Catalytic behaviour of NiAl$_2$O$_4$ spinel upon hydrogen treatment

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The effect of reduction on the catalytic activity and selectivity of nickel aluminate spinel has been reported using the 2-propanol decomposition reaction. The unreduced catalyst showed only dehydration activity. When reduced in hydrogen at different temperatures starting from 200 °C, dehydrogenation activity was observed. After reduction at 450 °C, the activity completely transformed into dehydrogenation, while the spinel structure remained unchanged. The unreduced and reduced catalysts were characterized by X-ray diffraction, temperature-programmed reduction, diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. The mechanism for the decomposition is discussed in terms of the coordination of aluminium ion and reducibility of nickel.

1. Introduction

Supported nickel catalysts are extensively used in reactions like hydrogenation of organic compounds, methanation, steam reforming and nitrous oxide decomposition [1–4]. Several studies on alumina-supported nickel catalysts revealed that their surface consisted of nickel aluminate spinel, NiAl$_2$O$_4$ [5–8] and when reduced, they were found to possess well-dispersed nickel species on their surface [8–10]. In a recent study on catalysts with varying stoichiometries of nickel and aluminium, Al-Ubaid [11] and Al-Ubaid and Wolf [12] observed that the catalyst having a composition corresponding to NiAl$_2$O$_4$ after reduction showed the highest activity for steam reforming of methane.

In the present communication, we report the effect of hydrogen treatment on the activity of NiAl$_2$O$_4$ spinel in the decomposition of 2-propanol.

2. Experimental procedure

NiAl$_2$O$_4$ was prepared by coprecipitating a stoichiometric mixture of nitrates of nickel and aluminium using 1 N ammonium hydroxide solution to a final pH of 8.2 [8]. The hydroxide precursor thus obtained was calcined at 800 °C for 24 h with intermittent grinding. The sample was quenched to room temperature by removing from the furnace. Pelletized samples were used for reduction and characterization. Reduction treatment was given in a tubular furnace by passing hydrogen through it for 3 h at various temperatures starting from 200 °C. The unreduced catalyst will be referred to as calcined NiAl$_2$O$_4$ and that reduced at 450 °C as reduced NiAl$_2$O$_4$.

Catalytic activity studies were carried out at atmospheric pressure in an all-glass fixed-bed continuous-flow reactor employing 1 cm^3 of the catalyst in powder form. The reactant was introduced into the re-

actor by means of an infusion pump. No carrier gas was used. Details of the experimental set-up are described elsewhere [13]. The experiments were performed at 250 °C with a contact time of 1.18 s. The experiments were initially carried out on the calcined sample after activation in air at 400 °C for 3 h. Subsequent experiments involved pretreatment *in situ* with hydrogen at various temperatures. In the case of reduction at 200 °C, the temperature was raised to the reaction temperature (250 °C) in a flow of nitrogen, since the temperature of reduction was less than that of the reaction. The gaseous products were analysed in an Orsat apparatus and the liquid products in a gas chromatograph [13]. Temperature-programmed reduction (TPR) studies were performed in a Perkin Elmer TGA-7 thermal analyser at a heating rate of 10 °C min^{-1} and a hydrogen flow rate of 25 cm^3 min^{-1}. A Perkin Elmer 3700 data station was used for processing the spectra after recording.

X-ray diffraction (XRD) patterns were recorded in a Phillips (PW 1140) X-ray diffractometer using nickel-filtered CuK$_\alpha$ radiation ($\lambda = 0.15418$ nm). The inversion parameter of the spinels was calculated by considering the line intensities of 2 2 0 and 4 4 0 planes [14].

Diffuse reflectance spectra (DRS) were recorded in a Cary 2300 u.v.–visible spectrophotometer equipped with a spherical integrator. BaSO$_4$ was used as standard. Necessary correction was applied before plotting the spectra.

Surface areas were estimated by the BET (N$_2$) method in a BET sorptometer (PMI Inc., USA).

Ion-exchange and n-butyl amine titration methods were used in determination of surface protonic and Lewis acidities, respectively [15].

