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Thermochimica Acta 256 (1995) 457–465

thermochimica
acta

Temperature-programmed-reduction studies of nickel oxide/alumina catalysts: effects of the preparation method

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Received 13 June 1994; accepted 6 November 1994

Abstract

Two series of NiO/Al₂O₃ catalysts with various metal loadings were prepared by incipient-wetness impregnation and coprecipitation methods. The reducibilities of NiO over these catalysts were investigated by the temperature-programmed reduction (TPR) technique. For impregnated Ni/Al₂O₃ catalysts, more than one species was detected by TPR. At low nickel loadings, the NiO–Al₂O₃ interaction is strong, and at high Ni loadings NiO is observed. NiAl₂O₄ was not detected at all Ni loadings. For precipitated Ni/Al₂O₃ catalysts, three NiO species are present in the TPR profiles. NiAl₂O₄ was detected at all Ni loadings. The rate of reduction of NiO on the support depends not only on the chemical nature of the NiO species but also on the rate of nucleation of metallic nickel. At high nickel loadings, owing to the presence of easily reduced Ni species, the rate of reduction is enhanced.

Keywords: Catalyst; Nickel/alumina; Nickel oxide; TPR

1. Introduction

Nickel catalysts have gained tremendous attention because they are active in hydrogenation, hydrotreating, and steam-reforming reactions. The basic idea of supporting nickel catalysts on high surface area ceramic substrates, such as silica

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and alumina, is to increase the surface area of nickel. Studies have shown that NiO is usually the major surface species at high levels on all supports, but species arising from Ni–support interaction vary depending on the chemical and physical properties of the support [1–9].

For supported nickel catalysts, reduction of nickel is difficult [5], and the equilibrium between oxidic Ni and H₂ varies depending on the extent of interaction between Ni and the support. Therefore, Ni–support interactions can be characterized by the reducibility of nickel. Previous studies [5,10] have indicated that nickel supported on alumina is not completely reduced to the metallic state due to a strong oxide–support interaction. This reduction depends on metal loading and calcination temperature and has been attributed to the formation of nickel aluminate spinel [1], or to nickel ions in the tetrahedral and octahedral sites of alumina [2], or to a modification of the electronic properties of nickel oxide due to reduction with alumina [3]. Zielinski [11] studied the effect of the morphology of nickel oxide on alumina catalysts. Nickel oxide existed on the support in two states: in free form as nickel oxide and in fixed form as a stoichiometric and/or non-stoichiometric nickel aluminate. The process of reduction causes a bi-dispersed structure of large and small nickel crystallites to form on the support. Small and large nickel oxide crystallites were found to undergo reduction with the same ease. The difficulty in the reduction of the supported catalysts is reported to be due to the chemical interaction of nickel oxide with the Al₂O₃ support.

In general, the interaction between the metal oxide and the carrier may be classified into three categories: (a) very weak interaction in which the support acts only as a dispersing agent, (b) solid solution formation, and (c) strong interaction or surface compound formation. The major interest in Ni/Al₂O₃ catalysts has centered on interactions between the metal and the support. It is known that metal–support interactions appreciably affect the surface properties of these catalysts and, hence, their catalytic properties. This results from the migration of nickel ions into alumina lattice sites of octahedral or tetrahedral symmetry. In the present paper, effects of preparation method and metal loading on the extent of interaction between nickel and alumina are investigated using the temperature-programmed-reduction (TPR) technique.

2. Experimental

2.1. Materials

Analytically pure Ni(NO₃)₂ · 6H₂O and Al(NO₃)₃ were obtained from Wako Chemical Co., Japan. A Harshaw Al-3945 γ -alumina (234 m² g⁻¹) was used as a support. The chlorine content in the bulk of this material was 45 ppm as determined by bulk analysis. Ultrapure argon and pre-mixed 10% hydrogen in argon (99.99% purity) used in this study were from Air Products and were further purified by passage through a Deoxo unit at 25°C and a 5A molecular sieve trap at –77°C.

