Characteristics of Fe/AlPO$_4$-5 catalyst prepared with organic solution

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Received 10 May 1993; accepted 10 August 1993

The Fe/AlPO$_4$-5 catalysts are prepared by impregnation with aqueous and organic solution (acetic acid, alcohol and acetone) of iron(III) nitrite respectively. The characterization of catalyst by means of XPS, Mössbauer spectroscopy, TPR and CO hydrogenation is reported. The catalyst prepared with the aqueous solution has no activity for CO hydrogenation because the Fe(III) in the catalyst cannot be reduced to α-Fe. However, the catalysts prepared with organic solution possess obvious hydrogenation activity, in which α-Fe is present in the initial reduced catalyst besides Fe^{3+} and Fe^{2+}. The results may be explained by the interaction degrees between the metal and the support induced by the different impregnation solvents.

Keywords: Catalyst preparation; Fe/AlPO$_4$-5 catalyst; CO hydrogenation

1. Introduction

Since the first synthesis of microporous aluminophosphate molecular sieves (designated AlPO$_4$-*n*) in 1982 [1,2], numerous papers have been published in which the synthesis and the structural characterization of AlPO$_4$-*n* were mainly reported. These solid materials exhibit some microporous characteristics of zeolites and also show the unusual physicochemical composition. The ideal AlPO$_4$-*n* have three-dimensional microporous crystal frameworks consisting of tetrahedra of oxygen surrounding aluminum and phosphorus ($Al/P = 1$). Because of its neutral network, the AlPO$_4$ molecular sieves have no ion exchange capacity. In order to create potential acidity, a portion of the aluminum and/or phosphorus must be substituted with the other elements by the synthesis. Therefore, the application of AlPO$_4$ molecular sieves in catalysis is limited.

In our work, Fe$_2$O$_3$/AlPO$_4$-5 and Fe/AlPO$_4$-5 catalysts were prepared by solid reaction and solvated metal atom impregnation (SMAI) methods respectively [3,4]. It has been shown that AlPO$_4$-5 molecular sieve exhibits shape selective behavior and enhances the yield of product in CO hydrogenation to light hydrocarbons. However, the dispersion of Fe_2O_3 on the surface of $AlPO_4$-5 was affected by the strong action of the support in Fe_2O_3/$AlPO_4$-5 catalyst. In Fe_2O_3/$AlPO_4$-5 catalyst prepared by SMAI, the loading amount of active components is limited by the preparation method. Recently, we have discovered that the Fe_2O_3/$AlPO_4$-5 catalyst prepared by impregnating $AlPO_4$-5 into the aqueous solution of iron nitrite cannot make CO convert under the usual reaction conditions [5]. The objective of this work is to establish a preparation method of the Fe impregnated $AlPO_4$-5 molecular sieve as catalysts for CO hydrogenation toward the formation of light hydrocarbons. Organic solvents are used as impregnation media in the preparation of the catalyst, such as acetic acid, alcohol, acetone. The prepared catalysts are characterized by XPS, Mössbauer, TPR and TPD; their catalytic properties in CO hydrogenation are reported.

2. Properties of Fe/$AlPO_4$-5 catalyst in CO hydrogenation

Fe/$AlPO_4$-5 catalysts ($AlPO_4$-5 was synthesized in our laboratory) prepared by the impregnation with aqueous solution, acetic acid, alcohol and acetone solution are designated as Fe/$AlPO_4$-5 (A), Fe/$AlPO_4$-5 (O_1), Fe/$AlPO_4$-5 (O_2), and Fe/$AlPO_4$-5 (O_3), respectively. The precursor was dried by evacuation to remove solvent, followed by reduction in flowing hydrogen. The loading amount of iron in the catalysts is 9 wt%. The measurements of activity and selectivity of catalysts are performed in a stainless-steel microreactor at $P = 1.1$ MPA, $T = 598$ K, SV = 1200/h, H_2/CO(mol) = 1. The catalytic results are shown in table 1. It is indicated that the Fe/$AlPO_4$-5 (A) catalyst has no catalytic activity in CO hydrogenation, but the Fe/$AlPO_4$-5 (O) catalysts can convert CO to hydrocarbons. In these catalysts Fe/$AlPO_4$-5 (O_2, O_3) catalysts are much more active in the reaction. The product distribution of CO hydrogenation over Fe/$AlPO_4$-5 (O) catalysts shows the high selectivity to C_1–C_5 alkanes and no liquid product at the steady state for all catalysts. The results are determined by both the surface property, pore size and pore structure of the molecular sieve and the properties of impregnation solvents.

