Fabrication of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ ($\text{M} = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$ and Ru^{3+}): catalytic effects for the reduction of 2- or 4-nitroanilines in water

SERKAN DAYAN¹, SEVGİ ÖZTÜRK¹, NILGÜN KAYACI¹,
NILGÜN KALAYCIOĞLU ÖZPOZAN^{1,*} and ESRA ÖZTÜRK²

¹Department of Chemistry, Faculty of Science, Erciyes University, Kayseri 38039, Turkey

²Karamanoglu Mehmetbey University, Faculty of Engineering, Department of Materials Science and Engineering, TR-70200 Karaman, Turkey

MS received 16 March 2015; accepted 2 July 2015

Abstract. Five new $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ ($\text{M} = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$ and Ru^{3+}) materials were developed for the reduction of nitroarenes as catalysts by conventional solid state reaction at 1300°C. The prepared materials were characterized by thermal analysis, Fourier transform infrared spectroscopy, X-ray powder diffraction analysis, scanning electron microscopy, energy-dispersive X-ray analysis and nitrogen adsorption–desorption analysis. The catalytic activities of the prepared catalysts were tested in the reduction of 2- or 4-nitroanilines in aqueous media at ambient temperature in the presence of NaBH_4 by UV–vis spectrophotometer. Furthermore, the $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ catalysts can be recovered by filtration and reused for five cycles for the reduction of 2-nitroaniline. These results show that the $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ catalysts can be used in practical applications in the reduction of nitroanilines.

Keywords. Chemical synthesis; catalytic properties; solid state.

1. Introduction

It is well known that many inorganic substances with the desired structure, properties and surface morphology have attracted considerable interest among scientists.^{1–3} Silicates are also suitable for applications in luminescence, catalysis, UV absorption, the preparation of zeolite materials, photocatalysis, etc.^{4–9} Additionally, silicates have properties of high physical and chemical stability. Among these silicate materials, aluminosilicates, in particular are widely used as catalysts in various reactions. In addition, the preparation of aluminosilicates is possible by methods such as sol–gel, coprecipitation, substitution, hydrothermal routes, conventional solid state, etc. Aluminosilicates materials can be used for the simple impregnation process, whereby combined materials can be synthesized and used as a long lasting catalyst.^{10–17} Furthermore, materials including nickel, copper, platinum, palladium and ruthenium have also been used as catalysts for the transfer of hydrogenation of ketones, hydrogenation of aldehyde, hydrosilylation of alkynes, methanol decomposition, Suzuki–Miyaura cross-coupling reaction, solvent-free oxidation of aromatic alcohols, etc.^{18–23}

Nitroarenes are a widely organic pollutant in waste water. Thus, the removal of nitroarenes is evermore an important issue. Various processes have been developed, including adsorption, photocatalysis, electrochemical treatment, the electro-Fenton method, electrocoagulation, catalytic hydrogenation, etc.^{24–35} Also, nitroaniline derivatives have been used as a precursor in the chemical synthesis of azo dyes, antioxidant compounds, poultry medicine, antiseptic agents, etc.³⁶ However, avoiding the use of organic solvents, the improvement of suitable processes for removing nitroarenes in aqueous media under mild conditions is still needed.

In this study, the $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ ($\text{M} = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$ and Ru^{3+}) materials were synthesized via solid-state method and characterized by thermogravimetry/differential thermal analysis (TG/DTA), Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD) analysis, scanning electron microscopy (SEM)–energy dispersive X-ray (EDX) analysis and nitrogen adsorption–desorption (BET) analysis. The prepared catalysts show good efficiency for the hydrogenation of 2-nitroaniline to 1,2-diaminobenzene and 4-nitroaniline to 1,4-diaminobenzene. Also, to our knowledge, this is the first report on the reduction of nitroanilines by using $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials as highly active catalytic systems.

* Author for correspondence (nozpozan@erciyes.edu.tr)

2. Experimental

2.1 Preparation and characterization of materials

All the chemicals and solvents used were of reagent and analytical grade. $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ materials were synthesized at 1300°C.

