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Mesoporous Nickel–Aluminosilicate Nanocomposite: A Solid Acid Catalyst for Ether Synthesis

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Mesoporous nickel aluminosilicate, a solid acid catalyst prepared by sol-gel technique was utilized as a heterogeneous catalyst for the synthesis of symmetrical ethers by dehydro-condensation of alcohols. The prepared catalysts were characterized by Fourier-transform infra red spectroscopy (FT-IR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), N₂ adsorption-desorption analysis, temperature programmed desorption of ammonia (TPD) and X-ray photoelectron spectroscopic techniques. The presence of the catalyst assisted the etherification reaction in 30 minutes. Ethers formed in these reactions were quantified by gas chromatography (GC) and the identities of few of them were confirmed by nuclear magnetic resonance spectral data (NMR).

Keywords: Mesoporous Materials, Nickel Aluminosilicate, Nanocomposites, Ether Synthesis, Heterogenious Catalysis.

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1. INTRODUCTION

Some organic reactions catalyzed by mineral acids have also been successfully carried out using solid acids like clays, aluminosilicates, heteropolyacids and ion exchange resins.¹ Besides the strong acidity and heterogeneous nature of solid acids, they do not require neutralization step at the end of the reaction and also can be reused. From the literature reports it is inferred that solid acid catalysts are extremely useful for alkylation, isomerisation and cracking reactions in petroleum industries.^{2–5} Among the available solid acids, aluminosilicates are the promising materials because of their tunable acidic properties. Negative charge created on the surface during the incorporation of AlO_4^{5-} for SiO_4^{4-} led to the surface acidity of these materials, the concentration and strength of the acidic sites can be altered by changing the Si/Al ratio.⁶

Ether preparation is one of the most important reactions in chemical industries since long time. Though many methods available for ether synthesis, Williamson's method⁷ is the most commonly employed one and requires the conversion of an alcohol to their corresponding halides or tosylates followed by their displacement with more basic alkoxides or phenoxides which causes some limitations in their industrial applicability. Alternative strategy involving the direct condensation of alcohols in presence of an organic or inorganic protic acid catalyst such as p-toluene sulphonic acid or sulphuric acid has been employed.⁸⁻¹⁰ Bronsted acids have also been utilised for the direct condensation of alcohols to ethers but are limited to vapour phase reactions alone.¹¹ However, Lewis acids have been applied for the preparation of ethers from alcohols in both vapour and liquid phases¹² but in stoichiometric ratio. Later, to overcome the above mentioned difficulties, organic resins (Nafion H) loaded with both Lewis and Bronsted acids were used for the preparation of methyl isobutyl ethers but with less selectivity.¹³⁻¹⁴ Inorganic catalysts like sulfated zirconia, sulphonic acid loaded MCM-41, HZSM-5 etc., were tested for the condensation of alcohols, in which case the yield of the ether formed was very low.¹⁵⁻¹⁷ Sulfonic acid functionalized mesoporous silica¹⁸ and SBA-15 were also active for ether synthesis only under vapour phase conditions.¹⁹ Aluminum dodecatungstophosphate was used for the condensation of alcohols to ethers in liquid phase but the amount of catalyst required is a limiting factor.²⁰ Hence, it is necessary to introduce a highly active catalyst system for ether synthesis in liquid phase. Recent reports by some researchers revealed that mesoporous materials register their role both as catalyst and as support for various industrially important reactions.²¹⁻²⁴ Based on the belief that the incorporation of a bivalent cation like Ni²⁺ into the aluminosilicate

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framework will alter the total acidity of the catalytic system, we herein present the catalytic applications of mesoporous nickel aluminosilicate nanocomposites for the preparation of ethers from alcohols by dehydrocondensation in liquid phase.

2. MATERIALS

All the chemicals used were of reagent or analar grade. Tetraethyl orthosilicate (TEOS) and aluminium nitrate were purchased from Sigma-Aldrich and used as received without any further purification. Absolute alcohol, nickel chloride and ammonia were obtained from Merck India Pvt. Ltd. and used as such.

