Journal of the Chinese Chemical Society, 1995, 42, 31-36

Effect of the Phase of Titanium Oxide on Metal-Support Interaction

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The metal-support interaction in the system of platinum supported on titanium oxides of different crystalline structures was investigated. Titanium oxide powders used as supports were prepared by neutralization of $TiOCl_2$-analogue solution with either NaOH or NH_3 base at varied pH. Pt was introduced onto the supports by impregnation. The phenomenon of strong metal-support interaction (SMSI) was determined by the suppression of chemisorption of H_2 over samples reduced at 773 K, in comparison with the behavior of samples reduced at 473 K. The loss of adsorption capacity was proved not due to metal sintering by examining the recovery of adsorption capacity after reduction, reoxidation and reduction cycle, accompanied with examination of the size of Pt particle with an x-ray diffractiometer and a transmission-electron microscope. The results showed that SMSI phenomenon was common to Pt supported on titanium oxides of all the varied crystalline structures. However, the chemisorption capacity of Pt reduced at 473 K varied greatly with the sodium content in the supports, which in turns affects the crystalline structure of titanium oxide. These results are attributed mainly to electronic effect endowed by the support.

INTRODUCTION

High surface area supports are widely used in industrial catalysts to achieve a large dispersion of costly precious metals. Support materials were considered inert in catalytic reactions until the strong metal-support interaction (SMSI) was reported for group VIII metals supported on TiO_2 by Tauster et al.[1] Since then, this subject has attracted great attention in catalysis research. The SMSI phenomenon was signified that the chemisorption capacities of noble metals supported on titania were greatly suppressed after reduction with hydrogen at temperatures near 773 K; the suppression was not due to sintering of metal particles according to the results of transmission electron microscopy and x-ray diffraction. Similarly decreased capacities of chemisorption after reduction at high temperatures were later noted on noble metals supported on transition-metal oxides,[2,3] and even extended to some supports that were not composed of compounds of transition metals and were nominally not reducible (e.g. La_2O_3[3] and Al_2O_3)[4]. Among several possible interpretations of this phenomenon, two are most popularly adopted. Because the extent of chemisorption suppression correlates well with the reducibility of the support, several authors proposed an electronic interaction between the metal and its support as the origin of SMSI.[5-9] On the other hand, from work on model catalysts, authors attribute the decreased adsorption capacity to site blockage, i.e. a migration of suboxide species of support (e.g. TiO_x, $1 < x < 2$) onto the overlying metal.[10-15] Some authors speculated that special active sites are created at the metal-migrated oxide border that cause high activity for methanation.[16,17]

Little attention is devoted to the influence on SMSI of various crystal form and particle size of titanium oxide. Lane and Wolf[18] reported that it was more difficult for TiO_x species to migrate onto the Pt surface when the latter were supported on rutile than on anatase; they also observed various CO adsorbed species formed on different crystal phases. On the other hand, the dependence of metal-TiO_2 interaction on the preparation and thermal history of TiO_2 is controversial.[19,20] Our objective was to examine the interaction between Pt and titanium oxide supports of various crystal structures to clarify the effect of structure and composition of titanium oxide.

EXPERIMENTAL METHODS

Catalyst Preparation

Reagent grade chemicals were used without further purification. $TiCl_4$ (Merck) was dissolved in HCl (1 M) to make up $TiOCl_2$-analogue solution (ca. 5 M). NaOH (5 M) or NH_3 (15 M) solution was added dropwise to a 40 mL portion of $TiOCl_2$ solution with stirring until the desired pH was attained. The pH value was set to be 3, 7, 10 and 13 with NaOH, but 10 was the maximum pH with NH_3. The precipitate was sealed in a polypropene bottle and underwent hydrothermal treatment at 373 K for 24 h in order to obtain

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Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

crystalline structure. The resultant solid was filtered, washed with deionized water until free of Cl^- ions, dried in air, and finally calcined at 873 K for 5 h. These titanium oxide compounds are designated Na/Ti/3 to Na/Ti/13 and NH/Ti/3 to NH/Ti/10 corresponding to the NaOH and NH_3 bases and the varied pH conditions.

