

Nafion/SiO₂ Nanocomposites: High Potential Catalysts for Alkylation of Benzene with Linear C₉-C₁₃ Alkenes

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Abstract: High surface area Nafion/SiO₂ nanocomposites with nano-sized Nafion resin particles entrapped and dispersed within the highly porous silica matrix exhibited significantly enhanced activity, high selectivity and long-term stability for the alkylation of benzene with linear C₉-C₁₃ alkenes owing to the increased accessibility of Nafion resin-based acid sites to reactants.

Keywords: Nafion/SiO₂ nanocomposites, Friedel-Crafts alkylation, linear alkylbenzenes.

Linear alkylbenzenes (LAB), the most important intermediates for biodegradable detergents, are produced industrially *via* the alkylation of benzene with linear C₉-C₁₄ alkenes¹. The conventional processes using AlCl₃ or HF as catalysts have many drawbacks, *viz.* corrosion, pollution, high catalyst consumption, separation and post-disposal problems^{1,2}. Besides, these catalysts also present low selectivity to 2-phenylalkanes, which are the key components that can greatly improve the biodegradability of the detergents. Thus, it is critical and desirable to develop solid acid catalysts for LAB synthesis. Over the years, various solid acid catalysts have been investigated, including clays², heteropolyacids, zeolites^{3,4} and immobilized homogeneous acids⁵. The first industrial process using fluorided SiO₂-Al₂O₃ as catalyst (the Detal[®] process) has been realized by UOP/Petresa¹. However, the Detal[®] process suffers from fast deactivation of the catalyst. Nafion[®] NR50 resin is known as a very strong Brønsted acid catalyst ($H_0 \approx -12$) which catalyzes many reactions in organic synthesis⁶. But its activity is limited in less polar solvents or in gas phase reactions owing to its extremely low surface area (0.02 m²/g). Recently, Nafion entrapped within the porous silica matrix (Nafion/SiO₂ nanocomposite) gave rise to significantly enhance activity for alkylation⁷, acylation⁸, isomerization⁹, rearrangement¹⁰ and dimerization¹¹ because it combined the strong acidity of Nafion resin with the desirable porosity of the silica support¹². In the present study, home-made Nafion/SiO₂ nanocomposite catalysts were used for the first time for the alkylation of benzene with linear C₉-C₁₃ alkenes. The results showed that Nafion/SiO₂ nanocomposite had high potential for this important

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alkylation reaction.

The Nafion/SiO₂ nanocomposites were prepared using an *in situ* sol-gel technique with tetraethoxysilane and 5% Nafion solution as silica and Nafion sources, respectively¹³. The alkylation reaction was carried out in a down-flow fixed bed reactor operating at 150°C and 4.5 MPa with 4 g catalyst. *Prior to* the reaction, the catalyst was *in situ* pretreated at 150°C for 4 h under nitrogen stream. A mixture from an industrial thermal cracking of paraffin oil (Yanshan Petrochemical Corporation) was directly used as the source of alkene reactants, which contained an approximately equal amount (50/50) of C₉-C₁₃ alkenes and C₉-C₁₃ alkanes. The reaction feed was the mixture of benzene (Yanshan Petrochemical Corporation, 98.5%) and the alkene source, which was previously dehydrated over 5 Å molecular sieve. The molar ratio of benzene/alkenes in the feed was always 45 and the reaction WHSV was 2 h⁻¹. During the reaction, samples were taken at certain time intervals and analyzed by GC and GC/MS for product quantification and identification, respectively.

By varying the ratio of Nafion resin solution to tetraethoxysilane, Nafion/SiO₂ nanocomposites with different Nafion contents (5~20%) have been prepared. Values of surface area/m² g⁻¹, pore diameter/nm and pore volume/cm³ g⁻¹ for these catalysts are as follows: 5% (415, 7.26 and 0.77), 13% (374, 7.15 and 0.68) and 20% (352, 5.71, and 0.55). It is seen that surface area, pore diameter and pore volume gradually decrease with the Nafion loading while the surface area can remain at high enough level. Compared to Nafion[®] NR50 resin with a surface area of about 0.02 m²/g, an increase of several orders of magnitude in surface area is obtained in the nanocomposites. Although the surface area of the nanocomposite is the additive value for both silica and Nafion[®] NR50 resin, the improved Nafion dispersion and the accessibility of Nafion resin-based acid sites to reactants in Nafion/SiO₂ nanocomposites have been demonstrated by TGA/TPD experiments (adsorption/temperature programmed desorption) using isopropanol as the reactant^{11,12} and catalytic reactions^{7-12,15}. Physical and chemical characterizations of the present samples showed that nano-sized Nafion particles were entrapped and dispersed in the highly porous silica matrix¹³.

