ABSTRACT

A variety of methods are available today for the synthesis of nanostructured materials, which can be used directly or in some supported form as catalyst. However, the mechanical alloying (MA) route for the production of such catalyst is very attractive because of its flexibility, inherent good intermixing, low capital cost, good production rate and ease of scaling up; although, contamination from the milling media may be a problem in some cases. In the present investigation, therefore, mechanical alloying has been used to generate Ni-based nanostructured catalysts.

Taking into account of the well documented structure and applications of NiAl, a precursor of Raney nickel, it was considered a useful model system for the present study of the catalytic activities, deactivation characteristics and their relationship with the surface and bulk structure / composition of the catalysts. Besides, the influence of defect structures on catalysis can be conveniently studied with mechanically alloyed phases in Ni-Al system. In particular, NiAl phase can exist as a single phase partially ordered B2-intermetallic compound over a wide composition range of 30 to 65 at. % Ni in the mechanically alloyed state, as against the equilibrium composition of 45 to 59 at. % Ni.

It is known that NiAl phase cannot be disordered even by rapid solidification. Binary NiAl also remains partially ordered in the mechanically alloyed state. Interestingly, Cr addition tends to disorder mechanically alloyed NiAl phase and therefore, influence of this disordered structure on the catalytic activity is also investigated in the present work. Besides, a simple method of pretreatment for increasing the activity of some Ni-Al phase is also reported.

The reaction chosen for this catalytic study is the decomposition of H_2O_2, which is a well-characterized model reaction, as well as a route for the production of oxygen. In the present work, a detailed systematic investigation of the catalytic characteristics of nanostructured Ni-Al phases in the decomposition of H_2O_2 has been undertaken to achieve an insight into this catalytic reaction.

Pure (> 99.5%) elemental Ni and Al powder of -300 mesh size (≤45 μm) were taken in the atomic proportions of $Al_{100-x}Ni_x$ (x= 10, 18, 21, 25, 30, 40, 50, 65, 68, and 90) in cemented carbide containers of a Fritsch Pulverisette-5 planetary mill and were mechanically alloyed for 30 hours at a mill-speed of 300 *rpm* in toluene medium using 10 mm diameter cemented carbide balls with ball to powder ratio of 10:1. In one case a pre-alloyed $Ni_{30}Al_{70}$ powder was used as a charge for milling. The mechanically alloyed powders were characterized by a Philips PW 1710 x-ray diffractometer with PW 1729 x-ray generator working at 40 kV using CoK_α (λ=0.179 nm) radiation. X-ray peak broadening has been used to calculate the effective crystallite size using Scherrer formula after separation of the contributions of strain and instrumental broadening by a standard procedure. The x-ray photoelectron spectroscopy (XPS) was done with a VG ESCA LAB MKII spectrometer using aluminum anode. Integrated peak areas of Ni 3*p* and Cr 2*p* peaks were used along with Al 2*p* peaks for quantitative analysis. Surface area measurements were carried out by BET method using GEMINI 2360 V2.01 analyzer. Particle size measurements were carried out using MALVERN Instrument M7.06 particle size analyzer.

It is found that liquid phase catalytic decomposition of H_2O_2 is marginally effected by the microcrystalline pre-alloyed-$Ni_{30}Al_{70}$ powder (particle size ≤45 μm) containing NiAl, Al_3Ni_2 and Al_3Ni phases. High-energy ball milling of this pre-alloyed-$Ni_{30}Al_{70}$ generated nano-sized (~12 nm) NiAl particles, which manifested a remarkable catalytic activity, similar to that of NiAl phase of $Ni_{30}Al_{70}$ composition synthesized by mechanical alloying of elemental blend. The appearance of the disordered Ni_3Al (or solid solution of Al in Ni) in $Ni_{68}Al_{32}$ diminished the activation energy appreciably as compared to $Ni_{65}Al_{35}$ nanocatalyst; although, the catalytic activity did not show any notable improvement as compared to that of $Ni_{65}Al_{35}$ composition.

The XPS indicates that in binary Ni-Al nano phases, Ni present as alloyed-Ni is possibly responsible for the catalytic activity. The negative shift of the XPS peaks of alloyed-Ni may be due to electron transfer from

Al to Ni on the surface, and its magnitude remains almost identical for a particular phase. The magnitude of electron transfer from Al to Ni on the surface in NiAl phase seems to be much higher than that in Al_3Ni and disordered Ni_3Al phase. The activity of the nanocrystalline Ni-Al phases seems to depend on the electronic state and the amount of the surface Ni bonded to Al, as well as the defect structure of the catalyst. The active sites for the H_2O_2 decomposition reaction on the surface nanostructured NiAl phase appear to consist of ~4 nickel atoms. All the catalysts get gradually deactivated with the formation of Al_2O_3 enriched surface layer possibly by the migration of Al atoms from the interior to the surface.

In NiAl(Cr) system, Cr in the NiAl phase seems to interact more with Al than with Ni, and the negative shift of Cr peaks may be due to the electron transfer from Al to Cr on the surface. The Cr^{+3} state on the surface of disordered NiAl(Cr) may be correlated with the observed catalytic activity in the decomposition reaction of H_2O_2. Presence of 20 at.% Cr in the nano-NiAl phase remarkably retards the deactivation of the catalyst.

The as-milled disordered Ni_3Al phase (or solid solution of Al in Ni) has very poor catalytic activity; but it has shown profound catalytic activity after a simple pretreatment in H_2O_2, apparently due to the formation of non-stoichiometric NiO on the surface of the catalyst in course of this pretreatment.