Clear solutions of aluminium nitrate (0.32 M) and TEOS (0.63 M) in ethanol were prepared separately and mixed with continuous stirring and pH of the medium was adjusted to 9 with ammonia. To the above aluminosilicate sol, NiCl₂ (0.05 M) in ethanol was added slowly with stirring and the resulting nickel aluminosilicate sol obtained was allowed to remain for 5 days at room temperature to get the gel. Since the concentration of water affects the rate of hydrolysis and condensation, ratio of TEOS to water was maintained as 1:16. The gel obtained was dried at 100 °C for one hour, calcined at various temperatures such as 800 °C, 1000 °C and 1200 °C to get the nickelaluminosilicate nanocomposites and were labeled as NAS-A, NAS-B and NAS-C respectively and were used as heterogeneous catalysts for the synthesis of a series of ethers from respective alcohols.

2.1. Catalyst Characterization

Thermal analysis and the TG-DTA of the samples were recorded with PYRIS/DIAMOND thermal analyser. Infrared spectral studies of different samples were recorded as KBr discs with Nicolet Avatar model FT-IR spectrophotometer between 400 and 4000 cm⁻¹. Powder X-ray diffraction patterns of the nanocomposites were obtained using X'PERT PANALYTICAL X-Ray diffractometer (Cu-K α radiation $\lambda = 1.54056$ Å) equipped with a scanning rate of 0.02 °/sec in 2θ range from 10°-90°. The textural properties of the materials were analyzed by N₂ adsorption/desorption measurements using MICROMERITICS ASAP 2020 POROSIMETER instrument. Pore size distribution was obtained by applying the BJH pore analysis to the adsorption branch of the nitrogen adsorption-desorption isotherms. Scanning electron microscopic (SEM) images were recorded on JEOL JSM-6390 instrument equipped with an energy dispersive X-ray analvsis (EDAX). Temperature programmed desorption (TPD) of ammonia was carried out in a U-shaped quartz reactor with 10% ammonia/Helium gas flow of 25 cm³/min, the sample was pretreated with a constant heating rate of 10 °/min to 500°. Ammonia consumption was monitored as a function of temperature with thermal conductivity detector in a Micromeritics autochem II chemisorption instrument. Gas chromatographic analysis of the alcohols and the products was done in Shimadzu-2010 gas chromatograph (GC). Nuclear magnetic resonance (NMR) spectra of selected products were recorded with BRUKER AMX 500 at 500 MHz with tetramethyl silane as internal standard in CDCl₃ solvent.

2.2. Catalytic Experiments

0.5 mM substrate (alcohol) was added to suitable quantity of nickel aluminosilicate catalyst and refluxed at 110 °C with 5 mL of toluene as solvent for 30 min. The reaction mixture was centrifuged and the centrifugate was quantified by GC. After the completion of catalytic experiment the used catalyst was filtered, washed with toluene, dried at 100 °C for one hour and utilized in reusability test.

2.3. Product Analysis

Gas chromatograph equipped with 5% diphenyl and 95% dimethyl siloxane, Restek capillary column (60 m length, 0.32 mm dia) and a flame ionization detector (FID) with nitrogen as a carrier gas. The initial column temperature was increased from 60 to 150 °C at a rate of 10 °C/min and then to 220 °C at the rate of 40 °C/min. The temperatures of the injection port and FID were kept constant at 150 and 250 °C, respectively during the product analysis.

3. RESULTS AND DISCUSSION

Thermogram of nickel aluminosilicate gel (Fig. 1) showed a set of plateaus respectively around 80 °C and 280 °C with corresponding endotherm and exotherm in the DTA due to the loss of water molecules and the decomposition of organic moieties in the gel respectively. Another endotherm appeared around 700 °C in the DTA without corresponding weight loss in the TGA suggested the occurrence of phase transformation of the formed nickel aluminosilicate nanocomposite from amorphous to crystalline. Based on the knowledge of TGA/DTA, the as-prepared gel



Fig. 1. Thermogram of nickel aluminosilicate gel.

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was calcined at three different temperatures with 800 °C as the lowest and 1000 °C and 1200 °C as the other two temperatures.