Figure 1 plots the conversion of alkenes *vs.* the reaction time over Nafion/SiO₂ nanocomposites with different Nafion loadings. The 5% Nafion/SiO₂ nanocomposite with fewer acid sites showed lower catalytic activity than the other ones (the conversion of olefins was 90.6% and 92.3% over 13% and 20% Nafion/SiO₂ nanocomposites, respectively) and deactivated rapidly. With increasing the Nafion loading from 5% to 20%, the nanocomposite showed higher activity and longer stability in the alkylation of benzene with the mixed olefins. However, there was not a linear correlation between the Nafion content and the catalyst stability. In comparison with the pure Nafion resin, the catalytic activity of the nanocomposite was greatly enhanced due to the increased accessibility of Nafion resin-based acid sites to the reactants. On the other hand, the preparation of the nanocomposite also provided the opportunity of intimate interaction between the hydroxyl group of silica and the -SO₃H contained in the pockets of the highly dispersed Nafion resin, which resulted in decline to some extent in the acidity of the sulfonic acid groups¹⁴. In the nanocomposites with similar surface areas, somewhat lower acid site dispersion, stronger acidity and higher catalytic activity could be expected

as the Nafion content was increased. Thus, it was not surprising that the 20% Nafion/SiO₂ nanocomposite presented a more than fourfold enhancement in the catalyst longevity than the 13% Nafion/SiO₂ nanocomposite. As compared with a TH-06 catalyst (a zeolite-Y based catalyst with the catalyst longevity of *ca.* 24 h at WHSV=1 h⁻¹), the 20% Nafion/SiO₂ nanocomposite also showed much longer catalyst stability although the WHSV value over this catalyst (2 h⁻¹) was twice that over TH-06.

Figure 1 The conversion of alkenes vs. time on stream over Nafion/SiO₂ catalysts

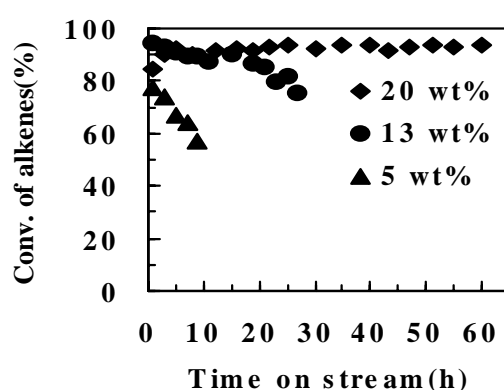


Table 1 The isomer distribution in the alkylates over different catalysts

Catalyst	Isomers distribution (%)				
	2-phenyl	3-phenyl	4-phenyl	5-phenyl	6-phenyl
5% Nafion/SiO ₂	36.2	26.7	14.8	18.7	3.6
13% Nafion/SiO ₂	34.6	27.7	14.1	19.4	4.2
20% Nafion/SiO ₂	31.7	28.1	14.7	20.7	4.7
HF ^a	15~18	15~18	-	-	-
AlCl ₃ ^a	30	20	-	-	-
Fluorided SiO ₂ -Al ₂ O ₃ ^{a,b}	25	-	-	-	-
TH-06 ^c	50	27	-	-	-

^aValues obtained from literature¹.

^bThe Detal[®] process running under similar conditions as used in the present work.

^cThe alkylation over TH-06 catalyst conducted with identical conditions (except WHSV=1 h⁻¹) to that employed in the present work.

The examination of the coke using solvent extraction method revealed that the deposition of heavy molecules formed by oligomerization of olefins was the most important factor leading to the deactivation of Nafion/SiO₂ nanocomposites. Another factor accounted for the catalyst deactivation was the poison level in the reaction feed. Because the industrial olefin mixtures containing a certain amount of poison (*e.g.* organic sulfur) were not purified *prior to* the reaction, poisoning of the acid sites might be also an important factor leading to the catalyst deactivation. This latter case was verified by the fact that the stability of TH-06 catalyst was greatly improved when the reactant mixture was desulfurized *prior to* the reaction test.

The isomer distribution of LAB over Nafion/SiO₂ nanocomposites is given in **Table**

1. It appeared that Nafion/SiO₂ nanocomposite catalysts produced significantly higher selectivity toward 2-phenylalkanes than HF and AlCl₃. Likewise, the selectivity to 2-phenylalkanes was higher than that in the Detal[®] process with a fluorided SiO₂-Al₂O₃ catalyst. The selectivity to 2-phenylalkanes slightly declined with increasing the Nafion content in the nanocomposites. This result could be explained by the fact that a slightly more aggregated form of the Nafion resin with stronger acidity, *i.e.* Nafion/SiO₂ nanocomposites with higher Nafion loading, readily catalyzed the skeletal isomerization of alkenes. Certainly, other textural differences might also influence the isomer distribution. The higher selectivity toward 2-phenyl and 3-phenyl isomers over the Nafion/SiO₂ catalysts might suggest some kind of shape-selectivity in the nanocomposites. TH-06 catalyst gave more 2-phenylalkanes than the Nafion/SiO₂ nanocomposites owing to its higher shape-selective catalysis as often observed with zeolite catalysts. Furthermore, BET measurements showed that there was little difference in the pore structure between fresh and deactivated catalysts. Our results also showed that coking had little effects on the isomer distribution in the alkylation of benzene with linear C₉-C₁₃ olefins. More detailed studies on the effect of reaction conditions and the composition of coke in the alkylation reaction are in progress.

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