

NOTE

Catalytic Methylation of 1-Naphthol over Iron Oxide

Selective ring alkylation of naphthols is difficult because these are typical multireactive substrates. They react with a variety of electrophilic reagents giving mixtures of mono- and polysubstituted isomers. Usually the alkylation of aromatic substrates is a process of low selectivity because an alkylated ring is more susceptible to a subsequent electrophilic attack than a nonalkylated one.

It seems that the only systematic data published so far that concern the gas phase alkylation of naphthols with methanol in the presence of Al_2O_3 are those of Klemm *et al.* (1, 2). Their results confirm the above observations, as besides numerous ring alkylated products the reaction mixtures also contained products of O-alkylation and dehydroxylation as well as methyl-naphthalenes. For 1-naphthol, 2-methyl-1-naphthol was obtained with a maximum yield of 37%. In the crude mixture nearly 20 other ring alkylated products could be found and in addition about 30% of this mixture consisted of undefinable compounds. Therefore, this reaction has not found an industrial application.

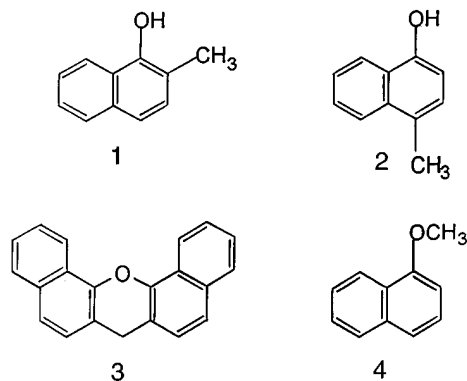
Some of the present authors have developed an oxide catalyst that contains iron, chromium, silicon, and potassium (3). It was active in the alkylation of phenol with methanol or higher alcohols as well as in the alkylation of other hydroxyarenes with good selectivity (4, 5).

In this Note are presented experimental results of the reaction of 1-naphthol with methanol in the presence of an iron oxide catalyst that contains additives, namely, Cr- and Si-oxides to prevent sintering and K_2O as an activator. The catalyst was obtained at room temperature by coprecipitation, until pH 7 was reached, from aqueous solutions of Fe and Cr nitrates and sodium silicate with aqueous ammonia solutions (1:1). After filtering the precipitate, nitrate ions were removed by washing and potassium carbonate was added. The dried precipitate was then powdered and pelletized with 3% addition of graphite. The solid mixture was next calcined at 743 K for 5 h. The resulting catalyst was composed of Fe, Cr, Si, and K oxides in a molar ratio of 100:2:1:0.1. X-ray diffraction showed that the fresh catalyst was amorphous. Its specific surface area (nitrogen BET method) was $107 \text{ m}^2/\text{g}$. After use the structure of the catalyst changed to magnetite (Fe_3O_4) with a specific surface area of $40 \text{ m}^2/\text{g}$. From the broadening of the (104) X-ray line, the average size of the crystallites was calculated to be about 30 nm.

The reaction was carried out in an electrically heated, steel flow reactor with a length of 70 cm and an inner diameter of 22 mm. Due to a coaxially positioned thermocouple it was possible to measure temperature along the length of the reactor. A volume of 25 cm^3 of catalyst with a grain size of 2–4 mm was placed in the middle of the reactor. The space over and below the catalyst was filled with an inert material. The reactants (substrates) at molar ratio of 1-naphthol: CH_3OH (1:10) were introduced through the top of the reactor using metering pumps. The experiments were carried out continuously, beginning with the reduction of the catalyst with methanol or reactant mixture at 473 K. Then the reaction was carried out for 1–2 h under steady conditions, the products being collected after condensation. They were analyzed by gas chromatography. The compounds resulting from the reaction of 1-naphthol with methanol are presented in Scheme I.

Compounds **1** and **3** and the remaining 1-naphthol were also isolated from the product mixture by medium pressure column chromatography on silica gel as adsorbent. The results obtained by preparative column chromatography were consistent with those obtained by gas chromatography, in reasonable approximation. Compound **1** was identified by comparison of its spectral (IR, ^1H NMR) and other physical properties with those described in the literature (1). Compound **3** was synthesized by a known method (6). Both samples of compound **3**, the synthetic one and that isolated from the reaction mixture, were shown to be identical by comparison of their physical properties (mp, IR, ^1H NMR and MS spectra). Compounds **2** and **4**, being present in the reaction mixture in small amounts, were not isolated. They were identified by comparison of their gas chromatographic retention times with the retention times of original samples synthesized in our laboratory. The other compounds existing in trace amounts were not identified.

