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Characterization of K-Fe/silicalite catalyst prepared via SMAI

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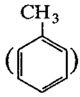
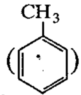
Highly dispersed supported metal catalyst K-Fe/silicalite are prepared via SMAI method, and characterized by TEM, XRD, XPS and magnetic measurements techniques. Its catalytic properties in the CO hydrogenation making olefin reaction are also studied. The results show that the iron on the surface of the catalyst which has superparamagnetism, almost existed as the Fe^0 before reacting. The catalyst exhibited high activity and selectivity for light olefins in $CO + H_2$.

Keywords: K-Fe/silicalite catalyst; SMAI; CO hydrogenation

1. Introduction

The solvated metal atom dispersion techniques used to prepare the supported catalyst as first developed by Klabunde, Ozin and their co-workers, had advantage over the classical ones [1,2]. However, the method made an amount of metal atom cluster and large metal particles were produced on the support surface, which were not easy to disperse to the pores of the catalyst supports. We improved the SMAD (Solvated Metal Atom Dispersion) method and designed the Solvated Metal Atom Impregnation method (SMAI), similar to the conventional impregnation. The sizes of the metal particles on the surface of the catalyst prepared by SMAI were below 2.5 nm [3].

Previously, we have shown that the pentasil zeolites indicated their unique characteristics as catalyst support for making light olefin from syngas, the pore structure of the zeolite products [4]. However they appeared as reduced incompletely, caused by the inferior dispersion of active components on the surface. By the SMAI method, the metal of the surface appears as atomic state, i.e. zero valence. In this paper, the silicalite is used as catalyst support. First, metal iron encounters with toluene gas, and produces ()$_n$ (Fe)$_x$ under liquid nitrogen. When silicate is introduced to the system at −78°C, ()$_n$ (Fe)$_y$/silicalite is prepared. Furthermore, when toluene is removed under vacuum at room temperature, we obtain the catalyst Fe/silicalite. Using the same method, potassium is introduced. The above processes are performed in the Static Apparatus for Metal Atom Synthesis [3]. The contents of the active component iron and the promoter potassium are 7.0 wt% and 0.8 wt%, respectively, as determined by atomic adsorption spectroscopy.

2. Dispersion of iron metal particles

1. TEM

TEM techniques are used to observe the dispersiveness of iron particles on the catalyst surface. The photos are of iron particles on the catalyst surface and are amplified 5 million times for the statistics of iron particles. 442 and 220 particles on the surface have respectively been counted before and after the catalysts were used in CO hydrogenation. According to the limited diameter range of Fe particles, the percentage of various sized Fe particles in the total number of calculated Fe particles is indicated in fig. 1. The average diameter

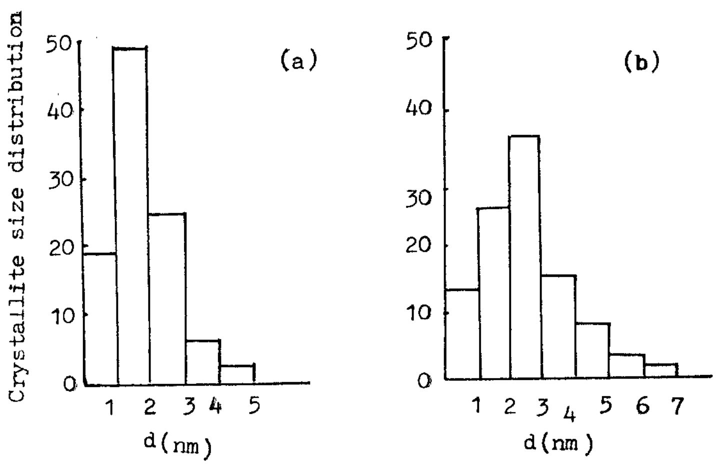


Fig. 1. Crystallite particles distribution on the surface in SMAI catalyst; a. before and b. after reacting.

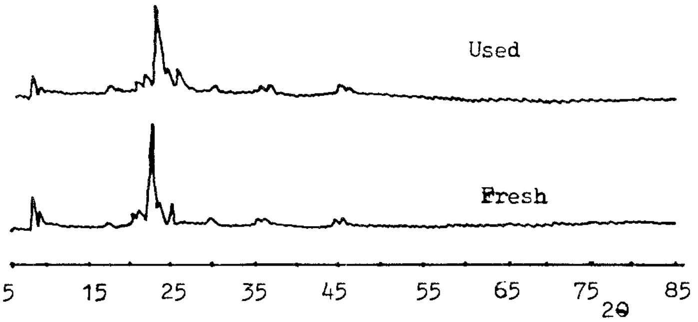


Fig. 2. XRD spectra of fresh and used SMAI catalysts.

