

Characterization of Nb₂O₅-ZrO₂ Catalyst*

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<Abstract>

Nb₂O₅-ZrO₂ was prepared by adding the Zr(OH)₄ powder into Nb(OC₂H₅)₅ solution followed by drying and calcining at high temperatures. The characterization of the prepared catalysts was performed using FTIR, XRD. Nb₂O₅ series catalysts exhibited the effective catalytic activity for propylene partial oxidation and the activity increased with increasing Nb₂O₅ content.

1. Introduction

Supported metal oxides exhibit interesting catalytic behavior depending on the kind of support, the content of active component and the preparation method[1,2]. Much of the current interest in the catalytic activity of niobium compounds stems from the work performed by Tanabe and coworkers[3,4].

Niobium compounds exhibit special properties not shown by the compounds of neighboring elements of niobium in the periodic table. Niobium oxide and its mixed oxides have very interesting properties, acting as supported and promoters. Niobium can also form layered structures with unique catalytic behavior. As a result of these different structures and properties, niobium compounds exhibit unique activity, selectivity and stability for many different catalytic reactions[5,6]. Nevertheless, for the Nb compounds to be competitive catalysts, requires that its preparation methods are easy to handle, with the cheapest starting Nb compounds, and resulting materials with high surface area. Niobic acid has been prepared in several ways. Usually, niobium ethoxide has been used as precursor, and very high surface areas have been obtained when supercritical extraction with CO₂ has been performed[7]. The starting material, the impurities and the preparation method influence not only the textural properties, but also the structure and hence the acidic properties of Nb₂O₅[8].

* This work was supported by University of Ulsan Research Fund of 2001.

Many researches have been done to understand the nature of active sites, the surface structure of catalysts as well as the role played by the promotor of the supported catalysts, using infrared(IR), X-ray diffraction(XRD), electron spin resonance(ESR) and Raman spectroscopy.

The present paper is concerned with the preparation of new catalyst system, $\text{Nb}_2\text{O}_5\text{-ZrO}_2$ and the structure properties have been studied by surface area, XRD, FTIR spectroscopy. Finally, catalytic activity of the prepared samples has been tested in the propene partial oxidation.

2. Experimental

Precipitate of $\text{Zr}(\text{OH})_4$ was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at 100°C for 12h. The dried precipitate was powdered below 100mesh. $\text{Nb}_2\text{O}_5\text{-ZrO}_2$ catalysts containing various Nb_2O_5 content were prepared by adding $\text{Zr}(\text{OH})_4$ powder into a $\text{Nb}(\text{OC}_2\text{H}_5)_5$ solution followed by drying and calcining at high temperature for 1.5h. in air. These series of catalysts are denoted by their weight percentage of Nb_2O_5 . For example, 10- $\text{Nb}_2\text{O}_5\text{-ZrO}_2$ indicate the catalyst containing 10 wt% Nb_2O_5 .

FTIR absorption spectra of catalyst powders were measured by KBr disk method over the range of $2000\text{-}400\text{ cm}^{-1}$. The samples for the KBr disk method were prepared by grinding a mixture of the catalyst and KBr powders in an agate mortar and pressing them in the usual ways. Catalysts were checked in order to determine the structure by means of Jeol JDX-8030 diffractometer, employing $\text{CuK}\alpha$ (Ni-filtered) radiation. The specific surface area was determined by applying the BET method to the adsorption of N_2 at 77K.

The catalytic activities were measured in a continuous flow reactor at atmospheric pressure, using a mixture of propene and oxygen. The ratio propene/oxygen was 1.0. The amount of catalyst(0.1-0.5g) was chosen so as to obtain less than 10% for the conversion of propene at $200\text{-}350^\circ\text{C}$. The catalyst was activated by heating the sample under a flow of a mixture of O_2 and He(the ratio of $\text{O}_2/\text{H}_2=1/4$) for 15hr. at 350°C prior to reaction. Reaction products were analyzed by gas chromatography(Hewlett Packard 5890II) with a Porapak P column at 100°C .

3. Result and Discussion

Table 1 presents the surface area of all the samples prepared. In order to study the

effect of the calcination temperature on niobia properties, the sample with the highest surface area was calcined at different temperatures. The increase of the calcination temperature produced a decrease in the surface area.

