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NOTE

Catalytic Organic Synthesis: An Eco-Friendly Approach

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Ni/Kieselguhr represents an important class of catalysts that offer an attractive alternative to the conventional Friedel-Crafts catalyst used for alkylation, which are corrosive and environmentally hostile. Exchanged Ni/kieselguhr catalyst is extensively used for alkylation, isomerization and molecular transformation. The techniques of electron microscopy and X-ray diffraction are used for obtaining information regarding the microstructure and interplanar spacing in the catalyst. Study of kinetics of reaction in the presence of catalyst provides parameters needed for reactor design.

Key Words: Ni/Kieselguhr, Catalyst.

The demand for design and development of new and environmental friendly catalysts is escalating day by day because of their extensive applications in chemical industries. Ni/Kieselguhr is proved as an excellent catalyst for reductive alkylation of aromatic and aliphatic amines. Nickel catalysts supported on kieselguhr offer an attractive alternative to the conventional Friedel-Crafts catalysts used for alkylation which are corrosive and environmentally hostile.

Alkylation is a process of introducing an alkyl group at carbon, oxygen, nitrogen or sulphur atom. Generally, the alkylating agents are alkenes, alcohols, alkyl halides or aldehydes and ketones. Alkylation reactions over heterogeneous catalysts have wide application in industrial processes. Heterogeneous catalysts are not easy to design because the active sites of the catalysts are not well defined and surface reaction mechanisms are not well understood. Homogeneous catalysts have many practical problems including corrosion, deactivation, waste disposal and recovery of the catalyst from the reaction mixture. The use of a catalyst aims not only at making a reaction faster but also to make the reaction selective.

As optimized earlier, nickel was co-precipitated on kieselguhr using a Heidolph rotary vacuum evaporator with electronically controlled temperature and agitation and incorporating various attachments and fittings[1]. The catalyst has been reduced in stainless steel reactor and the reaction was carried out in a microprocessor controlled 450 mL Parr Reactor assembly (USA). The technique of Thin Layer Chromatography (TLC) coupled with Flame Ionization Detector (FID) has been used for analysis of the products.

Ni/Kieselguhr catalyst: Depositing catalytically active metal on a support such as kieselguhr, silica, alumina or charcoal is advantageous in a number of ways. The metal can be highly dispersed throughout the pore system of the support yielding a large active metal surface per unit weight of the metal. This is especially advantageous when recovery of the precious metal is impossible. Although Kieselguhr has been extensively used as a support for catalysts, its X-ray data are rarely available in literature. It mostly contains various forms of silica and some other materials in traces. The exact composition of Kieselguhr is not definite and depends on the source. Their d_{hkl} values and relative intensities for Kieselguhr samples used in this study are shown in Table-1. An analysis of these d_{hkl} values revealed the presence of SiO_2 low or α-cristobalite, SiO_2 tridymite, SiO_2 kealite, Fe_2O_3 iron oxide components in the kieselguhr.

TABLE-1
PEAKS OF KIESELGUHR (RADIATION MONOCHROMATIC BEAM, $\lambda = 1.542$ Å)

No.	d	Intensity	No.	d	Intensity
1.	12.152	4	24.	3.838	2
2.	10.783	3	25.	3.770	4
3.	9.510	2	26.	3.685	4
4.	8.008	4	27.	3.619	2
5.	7.500	4	28.	3.503	2
6.	7.053	1	29.	3.440	—
7.	6.645	1	30.	3.417	2
8.	6.633	3	31.	3.355	2
9.	6.349	1	32.	3.320	5
10.	6.030	3	33.	3.317	2
11.	5.744	—	34.	3.288	1
12.	5.583	3	35.	3.238	—
13.	5.389	3	36.	3.221	—
14.	5.046	—	37.	3.126	12
15.	4.997	2	38.	2.969	2
16.	4.849	2	39.	2.964	2
17.	4.739	—	40.	2.955	—
18.	4.484	2	41.	2.938	1
19.	4.354	2	42.	2.840	12
20.	4.323	—	43.	2.814	10
21.	4.058	100	44.	2.722	5
22.	4.022	—	45.	2.657	2
23.	3.879	—	46.	2.560	2

Kieselguhrs are highly porous crystalline aluminosilicates. Ni support on kieselguhr may be visualized as being derived from a three-dimensional silica framework. The building units are silica components. Ni/Kieselguhr has intracrystalline pores of well-defined uniform shape and size. The unreduced catalyst consists of some circular disc type particles of about 60 μm dia along with large number of symmetrically positioned 3 μm dia circular holes in them.

On reduction the morphology of the catalyst particles changes from round particles of varying sized into rod-like particles of almost same size of about 5 μm. Deactivation was negligible due to small pore size and coke formation. Ni/Kieselguhr selectivity arises from a more uniform and strength distribution within the structure compared to the amorphous silica-alumina catalyst.

Alkylated amines and alkylated heterocycles are industrially important chemicals because of their extensive application in the synthesis of dyes, antioxidants and pharmaceuticals. So far, only scanty attention has been made to tap the potential of Ni catalyst in the synthesis of alkyl anilines. Alkylation of aniline with alcohol over Ni catalyst produced N-alkyl and C-alkyl derivatives as shown in Table-2.

TABLE-2
PERCENTAGE SELECTIVITY OF PRODUCTS AFFECTED BY ALKYLATION OF ANILINE

Catalyst	Temp. (°C)	Mol (%) conversion of aniline	Percentage selectivity of products					
			1	2	3	4	5	6
Ni/Kieselguhr	250	15.6	70.0	6.4	4.4	11.2	5.2	2.8
Ni/Kieselguhr	300	24.3	66.9	7.7	5.2	10.3	6.6	3.3
Ni/Kieselguhr	350	36.6	64.6	8.8	6.1	8.5	8.4	3.6
Ni/Kieselguhr	400	41.5	63.3	9.4	7.3	7.4	9.2	3.4

Wt. of catalyst = 4 g; aniline : n-propanol = 1 : 2 (mole)
Selectivity = (mole % yield of product/mole % conversion of aniline) × 100
1 = N-propylaniline 2 = *o*-propylaniline 3 = *p*-propylaniline
4 = N-isopropylaniline 5 = *o*-isopropylaniline 6 = *p*-isopropylaniline

In conclusion, the reductive alkylation with Ni/kieselguhr catalyst has been found to be a single-step and selective environmental-friendly reaction. The disposal of used catalyst is not arising on using these oxide catalysts. The regeneration of the catalyst is found to be a major advantage.

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