A New Method for Preparing Nickel Oxide Supported Silica Pillared Phosphates with High Surface Area

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A novel procedure was developed to prepare nickel oxide supported silica pillared zirconium phosphates whose surface areas and d-spacings are 125-198 m^2/g and 2.1-2.3 nm respectively, whereas the samples prepared by conventional method only have surface areas less than 20 m^2/g and d-spacings 1.8 nm. X-Ray diffraction (XRD), N_2 adsorption and temperature programmed reduction (TPR) indicated that the materials obtained by the new method have better nickel oxide dispersion than those obtained by the conventional method.

Pillared layered metal (IV) phosphates are a new type of catalytic materials with the versatility in structure and composition that are very important for catalysis.[1-5] Many metal (Ni, etc.) pillared layered materials,[6] especially stable silica pillared phosphates[7] with high surface areas have been prepared successfully until now. But not all catalytically interesting transition elements form polynuclear cations appropriate for intercalation. So incorporation of transition metals into the two-dimensional nano cavities opens a new way to versatile potential applications of pillared materials in catalysis and in molecular devices,[8] Some approaches have been carried out by impregnating the support with ethyl alcohol solution of metal salt,[9,10] reacting metal-cluster carbonyls with hydroxyl groups of pillared clay,[11] and intercalating metal ion-anchored diaminosiloxane into the interlayer region,[12] etc. However, the loading of metal species on the intracrystalline walls seems difficult, partially because the interlamellar region is easily "stuffed" with the metal oxide, which causes a dramatical decrease in the surface area and pore volume. In this paper, we have developed a new method, i.e., directly impregnating $Ni(OAc)_2$ on the $NH_2(CH_2)_3Si(OEt)_3$ (APS) pillared phosphate before calcination, to prepare the nickel oxide supported silica-pillared metal(IV) phosphates with larger surface area and relatively higher nickel oxide dispersion.

Nickel oxide supported silica pillared zirconium phosphates were prepared using the following procedure: 1 g of zirconium phosphate (ZrP) was mixed with 100 ml of 1 mol l^{-1} ethylamine solution and stirred vigorously at room temperature until ZrP was exfoliated completely, then refluxed with 74 g of 10 wt% aqueous APS solution for 24 h. The solid product (designated as Si-ZrP) was separated by centrifugation, then washed and dried at 323 K. Different from the conventional method for preparing NiO supported samples, we impregnated $Ni(OAc)_2$ solution directly to APS intercalates by the incipient wetness technique, then calcined them at 773 K for 3 h. The samples obtained were named as Si-ZrP-X-N before calcination and SiO_2-ZrP-X-N after calcination respectively (X means the weight percentage of NiO in wt%). For comparison, the samples with the same NiO contents were also prepared by the conventional method, i.e., the APS intercalates were firstly calcined at 773 K for 12 h to obtain silica pillared ZrP, followed by impregnation of $Ni(OAc)_2$ solution, drying and calcination at 773 K for 3 h. The samples prepared were designated as Si-ZrP-X-C before calcination and SiO_2-ZrP-X-C after calcination respectively.

Figure 1 depicts XRD patterns of the samples prepared by the new and conventional methods. Samples obtained by the new method possess larger d-spacing (Table 1), indicating that the existence of Ni^{2+} (new method) affects the formation of the SiO_2 pillar either by the incorporation of Ni^{2+} into SiO_2 pillars or by the interaction of Ni^{2+} with P-OH, which shields the P-OH groups from interacting with the SiO_2 pillars, thus restricts the spreading of the SiO_2 pillars. On the other hand, The peaks of NiO phase do not emerge until the loading is up to 20 wt% in the new method comparing to 15 wt% in the conventional method. This indicates new method can achieve a relatively higher NiO dispersion than conventional method.

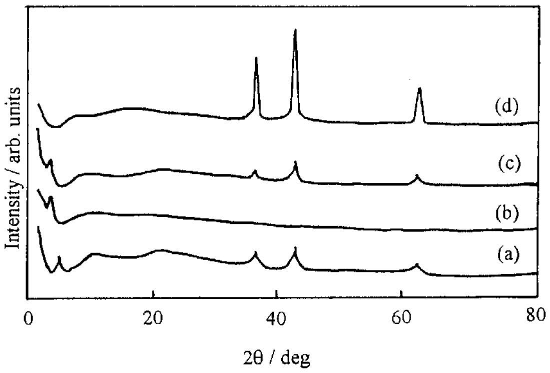

Figure 1. X-Ray diffraction patters of (a) SiO_2-ZrP-15-C (b) SiO_2-ZrP-15-N (c) SiO_2-ZrP-20-N (d) NiO .

