other groups; however, due to

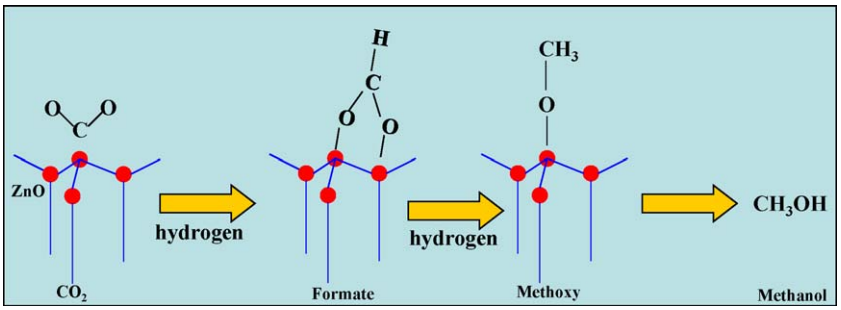

Fig. 1. Simplified reaction schematics for the synthesis of methanol [117].