All the starting materials, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (A.R.), Al_2O_3 (99.0%), SiO_2 (99.8%), NiCl_2 , CuCl_2 , PdCl_2 , PtCl_2 and RuCl_3 were weighed according to the nominal compositions of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ (This 1% ratio was selected randomly with the aim of setting the amount of catalyst used in each catalytic experiment). These powders were mixed homogeneously in an agate mortar for 2 h. Small quantities of H_3BO_3 (A.R.) were added as a flux during the mixing. A small amount of each sample was taken for DTA/TG to study the phase-forming process. TG and DTA were recorded on a DTA/TG system (Perkin-Elmer Diamond type). All the samples were heated at a rate of $10^\circ\text{C min}^{-1}$ from an ambient temperature to 1300°C in nitrogen atmosphere. After analysis, the sintering conditions of the materials, including the pre-firing temperature and the synthesizing temperature, were performed in three steps. First of all, the solid mixtures were pre-fired at 1300°C for 3 h in a porcelain crucible in air and milled with 5 ml analytically pure ethyl alcohol in an agate mortar to increase the surface area. Following this, the pre-fired substances were heated at 1100°C for 3 h and milled again with 5 ml analytically pure ethyl alcohol. Lastly, the materials were sintered at 1300°C for 3 h.^{10–13}

After these steps, the substances were obtained and all the compounds were examined with XRD analysis using a Bruker AXS D8 Advance diffractometer which was run at 20–60 kV and 6–80 mA, $2\theta = 10\text{--}90^\circ$ and a step of 0.002° using $\text{Cu K}\alpha$ X-ray. The SEM images and EDX analysis were performed on a LEO 440 model scanning electron microscope using an accelerating voltage of 20 kV. The infrared spectra were measured with a Perkin-Elmer Spectrum 400 FTIR system and recorded using a universal ATR sampling accessory within the range $550\text{--}4000\text{ cm}^{-1}$. Surface area, pore volume and pore width were calculated using the nitrogen adsorption–desorption (BET) isotherm with a Micromeritics Gemini VII Surface Area and Porosity system.

UV–vis absorption measurements for the catalytic experiments were performed with Perkin-Elmer Lambda 25 UV/vis spectrophotometers.

2.2 Reduction of nitroanilines

The catalytic activity of the prepared $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ was carried out for the reduction of nitroanilines with NaBH_4 . As a model reaction, the mixture consisting of respective catalyst $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ (10 mg), substrate

($2.5 \times 10^{-4}\text{ M}$) and NaBH_4 (0.01 M) in water (10 ml) were stirred at ambient temperature for a period of 12 min. After the desired reaction time, the sample was quickly filtered from a mini-column. The residue was monitored by ultraviolet-visible (UV–vis) spectrometry (figure 1).

3. Results and discussion

$\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ were prepared in accordance with the published procedure.^{10–13} All the prepared materials were characterized by XRD analysis, FT-IR, TG/DTA, SEM, EDX and nitrogen adsorption–desorption (BET) analysis. Moreover, the materials were used as catalysts in the reduction of nitroanilines.

3.1 Thermal behaviour

The thermograms of the prepared catalysts are given in figure 2. According to the obtained TG curves, $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ materials are quite stable up to at 1000°C and there are only mass losses of between 1 and 4%.

3.2 XRD analysis

The XRD patterns of the materials are seen at 1300°C in figure 3. The results show that the materials were successfully prepared and are in concordance with the literature.^{10–13} The diffraction patterns of the $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ materials showed that all the peaks had a general similarity to that of $\text{MgAl}_2\text{Si}_2\text{O}_8$. Concurrently, the unit cell parameters of materials crystallized in the triclinic system are listed in table 1. The data

Figure 1. The reduction of nitroanilines with $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ catalysts.

Figure 2. TG/DTA curves of (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

of the XRD pattern are attached in table 1. The representative (*hkl*) values are marked in figure 3 and supplementary tables S1–6.