2.2. Catalysts preparation

NiO reference material was prepared by decomposition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 400°C for 4 h. This temperature is high enough to decompose it [5]. Impregnated catalysts were prepared by the standard incipient-wetness (IW) method using an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [12,13]. A γ -alumina support with a particle size of 0.225 μm was used to ensure the existence of uniform metal profiles throughout the particles [14,15]. The coprecipitated Ni/ Al_2O_3 catalysts (designated as CP) were prepared by coprecipitation of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3$ in an aqueous solution with NaOH (Merck) at 0°C [11]. The final pH of the solution after precipitation was 11 ± 0.3 . NiAl_2O_4 was prepared by a coprecipitation method followed by heating to 850°C [14,15]. All catalysts were dried at 120°C for 24 h and calcined at 450°C for 6 h before use. The bulk Ni concentration of the catalysts was determined by atomic absorption (AA) spectroscopy after digestion of catalyst samples in concentrated HNO_3 for 24 h, and found to be within $\pm 0.2\%$ of the stated value.

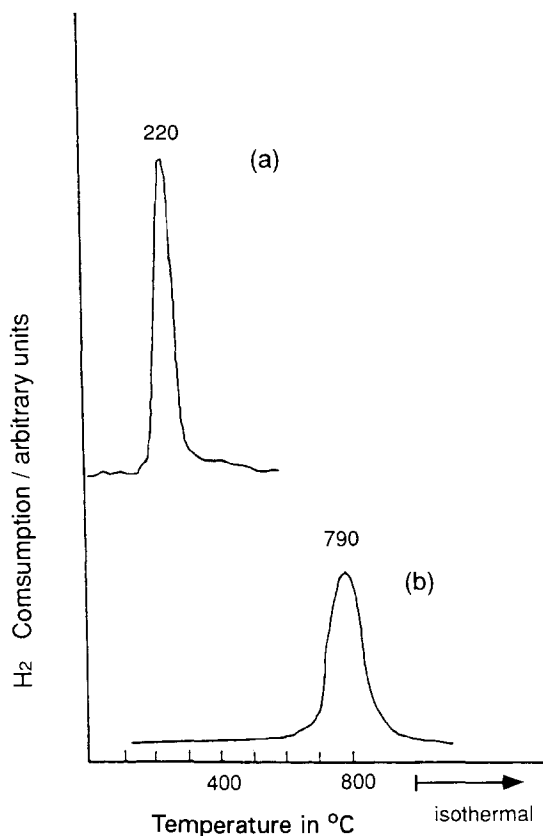


Fig. 1. (a) TPR of unsupported NiO. (b) TPR of unsupported NiAl_2O_4 .

2.3. TPR

The TPR experiments were made using a quartz U-tube reactor, similar to that described by Jenkins et al. [16] and Menon et al. [17]. The H₂/Ar carrier gas is further purified by passing through an oxisorb (Alltech) and a 5A molecular sieve trap to remove trace amounts of oxygen and water. This gas stream is then split, one path leading to the reference arm of the thermal conductivity detector (TCD, Shimadzu GC-8A) and the other passing through the reactor before going to the detector. Any reaction products generated during TPR can be trapped by a dry ice trap located between reactor and TCD. The signals for TCD can be calibrated by injecting pure sample by using a Valco sampling valve of known volume. Because reduction is an exothermic reaction, a minimum amount of sample (about 50 mg) is used to ensure no mass transfer limitations and also to satisfy differential bed conditions. The reactor is made of quartz and includes a small thermo-well for continuous temperature measurement. Several millimeters of glass wool were added at each end of the reactor to avoid entrance and exit effects, but there was no dilution of the catalysts. Mears criterion [18] indicated temperature gradients should be negligible. Application of appropriate criteria indicated that mass and heat transport effects were also negligible. Before starting the TPR experiments, the catalysts were dried in flowing Ar at 400°C for 1 h. 10% H₂/Ar was used as the reducing gas at a flow rate of 40 ml min⁻¹. The rate of temperature rise in the TPR experiment was 10°C min⁻¹ up to 900°C.

3. Results and discussion

3.1. Unsupported NiO and NiAl₂O₄

The TPR profiles of unsupported NiO and Ni/Al₂O₄ are illustrated in Fig. 1. The results are in agreement with those reported in the literature [19,20]. These peaks can be used to identify bulk NiO and Ni/Al₂O₄ species on catalyst samples.

