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In situ DRIFTS studies of high-temperature water-gas shift reaction on chromium-free iron oxide catalysts

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ABSTRACT

The identification of reaction surface intermediates in the high-temperature water-gas shift reaction on iron oxide unpromoted and promoted MgO, SiO_2 and TiO_2 has been studied via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The dosing of the gas mixture $CO + H_2O$ onto reduced Fe_2O_3/MgO as a function of reaction temperature produced formate species (1720, 1630 and 1370 cm^{-1}) as a surface intermediate. On reduced Fe_2O_3/TiO_2 only bands characteristic of carbonate species (1630 and 1550 cm^{-1}) are observed. A direct correlation between catalytic activity and acid/base properties of our catalysts is established. The Fe_2O_3/MgO basic catalyst is 100 times more active than the acidic catalyst Fe_2O_3/SiO_2.

RÉSUMÉ

L'identification des intermédiaires de surface en réaction de conversion du gaz à l'eau, dans le domaine des hautes températures, sur l'oxyde de fer seul et supporté par MgO, SiO_2 et TiO_2 a été étudiée par spectroscopie infrarouge en réflexion diffuse (DRIFTS). Le dosage de Fe_2O_3/MgO par le mélange gazeux $CO + H_2O$ en fonction de la température de réaction alimente la surface en espèces formiates (1720, 1630 et 1370 cm^{-1}). Sur le système Fe_2O_3/TiO_2, seules les bandes caractéristiques des espèces carbonates (1630 et 1550 cm^{-1}) sont observées. Une corrélation directe entre l'activité catalytique et les propriétés acido-basiques est établie. Le catalyseur basique Fe_2O_3/MgO est 100 fois plus actif que le catalyseur acide Fe_2O_3/SiO_2.

1. Introduction

The water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is generally operated according to a two-step process, namely at high (HTS, 350-450 °C) and low (LTS, 250–300 °C) temperatures, over two main types of catalysts, Fe-Cr and Cu-Zn systems, respectively. Iron oxide based HTS catalysts, Fe_3O_4 [1,2] or Fe_2O_3 [3], are generally doped with Cr_2O_3 [4–7]. The recognized role of chromium is preventing iron oxide from sintering as well as catalyzing the WGS reaction. However, catalysts based on Fe-Cr-O have ecological and safety problems linked to chromium compounds. For this reason, development of chromium-free iron-based catalysts with high HTS performance is suitable [3,8,9].

The WGS reaction is thought to occur principally through two main types of mechanisms, the regenerative or redox mechanism [1,10] and the associative mechanism

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[1]. In the regenerative mechanism the catalyst surface is successively oxidized by H_2O and reduced by CO. In turn, the associative mechanism assumes that CO and H_2O interact to form a reaction intermediate, such as an adsorbed formate species, which then decomposes to CO_2 and H_2. It was found by Rethwisch and Dumesic [1] that Fe_3O_4 catalyzed the water-gas shift reaction via the regenerative mechanism while $MgFe_2O_4$, ZnO, MgO, TiO_2, SiO_2 catalyzed the water-gas shift reaction mainly via the associative mechanism. It was also established that basic oxides were more active than acidic or amphoprotic ones. This can be related to the weaker metal-oxygen bonding in basic oxides.

The associative mechanism generally considers a kind of bifunctional sequence with a specific role of metal and support. Thus, the formate can form from the surface reaction of CO bonded to the metal with OH groups located at the metal-support interface, as follows: $CO_{ad} + OH_{ad} \rightarrow HCOO_{ad}$. The formate bonded on the metal then spills over to the support where it decomposes to CO_2 and H_2 [11].

In the present paper, we give the effect of the acid/base properties of various supports on chromium-free iron-based catalyst in the WGS Reaction. Besides the determination of catalytic activity and acid/base properties, catalysts were subjected to in situ DRIFT measurements in order to obtain the type of active sites and the part of these interfaces in the water gas shift reaction.

2. Experimental

2.1. Catalysts preparation

Fe_2O_3/SiO_2, Fe_2O_3/TiO_2 and Fe_2O_3/MgO systems were prepared by the incipient wetness impregnation method. The 30 wt.% Fe_2O_3/support catalysts were prepared by impregnation of SiO_2, TiO_2 or MgO with an appropriate concentration of $Fe(NO_3)_3.9\ H_2O$. After drying at 80 °C overnight, the resulting solid was calcined in air at 400 °C for 2.5 h [12].

