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A novel *N*-alkylation of amines by alkyl halides on mixed oxides at room temperature

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Abstract

Selective liquid phase *N*-alkylation of amines by alkyl halides using Al_2O_3–OK as a catalyst in the presence of acetonitrile at room temperature (30 °C) is described. The Al_2O_3–OK catalyst was characterized by XRD, SEM–EDXS, elemental analysis, particle size analysis, BET surface area, pore size and average pore diameter. The catalyst used for this synthetically useful transformation showed a considerable level of reusability as well as good activity.

Keywords: *N*-Alkylation; Mixed oxides; Tertiary amines; Liquid phase reaction; Room temperature (30 °C)

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1. Introduction

The development of simple, efficient and highly selective methods for widely used organic compounds from readily available reagents is one of the major challenges in organic synthesis. The reactions of amines have been a topic of immense research interest due to their synthetic utility [1] and biological activity [2]. Among these, C–N bond formation is one of the most important transformations in organic synthesis. Amines are widely used as intermediates to prepare solvents, fine chemicals, agrochemicals, pharamaceuticals and catalyst for polymerization [3].

The nucleophilic attack of alkyl halides by primary and secondary amines is useful for the preparation of tertiary amines but the reactions are invariably slow and give rise to a mixture of secondary and tertiary amines [4]. Thermal reaction between alkyl halides and amines in the presence of a base requires longer reaction time period and affords lower yields of desired product [5,6]. Although the relatively similar Ullman and Goldberg reactions with copper catalysts [7,8] and the Pd catalyzed Buchwald–Hartwig reaction have been studied in detail [9,10] transition metal-free amination of electron rich benzylic halides has been largely unexplored [11]. The alkylation of amines has also been accomplished by the reaction of an alkylating reagent and an amine in the presence of base like sodium hydride or potassium carbonate [12,13]. *N*-Alkylation of carbamates was reported using cesium carbonate in presence of a phase transfer catalyst [14].The *N*-alkylation can be also accomplished by bases like $CsOH \cdot H_2O$, $CsCO_3$ and various ionic liquids [15–19]. Recently Varma et al. and his coworker studied the direct generation of tertiary amines under microwave irradiation, but recycling of this catalyst was hampered by the homogeneous medium of the catalyst [20].

However, some of these methods are limited by harsh reaction conditions, low yields, long reaction time and use of toxic solvents or catalysts and many of which do not show recyclability. Therefore, the development of mild, efficient, environmentally more benign method of *N*-alkylation of heterocyclic compounds which bear an acidic hydrogen atom attached to nitrogen is still a major challenge in organic synthesis.

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We recently reported several transition metals based mesoporous silicates, aluminophosphate molecular sieves and mixed oxides, as catalysts for a variety of industrially important organic reactions as possible alternatives to standard synthesis of a wide variety of precursors and intermediates. Reactions like reduction of aromatic nitro and carbonyl functions and alkylation have been successfully carried out with these metal oxides [21–26].

In continuation of our earlier work, we report herein an efficient method for the synthesis of tertiary amines via *N*-alkylation of amines by alkyl halides in liquid phase using acetonitrile on reusable Al_2O_3–OK catalyst at room temperature (30 °C).

2. Experimental

2.1. Catalyst preparation

The preparation of Al_2O_3–OK was carried out in the same manner as described in the previous report [27,28]. 26 g KNO_3 and 74 g Al_2O_3 were crushed in mortar, and then appropriate deionised water was added which can be absorbed by Al_2O_3. After grinding, the mixture was dried at 110 °C for 1 h, and then activated at 600 °C for 3 h. When the loading of KNO_3 is above the threshold, only about 7% of KNO_3 can be dispersed through the interaction with Al_2O_3 support and decomposed in a mild pretreatment such as evacuation at room temperature, while a lot of undispersed KNO_3 located in the pores of Al_2O_3 forms a new phase such K_2 [$Al(NO_3)]_5$. Both the residual KNO_3 and K_2 [Al $(NO_3)]_5$ decomposed during evacuation at 600 °C and potassium ion migrate from the inner to the external surface of Al_2O_3 during evacuation process. Consequently, several layers of basic materials such as K_2O overlap on the Al_2O_3 result in some basic sites with basic strength [H^-] of 27.0.

Table 1
BET surface area and pore size analysis of Al_2O_3–OK

Catalyst	BET surface area (m^2/g^{-1})	Pore volume V_p (cm^3/g^{-1})	Average pore diameter D_p (Å)
Al_2O_3–OK	78.56	0.098	51.53

2.2. Catalyst characterization

To study the textural characterization of catalyst, surface area measurement and pore size distribution analysis were done, after degassing the sample under high vacuum at 300 °C for 4 h, by nitrogen adsorption on a micromeritics ASAP 2010 instrument at an adsorption temperature of 77 K. (Table 1). The elemental analysis of Al and K was done using a ICP-AES Spectrometer. It was found to be (Al = 27.00%; K = 39.12%). The morphology of catalyst was evaluated by scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDXS) analysis were done. The particle size of the catalyst was determined on computerized Inspection system (Galai–Cis–1).

2.3. X-ray diffraction

The X-ray powder diffraction pattern was obtained using a conventional powder diffractometer (Philips 1050) using graphite monochromatised Cu Kα radiation operating in Bragg-Brentano ($\theta/2\theta$) geometry. The crystallite size of the catalyst (calcined 600 °C) was found to be 1.40 nm (see Fig. 1).

2.4. Particle size analysis

The Al_2O_3–OK catalyst was ground to # 100 mesh size. The particle size analysis of the Al_2O_3–OK is shown in

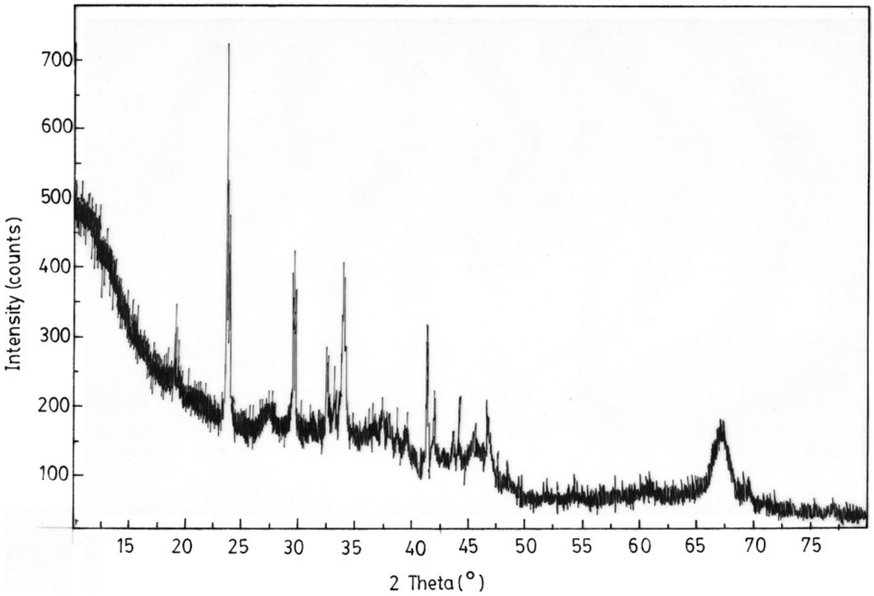

Fig. 1. Catalyst calcined at 600 °C.