A Novel Method for Measuring Active Sites of Fe_3O_4 for WGS Reaction

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Introduction

The measurement of active sites on the catalyst surface is of great importance as it reveals the features of the catalyst and relates to the catalytic performance. Chemisorption of a suitable adsorbate on catalyst surface is the conventional route used for these measurements.

Magnetite (Fe_3O_4) is the well known active phase of iron oxide-based catalysts in high temperature shift reactions. Nitric oxide (NO) was reported to adsorb on Fe_3O_4 in one-to-one correspondence with the surface iron cations [1]. NO adsorption on Fe_3O_4 is dependent on sample pretreatment. Extended evacuation causes reduction of the magnetite surface and results in excessive NO uptakes. Chemisorption of NO at 273 K and evacuation for 0.5 h were shown to yield an NO uptake equal to the N_2 uptake in the BET monolayer [2]. NO adsorption is useful for the measurement of the magnetite surface area, however, it does not selectively titrate the active sites for WGS reactions. It was reported that adsorption of CO and CO_2 from a CO_2/CO mixture could be used as a probe to identify the anion-cation pair-sites on the magnetite surface [3].

In this communication, a new method for measuring active sites on a magnetite surface for WGS reactions is revealed. A concept similar to that used for the measuring Cu surface area [4] wherein the decomposition of nitrous oxide (N_2O) on metallic Cu is used to measure Cu surface area was used to measure the active sites as the activated magnetite surface.

Materials and Methods

Iron oxide precursors (magnetite, maghemite and hematite) were prepared with ferrous nitrate and sodium hydroxide solutions. One reference magnetite sample was purchased from Aldrich. Iron oxides were reduced at 385 °C with $5\%H_2+2\%H_2O$ in N_2 for 1 hour. The reduced samples were flushed with He followed by cooling down to designated N_2O decomposition temperature.

A pulse chromatographic method was employed for the study of N_2O decomposition. The experiment was performed with a modified AMI-90 Catalyst Characterization System (ZETON ALTAMIRA).

Results and Discussion

TPR profiles indicated that γ-Fe_2O_3 and α-Fe_2O_3 were completely converted to Fe_3O_4 at <365 °C and <385 °C with $5\%H_2$ in N_2, respectively. To ensure that the iron was in the Fe_3O_4 phase, iron oxides used in this study were reduced at 385 °C with $5\%H_2+2\%H_2O$ in N_2 followed by He flushing at the same temperature.

The pulse chromatographic experiments showed that there was no decomposition of N_2O over unreduced Fe_2O_3 (pretreated at 385 °C with He). N_2O decomposition was observed over Fe_3O_4 that was obtained by reduction of Fe_2O_3 (Table 1). At 30 °C the combined consumption of N_2O (second to sixth pulse) was less than 5% of that in the first pulse. This implies that decomposition of N_2O on Fe_3O_4 surface is rapid.

The decomposition of N_2O on Fe_3O_4 surface is tentatively proposed as an equation:

$$N_2O(g) + 2(Fe_3O_4)_s \rightarrow N_2\ (g)+ [Fe_2^{3+} Fe^{2+}O_4]_s\ [Fe_2^{3+}Fe^{2+}O_4]_s \quad \ldots\ldots\ldots (1)$$
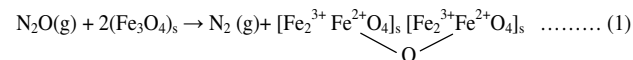
Symbol "g" and subscribe "s" signify gas phases and surface atoms, respectively.

An average Fe atom density of 9.8×10^{18}/m^2 on Fe_3O_4 surface [1] is assumed. If it is assumed that Fe atoms with different coordination are present on Fe_3O_4 surface evenly, an oxygen coverage on the active sites $\theta=1$ will correspond to a surface stoichiometry of $Fe/N_2O=6$. Based on this definition, the θ obtained from this study is listed in table 1.

Table 1. Effect of temperature on N_2O decomposition

Temperature (°C)	30	50	70	90	110	130
N ($\times10^{-2}$ mmol/g)	8.65	9.02	9.26	9.45	10.3	16.4
θ, oxygen coverage	0.96	0.99	1.02	1.04	1.14	1.81

θ: oxygen coverage on active sites, see text.

There was insignificant N_2O decomposition in the second and subsequent pulses at temperature below 90 °C. At 110 °C and 130 °C the combined N_2O decomposition in the second and subsequent pulses was more than 10% and 30% of that decomposed in the first pulse. This implies that oxidation of bulk Fe_3O_4 probably occurred at those high temperatures.

It is commonly accepted that WGS reaction over Fe-Cr catalysts predominantly follows the regeneration mechanism. The catalyst surface undergoes successive oxidation and reduction cycles by H_2O and CO to produce H_2 and CO_2 respectively, with Fe^{3+} and Fe^{2+} occupying the octahedral sites in the magnetite structure constituting a "redox" pair [5]. Therefore, the sites on Fe_3O_4 surface that decompose N_2O by capturing the oxygen atom are the active sites for WGS reactions.

N_2O decomposition on magnetite surface was also studied on the Fe_3O_4 obtained from different precursors. Attempts will be made to correlate WGS activity with active sites on Fe_3O_4 surface measured by the N_2O decomposition method.

Significance

An adequate and practical method for measurement of active sites on Fe_3O_4 surface for WGS reactions was developed.

References

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