The IR spectra of as-prepared nickel aluminosilicate gel and the calcined samples NAS-A, NAS-B and NAS-C were given in Figure 2. A broad band found around 3137 cm⁻¹ due to the asymmetric stretching of free silanol groups in the spectra of as-prepared gel was disappeared in the case of calcined samples indicating the condensation between them to form silicate structures upon calcinations. However, a new broad band around 3410 cm⁻¹ was found in the spectra of calcined samples corresponding to the surface hydroxyl groups even after calcination. In addition, the band appeared around 1360 cm⁻¹ due to the nitrate vibrations in the gel was not seen in the calcined samples that can be due to the complete decomposition of the organic residues during calcination. Absorptions occurred between 1110 cm^{-1} and 1030 cm^{-1} and around 730 cm^{-1} in the infrared spectra of NAS-A, NAS-B and NAS-C were respectively assigned as due to the stretching and bending vibrations of internal tetrahedral units that are typical of zeolites. Vibrational bands corresponding to the tetrahedral linkage atoms appeared in the region of $498-550 \text{ cm}^{-1}$. These IR spectral features were characteristic of zeolite like structure in the calcined nickel aluminosilicates.⁶

An increase in the crystallinity of the aluminosilicate nanocomposites, NAS-A, NAS-B and NAS-C as a function of calcination temperature was evidenced from the XRD patterns presented in Figure 3. Diffraction patterns obtained were compared with the standard JCPDS file and it was found that diffraction is similar to that of nickel aluminium oxide (JCPDS No.: 78-2180), nickel silicate (JCPDS No.: 83-1646) and also orthorhombic nickel aluminosilicate (JCPDS No.: 74-0731). Further, diffraction lines corresponding to either alumina or silica have not been observed suggesting that no phase separation of the catalyst occurred during the crystallization. The observed



Fig. 2. FT-IR spectra of nickel aluminosilicate.

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Fig. 3. Powder X-ray diffraction of nickel aluminosilicate nanocomposite calcined at different temperature.

powder XRD diffractions of the prepared NAS confirmed the presence of Ni ion in the aluminosilicate framework.

Layered, porous morphology of the prepared samples was identified from the SEM images (Fig. 4). The elemental composition of the catalysts were analysed using energy dispersive X-ray analysis technique and the results were tabulated (Table I). It was observed from the elemental analysis that the ratio of Si/Al decreases slightly and amount of nickel on the surface increases with an increase in the calcination temperature. Though a constant quantity of nickel was loaded during the sol preparation, variation in its concentration on the surface of the catalytic system was observed depending upon the calcination temperature





Fig. 4. SEM images of nickel aluminosilicates calcined at (a) 800 °C, (b) 1000 °C and (c) 1200 °C.

Table I. Elemental composition of NAS.

Sample code	O (mass %)	Al (mass %)	Si (mass %)	Ni (mass %)
NAS-A	65.04	29.7	3.97	0.41
NAS-B	61.73	32.45	4.07	0.57
NAS-C	58.94	33.79	3.62	1.21

nickel

aluminosilicate

nanocomposites.					
Catalyst	BET surface area $(m^2 g^{-1})$	BJH pore volume (cm ³ g ^{-1})	BJH pore radius (nm)		
NAS-A	210.16	0.2862	1.8		
NAS-B	131.57	0.3659	4.0		
NAS-C	33.36	0.0902	3.0		

of

characteristics

Table

II. Sorption

that can be ascribed to the sintering of the material at higher temperature that changed the composition of the constituent elements at the surface level.

Surface area, pore diameter, pore volume and pore size distribution were determined using the nitrogen adsorption–desorption isotherm and the results were summarized in Table II. The BET isotherms (Fig. 5) of the



Fig. 5. N_2 adsorption–desorption isotherm of nickel aluminosilicates calcined at (a) 800 °C, (b) 1000 °C and (c) 1200 °C, BJH pore volume distribution (d) catalyst NAS-A, (e) catalyst NAS-B and (f) catalyst NAS-C.

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Scheme 1. Transfer hydrogenation of acetophenone followed by dehydro-condensation.