Table 1
Catalytic properties of the Fe/$AlPO_4$-5 catalysts for CO hydrogenation

Catalyst	Impregnation solvent	CO conv. (%)	Hydrocarbon distribution (wt%)				
			C_1	C_2	C_3	C_4	C_5
A	water	tr	–	–	–	–	–
O_1	acetic acid	5.8	35.6	20.4	21.1	13.4	7.39
O_2	alcohol	20.1	32.3	23.0	22.4	13.9	5.67
O_3	acetone	23.0	3.90	21.4	22.0	11.2	6.39

3. Dispersion of iron in the surface of Fe/AlPO$_4$-5 catalysts

The states of the iron particle existing on the prepared catalyst surface are distinguished with the Mössbauer and XPS techniques. Transmission Mössbauer spectra are obtained with a constant acceleration spectrometer MS-500. XPS spectra are recorded on the PHI 5300 spectrometer using Mg K_α X-ray, the binding energies are corrected by reference to the binding energy of C_{1s} (284.6 eV). Fig. 1 shows the Mössbauer spectra of the prepared Fe/AlPO$_4$-5 (A) and Fe/AlPO$_4$-5 (O$_3$) catalysts. Both catalysts contain a symmetric quadrupolar splitting doublet. Their values of the isomer shift and the quadrupolar splitting are respectively 0.3273 mm/s, 0.8302 mm/s for Fe/AlPO$_4$-5 (A) and 0.2773 mm/s, 0.7562 mm/s for Fe/AlPO$_4$-5 (O$_3$). The doublet is attributed to the superparamagnetic Fe^{3+}. The results indicate that the iron phase is present as very small particles. Another interpretation of the doublet could be the surface phase in strong interaction with AlPO$_4$-5 molecular sieve [6]. It is possible to conclude that the iron phase could be highly dispersed in the catalysts prepared with both aqueous solution and organic solution. However, the $Fe_{2p_{3/2}}$ XPS spectra of the catalyst show that the existing states of iron species in two kinds of catalysts are distinct (fig. 2), the two peaks in the $Fe_{2p_{3/2}}$ region are observed for the Fe/AlPO$_4$-5 (A), binding energies of the $Fe_{2p_{3/2}}$ lines are 712.2 and 711.2 eV respectively. For the Fe/AlPO$_4$-5 (O$_3$) catalyst, only one iron line is present, the binding energy of which is 711.5 eV. The appearance of the higher binding energy peak in the $Fe_{2p_{3/2}}$ region demonstrates the strong interaction between the metal and the support in the Fe/AlPO$_4$-5 (A) catalyst. As a conclusion, it is indicated that the iron phases in the Fe/AlPO$_4$-5 (O$_3$) and Fe/AlPO$_4$-5 (A) catalysts exist in different states, although the Fe/AlPO$_4$-5 catalysts prepared by impregnation with the aqueous solution or with the organic solution, have the similar superparamagnetic characteristics.

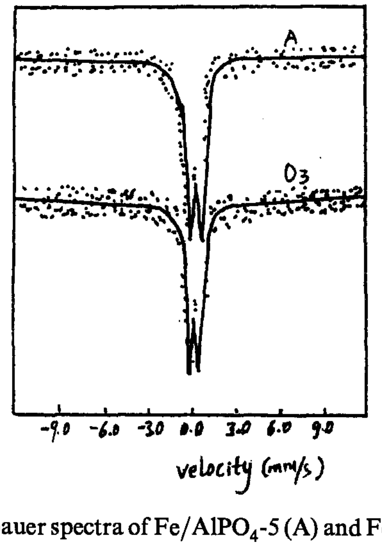

Fig. 1. Mössbauer spectra of Fe/AlPO$_4$-5 (A) and Fe/AlPO$_4$-5 (O$_3$).

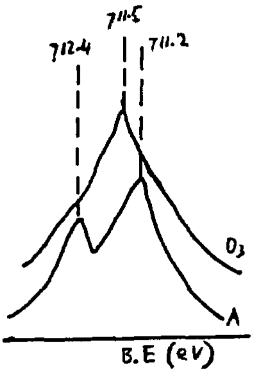

Fig. 2. XPS spectra of Fe/AlPO$_4$-5 (A) and Fe/AlPO$_4$-5 (O$_3$).

4. Reducibility and adsorbability of the catalyst

To investigate further the interaction between the surface iron phase and the AlPO$_4$-5 support, the Mössbauer spectra of the catalysts were recorded after H_2 reduction at 623 K for 12 h (fig. 3). The Fe/AlPO$_4$-5 (A) catalyst spectrum presents a single and doublet lines which are analysed in terms of the following additional contribution: (i) the doublet corresponding to Fe^{2+} in octahedral and tetrahedral sites of the spinel structure and (ii) the single corresponding to the superparamagnetic Fe_2O_3. The reduced Fe/AlPO$_4$-5 (O$_3$) catalyst spectrum presents an α-Fe sextuple besides a single and doublet lines. It is indicated that the iron phases in the Fe/AlPO$_4$-5 (A) cannot be reduced to α-Fe, but in the Fe/AlPO$_4$-5 (O) this can be done under the same reducing conditions.