Pt (1% by mass) was impregnated onto the titanium oxide support by the method of incipient wetness. For each portion (1 g) of support, 0.8 mL of $PtCl_4$/HCl solution (Janssen) was added dropwise under vigorous stirring. Then, the mixture was heated until the solvent was evaporated, followed by calcination at 393 K for 12 h.

Catalyst Characterization

The crystal structures were examined with a Phillips 1792 x-ray diffractometer and Cu Kα radiation. The BET surface areas were determined by physical adsorption of N_2 at liquid N_2 temperature in a volumetric system. The particle sizes of Pt metal were determined with the transmission electron micrographs (Hitachi H-600 TEM). The sodium content was analyzed with an inductively-coupled plasma atomic emission spectrometer (Allied Analysis System, model ICAP 9000).

Studies of SMSI Phenomena

The capacity to chemisorb H_2 on the supported Pt catalysts was measured at ambient temperatures with a circulatory system; the hydrogen pressure was monitored with a pressure transducer (MKS type-122AA). Before being admitted to the system, H_2 gas was purified by passage through a molecular-sieve column and a liquid-N_2 trap. A portion (1.5 g) of the supported Pt catalyst was packed in a quartz reactor. After preheating at the reduction temperatures in vacuum, the supported Pt catalysts were reduced at either 473 or 773 K; these processes are briefly termed as LTR and HTR conditions, respectively. The reduced samples were pumped to a pressure less than 10^{-5} torr for 8 h before capacity to chemisorb H_2 was measured; the pressure of H_2 was varied in the range 0-200 torr and 20-30 min was typically required to attain equilibrium at a specific pressure. The amount of chemisorbed H_2 was determined by extrapolating the plateaus of isotherms to the point of zero pressure so that interference from physisorption was excluded.

RESULTS AND DISCUSSION

The crystal phase of titanium oxide powders as synthesized varied greatly with pH of the solution when NaOH was used for neutralization of $TiOCl_2$ (Fig. 1), but was nearly independent of pH when NH_3 was the base (Fig. 2). In the latter case, anatase was the predominant phase of titanium oxide formed, and a little rutile phase was present only at low pH. With NaOH as the base, the diffraction pattern shows that rutile was the predominant phase at pH 3. The phases are a mixture of rutile, anatase and layered titanates at pH 7, and mainly layered structures at pH greater than 10.

Table 1 shows that the sodium content of titanium oxide powders prepared with NaOH was directly proportional to the pH of the solutions, or to the amount of NaOH added. Based on the diffraction patterns and comparison with the theoretical sodium content in various layered titanates, sample Na/Ti/13 is composed mainly of mixed phases of $Na_2Ti_3O_7$ and $Na_2Ti_5O_{11}$, whereas the latter is dominant in sample Na/Ti/10.

The metal-support interaction was investigated with 1 wt. % Pt supported on the synthesized titanium oxide powders. The capacities of hydrogen chemisorption were compared among supported Pt catalysts reduced at 473 and 773 K and also subjected to reduction at 773 K, followed by reoxidation at the same temperature, then reduction at 473 K (termed as a HTR-HTO-LTR cycle). Because the SMSI phenomenon is not due to sintering of Pt particles, the capacity for hydrogen chemisorption is expected to be reversible. Hence, the chemisorption capacity that is suppressed