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samples, NAS-A, NAS-B and NAS-C were found to be of type-IV in nature and confirmed the mesoporous nature of these catalysts.²⁵ Nickel aluminosilicate nanocomposites experienced a decrease in surface area with rise in calcinations temperature, whereas pore size and pore volume is maximum for the sample calcined at 1000 °C than the other two samples. As observed in the case of TG/DTA analysis, phase transformation occurred at 800 °C and hence above this temperature sintering takes place that led to a decrease in the surface area of the catalysts. Further, the broad distribution of the pore size obtained (Figs. 5(d)–(f)) is attributed to the disordered pores formed during the capillary evaporation of the solvent in the absence of any external templates.

Oxidation state of Ni in nickel aluminosilicate composite NAS-A was identified from the XPS spectra. Figure 6 depicts the XPS spectra of C1s, Ni 2p and survey plot of the catalyst. Ni $2p_{3/2}$ peak appered at 855.7 eV and 872.9 eV with their corresponding shake up peaks at 861.75 eV and 879.65 eV respectively. Binding energies of these peaks are assigned to the oxidized form of nickel.²⁶ Further, the 2p binding energy of NiO obtained for the nanocomposites NAS-A was higher than that of the free NiO (853.5 eV), indicating a strong interaction between NiO and the aluminosilicate support leading to an enhanced binding energy of the NiO incorporated on to the framework.²⁷

Acidity of the prepared nickel aluminosilicate nanocomposites NAS-A, NAS-B and NAS-C was determined by TPD of ammonia (figure not included). Ammonia TPD of each sample exhibited three desorption peaks out of which the low temperature peak appeared in the region 202 to 297 was ascribed to the weakly adsorbed ammonia on the surface silanol groups of the samples.²⁸ Desorptions appeared around 397 °C and 538 °C in the case of sample NAS-A were assigned to the chemisorbed ammonia on the strong acidic sites formed by the incorporation of Al³⁺ and Ni²⁺ in to the Si⁴⁺ framework respectively. However the same peaks due to the desorption of adsorbed ammonia at respective acidic sites in the samples NAS-B and NAS-C appeared at little lower regions owing to the reason that these samples possess less acidity than the other sample. In general, a decrease in respective desorption temperature for the three peaks was observed with increase in the calcination temperature of them because of both the decreased acidic strength and concentration of acidic sites of the catalyst.

3.1. Catalytic Reactions

In this study, an attempt was made for the transfer hydrogenation of carbonyl compounds in presence of catalyst NAS-A by choosing acetophenone as a model substrate and isopropanol as a hydrogen donor to yield phenylethanol.



Scheme 2. Mechanism for the etherification of alcohols.

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Table III. Transfer hydrogenation of acetophenone.						
	Catalyst		Reaction	Yield of phenyl	Yield of	
S. no.	(mg)	Base	(Hrs)	ethano (1%)	product (%)	
1	50	КОН	12	11.6	_	
2	50	KOH	24	58.3	16.9	
3	100	KOH	24	16.5	48.1	
4	100	-	24	2.0	-	

But, during the course of the reaction, examination of thin layer chromatography (TLC) revealed the formation of phenylethanol in very low yield along with another low polar compound as a major product. Analysis of the above reaction mixture by GC registered a maximum intense peak at 9.6 min as retention time corresponding to the above said low polar product. Based on the knowledge gained from the results of TLC and GC, the above reaction mixture was subjected to column chromatography over silica gel and the low polar product was isolated with high purity which did not answer any of the tests for alcohols. In order to identify it, ¹H and ¹³C NMR spectra were recorded and interpreted. The spectral features revealed that the product is $bis(\alpha$ -methylbenzyl)ether. Further proof for the structure of $bis(\alpha$ -methylbenzyl)ether was also derived from the ¹H NMR spectrum of the same compound reported by Kim et al. in a reaction using ZnCl₂ as a Lewis acid catalyst for ether synthesis.¹² Hence, we believed that the selected catalyst NAS-A initially promoted the transfer hydrogenation reaction to afford the phenylethanol which underwent insitu dehydro-condensation to afford bis(α -methylbenzyl)ether as identified above (Scheme 2) (Table III).