The textural properties of support SiO_2-ZrP and two series of samples are listed in Table 1. After loading by the conventional method the surface areas and pore volumes of the samples decrease dramatically (<20 m^2/g and <0.04 cm^3/g) comparing to those of the support SiO_2-ZrP (297.1 m^2/g and 0.16 cm^3/g). However, the surface areas and pore volumes of the

Table 1. Textural properties of the samples with different NiO loading prepared from different method

NiO	Conventional method			New method		
content / wt%	S_{BET} / m^2/g	V_{Pore} / cm^3/g	d / nm	S_{BET} / m^2/g	V_{pore} / cm^3/g	d / nm
0	297.1	0.163	1.8			
10	19.9	0.0304	1.8	197.6	0.104	2.2
15	20.7	0.0358	1.8	161.2	0.089	2.3
20	15.7	0.0239	1.8	140.9	0.101	2.1
25	18.8	0.0312	1.8	125.1	0.109	2.1

samples prepared by the new method are all in the range of 198-125 m^2/g and 0.09-0.11 cm^3/g, respectively. The great difference could be explained by the different disperse state of NiO (cf. XRD and TPR results). In the conventional method, NiO exists mainly in aggregated state which might result from the crystal growth of NiO and lead to a stuffy structure, while in the new method the NiO tends to form a disperse state which makes the samples keep a more open structure.

Results of TG/DTG analysis in flowing air are shown in Figure 2. There are three peaks on the DTG profile of Si-ZrP (curve a). The first peak at 443 K corresponds to the dehydration of the pillared material and the elimination of ethylamine residue. The second peak at 674 K and the third peak at 899 K correspond to the removing of propylamine groups from APS.[7] However, when Ni^{2+} is supported, the temperature of all the peaks shifts to lower temperature (curve b) and no organic residue was left after calcination at 773 K for 3 h (curve d). It could be concluded that Ni^{2+} might act as a catalyst during the elimination of organic species. Because the silica pillared material had been pre-synthesized before the impregnation of $Ni(OAc)_2$ solution in the conventional method, the curve c only shows the decomposing peak of $Ni(OAc)_2$ besides the low temperature peak ascribed to water desorption.

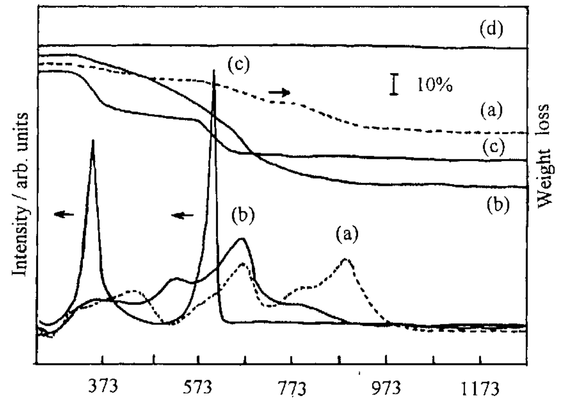

Figure 2. TG/DTG profiles of samples : (a) Si-ZrP (b) Si-ZrP-20-N (c) SiO_2-ZrP-20-C (d) as Si-ZrP-20-N calcined in air at 773 K for 3 h .

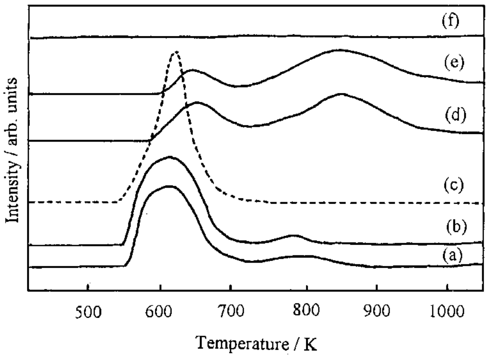

Figure 3. Temperature-programmed reduction (TPR) spectra for (a) SiO_2-ZrP-15-C (b)SiO_2-ZrP-20-C (c) NiO (d) SiO_2-ZrP-20-N (e) SiO_2-ZrP-15-N (f)support SiO_2-ZrP

The TPR spectra of the samples are very different (Figure 3). No peak was found in the curve of support silica pillared ZrP. The samples prepared by the new method show an intense peak at about 838 K and a smaller peak at 632 K, and the peak area ratio of low temperature to high temperature increases with the increase of NiO loading, while the samples prepared by the conventional method show a much larger peak at about 617 K and a very small peak at 797 K. Comparing with the TPR spectrum of bulk NiO (only one peak at 612 K), the peaks at low temperature could be attributed to the aggregate of NiO, and the peaks at high temperature could be attributed to the dispersed NiO species . Because of the strong interaction of dispersed NiO species with the support surfaces, its reduction temperature is delayed. The above TPR results show that the samples prepared by the new method have higher degree of dispersion than those samples prepared by the conventional method, which is consistent with the results of BET and XRD.

It can be concluded that the new method reported here, i.e., to load metal salt directly on the APS intercalate followed by calcining it to form the pillar and the supported metal oxide simultaneously, is an effective way to prepare metal oxide supported layered silica pillared materials with high surface area, large pore volume and better metal oxide dispersion.

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