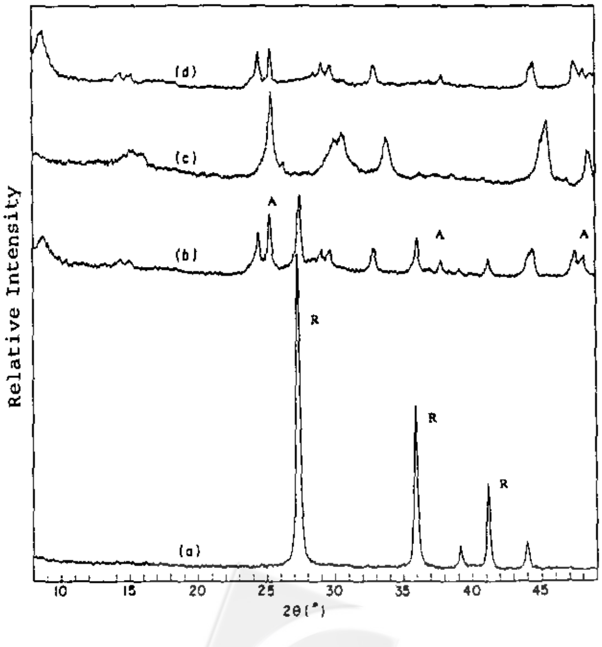

Fig. 1. X-ray diffraction patterns of titanium oxide compounds prepared with NaOH; (a) Na/Ti/3, (b) Na/Ti/7, (c) Na/Ti/10 and (d) Na/Ti/13. (A-anatase; R-rutile).

Table 1. Na Content of Pt Catalysts (1 wt%) Supported on Titanium Oxide Prepared with NaOH

Support	Na/%
Na/Ti/3	1.48
Na/Ti/7	5.2
Na/Ti/10	8.8
Na/Ti/13	13.6
$Na_2Ti_3O_7$	15.1^{t}
$Na_2Ti_4O_9$	11.9^{t}
$Na_2Ti_5O_{11}$	9.8^{t}

[t] theoretical values

after 773 K reduction is expected to recover when the Pt catalyst is re-oxidized and then reduced at 473 K.

Table 2. Physical Properties and Hydrogen Chemisorption Capacity of Pt Supported on Titanium Oxide Prepared with NaOH

Support	BET Surface area $/m^2g^{-1}$	Treatment	H/Pt	Pt diameter[a]/nm
Na/Ti/3	16	LTR[b]	0.62	6.6
		HTR[c]	0.13	2.0
		HTR-HTO-LTR[d]	0.54	12.1
Na/Ti/7	38	LTR	0.48	2.4
		HTR	0.06	3.8
		HTR-HTO-LTR	0.40	-
Na/Ti/10	6	LTR	0.19	5.0
		HTR	0.00	5.0
		HTR-HTO-LTR	0.14	3.0
Na/Ti/13	13	LTR	0.09	2.6
		HTR	0.00	2.3
		HTR-HTO-LTR	0.07	2.9

[a] Average diameter of 100 Pt particles observed in TEM photographs.
[b] Reduction at 473 K.
[c] Reduction at 773 K.
[d] The reduction cycle included reduction and re-oxidation at 773 K and reduction at 473 K.

The results are tabulated in Tables 2 and 3, in which the chemisorption capacity is expressed as the H/Pt ratio. All titanium oxide supports demonstrated suppression of hydrogen chemisorption capacity after reduction at 773 K. However, the chemisorption capacity after reduction at 473 K and the extent of chemisorption suppression after reduction at 773 K varied much for titanium oxide samples prepared with varied bases. With NH_3, the three catalysts have H/Pt ratios near 0.4 after reduction at 473 K. The chemisorption capacities were almost completely suppressed after reduction at 773 K. The similarity of chemisorption behavior among these three catalysts is explained by their similarity of crystal structures of titanium oxide supports. However, the extent of recovery of chemisorption capacity after