The formation of ether gave an idea that the phenylethanol formed by transfer hydrogenation of acetophenone involved in intermolecular dehydration to yield $bis(\alpha$ methylbenzyl)ether. However, to ascertain whether the catalyst promotes both transfer hydrogenation as well as intermolecular dehydration of alcohols exclusively, the later reaction was carried out by utilizing phenylethanol as a substrate under various conditions (Table IV). From the results obtained, it was evident that the reaction carried out in toluene was more successful without the addition of any base to promote the dehydration. Similar results were

Table IV. Etherification of phenylethanol.

S. no.	Catalyst quantity (mg)	Additive	Solvent	Reaction time (Hrs)	% yield of ether
1	50	H_2O_2	Water	24	_
2	100	H_2O_2	Water	24	_
3	100	KOH	Toluene	15	50.3
4	100	_	Toluene	1	73.2
5	100	HIO_4	Water	24	14.0
6	100	_	Acetone	24	2.1
7	100	KOH	Acetone	24	8.5

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 Table V. Effect of calcination temperature on the etherification of phenylethanol.

S. no.	Catalyst	Calcination temperature of support (°C)	Substrate	Yield (%)	Selectivity
1	NAS-A	800	Phenylethanol	49.7	80.4
2	NAS-B	1000	Phenylethanol	96.9	97.6
3	NAS-C	1200	Phenylethanol	1.6	53.7

reported during the attempted oxidation of phenylethanol using $HAuCl_4$ as catalyst.²⁹ However, to the best of our knowledge, there is no report on the utility of nickel aluminosilicate for ether synthesis. Hence, for the first time we herein present a detailed investigation on the utility of mesoporous nickel aluminosilicate as heterogeneous solid acid catalyst system towards ether synthesis from alcohols.

3.2. Optimisation of Reaction Conditions

3.2.1. Selection of Catalyst

In order to identify the most efficient catalyst system for the ether synthesis among the available three catalysts NAS-A, NAS-B and NAS-C prepared at different calcination temperatures, all of them were tested by refluxing 0.5 mM phenylethanol in toluene with 100 mg of the catalyst and the results obtained were given in Table V. From the results given in the table, it was evident that the catalyst obtained after calcination at 1000 °C (sample NAS-B) showed superior performance than the remaining two samples (NAS-A and NAS-C) indicating that not only the surface area but also the dimension of pores of the catalyst do have a significant contribution towards its efficiency in the ether formation reaction.

To confirm the role of the catalyst in this reaction, substrate (phenylethanol) alone was refluxed in toluene without catalyst NAS-B, wherein the reaction did not proceed highlighting the presence of the catalyst is vital for the expected transformation. However, an increase in the quantity of the catalyst had a linear correlation with the yield of the product until the loading of 100 mg catalyst beyond which no significant impact was observed (Table VI). Further, with a view to know whether the reaction proceeds at room temperature, the same was carried out at by stirring at room temperature with 100 mg of catalyst in which case no ether formation was observed even after

 Table VI. Effect of catalyst quantity on the etherification of phenylethanol.

S. no.	Catalyst quantity (mg)	Substrate	Yield (%)
1	0	Phenylethanol	0
2	50	Phenylethanol	88.6
3	100	Phenylethanol	96.9
4	150	Phenylethanol	98.2

Table VII.	Etherification of alcohols.				
S. no.	Substrate	Product	Reaction time (min)	Yield ^a	Selectivity
1	OH		30	96.9	97.6
2	OH Cl		30	74.6	66.4
3	OH Br	Br	30	72.8	90.4
4	H ₃ CO	H ₃ CO OCH	30	88.1	73.1
5	ОН		30	3.7	97.0
6	OH Deliv	rered by Ingenta to Naryang Tec IP: 95.18 175.31 On: Lat 18 Jun Copyright: American Scientifi	hnological Un ¹⁸⁰ ersity n 2016 22:17:01 c Publishers	92.8	92.8
7	Н3СО	H ₃ CO	180	71.7	84.1
8	OH		30	71.6	100
9	ОН		30	98.3	96.6
10	ОН		30	93.7	94.9
11	OH OH	0-0-	30	99.1	99.8

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Notes: ^aDetermined from GC; ^bDetermined from GC peak area; Selectivity = [(area of substrate + area of product)/total peak are ×100.