3.3 Infrared spectra

The IR spectra of the $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials are presented in figure 4. The IR absorption peaks were obtained as 1197, 1084, 954, 910, 858, 775, 619, 549 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8$; as 1206, 1084, 954, 901, 858, 793, 702, 623, 545 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$; as 1210, 1154, 1071, 1014, 936, 893, 793, 736, 693, 649, 623 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$; as 1201, 1080, 949, 910, 780, 675, 623, 571 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$; as 1201, 1080, 949, 910, 858, 780, 675, 623, 549 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and

as 1201, 1080, 949, 910, 858, 780, 675, 623, 549 cm^{-1} for $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

3.4 SEM–EDX analysis

The morphologies and microstructures of the obtained $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ were investigated by SEM as shown in figure 5. The low-magnification SEM image shows that the synthesized $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials are generally homogeneous and have an similar surface morphology. The average sizes of the compounds were found to be between 100 nm and 1.5 μm for $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$. It is clearly seen that the SEM images are quite unlike those in the

Figure 3. XRD patterns of (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

literature, owing to the fact that the synthesis-procedure proposed by this paper increases the surface area and decreases particle size compared to classic $\text{MgAl}_2\text{Si}_2\text{O}_8$ analogues.^{10–13}

In addition to SEM images, the elemental composition of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ was determined by EDX elemental analysis. The EDX analysis images belonging to

$\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ compounds are shown in figure 6. The data supported the structure of the materials. In addition, the analytic data of Mg, Si, Al, O and metal are shown in table 2.

The EDX spectra given in figure 6b revealed that $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$ consists of Mg, Si, Al, O and Ni, as expected. Similarly, figure 6c–f revealed that

Table 1. Unit cell parameter and crystal systems of materials.

Compounds	Crystal system	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>V</i> ($\times 10^6$ pm ³)	α (deg)	β (deg)	γ (deg)
$\text{MgAl}_2\text{Si}_2\text{O}_8$	Triclinic	758.28	1455.82	1472.20	940.20	46.99	84.15	77.68
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$	Triclinic	399.95	485.60	1301.97	239.19	101.73	100.51	98.12
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$	Triclinic	931.07	2083.19	2040.52	837.57	153.75	148.10	30.62
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$	Triclinic	533.99	872.47	1104.10	362.09	121.98	57.05	113.02
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$	Triclinic	586.73	161.04	190.74	794.29	147.42	56.79	123.69
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$	Triclinic	629.75	176.93	234.15	699.39	155.84	41.03	132.10

Figure 4. FT-IR spectra of (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}_{0.01}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ consists of Mg, Si, Al, O, Cu, Pd, Pt and Ru as expected, respectively.

3.5 BET analysis

Surface area ($\text{m}^2 \text{g}^{-1}$), pore volume ($\text{cm}^3 \text{g}^{-1}$) and pore width (nm) were calculated by the nitrogen adsorption–

desorption (BET) isotherm and the results are summarized in table 3. The BET isotherms (figure 7) of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ were found to be of the type-III adsorption isotherm according to IUPAC, which is related to the formation of multilayer adsorption. When the results were investigated, the synthesized $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials were found to have lower surface areas. However, the $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials could be used as active catalysts in this study.

Figure 5. SEM image of (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

3.6 Catalytic activity

For catalytic and UV-vis studies, 2-nitroaniline and 4-nitroaniline were selected, respectively. The catalytic activities of $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ were observed in the reduction of nitroanilines using NaBH_4 according to the optimized model reaction conditions. The colour of solution gradually vanished as the reaction proceeded. Concurrently, the UV spectra of reaction mixture were recorded at different times after the addition of the $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$.

Five repeated runs were examined on the same system for the reduction of 2-nitroaniline with the best catalyst. Figure 9 shows that there is no significant loss of catalytic activity in the synthesized $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}_{0.01}$.

3.7 Catalytic effects of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ for the reduction of 2-nitroaniline

The catalytic effects of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ were examined in the reduction of 2-nitroaniline by comparing the bands, which appear and disappear after

Figure 6. EDX analysis of (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

Table 2. EDX analysis data for $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ compounds.

Compounds	Mg (calc.)	Mg (obs.)	Al (calc.)	Al (obs.)	O (calc.)	O (obs.)	Si (calc.)	Si (obs.)	Metal (calc.)	Metal (obs.)
$\text{MgAl}_2\text{Si}_2\text{O}_8$	10.37	10.12	23.03	23.24	54.62	55.08	11.98	12.07	—	—
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$	10.35	10.06	22.97	23.20	54.48	54.22	11.95	12.11	Ni: 0.25	Ni: 0.25
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$	10.34	10.51	22.96	22.78	54.47	54.97	11.95	12.23	Cu: 0.27	Cu: 0.30
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$	10.32	10.18	22.92	23.10	54.37	54.59	11.93	11.74	Pd: 0.45	Pd: 0.42
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$	10.29	10.09	22.84	23.09	54.17	53.97	11.89	11.77	Pt: 0.83	Pt: 0.82
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$	10.33	10.53	22.93	22.69	54.38	54.09	11.93	12.08	Ru: 0.43	Ru: 0.44

Table 3. Adsorption–desorption characteristics of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$.

