



## Short Communication

# Advantage of Ni/SBA-15 catalyst over Ni/MgO catalyst in terms of catalyst stability due to release of water during nitrobenzene hydrogenation to aniline

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## ABSTRACT

Two catalysts, Ni/SBA-15 and Ni/MgO were prepared by wet impregnation technique with 5 wt.% Ni loading in each catalyst. These were tested for nitrobenzene hydrogenation to aniline reaction under vapor phase at atmospheric pressure. Ni/MgO suffered a huge loss in the activity (conversion) during time on stream study even though the Ni dispersion is larger compared to that in SBA-15 supported catalyst. TPR studies of used catalysts confirm coking of the catalysts. The superior catalytic activity in terms of conversion and selectivity during time on stream operation exhibited by Ni/SBA-15 catalyst is due to the hydrophobic nature of this catalyst (resistant to water generated during the reaction) and the effect of coking is not significant.

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## 1. Introduction

Aniline (AN) is an important intermediate for preparation of polyurethanes, dyes, pharmaceuticals, explosives, methylene diphenyldiisocyanate (MDI) and agricultural products. Hydrogenation of nitrobenzene (NB) is a convenient route to produce aniline (AN) over a variety of supported metal catalysts both in vapor and in liquid phase conditions [1–5]. The catalyst deactivation is mainly due to coking of the catalyst or sintering of active metal. There is no systematic study over the influence of water released during the reaction on the activity. The present investigation highlights this point for which Ni/SBA-15 and Ni/MgO catalysts have been selected.

## 2. Experimental

## 2.1. Catalyst preparation

The mesoporous SBA-15 support was prepared by using triblock copolymer (P123) as a structure directing agent and Tetra ethyl ortho silicate (M/s. Sigma Aldrich Chemicals, USA) as reported by Zhao et al. [6]. MgO was prepared by precipitation of  $\text{Mg}(\text{NO}_3)_2$  (M/s. Loba chemie, India) with 5%  $\text{Na}_2\text{CO}_3$  solution (M/s. Loba chemie, India) followed by washing, drying (393 K for 12 h) and calcining (773 K for 5 h) the precipitate. The Ni based catalysts were prepared by wet impregnation method using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M/s. Loba chemie, India) and the excess

water was removed by evaporation followed by drying at 393 K for 12 h and calcination at 723 K for 5 h.

## 2.2. Catalyst characterization

The catalysts were digested in aquaregia and the diluted solution was tested by AAS (M/s. Perkin–Elmer A-300) for Ni content. XRD patterns of the catalysts were recorded on a Ultima IV diffractometer (M/s. Rigaku Corporation, Japan) with 40 kV and 20 mA, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Water adsorption experiment was carried out on a homemade pulse reactor. In a typical experiment, about 100 mg of support/catalyst was placed in a micro-reactor (8 mm. i.d. and 250 mm long). The support was first pre-treated in He flow for 1 h at 523 K. The outlet of the reactor was connected to a TCD equipped GC-17A (M/s. Shimadzu Instruments, Japan) through an automatic six-port valve (M/s. Valco Instruments, U.S.A.). Pulses of water by passing He through the water trap at room temperature were injected into the reactor until there is no further change in the TCD signal intensity (monitored by using a Class-5000 software). Surface area of the catalysts was measured by nitrogen adsorption at 77 K using SMART SORB 92/93 (M/s. Smart Instruments Co (P) Ltd, India).

A homemade pulse reactor was used for  $\text{H}_2$  pulse chemisorption experiments at 300 K. Prior to the experiment, the catalyst was reduced in  $\text{H}_2$  flow at 773 K for 1 h and finally brought to room temperature at which 4.95%  $\text{H}_2$  balance argon was injected in pulses until no further change in the TCD signal intensity.

Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 5%  $\text{H}_2/\text{Ar}$  mixture gas at a rate of  $30 \text{ cm}^3 \text{ min}^{-1}$  with a temperature ramping of  $10 \text{ K min}^{-1}$ . The hydrogen consumption was monitored using a TCD equipped GC.