X-ray photoelectron (XP) spectra (XPS) were recorded in an Escalab Mark II instrument (Vacuum Generators, UK) at an operating pressure of

10^{-8} mbar or less. The radiation used was MgK_α with an energy of 1253.6 eV. XP spectra were also recorded after sputtering the sample with argon ions for 5 min at a pressure of 5×10^{-6} mbar and at an accelerating voltage of 8 kV. The resultant beam current was 50 μA. The binding energy (BE) scale was calibrated against the 2p line of aluminium in the sample, centred at 74.5 eV [16].

3. Results and discussion

3.1. Catalytic activity

Calcined $NiAl_2O_4$ showed only dehydration activity, giving propene and water. After a few experiments on this catalyst which gave reproducible results, it was subjected to reduction. This treatment was found to induce dehydrogenation activity in the system. Experiments carried out after reduction at 200, 300, 400 and 450 °C showed increasing activity for dehydrogenation. The overall conversions, yields of propene and selectivity for dehydrogenation are given in Table I. The percentage selectivity is defined as

$$\frac{\text{Yield of hydrogen or acetone}}{\text{Total conversion}} \times 100$$

The trends in the yields of hydrogen and selectivity for dehydrogenation are shown in Fig. 1 as a function of reduction temperature (T_r). The results indicate that both activity and selectivity for dehydrogenation increased with increase in T_r. It is interesting to note that the selectivity for dehydrogenation reached 100% as dehydration activity completely disappeared after reduction at 450 °C. Such transformation of selectivity of an aluminate spinel is reported for the first time in this communication.

In view of this change in selectivity upon reduction, characterization of the calcined and reduced catalysts was undertaken with the help of XRD, TPR, DRS and XPS techniques.
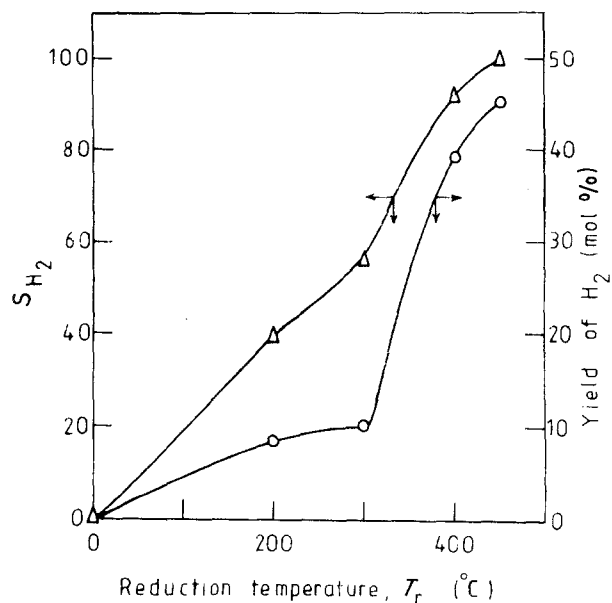
3.2. XRD patterns

Calcined $NiAl_2O_4$ was blue in colour. The catalyst reduced in the tubular furnace as well as the catalyst reduced in the catalytic reactor at 450 °C were bluish-black in colour. Phase identification of these two catalysts was done by XRD. The XRD patterns of the calcined catalyst and the catalyst reduced in situ in the catalytic reactor are shown in Fig. 2. In both cases, only the spinel phase was observed. Increasing the sensitivity in the case of reduced $NiAl_2O_4$ did not reveal any extra peaks that might arise due to crystalline Ni or NiO. Hence, it may be understood that the spinel network remained intact even after reduction. The colour change suggests that the reduction was confined only to the surface layers.

3.3. TPR studies

The extent to which the catalyst was subjected to reduction was estimated by TPR studies. Fig. 3 shows the TPR profiles of calcined $NiAl_2O_4$ and its derivative. Although there seems to be an initial baseline drift as indicated by the derivative curve (Fig. 3b), a general loss of weight can be observed. The rate of reduction

TABLE I Activity of $NiAl_2O_4$ catalyst before and after reduction for the decomposition of 2-propanol

T_r (°C)	Yield (mol %)		S_{H_2}	Total conversion (mol %)
	Propene	Hydrogen		
–	13.17	–	0.0	13.17
200	12.95	8.61	40.0	21.56
300	7.62	10.03	56.8	17.65
400	3.59	39.29	91.6	42.88
450	–	45.17	100.0	45.17

Figure 1 Influence of reduction temperature on the selectivity and yields of acetone formation on $NiAl_2O_4$.