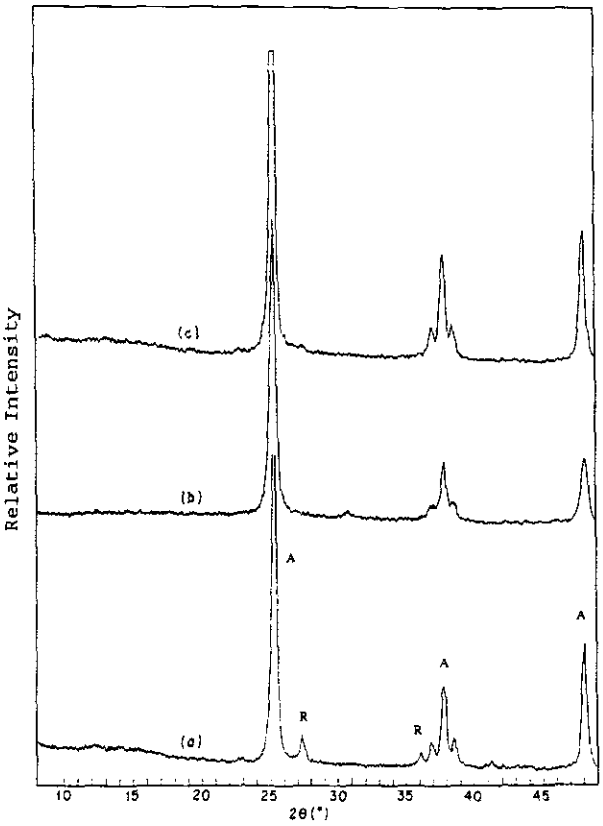

Fig. 2. X-ray diffraction patterns of titanium oxide compounds prepared with NH_3; (a) NH/Ti/3, (b) NH/Ti/7 and (c) NH/Ti/10. (A-anatase; R-rutile).

Table 3. Physical Properties and Hydrogen Chemisorption Capacity of Pt Supported on Titanium Oxide Prepared with NH_3

Support	BET Surface area $/m^2g^{-1}$	Treatment	H/Pt	Pt diameter[a]/nm
NH/Ti/3	45	LTR[b]	0.33	-
		HTR[c]	0.00	5.0
		HTR-HTO-LTR[d]	0.48	-
NH/Ti/7	53	LTR	0.40	1.5
		HTR	0.05	2.5
		HTR-HTO-LTR	0.17	3.0
NH/Ti/10	45	LTR	0.40	2.5
		HTR	0.00	1.7
		HTR-HTO-LTR	0.12	-

[a] Average diameter of 100 Pt particles observed in TEM photographs.
[b] Reduction at 473 K.
[c] Reduction at 773 K.
[d] The reduction cycle included reduction and re-oxidation at 773 K and reduction at 473 K.