Bulk Fe_2O_3 catalyst was synthesized by the co-precipitation method. The starting reagents of high purity $FeSO_4.7\ H_2O$ and $Fe_2(SO_4)_3.5\ H_2O$ with a molar ratio (1/1) were dissolved in water to which 100 mL of NH_4OH was added as a precipitant agent. The mixture was vigorously stirred for 30 min. The resulting powder was washed several times with deionized water, and dried at 110 °C. Subsequently, the powder was calcined at 400 °C in air (33 mL/min) with a rate of 5 °C/mn for 2.5 h [9].

2.2. Apparatus and procedure

X-ray powder diffraction patterns were obtained with a Philips PW 1050/81 automated powder goniometer, equipped with diffracted-beam graphite monochromatic Cu (K_α) radiation.

H_2- TPR profiles were determined using a laboratory-made apparatus equipped with a TCD detector. The catalyst sample (200 mg) was loaded into a U-shape quartz reactor, then heated at 200 °C under argon flow with a rate of 5 °C/min for 1 h and cooled to room temperature. Next, the sample was submitted to a flow of 5% H_2/Ar from room temperature to 800 °C. A cold trap was placed downstream of the sample to capture any water that evolved from catalyst prior to entering the TCD detector.

Catalysts were tested under atmospheric pressure between 350 and 450 °C after being activated in situ under a flow of 48% H_2/N_2 using an amount of catalyst of 250 mg for all runs. After reduction, the reacting gases (H_2O/CO = 4.4) were introduced into the reactor at a total flow rate of 33 mL/min. Before each analysis, the effluent passed through a water-trap at 0 °C to remove the water of the reaction. The gas composition was analyzed by a TCD chromatograph containing two 4 m carbosieve B columns (1/8 inch, 100 to 200 meshes).

In situ DRIFT studies were performed on a Nicolet Magna IRTF spectrometer with OMNIC software. The reaction was performed in a high temperature Spectra-tech cell equipped with a ZnSe window. The sample (~50 mg) was first treated in a flow of (~35 mL/min) H_2 at 400 °C for 30 min (high-temperature treatment) before each experiment. The heating rate during the treatment was 10 °C/min. After this treatment, the sample was cooled under He and then put in contact with the reacting mixture CO/H_2O at increasing temperature (25–450 °C). Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were recorded with co-addition of 64 scans in single-beam spectra or absorbance spectra, by applying a resolution of $4\ cm^{-1}$.

3. Results and discussion

3.1. XRD and H_2- TPR measurements

The X-ray phases of Fe_2O_3-only and Fe_2O_3-promoted freshly calcined samples are given in Table 1. α-Fe_2O_3 hematite is the mainly crystalline phase in Fe_2O_3, Fe_2O_3/SiO_2 and Fe_2O_3/TiO_2. For the system doped with MgO, at higher Fe_2O_3 loading (30 wt.%) the band characteristic of MgO decreased while new bands assigned to $MgFe_2O_4$ are formed [9]. This indicates that iron oxide is in strong interaction with MgO, leading to a mixed oxide formation.

H_2- TPR results of the four catalysts are reported in Fig. 1 and their peak maxima are summarized in Table 1. In all cases, three peaks of hydrogen consumption in a temperature range of 25–800 °C are observed [13,14]. For Fe_2O_3-only, the lower reduction temperature region (446 °C) of Fe_2O_3 is attributed to the reduction of Fe_2O_3 to Fe_3O_4 while the higher temperature region (606–684 °C) is credited to the reduction of Fe_3O_4 to FeO and Fe. The low temperature peaks of Fe_2O_3/TiO_2 and Fe_2O_3/MgO shifted to 340 and 368 °C respectively. On the other hand, MgO− promoted catalyst involved a shift of the reduction temperature to lower values as depicted in Fig. 1, curve c. XRD studies showed that $MgFe_2O_4$ crystalline phase is present in Fe_2O_3/MgO. Indeed, the presence of this phase improves the reducibility of Fe_2O_3/MgO. More detailed studies were reported elsewhere [9].