Table 1. Specific Surface Area and Activity of Catalysts

Catalyst	T _{calcine}	Sp.Sur.Area	Activity
10-Nb ₂ O ₅ -ZrO ₂	400 °C	27m ² g ⁻¹	5.6molh ⁻¹ g ⁻¹
20-Nb ₂ O ₅ -ZrO ₂	400 °C	30m ² g ⁻¹	12.2molh ⁻¹ g ⁻¹
30-Nb ₂ O ₅ -ZrO ₂	400 °C	43m ² g ⁻¹	16.1molh ⁻¹ g ⁻¹
30-Nb ₂ O ₅ -ZrO ₂	500 °C	18m ² g ⁻¹	6.5molh ⁻¹ g ⁻¹
30-Nb ₂ O ₅ -ZrO ₂	700 °C	10m ² g ⁻¹	6.5molh ⁻¹ g ⁻¹
30-Nb ₂ O ₅ -ZrO ₂	900 °C	4m ² g ⁻¹	1.1molh ⁻¹ g ⁻¹

In order to compare the effect of the temperature on the structural properties, The XRD patterns of the samples calcined at 673, 773, 973 and 1173K, were also measured. The changes observed in the XRD patterns are shown in Fig. 1. After heating at 673K, the sample remains amorphous, whereas at the other temperatures, it crystallizes in different phases. Upon heating at 773K the Nb₂O₅ adopts the hexagonal system. At 973K splitting of the peaks is observed and the new crystalline system is in agreement with the orthorhombic phase[9]. Finally, the sample calcined at 1173K crystallizes in the monoclinic system[10]. Ko and Weissman[11] compared the patterns of samples heated 773K and 973K and suggested that the broadening of peaks in the sample calcined at 773K can be due to the fact that the Nb atoms occupy a range of positions between two crystallographically equivalent sites. So, the splitting observed at 973K can be explained considering that the Nb atoms can occupy either of these two sites[12].

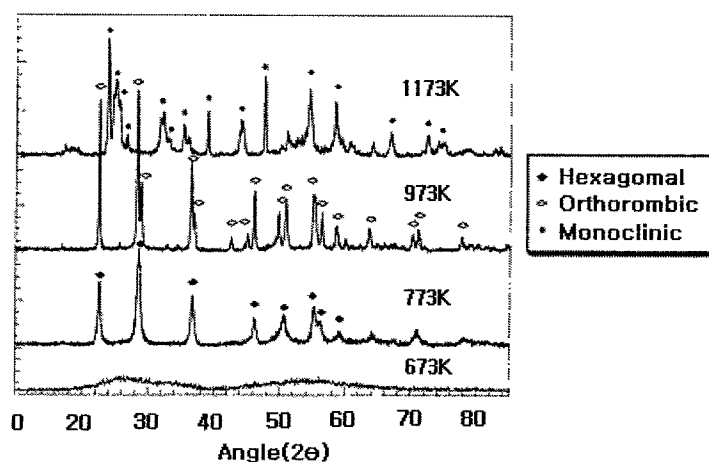


Fig. 1. XRD patterns of Nb₂O₅ samples calcined at different temperatures

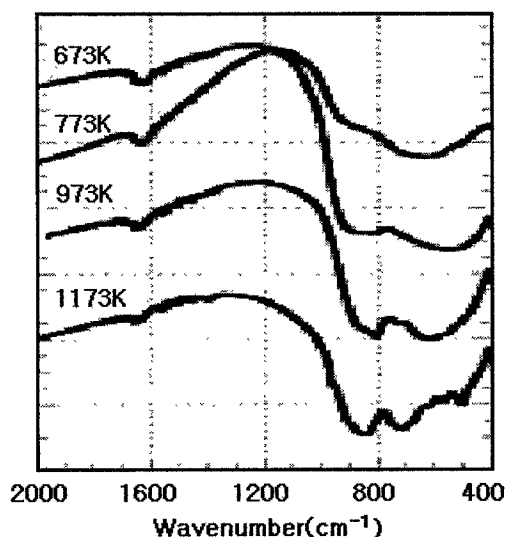


Fig. 2. FTIR spectra of Nb_2O_5 calcined at different temperature.