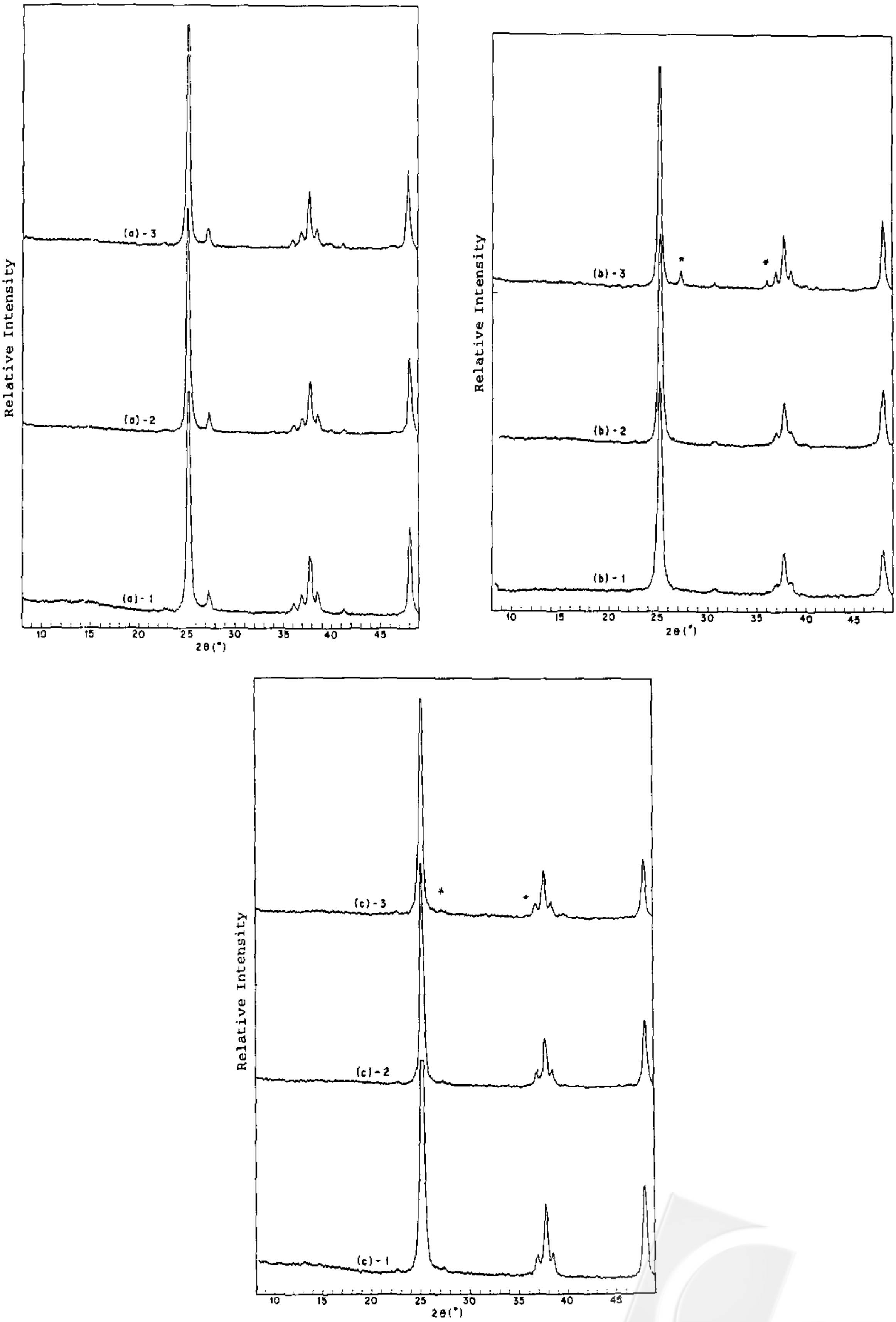

Fig. 3. X-ray diffraction patterns of Pt supported on titanium oxides prepared with NH_3 after various treatments; (a) NH/Ti/3, (b) NH/Ti/7 and (c) NH/Ti/10; **-1**: reduction at 473 K, **-2**: reduction at 773 K, -3: HTR-HTO-LTR cycle.

the thermal cycle of reduction and oxidation at 773 K and reduction at 473 K differed among them. Complete recovery was observed for Pt supported on NH/Ti/3, but less than half the capacity was recovered for supports prepared in more basic conditions, i.e. NH/Ti/7 and NH/Ti/10. This distinction cannot be due to the surface areas, which are all about 45-53 m^2/g, or to sintering of Pt particles as no growth of Pt particles was detected in either transmission electron micrography or diffraction patterns, but perhaps a phase transformation of the titanium oxide support was responsible. The most obvious alteration was found on sample NH/Ti/7. Fig. 3 shows an increased crystallinity of the original anatase phase and the appearance of new diffraction signals at $2\theta = 27$ and 36°, corresponding to the rutile phase, after the thermal cycle of reduction and oxidation. Hence, the capacity of hydrogen chemisorption was probably lost because some Pt atoms became embedded inside titanium oxide particles during phase transformation of the latter during the thermal cycle.

For catalysts with NaOH as base, the capacity of hydrogen chemisorption of supported Pt was found to be a function of Na^+ content in the titanium oxide supports and of the pH of the solution used for preparation. The H/Pt ratio decreased as the pH and Na^+ content increased, even after reduction at 473 K. The largest H/Pt ratio was obtained for Pt supported on Na/Ti/3. As this H/Pt ratio exceeded that obtained over any catalyst prepared with NH_3 base although the surface area of the former was smaller than that of the latter, ca. 1 wt. % Na^+ content in titanium oxide support enhanced the capacity of Pt to chemisorb H_2. However, when the Na^+ content exceeded 8.8% (sample Na/Ti/10 and Na/Ti/13), the capacity of Pt for H_2 was obviously suppressed even just through reduction at 473 K. As the particle size determined from TEM photographs showed no correlation with Na^+ content, the effect of Na^+ on the chemisorption capacity of Pt is likely due to electronic interaction. In contrast to the catalysts prepared with NH_3, the recovery of chemisorption capacity after the thermal cycle of oxidation and reduction was almost complete for all these samples. Fig. 4 shows no detectable phase transformation occurred during this cycle. These results indirectly support our proposal that phase transformation is responsible for the non-reversible adsorption behavior observed on Pt supported on NH/Ti/7 and NH/Ti/10.