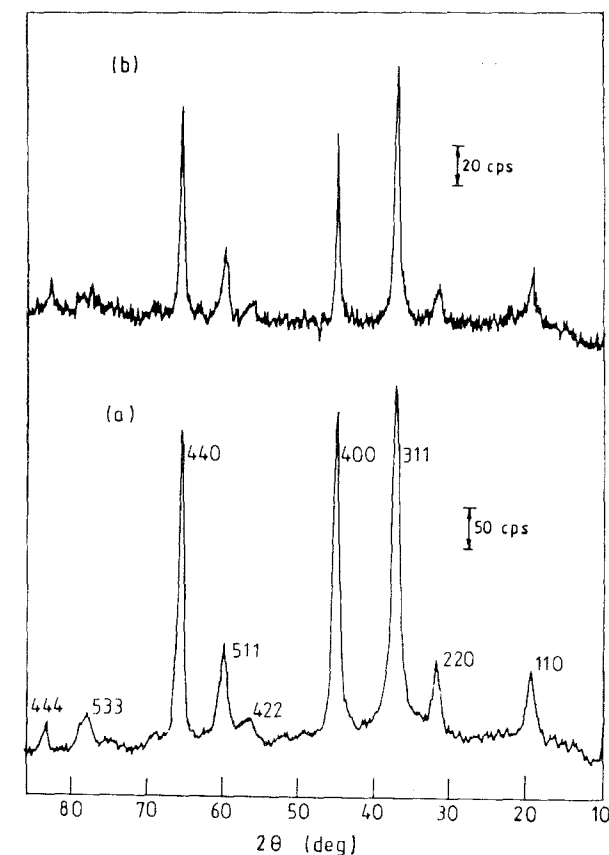*Figure 2* X-ray patterns of $NiAl_2O_4$: (a) calcined, (b) reduced.
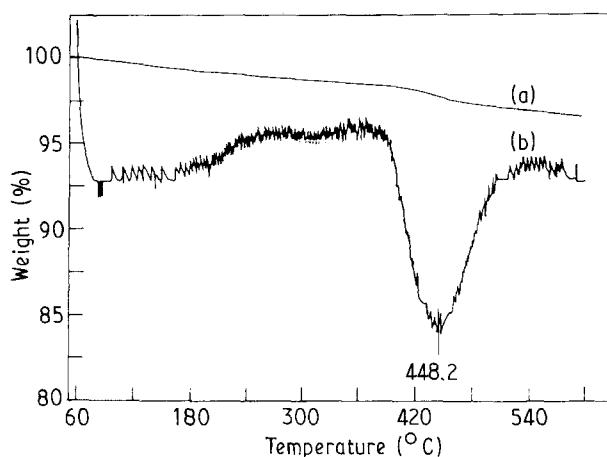
Figure 3 TPR spectra of (a) NiAl$_2$O$_4$, (b) derivative of (a).

Figure 4 DRS spectra of NiAl$_2$O$_4$: (a) calcined, (b) reduced.

was maximum at 448 °C. The extent of reduction at this temperature, indicated by the weight loss, was only 2.48%, as against the maximum possible weight loss of 9.06% which was calculated according to the equation

$$NiAl_2O_4 + H_2 \rightarrow Ni + Al_2O_3 + H_2O \uparrow$$

It may be noted that although the catalyst was partially reduced, its structure remained undisturbed, as revealed by the XRD.

3.4. Surface areas

Calcined NiAl$_2$O$_4$ had a surface area of 67.0 m^2 g^{-1} while it was 62.1 m^2 g^{-1} for the reduced catalyst. This indicates that the surface area was not affected by the reduction treatment.