3.2. Impregnated Ni/Al₂O₃

The TPR profiles for a series of impregnated Ni/Al₂O₃ catalysts are shown in Fig. 2. For 1.8% Ni/Al₂O₃, a broad peak is observed around 510°C (Fig. 2, curve (a)). As the Ni loading is increased, a peak starts to appear at around 250°C and the relative proportions of this peak increase as the Ni loading increases. In addition, this peak shifts to lower temperature as the nickel loading increases. The correspondence between the peak maximum of this low-temperature peak and that of the bulk nickel oxide (Fig. 1, curve (a)) makes it reasonable to assign this peak to large particles of nickel oxide which, although dispersed by the alumina, do not form significant chemical bonds with the underlying alumina surface. However, none of the TPR peaks at any Ni loading resembles that for NiAl₂O₄ ($T_{\max} = 790^\circ\text{C}$). This result indicates that bulk NiAl₂O₄ is not formed on the impregnated Ni/Al₂O₃.

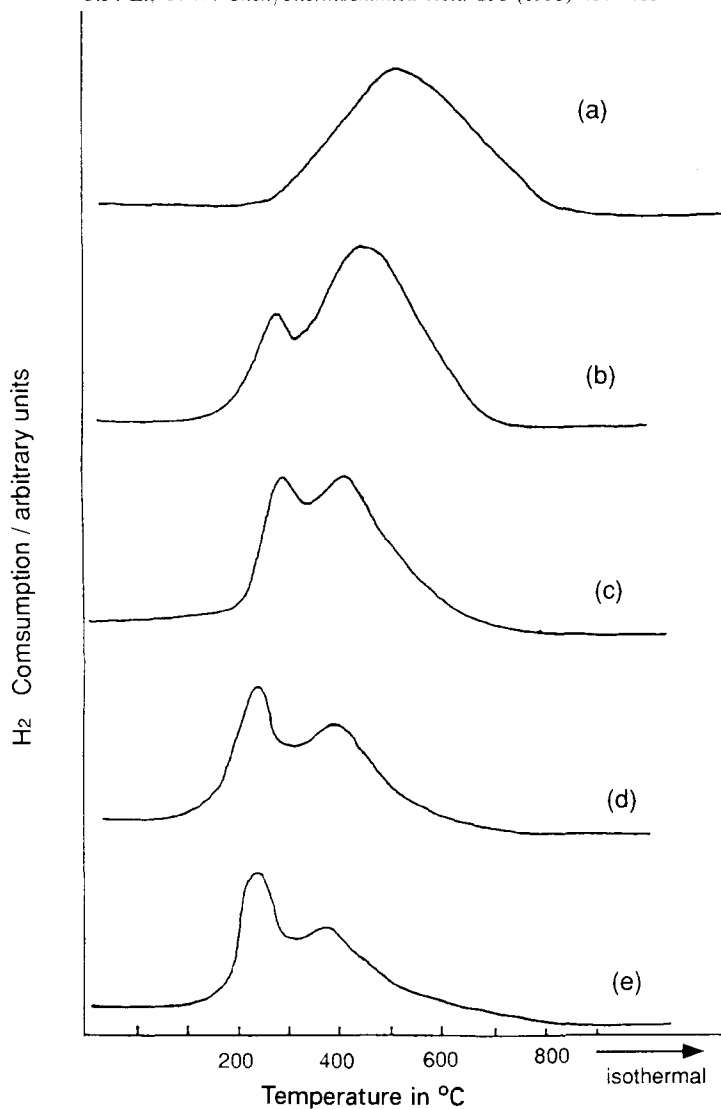


Fig. 2. TPR profiles for impregnated Ni/Al₂O₃ catalysts: (a) 1.8 wt% Ni; (b) 5.3 wt% Ni; (c) 11.3 wt% Ni; (d) 16.4 wt% Ni; (e) 24.8 wt% Ni.

catalysts. This is possibly due to the low calcination temperature used in this study or to the fact that surface nickel aluminate has a different reducibility than the bulk.