Materials	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	BJH pore volume ($\text{cm}^3 \text{ g}^{-1}$)	BJH pore width (nm)
$\text{MgAl}_2\text{Si}_2\text{O}_8$	0.1395	0.001145	29.4536
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$	0.1495	0.001139	15.6186
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$	0.2906	0.001515	9.0267
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$	0.1403	0.001941	21.8340
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$	0.1381	0.001153	29.3216
$\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$	0.0126	0.001120	70.1650

Figure 7. BET isotherms of $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

Figure 8. Time-dependent UV-vis absorption spectra of the *o*-nitroaniline reduced by NaBH_4 catalysed by the (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$, (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and (g) time-dependent absorbance data of materials.

Figure 9. (a–e) Time-dependent multiple runs of the *o*-nitroaniline reduced by NaBH_4 catalysed by $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$.

reduction on the UV–vis spectrum. The characteristic band arises at 410 nm from the $-\text{NO}_2$ group. While each reaction was realized, the UV–vis measurements were also performed at various minutes, as seen in figure 8.

On the basis of the results in figure 8, when $\text{MgAl}_2\text{Si}_2\text{O}_8$ material was used as a catalyst in the reduction of 2-nitroaniline for a 12-min period, there is no catalytic activity

of the $\text{MgAl}_2\text{Si}_2\text{O}_8$ material for this reaction. However, when $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ materials were used as catalyst for this catalytic reaction, the catalytic activity of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ increased in the order $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$. As is

Figure 10. Time-dependent UV-vis absorption spectra of the *p*-nitroaniline reduced by NaBH_4 catalysed by the (a) $\text{MgAl}_2\text{Si}_2\text{O}_8$, (b) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, (c) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, (d) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, (e) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$, (f) $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and (g) time-dependent absorbance data of materials.

shown in figure 8, the reduction peak almost disappears within 12 min after the addition of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ to the aqueous media.

To ensure the reliability of the results, the catalytic reaction was repeated four times in figure 9. It is understood that $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ completes the reaction without any significant loss of catalytic effect. After leaching, the catalyst $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ was still stabilized. This is due to the good organization of Ru on the structure of $\text{MgAl}_2\text{Si}_2\text{O}_8$.

3.8 Catalytic effects of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ for the reduction of 4-nitroaniline

We compared the catalytic activity of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ in the reduction of 4-nitroaniline. The characteristic UV-vis peak of 4-nitroaniline appears at around 380 nm. When investigating the catalytic experiment, the catalytic activities of $\text{MgAl}_2\text{Si}_2\text{O}_8$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ for the hydrogenation of 4-nitroaniline were similar to the reduction of 2-nitroaniline. Likewise, there was no catalytic effect of $\text{MgAl}_2\text{Si}_2\text{O}_8$ in the hydrogenation of 4-nitroaniline and the activity of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ increased in the order $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+} < \text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$, as is shown in figure 10. However, interestingly, the reduction peak is still present for up to 12 min after the addition of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ to the aqueous media. Therefore, the reduction of 2-nitroaniline to 1,2-diaminobenzene was easier than the reduction of 4-nitroaniline to 1,4-diaminobenzene.

All the catalytic experiments show that the $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$ materials are highly effective in the reduction of nitroanilines.

3.9 Proposed mechanism of reduction of nitroanilines with $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$

It is well known from the literature that catalytic activity is generally based on the composition of catalysts. In this context, the activity depends upon various factors like particle size, porosity, stability, the redox properties of metal ions and their distribution and electron charge potential.³⁷ In particular, materials containing Ru nanoparticles are known to be effective catalysts in the reduction of nitroanilines.³⁸ Herein, when $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{M}_{0.01}$ materials are added to the reaction media, the nitroaniline and the borohydride ions (produced by the ionization, of NaBH_4 in aqueous medium) diffuse from the aqueous solution towards the materials surface and around the metal ions. Therefore, the metal ions present act as a medium to transfer electrons from BH_4^- to nitroaniline which leads to the formation of aminoanilines (phenylendiamines). The aqueous medium provides the H^+ ions required for the reduction of nitroanilines. The faster the electron transfers, the higher the value of the rate constant. It is evident that the catalytic reaction was fastest in the case of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ as compared to other materials.