3.5. DRS studies

DRS studies were carried out in order to find out the environment in which the surface metal ions were present, by means of characteristic absorption bands. The DRS of the calcined and the reduced catalysts are shown in Fig. 4. The spectra obtained were similar to those reported by Scheffer et al. [17]. A decrease in intensity was observed after reduction, indicating the disappearance of surface species, while a band at 320 nm is still prominent, which is assigned to Ni^{2+} in NiO [17].

3.6. XPS studies

XPS studies were carried out with a view to knowing the oxidation state of nickel in the calcined and reduced catalysts. The results are tabulated in Table II. From the BE values of Ni 2p$_{3/2}$, observed at 856.4 eV, the surface of these catalysts was found to contain nickel in +2 state [7, 12]. The Ni 2p spectra are reproduced in Fig. 5. The spectra of the calcined and the reduced catalysts are nearly identical with respect to BEs and line shapes. This observation is consistent with the report of Al-Ubaid and Wolf [12]. No metallic nickel could be noticed in the XPS of reduced
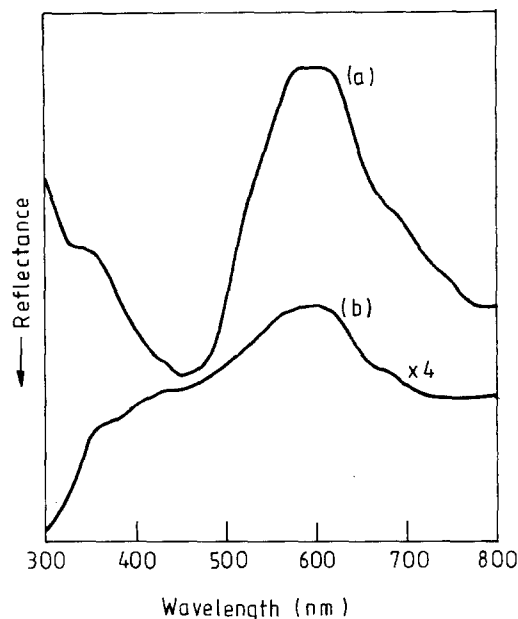
TABLE II XPS results on the NiAl$_2$O$_4$ system

Compound	BE (eV)[a]				
	Ni 2p$_{3/2}$	Ni 2p$_{1/2}$	ΔBE	Ni 3p$_{3/2}$	O 1s
NiAl$_2$O$_4$	856.4 (862.5)	874.2 (880.9)	17.8	68.8	531.4 (522.4)
Reduced NiAl$_2$O$_4$	856.5 (862.8)	874.1 (880.3)	17.6	68.8	531.5 (522.5)
Reduced NiAl$_2$O$_4$ after Ar$^+$ sputtering	856.6 (862.5)	874.1 (880.6)	17.5	68.8	531.2 (522.2)

[a] Values in parentheses correspond to the BEs of respective satellites.

NiAl$_2$O$_4$. This may be due to the aerial oxidation occurring during the transfer of the catalyst into the XPS instrument. If such oxidation was restricted to the surface layers, argon ion sputtering should expose the metallic species to the surface. The spectrum obtained after argon ion sputtering is shown in Fig. 5c. Here too, the +2 state of nickel dominates the surface. However, a clear shoulder can be seen at 853.5 eV which corresponds to metallic nickel [18, 20]. In a similar study on reduced nickel aluminates, Al-Ubaid and Wolf [12] were unable to observe this peak because no sputtering was done, which led them only to speculate on the existence of mono-dispersed nickel. The aerial oxidation during the transfer of the catalyst is evident because of the extremely active (pyrophoric) nickel species that developed as a result of the reduction. In situ reduction in the preparation chamber of the XPS instrument would have thrown more light on this aspect.