Variations of the TPR profiles of impregnated Ni/Al₂O₃ catalysts as a function of Ni loading can be interpreted as Ni species interacting with different Al₂O₃ sites. Shyu [21] has reported, based on his XPS studies, that the extent of the Ni/Al₂O₃ interaction depends on the Ni loading. At nickel loadings below 12%, nickel species interact with tetrahedrally coordinated sites of γ -Al₂O₃, while at nickel loadings above 12%, the Al₂O₃ is saturated with Ni and bulk NiO is formed on the Al₂O₃

surface. In addition, Ni(tetra) is not reducible at temperatures below 400°C. Based on the above discussion, the TPR peak for 1.8 wt% Ni/Al₂O₃ at 510°C can be attributed to Ni(tetra). Compared to unsupported NiO, the increased difficulty of Ni(tetra) reduction suggests that the Ni species in tetrahedral sites of the γ -Al₂O₃ is chemically modified. The difference in TPR between NiAl₂O₄ and the 1.8 wt% Ni/Al₂O₃ indicates that the strongly interacted Ni(tetra) phase is not bulk NiAl₂O₄. It is worth noting that the peak of Ni(tetra) shifts to lower temperature as the Ni loading increases. This is probably because the rate of reduction of Ni(tetra) depends not only on its chemical nature but also on the nucleation process by which metallic nuclei are generated. For high metal loading catalysts, a significant amount of reducible NiO species may serve as metallic nuclei to facilitate reduction of Ni(tetra).

Many investigators [22–25] have also found evidence for an NiO which is far less reducible than the bulk oxide. They proposed that this is an oxide present as very small particles and that the difficulty in reduction arises from the low rate of nucleation of these small-sized particles. Such an explanation is consistent with the high-temperature peak observed in the present work. However, we favor a more chemical reason for the high-temperature peak, namely the formation of amorphous surface nickel aluminate bearing some resemblance to bulk nickel aluminate. This type of structure is logical because the γ -Al₂O₃ crystal structure is that of a spinel with a deficit of cations. However, the diffusion of nickel ions during calcination into the alumina lattice sites is limited to the first few outer layers of the support. It must be recognized that the “surface spinel” in Ni/Al₂O₃ catalysts does not have long-range, three-dimensional order, because characteristic X-ray diffraction lines have not been observed. Turlier et al. [24] have suggested a similar explanation for the inhibition of nickel reduction on silica and alumina. Thomas et al. [26] proposed similar compounds to explain the decreased reducibility of Mo/Al₂O₃ catalysts. The difference between the two explanations may actually be semantic. It should be noted that, for hemispherical particles, 30% of the nickel oxide phase will be in contact with the alumina surface and even greater proportions will be in contact for raft-like particles. Such intimate contact between the two phases would result in moderately strong interaction and could lead to a reducibility intermediate between bulk nickel oxide and nickel aluminate.

3.3. *Precipitated Ni/Al₂O₃ catalysts*

To compare the effect of preparation method on the chemical nature of the Ni species on Ni/Al₂O₃ catalysts, a series of precipitated Ni/Al₂O₃ catalysts was studied by TPR, as shown in Fig. 3. There are two sets of peaks in the TPR profiles, 420–500°C and around 720°C. The latter peak around 720°C is close to that for NiAl₂O₄. It is noteworthy that TPR data show a broad peak at around 500°C at nickel loadings of 10 and 15 wt% (Fig. 3, curves (b) and (c)). However, at Ni loadings greater than 20%, two NiO components are observed and the peak widths decrease. This result clearly indicates that the nature of the Ni species on precipitated catalysts varies with Ni loading.

