A MECHANISM OF ETHENE HYDROGENATION OVER ZrO₂ STUDIED BY INFRARED SPECTROSCOPY

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Received 18 June 1993; accepted 6 July 1993

Abstract—Ethene hydrogenation, one of the most fundamental and well investigated heterogeneous catalytic reactions, on ZrO₂ has been studied by transmission infrared spectroscopy and herewith reviewed. Several key adsorbed species were identified during the reaction from ethene to ethane at low temperatures. The reaction mechanisms were examined based on the observed species.

INTRODUCTION

The mechanism for the hydrogenation of unsaturated hydrocarbons, especially ethene, have attracted a great deal of interest and have been investigated as one of the most fundamental catalytic reactions for several decades [1-3]. In the 1930's, several mechanisms for ethene hydrogenation were already proposed [4-6]. These were based on the results of isotopic and kinetic studies. In the 1960's, infrared (IR) spectroscopy, pioneered by Eischens, was employed to directly observe adsorbed species arising from ethene adsorption and hydrogenation over supported metal catalysts [2,3]. These IR studies seemed to support the mechanism proposed by Horiuti and Polanyi [4] described as follows,

\[
\begin{align*}
\text{C}_2\text{H}_4 & \xrightarrow{\text{M}} \text{CH}_2\text{CH}_2\\
\text{H}_2 & \xrightarrow{2 \text{M}} \text{CH}_3\text{CH}_2\text{M}\\
\end{align*}
\]

where M represents a metal atom. In this mechanism or in general, the alkyl intermediate was postulated during the olefin hydrogenation over metal catalysts.
Recent progress in surface science techniques has led to a reconsideration of the reaction mechanism of olefin hydrogenation on clean and well-defined metal surfaces. Vibrational studies such as high resolution electron energy loss spectroscopy (HREELS) and IR reflection absorption spectroscopy (IRAS) have enabled the direct observation of adsorbed species on metal surfaces. Ethene adsorbed on clean metal surfaces has been examined by HREELS [11-12] and by IRAS [13-15], coupled with low-energy electron diffraction (LEED). The observed species are π-bonded [6], di-σ-bonded [3] ones and/or ethyldyne [15] (M represents a metal atom).

\[
\begin{align*}
\text{CH}_2 &= \text{CH}_2 & \text{CH}_2 - \text{CH}_2 & \text{CH}_3 \\
&\downarrow M & / \downarrow M & | C \downarrow M \\
&\text{M} & \text{M} & \text{M} \\
\end{align*}
\]

π-bonded, di-σ-bonded ethyldene

These same adsorbed species that appear on ordered metal single crystal surfaces have also been observed on supported metals by transmission IR spectroscopy [17-27]. Although ethyldyne is the most stable species derived from ethene adsorption on many metal surfaces [11], it has been concluded that ethyldyne does not act as the direct intermediate during ethene hydrogenation [20,28-30]. In recent years, Madix et al. [7-10] have investigated olefin hydrogenation and the H-D exchange reaction of H(or D)-covered Fe(100) surface with olefins mainly by means of temperature-programmed reaction spectroscopy (TPRS). They observed the evolution of H2, HD, D2, ethene (d0-d4) and trace amounts of ethane with no ethene decomposition during TPRS from the C2H4 + D-Fe(100) reaction. On the basis of the existence of an exchange reaction of ethene with preadsorbed hydrogen they explained the reversible formation of the ethyl group. The observed ethyl species, however, was not necessarily regarded as the intermediate for hydrogenation as will be mentioned below. Actually, they did not observe ethane production in their experiments. High-pressure reactions over single-crystal metal surfaces have also been investigated relating the accumulated knowledge of adsorbates on well-defined surfaces to the practical use of supported catalysts [31]. The reaction kinetics and post reaction surface analysis over single-crystal metal surfaces have already been studied [28,22-36]. Among these, Backman and Masel detected ethyldyne and the ethyl species after high-pressure ethene hydrogenation at 298 K over Pt(111) by HREELS. The ethyl species disappeared with introduction of H2 onto the surface while the ethyldyne remained. They concluded that the ethyldyne was merely a spectator while the ethyl radical was the reactive intermediate. In this way, surface ethyl groups were now regarded as being the intermediates for ethene hydrogenation over metals.

The activity of metal oxides for olefin hydrogenation was first examined by Burwell et al. over Cr2O3 [37-41] followed by those over Al2O3 [42-44], ZnO [45-52], and other metals [53]. Subsequently, the mechanism of olefin hydrogenation over other nonmetals