4. Mechanism of 2-propanol decomposition
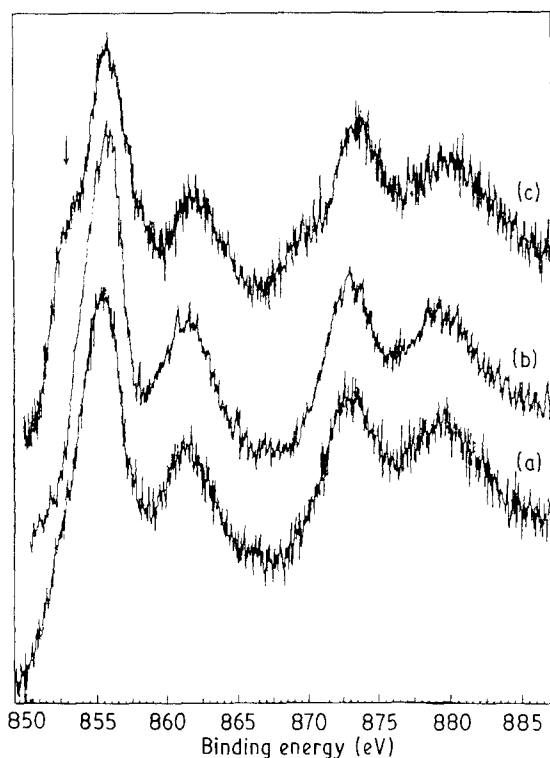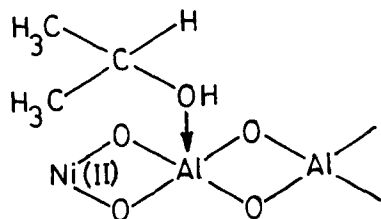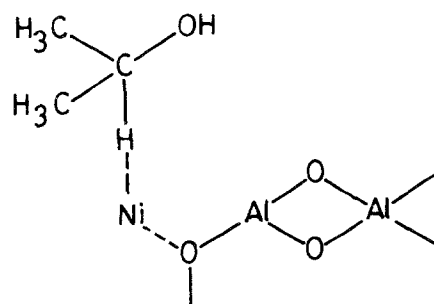
It is well known that NiAl$_2$O$_4$ is an inverse spinel

Figure 5 XPS (Ni 2p) of NiAl$_2$O$_4$: (a) calcined, (b) reduced, (c) reduced and Ar$^+$ ion etched.

In this case, the alcohol gets adsorbed through the hydrogen of the secondary carbon on to the Ni(0). Previous studies on reduced Ni–Al$_2$O$_3$ catalysts showed that the reduction treatment enhanced the chemisorption of hydrogen [12]. In the present case, dehydrogenation of alcohol must be occurring due to a similar tendency of the catalyst, wherein hydrogen was taken up from the alcohol.

5. Summary and conclusions

Calcined NiAl$_2$O$_4$ showed only dehydration activity towards the decomposition of 2-propanol. Reduction of this catalyst with hydrogen led to the generation of dehydrogenation activity. When reduced at 450 °C, the catalyst exhibited exclusively dehydrogenation activity. XRD of the reduced NiAl$_2$O$_4$ showed that the spinel structure remained unchanged after reduction, while TPR and DRS techniques indicated partial reduction of the spinel. XPS studies revealed the presence of metallic nickel species. Based on these studies, the dehydration activity was attributed to the tetrahedrally coordinated Al^{3+} ions acting as Lewis acid centres. The dehydrogenation reaction was catalysed by the surface nickel species.

To conclude, the reduction treatment of NiAl$_2$O$_4$ at 450 °C led to the formation of a system which was crystallographically the same but catalytically different.

[21]. In the present case, the inversion of calcined NiAl$_2$O$_4$ was found to be 0.76. An earlier report from this laboratory showed that dehydration activity of NiAl$_2$O$_4$ in 2-propanol was influenced by its inversion parameter [22]. Al^{3+} ions present in tetrahedral sites were found to act as Lewis centres on the surface and were responsible for this activity. In the present case, calcined NiAl$_2$O$_4$ was found to possess only Lewis acidity which was 0.50 mmol g^{-1}. Ross *et al.* [8] proposed a scheme to explain the participation of surface Al^{3+} ions in the steam reforming of methane. The scheme can well be extended here for the dehydration reaction of 2-propanol, as shown below:

In this process, the alcohol gets adsorbed through oxygen to the Al^{3+} ion which is deficient in electrons, while Ni^{2+} remains inactive. Upon reduction, nickel goes over to the metallic state and facilitates the dehydrogenation process, according to the scheme given below, which is again an extension of that suggested by Ross *et al.* [8].

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