The methanol alkylation of 1-naphthol was investigated as a function of temperature and space velocity (LHSV). Figure 1 shows the dependence on temperature of the conversion of 1-naphthol and the yield of the main product **1** and of the two derivatives **2** and **3**. At 550 K the selectivity of reaction is nearly 100%. The quantity of the collected liquid products was 95–98% which indicates that there is practically no methanol degradation. In the temperature range of 563–613 K 1-naphthol conversion increases with a



SCHEME I. The products of 1-naphthol methylation: 2-methyl-1-naphthol (**1**), 4-methyl-1-naphthol (**2**), 7H-dibenzo[c,h]xantheno (**3**), 1-methoxynaphthalene (**4**).

gradual decrease of the selectivity of the formation of compound **1**. At the same time, compounds **2** and **3**, as well as **4** (up to 0.1%), were detected in the condensates. The total yield of the liquid products obtained decreased to 70% with increase of temperature because methanol was partially decomposed. During the experiments, lasting tens of hours, no formation and accumulation of resin- or tar-type deposits on the catalyst were observed. After interrupting the experiment and cooling the reactor, the restarted system, after establishing stationary conditions (which took about 1 h), gave the same results as previously, suggesting no deactivation due to catalyst poisoning. The alkylation was also carried out at other LHSV loads (from 0.5 to 3.0 h⁻¹) and the results obtained at 603 K are given in Table 1.

The alkylation of 1-naphthol with our iron oxide catalyst runs quite differently from that in the presence of

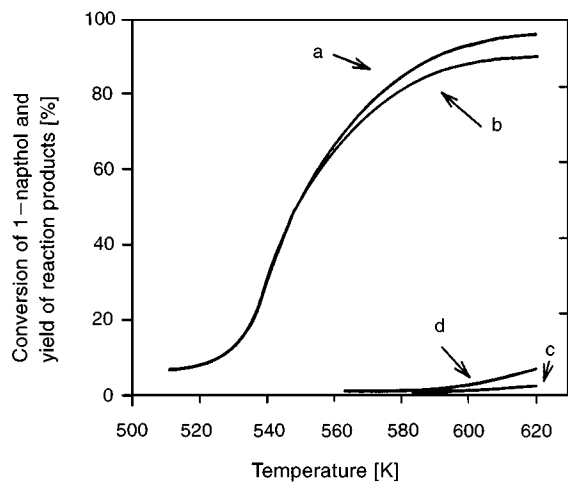
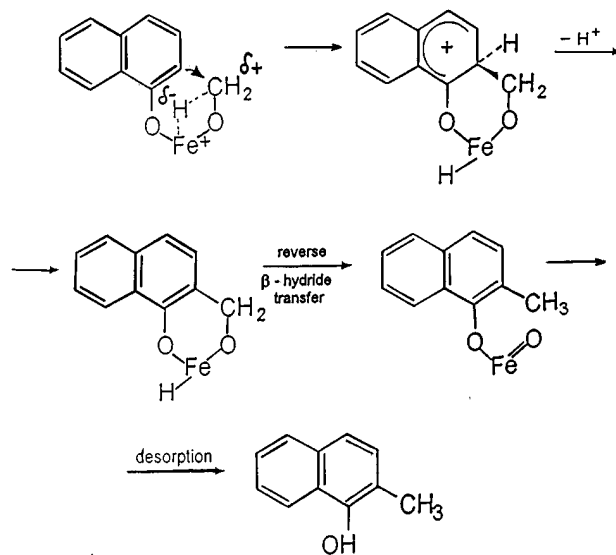
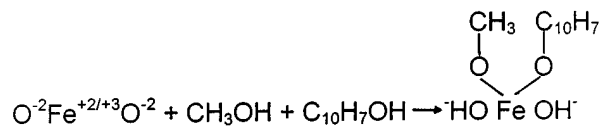


FIG. 1. Temperature dependence of the conversion of 1-naphthol and the yield of the main product **1** and of the two derivatives **2** and **3** at a LHSV load of 1.5 h⁻¹. (a) Conversion of 1-naphthol, (b) yield of **1**, (c) yield of **2**, (d) yield of **3**.