$d_n = \Sigma n_i d_i / \Sigma n_i$. The crystallite particles are below 3.0 nm. The average diameters are 1.7 nm and 2.1 nm, before and after reacting, respectively.

2. XRD

The phases of the catalyst are distinguished using an XRD instrument (D/MAX-RA, CuK, 40 kV, 103 mA). The results indicate that there are only the diffraction special peaks of support silicalite on the XRD spectra of the fresh and used catalyst, and no diffraction peaks of iron crystallite or iron oxide particles (see fig. 2). Therefore it is proposed that the crystallites on the surface are below 3.0 nm, which is in agreement with the result of TEM.

3. MAGNETIC MEASUREMENTS

The magnetic susceptibility of the catalysts is measured by the Faraday Magnetic Balance in different magnetic fields under different temperatures. The relation between the ratio of the specific magnetizing moment σ and the saturation specific magnetizing moment σ_s, and the ratio of the magnetic intensity H and Kelvin temperature T, are illustrated in fig. 3. The σ/σ_s vs. H/T curve has shown that the σ/σ_s ratios overlap in a same curve under different temperatures, no matter whether the catalyst is fresh or used, σ/σ_s is independent of the temperature and indicated that the SMAI K-Fe/silicalite catalysts are superparamagnetic [5].

The average diameter of the iron particles at the surface of the SMAI catalysts, which are superparamagnetic materials or magnetic-ordered materials, are calculated using the low-field approximation of the Langevin function [6]:

$$d_{\mathrm{LF}} = \left(\frac{18\,k}{\pi I_s} \frac{\sigma}{\sigma_s} \frac{T}{H} \right)^{1/8},$$

here k is the Boltzmann constant and I_s is the spontaneous intensity of

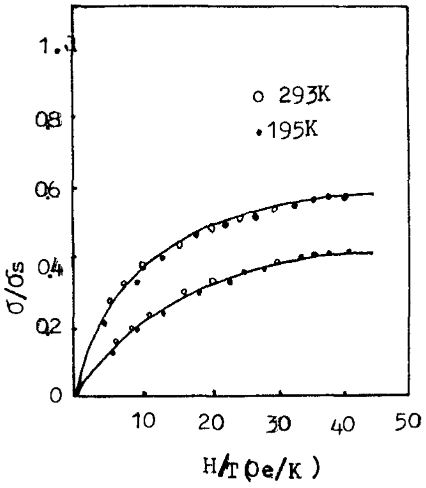


Fig. 3. $\sigma/\sigma_s - H/T$ curves of fresh and used catalysts.

magnetization. It is assumed that the value of I_s of various Fe particle sizes is constant 1707 Oe at room temperature. The average diameter of the iron particles has been calculated to be 2.2 nm and compared with the results of the TEM and XRD measurements in table 1.

4. XPS

XPS experiments are performed in a PHI-5300 ESCA spectrometer using monochromatic MgK_α radiation. The base pressure of the instrument is 10^{-8} Torr. The $Fe_{2p3/2}$ XPS spectra of K-Fe/silicalite treated by a special process of 2 minutes ion sputtering or not, are shown in fig. 4. The binding energy of the Fe lines are 706.9 eV, 711.5 eV and 708.8 eV, respectively, which suggested that Fe^0, Fe_2O_3 and FeO existed on the surface of the catalysts. After the catalyst is ion sputtered, the proportion of the Fe^0 phase on the surface of the SMIA catalyst rises greatly. This suggests that Fe^0 particles are covered by a thin oxide skin caused by micro-oxygen in high-purity nitrogen, which are removed by ion sputtering and easily by H_2 reduction before CO and H_2 mixture gas is

Table 1
Comparison of Fe average particle diameters measured by different methods for K-Fe/silicalite catalyst

States of catalyst	TEM		XRD	Magnetic
	ds	*dv*	*dv*	*ds*
before reacting	2.6	2.9	< 3.0	2.2
after reacting	3.0	3.4	< 3.0	3.2

Unit: nm; *ds*-face average diameter; *dv*-bulk average diameter.

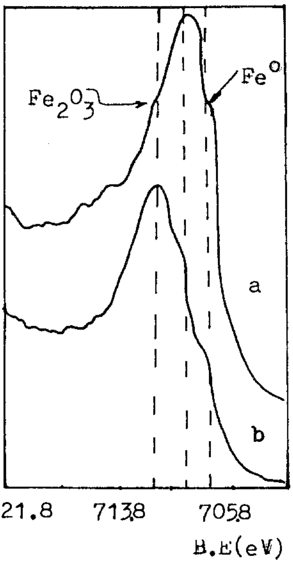


Fig. 4. $Fe_{2p3/2}$ XPS spectra of SMAI K-Fe/silicalite by ion sputtering for 2 min (a), and not sputtering (b).

introduced to the reactor. The surface component of the unused catalysts are mostly Fe^0 particles.