The results of the TPR spectra of the catalysts are in good agreement with those

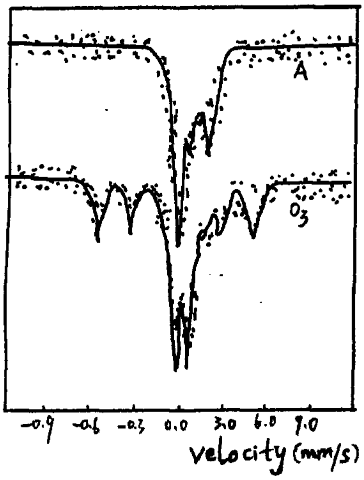

Fig. 3. Mössbauer spectra of Fe/AlPO$_4$- 5 (O$_3$) and Fe/AlPO$_4$-5 (A) reduced catalysts.

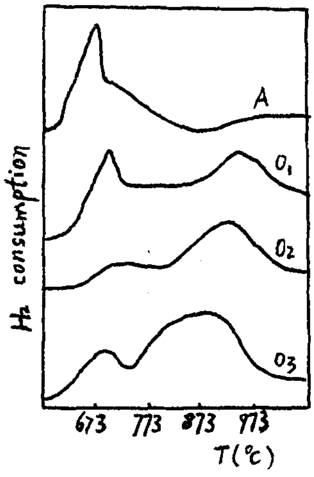

Fig. 4. TPR spectra of Fe/AlPO$_4$-5 (O) and Fe/AlPO$_4$-5 (A).

obtained from the Mössbauer spectra. Except the Fe/AlPO$_4$-5 (A) catalyst, the reduction of the Fe/AlPO$_4$-5 (O) catalysts occurs in the following sequence: Fe(III) → FeO → α-Fe (fig. 4).

The different surface compositions of the reduced catalysts result in their different adsorbability for CO. Fig. 5 illustrates the TPD spectra of CO for the Fe/AlPO$_4$-5 catalyst. Fe/AlPO$_4$-5 (O_3) exhibits the highest CO desorption capacity followed by Fe/AlPO$_4$-5 (O_2) and Fe/AlPO$_4$-5 (O_1). In the Fe/AlPO$_4$-5 (A) catalyst, there is hardly CO chemisorption. The result of the CO TPD is in excellent agreement with the catalytic results of CO hydrogenation.

The above results could be interpreted as follows. Although the AlPO$_4$-5 molecular sieve is electroneutral, Al^{3+} and P^{5+} have different electronegativity resulting in the different electropositivity between PO_4 and AlO_4 tetrahedral units. When the

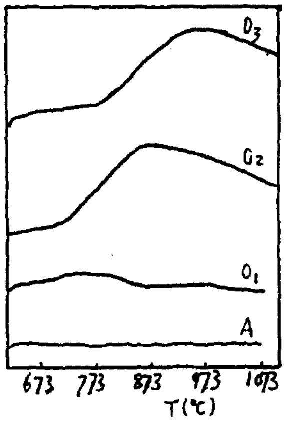

Fig. 5. CO TPD spectra of Fe/AlPO$_4$-5 (A) and Fe/AlPO$_4$-5 (O).

AlPO$_4$-5 molecular sieve is impregnated in the aqueous solution of the iron nitrite, H_3^+O have priority to occupying the AlO$_4$ unit, the Fe^{3+} present only to the PO$_4$ unit. The strong action of the PO$_4$ unit to Fe^{3+} restrains the reduction of Fe^{3+}. In organic solvents the Fe^{3+} could exist in the AlO$_4$ unit and be reduced to α-Fe because of the weak action of the AlO$_4$ unit to Fe^{3+}. The catalysts prepared with organic solvents exhibit catalytic activity in CO hydrogenation.

As a result, a preparing method of the supported AlPO$_4$-5 catalyst is shown in this work. Aluminophosphate molecular sieve can be used as the support altering the zeolite for CO hydrogenation in the aspect of the limiting growth of the carbon chain. The effect of the impregnation solvent on the preparation of AlPO$_4$-5 supported catalyst is very important to obtain high activity and selectivity. The application of organic solvent changes the adsorption of the ion in the progress of the impregnation and the existing states of the surface active components over the catalyst. Further work on AlPO$_4$-*n* catalyst is in progress.

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