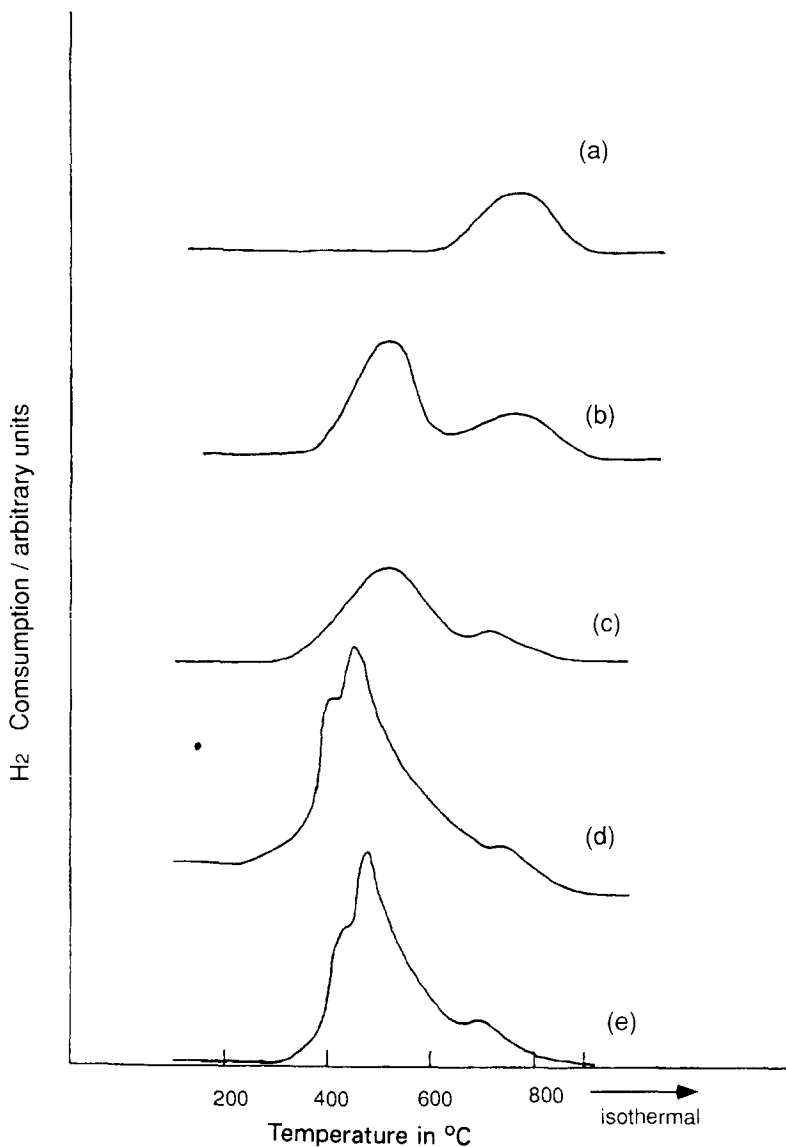


Fig. 3. TPR profiles for coprecipitated Ni/Al₂O₃ catalysts: (a) 1.9 wt% Ni; (b) 10.2 wt% Ni; (c) 14.8 wt% Ni; (d) 20.6 wt% Ni; (e) 26.7 wt% Ni.

At nickel loadings below 15 wt%, the peak at 750°C can be attributed to NiO–Al₂O₃ solid solution, because this solid solution is not reducible at temperatures below 700°C. The broad peaks at around 470°C should be attributed to Ni(tetra) as discussed in the previous section.

However, as the Ni loading is increased up to 20%, two peaks were observed between 400 and 460°C (Fig. 3, curves (d) and (e)). This is possibly due to the

increased nucleation rate of large NiO crystallites. This effect reduces the width of the TPR peaks and makes the broad peak resolvable at high Ni loadings. Fig. 2 also shows that the high-temperature peaks ($> 700^{\circ}\text{C}$) shift to lower temperature as the Ni loading increases. In addition, the area of this peak decreases as the Ni loading is increased. This result suggests that the presence of easy-to-reduce species may facilitate nucleation of other Ni nuclei which originally interact strongly with the support and thus enhance the reduction of the more strongly interacting Ni species [27].

4. Conclusions

TPR studies of Ni/Al₂O₃ catalysts lead to the following conclusions.

(1) For impregnated Ni/Al₂O₃ catalysts, more than one species was detected by TPR. At low nickel loadings, the Ni–Al₂O₃ interaction is strong and at high Ni loadings, NiO is observed. NiAl₂O₄ was not detected at all Ni loadings.

(2) For precipitated Ni/Al₂O₃ catalysts, three Ni species are present in the TPR profiles. NiAl₂O₄ was detected at all Ni loadings.

(3) The rate of reduction of Ni on the support depends not only on the chemical nature of the Ni species but also on the rate of nucleation of metallic nickel. At high nickel loadings, due to the presence of easily reduced Ni species, the rate of reduction is enhanced.

Acknowledgement

This research was supported by the National Science Council of the Republic of China.

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