4. Conclusion

Herein, we reported the novel preparation and characterization of $\text{MgAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ni}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Cu}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pt}^{2+}$, $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and their catalytic activities for the reduction of 2- and 4-nitroaniline with the use of NaBH_4 in water. The synthesized materials are easily synthesized with a modified-conventional solid state method and do not require an inert atmosphere.

The fabricated $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$ catalysts show a very high catalytic activity in the reduction reaction of 2-nitroaniline. The catalytic experiments show that because $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ is long lasting, the material is more effective than analogues. Additionally, the conversion of 2-nitroaniline compared with 4-nitroaniline was surprisingly higher under this reaction condition. The reason for this is that the position of the electron donor- NH_2 groups may be responsible for the catalytic activity of $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Ru}^{3+}$ and $\text{MgAl}_2\text{Si}_2\text{O}_8 : \text{Pd}^{2+}$. Also, these materials could be used in waste water treatment and in the conversion of 2- or 4-nitroanilines to 2- or 4-aminoanilines in aqueous media at ambient temperature. When examined in the context of the literature, it is clear that the metal complexes or materials used herein show good efficiency in reduction of nitroarenes.^{39–45}

Acknowledgement

We acknowledge the financial support granted by Erciyes University (ERUBAP).

Electronic Supplementary Material

Supplementary material pertaining to this article is available on the Bulletin of Materials Science website (www.ias.ac.in/matsersci).

References

1. Song-Song Z, Song J-M, Niu H-L, Mao C-J, Zhang S-Y and Shen Y-H 2014 *J Alloys Compd.* **585** 40
2. Zenga T, Zhanga X-L, Niua H-Y, Maa Y-R, Li W-H and Caia Y 2013 *Appl. Catal. B Environ.* **134–135** 26
3. Demirelli M, Karaoglu E, Baykal A, Sozeri H and Uysal E 2014 *J. Alloys Compd.* **582** 201
4. Aksekov S M, Rastsvetaeva R K, Rassyllov V A, Bolotina N B, Taroev V K and Tauson V L 2013 *Microporous Mesoporous Mater.* **182** 95
5. Neelakandeswaria N, Sangamia G, Emayavarambana P, Babub S G, Karvembub R and Dharmaraja N 2012 *J. Mol. Catal. A: Chem.* **356** 90
6. Ambrogi V, Latterini L, Marmottini F, Tiralti M C and Ricci M 2013 *J. Pharm. Innov.* **8** 212
7. Kim Y K, Rajesh K P and Yu J-S 2013 *J. Hazard. Mater.* **260** 350