SCHEME II. The proposed reaction pathway for catalytic methylation of 1-naphthol over iron oxide.

the alumina catalyst studied by Klemm *et al.* In our case there is no dehydroxylation of 1-naphthol, nor any formation of methylnaphthalenes. There are also no polymethylated naphthols among the reaction products. The presence of 2,4-dimethyl-1-naphthol could have been expected, but this compound was not found. Also O-methylation is an insignificant process.

Based on literature searching no direct information could be found which could explain our experimental data. Our suggestion on the reaction mechanism is based on the known fact that on basic metal oxide surfaces, preoxidized transition metal and clean transition metal surfaces, methoxy intermediates decompose via β -hydride elimination (β -hydride transfer), leaving positively charged carbon atoms (7–9). Such a mechanism in this reaction has been recently proved by Gellman *et al.* (10, 11). According to the author's hypothesis the β -hydride elimination is the reaction responsible for the transformation of the nucleophilic methoxide into an electrophile. It is assumed that the reaction of interest occurs on iron ion sites which are doubly occupied by both methoxide and naphthoxide, as proposed in Scheme II.

To sum up, in the presence of an iron oxide catalyst, the alkylation of 1-naphthol runs with high yield and selectivity. High contents of 2-methyl-1-naphthol in the reaction products allow for its easy separation and purification. This

TABLE 1
Iron Oxide-Catalyzed Methylation of 1-Naphthol at 603 K

Experiment No.	LHSV ^a (h ⁻¹)	Conversion of 1-naphthol (%)	Yield of 1 (%)	Yield of 2 (%)	Yield of 3 (%)	Unidentified compounds (%)	Selectivity of 1 (%)
1	0.5	97.0	85.4	2.6	6.3	2.7	88.0
2	1.0	94.5	87.2	2.0	4.1	1.2	92.0
3	1.5	93.2	88.6	1.0	2.5	1.1	95.1
4	3.0	92.6	89.8	0.5	1.5	0.8	97.0

^a LHSV, liquid hourly space velocity.

might be a raw material for further syntheses. It is the author's belief that the method of selective alkylation that they propose might be of potential significance in the syntheses of agrochemicals, dyes, and drugs. For example, 2-methyl-1-naphthol could be used in the manufacture of menadione, a precursor of vitamin K₃.

ACKNOWLEDGMENT

The research was performed with financial support from the Polish State Committee for Scientific Research under Grant 7S203 032 06.

REFERENCES

- Klemm, L. H., Shabtai, J., and Taylor, D. R., *J. Org. Chem.* **33**, 1480 (1968).
- Klemm, L. H., and Klopfenstein, C. E., *J. Org. Chem.* **35**, 1069 (1970).
- Grabowska, H., Kaczmarczyk, W., and Wrzyszczyk, J., *J. Appl. Catal.* **47**, 351 (1989).
- Grabowska, H., and Wrzyszczyk, J., *Res. Chem. Intermed.* **17**, 263 (1992).
- Grabowska, H., Miśta, W., Syper, L., Wrzyszczyk, J., and Zawadzki, M., EUROPACAT II Congress, (Maastricht, 1995), Book of Abstracts, p. 601 (1995).
- Kamel, M., *Helv. Chim. Acta* **42**, 58 (1959).
- Kizhakevariam, N., and Stuve, E. M., *Surf. Sci.* **286**, 246 (1993).
- Wiegand, B. C., Uvdal, P., Serafin, J. G., and Friend, C. M., *J. Phys. Chem.* **96**, 5063 (1992).
- Shen, B.-R., Chaturvedi, S., and Strongin, D. R., *J. Phys. Chem.* **98**, 10258 (1994).
- Gellman, A. J., and Dai, Q., *J. Am. Chem. Soc.* **115**, 714 (1993).
- Forbes, J. G., and Gellman, A. J., *J. Am. Chem. Soc.* **115**, 6277 (1993).

H. Grabowska*
W. Miśta*
L. Syper†
J. Wrzyszczyk*,¹
M. Zawadzki*

*W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences
P.O. Box 937, 50-590
Wrocław 2, Poland; and
†Institute of Organic Chemistry, Biochemistry, and Biotechnology,
Technical University of Wrocław,
Wybrzeże Wyspiańskiego Street 27
50-370 Wrocław
Poland

Received May 24, 1995; revised December 4, 1995; accepted December 28, 1995

¹ To whom correspondence should be addressed.