3. Catalysis of SMAI K-Fe / silicalite catalyst

5. TPR AND TPSR

TPR is used for characterizing the reducibility of SMAI K-Fe/silicalite catalysts. Fig. 5 shows that both Fe/silicalite and K-Fe/silicalite catalysts are easily reduced, in good agreement with the XPS results in which the surface is

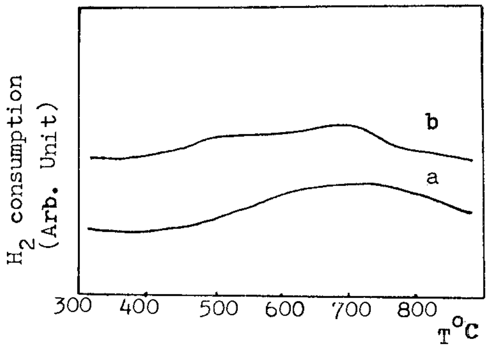


Fig. 5. TPR spectra of SMAI catalysts; a. Fe/silicalite; b. K-Fe/silicalite.

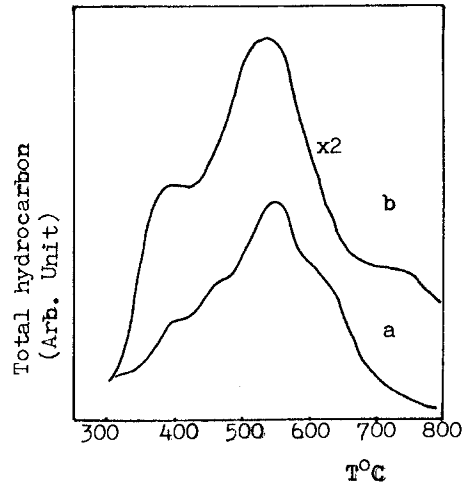


Fig. 6. TPSR spectra of carbonaceous species by CO adsorption at 100 ° C (a) and 250 ° C (b).

covered with a thin oxide skin. We have further shown, by temperature programmed surface reaction, that the reactivity of carbonaceous species formed species on the surface of SMAI catalyst by adsorption of carbon monoxide under different condition and reaction of the species with hydrogen. It has been found in fig. 6, that a very reactive carbon species, α, $T = 330°C$ in TPSR spectra, and iron carbide carbon species, $T = 410–450°C$ and unreactive carbon species $T = 550–600°C$ are formed [7], in which the carbon species in iron carbide is an important iron phase for making olefins from $CO + H_2$ [8].

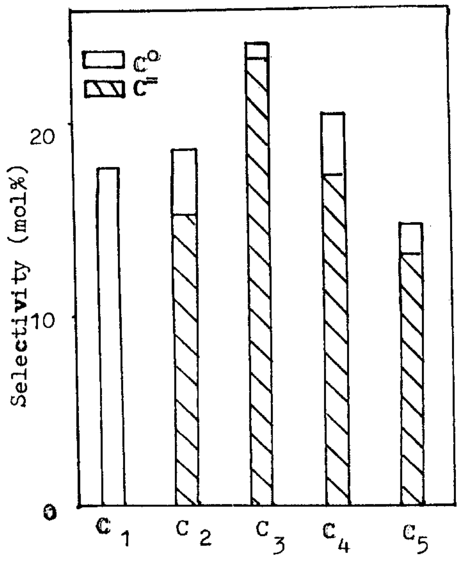


Fig. 7. Product distribution of CO hydrogenation.

6. CATALYTIC ACTIVITY AND PRODUCT DISTRIBUTION

Activity and selectivity measurements are performed in a stainless-steel microreactor at 1.1 MPa, 573 K, and H_2: CO = 1.0. While the catalyst is on a stable period, the conversion of carbon monoxide can reach over 80%, well over the data from the catalyst prepared by conventional impregnation [9]. The product distribution of the K-Fe/silicalite catalyst containing Fe 7.0 wt% and K 0.8 wt% is shown in fig. 7. The carbon monoxide-hydrogen produces mainly C_1-C_5 hydrocarbons, only trace amounts of C_5^+ hydrocarbons are detected. As controlled by the use of silicalite support and the selectivity of C_2-C_4 olefins is above 57.0% in the product, the olefin-to-paraffin ratio 9.6. The high activity of the catalyst relates to its highly active and high dispersion Fe^0 on the surface of the catalysts.

In conclusion: the SMAI method can be used to prepare highly dispersed zeolite supported metal catalyst to be used in F-T synthesis for the production of light olefins.

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