6 hrs of the reaction with or without a base. From these facts, it became obvious that 0.5 mM substrate in 5 mL of toluene was converted into its corresponding ether in 30 minutes using 100 mg of catalyst NAS-B at 110 °C.

3.3. Extension of the Scope

The generality of the reaction was tested by extending the reaction to various alcohols including both aliphatic and aromatic classes. In all the reactions, a smooth conversion of selected alcohols to respective ethers was realized in 30 min (Entries 1-5 and 8-14, Table VII) except benzyl alcohol or its derivative wherein it took 3 hrs (Entries 6 and 7, Table VII). The yield of ether decreased in the order phenylethanol > para-substituted phenylethanols > ortho-substituted phenylethanol. Generally, the presence of both electron withdrawing and electron releasing substituents at the para position of the alcohol resulted in low yield due to the fact that electron withdrawing substituents can weaken the O-H bond to make the substrates (alcohol) more acidic and thus became difficult to release -OH group that is a partial requirement to get symmetrical ethers by dehydro-condensation. In contrast, when electron releasing group is available on the *para* position, alcohol could behave better as a base to release -OH and consequently proton release would become unfavoured. Hence, there was a decrease in the yield of symmetrical ethers from the alcohols containing both electron withdrawing and electron releasing substituents at the para position (Entries 2-4 and 7 in Table VII) compared to unsubstituted one. Substitutional effect was more pronounced in the case of ortho position (Entry 5, Table VII) due to the steric hinderance at *ortho* position. Though the yield of respective ethers obtained with benzylalcohol or 4-methoxy benzylalcohol as substrates in our experiment was less, it appeared to be better than that reported using $ZnCl_2$ as a catalyst.¹²

Aliphatic alcohols have also been etherified under the same experimental conditions in excellent to moderate yield using the selected catalyst NAS-B. Among them, cyclopentanol was converted into its symmetrical ether in higher yield than that of cyclohexanol (Entries 11 and 12, Table VII), the fact that could be correlated to the reactivity of the aliphatic cyclic compounds based on the internal ring strain that is more effective in the case of five membered cyclopentanol than the six membered cyclohexanol that facilitates the former towards etherification at a faster rate than the later.

3.4. ¹H and ¹³C-NMR Spectral Data

Di(α-methyl benzyl)ether (Table VII, entry 1). ¹H NMR (CDCl₃): $\delta = 1.45$ (d, J = 6.5 Hz, 3 H, C1–CH₃), 1.54 (d, J = 6.5 Hz, 3 H, C8–CH₃), 4.32 (q, J = 6.5 Hz, 1 H, C1–H), 4.60 (q, J = 6.5 Hz, 1 H, C8–H) and 7.28–7.43 (m, 10 H, Ar–H).

¹³C NMR (CDCl₃): δ = 23.04 (C1–CH₃), 23.74 (C8–CH₃), 74.46 (C1), 74.68 (C8), 126.26 (C3, C5), 126.35 (C12, C14), 127.17 (C7), 127.41 (C10), 128.27 (C4, C6), 128.49 (C11, C13), 144.21 (C2) and 144.29 (C9).

Di(4-methoxy benzyl)ether (Table VII, entry 7). ¹H NMR (CDCl₃): $\delta = 3.84$ (s, 6 H, -OCH₃), 4.50 (s, 4 H, -CH₂), 6.92 (dd, J = 2 Hz, 6.5 Hz, 4 H, Ar-H) and 7.32 (d, J = 8.5 Hz, 4 H, Ar-H).

Dibenzylether (Table VII, entry 6). ¹H NMR (CDCl₃): $\delta = 4.72$ (s, 4 H, -CH₂) and 7.32-7.4 (m, 10 H, Ar-H).

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Fig. 7. Heterogeneity test.