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### 2.3. Activity test

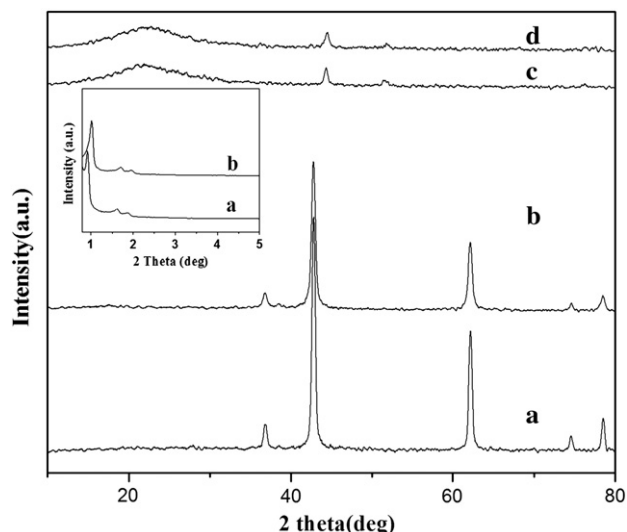
The hydrogenation of nitrobenzene was carried out in a fixed bed glass reactor (14 mm i.d.) at atmospheric pressure in the temperature range of 498–573 K with a liquid feed rate of  $1 \text{ cm}^3 \text{ h}^{-1}$  and  $\text{H}_2$  flow rate of  $18 \text{ cm}^3 \text{ min}^{-1}$  over 1 g of catalyst. In a separate experiment, co-feeding of  $\text{H}_2\text{O}$  ( $\text{H}_2\text{O}$ : NB = 2:3) along with NB is maintained. The product mixture was collected in ice trap. The product components were confirmed by GCMS-QP 5050A and analyzed by FID equipped GC-17A (M/s. Shimadzu Instruments, Japan).

### 3. Results and discussion

Table 1 indicates the Ni content, BET surface area, Ni dispersion by  $\text{H}_2$  pulse chemisorption, Ni particle size and water adsorption uptake of the supports and catalysts. The Ni content in both the catalysts is ~5 wt.% (Ni content in Ni/MgO is slightly higher than that in Ni/SBA-15). The decrease in BET surface area of Ni/SBA-15 is due to the pore blockage. It was reported that the considerable decrease in the surface area of the Ni/SBA-15 prepared by impregnation technique can be attributed to either the loss of crystallites or pore blockage [7]. MgO possesses low surface area and slight decrease in the surface area after incorporation of Ni may be due to the pore blockage. However, Ni dispersion and active metal area of this catalyst is nearly 3 times that of Ni/SBA-15 catalyst. This clearly indicates a strong interaction between Ni and MgO which dominates the pore blockage. The particle size of Ni in this catalyst is ~3 nm. Fig. 1 shows the XRD patterns of both the catalysts in reduced form and after the reaction. In Ni/MgO catalysts, reflections due to Ni metal are absent. The smaller Ni particle size as obtained from  $\text{H}_2$  chemisorption experiments prompts to think that Ni is in amorphous form. The reflections at  $2\theta$  values in the decreasing order of intensity:  $43.100$  (100%),  $62.599$ ,  $37.104$ ,  $79.053$  and  $75.092$  may be due to the presence of  $\text{MgNiO}_2$  (ICDD No.24-0712) or MgO (ICDD No.87-0653). It is reported that the XRD patterns of the (Mg, Ni)O system ( $\text{MgNiO}_2$ ) phase (cubic system, spatial group Fm3m and parameter  $a = 4.1922 \text{ \AA}$ ), its symmetry and unit cell parameter are essentially the same as those for the MgO (cubic system, spatial group Fm3m, parameter  $a = 4.209 \text{ \AA}$ ) phase and the incorporation of nickel to the structure of the MgO produces a shift of the diffraction peaks to higher  $2\theta$  values (lower crystalline plane distances) when the nickel content is higher. These findings indicate the formation of a solid solution,  $\text{NiO-MgO}$  [8–10]. In the case of Ni/SBA-15 catalyst, the reflections of Ni metal can be clearly seen in reduced and spent catalysts. A decrease in the intensity of reflections at lower  $2\theta$  with lower long-range order than the others (SAXS) for Ni/SBA-15 catalyst has been reported due to partial collapse of SBA-15 structure after the introduction of Ni salt by impregnation technique [7,11,12]. However in the present case, the low angle XRD patterns (inset in the main Fig. 1) of reduced and spent Ni/SBA-15 catalysts indicate the presence of mesoporous structure of SBA-15. This indicates the robustness of SBA-15 particularly in maintaining the mesoporous structure during the reaction.