8. Tušar N N, Laha S C, Cecowski S, Arcon I, Kaucic V and Glaser R 2011 *Microporous Mesoporous Mater.* **146** 166
9. Shao G N, Kim Y, Imran S M, Jeong Jeon S, Sarawade P B, Hilonga A, Kim J-K and Kim H T 2013 *Microporous Mesoporous Mater.* **179** 111
10. Ozpozan Kalaycioglu N and Circir E 2012 *J. Alloys Compd.* **510** 6
11. Circir E and Ozpozan Kalaycioglu N 2012 *Mater. Res. Bull.* **47** 1138
12. Ozpozan Kalaycioglu N and Circir E 2013 *J. Therm. Anal. Calorim.* **111** 273
13. Circir E and Ozpozan Kalaycioglu N 2012 *J. Therm. Anal. Calorim.* **110** 1179
14. Chang C F, Wu Y L and Hou S S 2009 *Colloids Surf. A* **336** 159
15. Viswanathan B, Sivasanker S and Ramasamy A V 2002 *Catalysis: principles and applications* (New Delhi: Narosa Publishing House)
16. Padmaja P, Warriar K G K, Padmanabhan M, Wunderlich W, Berry F J, Mortimer M and Creamer N J 2006 *Mater. Chem. Phys.* **95** 56
17. Ciuffi K J, Nassar E J, Rocha L A, da Rocha Z N, Nakagaki S, Mata G, Trujillano R, Vicente M A, Korili S A and Gil A 2007 *Appl. Catal. A: Gen.* **319** 153
18. Dayan S, Ozpozan Kalaycioglu N, Dayan O, Ozdemir N, Dincer M and Buyukgungor O 2013 *Dalton Trans.* **42** 4957
19. Pournara A, Kovala-Demertzi D, Kourkoumelis N, GeorgakopoulosIoannis S and Kostas D 2014 *Catal. Commun.* **43** 57
20. Rochaa B G M, Valishinaa E A, Chaya R S, Guedes da Silva M F C, Buslaeva T M, Pombeiroa A J L, Kukushkind V Y and Luzyanin K V 2014 *J. Catal.* **309** 79
21. Tsonchevaa T, Genovaa I, Stoyanovab M, Pohlb M-M, Nickolovc R, Dimitrova M, Sarcadi-Priboczkid E, Mihaylove M, Kovachevae D and Hadjiivanov K 2014 *Appl. Catal. B: Environ.* **147** 684
22. Kumbhar A, Jadhav S, Kamble S, Rashinkar G and Salunkhe R 2013 *Tetrahedron Lett.* **54** 1331
23. Wu G, Wang X, Guan N and Li L *Appl. Catal. B: Environ.* **136–137** 177
24. Marais E and Nyokong T 2008 *J. Hazard. Mater.* **152** 293
25. O'Connor O A and Young L Y 1989 *Environ. Toxicol. Chem.* **8** 853
26. Dieckmann M S and Gray K A 1996 *Water Res.* **30** 1169
27. Oturan M A, Peironten J, Chartrin P and Acher A J 2000 *Environ. Sci. Technol.* **34** 3474
28. Modirsshahla N, Behnajady M A and Mohammadi-Aghdam S 2008 *J. Hazard. Mater.* **154** 778
29. Canizares P, Saez C, Lobato J and Rodrigo M A 2004 *Ind. Eng. Chem. Res.* **43** 1944
30. Chiou J R, Lai B H, Hsu K C and Chen D H 2013 *J. Hazard. Mater.* **248–249** 394
31. Khan F, Pandey J, Vikram S, Pal D and Cameotra S S 2013 *J. Hazard. Mater.* **254–255** 72
32. Kamaraj R, Davidson D J, Sozhan G and Vasudevan S 2014 *J. Tai. Inst. Chem. Eng.* **45** 2943
33. Kamaraj R, Davidson D J, Sozhan G and Vasudevan S 2014 *J. Environ. Chem. Eng.* **2** 2068
34. Vasudevan S 2014 *J. Water Process Eng.* **2** 53
35. Vasudevan S and Oturan M A 2014 *Environ. Chem. Lett.* **12** 97
36. Sun J H, Sun S P, Fan M H, Guo H Q, Qiao L P and Sun R X 2007 *J. Hazard. Mater.* **148** 172
37. Goyal A, Bansal S and Singhal S 2014 *Int. J. Hydrogen Energy* **39** 4895
38. Sarmah P P and Dutta D K 2012 *Green Chem.* **14** 1086
39. Shah M, Guo Q-X and Fu Y 2015 *Catal. Commun.* **65** 85
40. Shokouhimehr M, Kim T, Jun S W, Shin K, Jang Y, Kim B H, Kim J and Hyeon T 2014 *Appl. Catal. A: Gen.* **476** 133
41. Shil A K, Sharma D, Guha N R and Das P 2012 *Tetrahedron Lett.* **53** 4858
42. Sharma R K, Monga Y and Puri A 2014 *J. Mol. Catal. A: Chem.* **393** 84
43. Salam N, Banerjee B, Roy A S, Mondal P, Roy S, Bhaumik A and Islam M 2014 *Appl. Catal. A: Gen.* **477** 184
44. Davarpanah J and Kiasat A R 2013 *Cat. Commun.* **41** 6
45. He G, Liu W, Sun X, Chen Q, Wang X and Chen H 2013 *Mater. Res. Bull.* **48** 1885