Di(diphenylcarbinyl)ether (Table VII, entry 9). ¹H NMR (CDCl₃): $\delta = 5.69$ (s, 2 H, CH), and 7.19–7.45 (m, 20 H, Ar–H).

Diindanylether (Table VII, entry 13). ¹H NMR (CDCl₃): $\delta = 2.16 \ (m, 2 \text{ H}, \text{C2-CH}_2), 2.54 \ (m, 2 \text{ H}, \text{C13-CH}_2), 3.01 \ (m, 2 \text{ H}, \text{C3-CH}_2), 3.11 \ (m, 2 \text{ H}, \text{C12-CH}_2), 3.36 \ (m, 1 \text{ H}, \text{C1-H}), 4.39 \ (t, J = 8.0 \text{ Hz}, 1 \text{ H}, \text{C14-H}) \text{ and} 7.15-7.43 \ (m, 8 \text{ H}, \text{Ar-H}).$

3.5. Heterogeneity Test

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In order to prove that the catalyst involved in the reaction **4. CONCLUSION** did not leach out during the course, heterogeneity test was performed by filtering the reaction mixture after 15 min. A novel, mesoporous solid acid catalyst composed of

did not leach out during the course, heterogeneity test was performed by filtering the reaction mixture after 15 minutes of the commencement and the filtrate was allowed to reflux at 110 °C for another 15 minutes (Fig. 7). Ether formed at the first 15 minutes and also at every 5 minutes interval for another 15 minutes after filtering the catalyst was quantified. Yield of symmetrical ether was found to be 48.25% after 15 minutes and no appreciable increase in the quantity of ether was noticed after the catalyst was removed by filtration even allowing the reaction up to 30 minutes indicating the concept of heterogeneity in these reactions.

3.6. Reusability

Main distinguishable property of solid acids than that of mineral acids is their reusability. Catalyst NAS-B almost retained its activity towards the etherification of phenylethanol to yield $bis(\alpha$ -methylbenzyl)ether even after five cycles. The corresponding yield obtained in each run was also presented in Table VIII. The reusability test proved that the nickel aluminosilicate nanocomposite is an excellent, reusable catalyst system.

3.7. Plausible Mechanism for the Ether Formation

Based on the reports on dehydro-condensation of alcohols,⁶ a typical mechanism for the etherification of

Table VIII. Results of reusability test using phenylethanol as a substrate.

Catalytic cycle no.	Yield (%)
1	97.7
2	97.6
3	96.9
4	96.2
5	95.3

alcohols on the surface of nickel aluminosilicate nanocomposite NAS-B is proposed and presented in Scheme 2. In the first step, weak hydrogen bonds were formed between the proton of a substrate alcohol and oxygen available on the catalyst surface and also between the oxygen or hydrogen of –OH group of silanol on the surface of the catalyst with a hydrogen or oxygen atom of another alcohol molecule. In the second step, interaction between the oxygen atom of an alcohol moiety and the α –C atom of the other alcohol occupying the neighbouring catalyst site occurred. Consequently, C—O bond formed in step 2 became much stronger with the cleavage of O—H and C—O bonds in the respective alcohols to form symmetrical ethers. At the end of the catalytic cycle, the catalyst was recovered and dried at 100 °C for next cycle.

nickel aluminosilicate was prepared by a simple solgel technique without employing any structure directing agents. The effect of calcination temperature of the asprepared gel on the surface area, porosity and acidity of the catalysts were analysed and the best one was applied as a heterogeneous catalyst for the preparation of ethers from both aliphatic and aromatic alcohols by dehydrocondensation. Interestingly, the chosen catalyst effected the dehydro-condensation of alcohols to the corresponding symmetrical ethers with a maximum of 99.1% yield from the cyclopentanol in 30 minutes. The effect of electron with drawing and electron releasing substituents present in the alcohols on the quantity of ether obtained was discussed in terms of the acidity or the basicity of the -OH group. The catalyst applied was highly selective towards the synthesis of symmetrical ethers and was reusable up to five cycles. Hence, this new catalyst could be utilized to prepare even complicated ethers at ambient reaction conditions in short time.

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