The present work shows that the crystal structure of titanium oxide has no exclusive impact on interaction between Pt and the support. Although Lane and Wolf[18] reported that suppression of chemisorption capacity was less for Pt supported on rutile than on anatase, a contrary result was observed for our catalysts. For instance, Pt on the

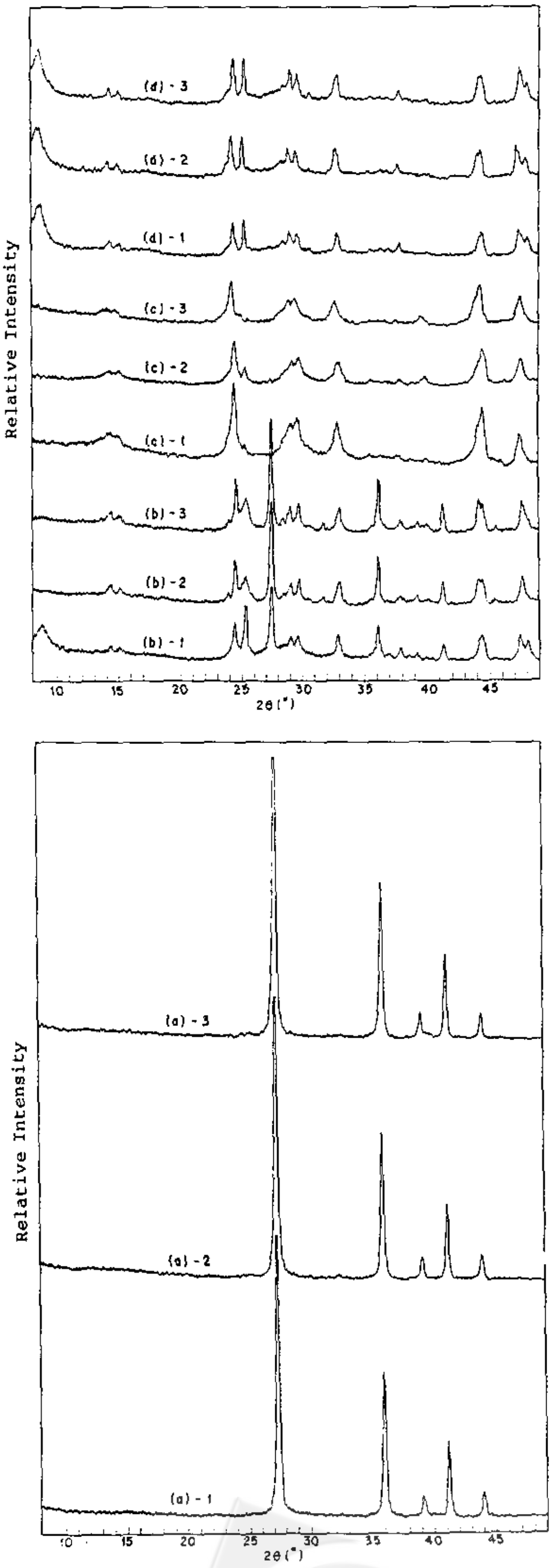

Fig. 4. X-ray diffraction patterns of Pt supported on titanium oxides prepared with NaOH after various treatments; (a) Na/Ti/3, (b) Na/Ti/7, (c) Na/Ti/10 and (d) Na/Ti/13; -1: reduction at 473 K, -2: reduction at 773 K, -3: HTR-HTO-LTR cycle.

Na/Ti/3 support, which has the rutile structure, showed more typical SMSI phenomenon than catalysts with anatase structure, such as NH/Ti/10. On the other hand, the capacity to chemisorb hydrogen on Pt supported on Na/Ti/7, which contains mixed phases of rutile, anatase and layered titanate, varied with reduction conditions similar to that on NH/Ti/3, which is mainly anatase and with slight rutile.

ACKNOWLEDGEMENT

We thank the National Science Council of Taiwan, R.O.C. for financial support.

Key Words

Titanium oxide; Metal-support interaction; Crystalline structure; Sodium content.

Received September 21, 1994.

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