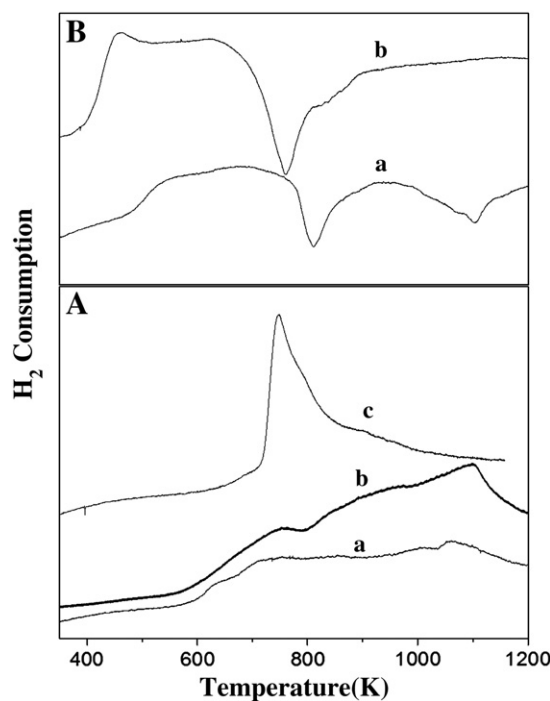
**Table 1**  
Physico-chemical properties of Ni/SBA-15 and Ni/MgO catalysts.

Property	Support		Ni/SBA-15		Ni/MgO	
	SBA-15	MgO	Fresh	Used	Fresh	Used
Ni content (wt.%)			5.05		5.30	
BET surface area ( $\text{m}^2 \text{ g}^{-1}$ )	546	51	427	325	45	42
Ni dispersion (%)	–	–	9.5	–	31.5	–
Ni particle size (nm)	–	–	10.6	–	3.2	–
Ni-metal area ( $\text{m}^2 \text{ g}^{-1}$ )	–	–	3.2	–	10.5	–
$\text{H}_2\text{O}$ adsorption capacity ( $\mu\text{mol g}^{-1}$ )	1.7	6.7	0	–	1.2	–



**Fig. 1.** XRD patterns of Ni catalysts. a) Ni/MgO (Reduced), b) Ni/MgO (Used), c) Ni/SBA-15 (Reduced) and d) Ni/SBA-15 (Used). Inset figure: SAXS pattern of a) Ni/SBA-15 (Reduced) and b) Ni/SBA-15 (Used).

TPR profiles of supported nickel catalysts (calcined and spent) are depicted in Fig. 2. In the case of Ni/SBA-15 catalyst, a single stage reduction peak at a  $T_{\text{max}}$  of 746 K is observed which corresponds to hydrogen consumption due to the reduction of  $\text{NiO}$  to  $\text{Ni}^0$ . It is reported that the TPR pattern of Ni/ $\text{SiO}_2$  catalyst presents two reduction peaks with  $T_{\text{max}}$  at 723 and 883 K. The low temperature signal is due to the reduction of NiO species of low interaction with the support, whereas the high temperature signal is due to the reduction of nickel oxide interacted chemically with the support which can be ascribed to the formation of nickel silicate [13,14]. Probably, a low intense shoulder peak at higher temperature region may be ascribed to the strongly interacted NiO with SBA-15. Whereas in the TPR pattern of Ni/MgO catalyst, a broad peak that could be attributed to strong interaction



**Fig. 2.** TPR patterns of Ni catalysts. A: Calcined catalysts. a) Ni/MgO, b) 10 wt.% Ni/MgO, and c) Ni/SBA-15. B: Used catalysts. a) Ni/MgO and b) Ni/SBA-15.

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