Fig. 2 shows the FTIR spectra of the niobia compounds calcined at 673, 773, 973 and 1173K. After calcining at 673K, an intense broad band centered around 655cm^{-1} with a shoulder near 800cm^{-1} is observed. The increase of the calcination temperature brings about splitting of the bands and a decrease in intensity of the band at the lowest frequency. Calcination of the sample at 1173K results in a new band at 724cm^{-1} . After calcining at 673K, we observe by IR that both bands are very broad. The width and the intensity of the bands are due to the amorphous nature at that temperature, in agreement with the XRD patterns. At increasing calcination temperature, the bands are not so broad and they are splitted, probably due to the greater asymmetry in the unit cell and the possible interaction between the Nb-O groups. The band near 850cm^{-1} appears in all spectra, which has been assigned to a highly distorted octahedral NbO_6 containing Nb=O bond, increasing for higher calcination temperatures[13]. In contrast, Mauer and Ko[7] reported that this band disappears at higher crystallinity. However, the relative intensity of the band at the lower frequency, near 600cm^{-1} , assigned to the Nb-O bond of the slightly distorted NbO_6 octahedra, decreases with the increase in the temperature. Furthermore, this band splits and shifts to the lower frequency. This fact suggests the existence of different Nb-O species or inequivalent Nb-O groups. The band at 724cm^{-1} can be assigned to Nb-O-Nb chain linkages[14]. The increase in the intensity of this band at increasing calcination temperature may be due to the existence of more Nb-O-Nb linkages, relative to Nb=O and Nb-O bonds in the structure adopted at 1173K.

The changes induced on the surface properties of Nb_2O_5 by an increase in the calcination temperature were evaluated by measuring its catalytic activity for the

propene partial oxidation. Table 1 presents the catalytic activity per gram of catalyst. The propene partial oxidation reactions were carried out at intervals of 30°C from 205 to 325°C. The catalysts activities for propene partial oxidation 235°C are measured and the results are illustrated. The various in catalytic activities of Nb₂O₅-ZrO₂ catalysts are roughly correlated with the change of their acidity and surface area. It was reported that the oxidation activity for olefins increases with an increase in the acidity of the catalyst[15]. Obviously, the decrease in specific surface area due to the calcination temperature causes a decrease in the catalytic activity.

Since the catalytic oxidation is a reaction between an organic compound and oxygen on the surface of metal oxide, oxidation activity is governed by two factors, that is, activation of the reactant and oxidizing power of surface oxygen. When the oxidizing power is weak, the reaction requires a sufficient activation of the reactant molecule. Thus, the oxidation is decided predominantly by the activation of the organic molecule rather than by that of oxygen. In this work, the catalytic activity for propene oxidation is correlated with acidity and acid strength of the catalysts, indicating that the activity is governed mainly by activation of the reactant by acidic sites.

It is well known that the acidic properties of niobium oxide results in its high catalytic activity for several reactions[16,17,18]. Tanabe proposed that the surface acid strength of niobic acid corresponds to Brønsted acid sites. On the other hand Jehng and Wachs[19] studied the acidity of bulk and supported Nb₂O₅ by Raman and IR of adsorbed pyridine. In their work they concluded that the highly distorted surface NbO₆ octahedral sites correspond to the Lewis acid sites and the Raman band between 850 and 1000cm⁻¹. Furthermore, the slightly distorted surface NbO₆ sites, as well as NbO₇ and NbO₈ sites are associated with Brønsted acid sites and Raman bands in the 500-700 cm⁻¹ region.

Table 2. Acid Strength of Catalysts

Hammet Ind.	ZrO ₂	30-NbO ₂ -ZrO ₂
Dimethylyellow	+	+
Dicinnamalacetone	+	+
Benzalacetophenon	+	+
Anthraquinone	-	+
p-Nitrotoluene	-	+
Nitrobenzene	-	+
2,4-Dinitrofluorbenzene	-	+

In general, the catalytic activity for olefin oxidation is different depending on the niobium content, acidity and acid strength of catalyst[20]. It was reported that the

oxidation activity for olefins increases with an increase in the acidity of the catalyst[21]. The acid strength of the catalysts was examined by the color change method using Hammett indicators as described in a previous paper[22,23]. ZrO_2 without Nb_2O_5 had an acid strength of $H_o \leq -11.35$, while $Nb_2O_5-ZrO_2$ samples were estimated to be $H_o \leq -14.5$. These results (Table 2) mean that the weak acid sites of ZrO_2 are converted into strong acid sites by means of modifying the sample with Nb_2O_5 .

4. References

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