

Alkylation of Benzene with 1-Dodecene over USY Zeolite Catalyst: Effect of Pretreatment and Reaction Conditions

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Abstract—Catalytic activity, stability and selectivity of USY zeolite catalyst for alkylation of benzene with 1-dodecene were investigated using a continuous fixed bed high pressure microreactor. It is found that the catalytic activity and stability depend closely on the pretreatment temperature of catalyst and reaction conditions. The best result was obtained at 120 °C and 3.0 MPa with 8 molar ratio of benzene to 1-dodecene, and 4 h⁻¹ weight hourly space velocity of reactant over the catalyst with the pretreatment temperature of 500 °C. Under this condition, the reaction conversion was nearly 100% and no deactivation was observed within the employed 50 h of time on stream with the selectivity of 2-phenyldodecane being 22%.

Key words: Linear Alkylbenzene, USY Zeolite, Alkylation, 1-Dodecene, Benzene

INTRODUCTION

Linear alkylbenzene (LAB) is the primary raw material used to produce LAB sulfonate (LAS), a surfactant detergent intermediate. Nowadays, most of LAB productions involve the utilization of hydrofluoric acid as the catalyst, which is a source of pollution and equipment corrosion. A great deal of effort has been concentrated on the development of solid acid catalysts for the process. Recently, UOP and CEPSA announced their new Detal process for the manufacture of LAB based on a fixed bed of solid acid catalyst, which is fluoride containing silica-alumina [Kocal, 1993; Sivasanker and Thangaraj, 1992].

Among various solid acid materials, zeolites have been extensively evaluated for the production of LAB [Kocal et al., 2001]. For example, H-ZSM-5 and H-ZSM-12 show little activity due to their small pore size, and dealumination of mordenite or Y zeolite can increase the catalytic activity and stability by opening up the mesoporosity with the zeolite [Jung et al., 2000; Meriaudeau et al., 1997; Sugi et al., 2000]. Zeolite Beta and EMT are also evaluated together with Y zeolite, and it is found that Beta and EMT catalysts are less active than Y zeolite [Cao et al., 1999].

So far, the catalytic stability of zeolite is still a key problem need to be solved for the future commercial utilization of zeolite catalysts in LAB production. However, only a few studies have adopted fixed bed reactor to evaluate the catalyst performance [Sivasanker and Thangaraj, 1992], and most of the previous experiments are carried out in batch reactors, which are inconvenient for testing the catalytic stability.

In this work, the activity, selectivity and stability of an USY zeolite catalyst are measured in detail in the alkylation of benzene with 1-dodecene under various pretreatment and reaction conditions. We consider that, during the water steam treatment for the preparation of USY zeolite, acid strength increases and acid number decreases, with the creation of secondary structured mesopores. These catalyst properties are indispensable for the high performance of the zeolite catalyst in the reaction of benzene alkylation with 1-dodecene.

EXPERIMENTAL

All experiments were carried out in a fixed bed microreactor. The reactant mixture of benzene and 1-dodecene was injected by a high pressure pump into the fixed bed reactor, in the middle stage of which was charged with 1.0 g of USY catalyst in the form of granules (40-60 mesh). The catalyst was initially pretreated in situ in air flow at a desired temperature before reactants enter the reactor. In order to measure the effect of reaction conditions, reactions were operated in a temperature range of 80-160 °C, at a pressure interval of 0.1-3.0 MPa, with the molar ratio of benzene to 1-dodecene (B/D) in a range of 2-8, and weight hourly space velocity (WHSV) of the reactant of 4-12 h⁻¹. Also, to keep the system at the required pressure, a small flow of N₂ was maintained from the reactor head. The reaction products were analyzed by the gas chromatograph (HP 5890 II) using FID as the detector furnished with a 30 m SE30 capillary column. The conversion and selectivity were calculated as follows. Conversion = $(M_{d0} - M_d)/M_{d0} \times 100\%$, where M_{d0} is the molar percentage of 1-dodecene before reaction, and M_d is the molar percentage of 1-dodecene after reaction. Selectivity of LAB isomer was defined as S = M_i/M_s × 100%, where M_i is the molar percentage of a LAB isomer in the final products, and M_s is the sum of molar percentage of all six phenyldodecane isomers.

Zeolite USY used in this work was from Zeolyst (Si/Al=40). Benzene was from Wako (99.0%) and 1-dodecene from Tokyo Kasei (95.0%). The reactants were dehydrated by 5A zeolite before use.

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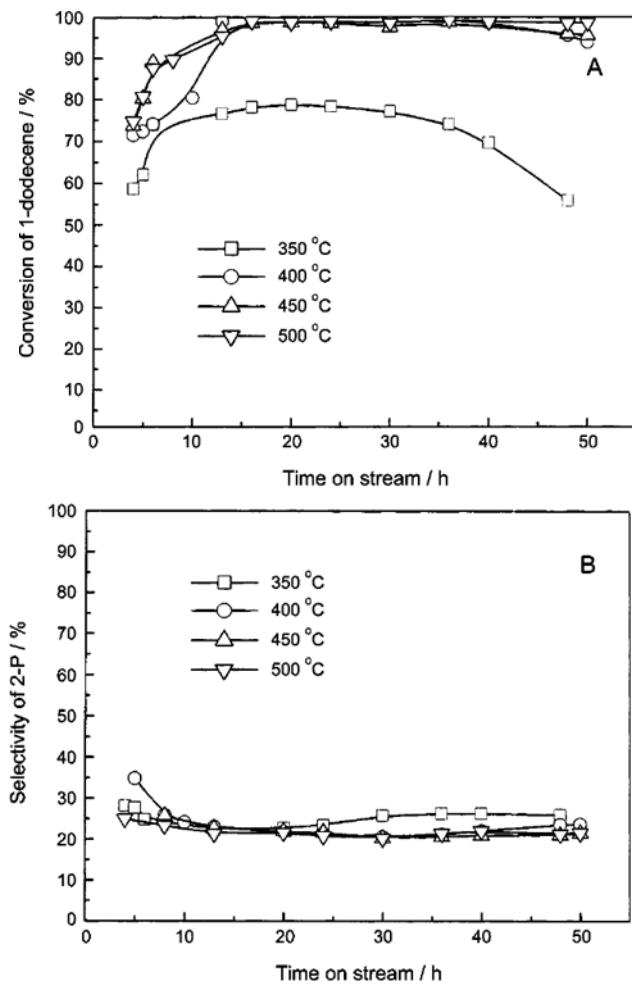


Fig. 1. Alkylation of benzene with 1-dodecene over USY zeolite catalyst: effect of pretreatment temperature of the catalyst in air flow for 4 h on activity and stability (A), and selectivity (B) (Reaction temperature=120 °C, Pressure=3.0 MPa, WHSV=4 h⁻¹, B/D=8).

RESULTS

1. Effect of Pretreatment Temperature of USY Catalyst

The experiment was carried out at 120 °C and 3.0 MPa, and with the WHSV of 4 h⁻¹ and the B/D of 8, which is the typical reaction condition in this work. Fig. 1 shows the influence of pretreatment temperature of USY zeolite in air on the reactivity of alkylation of benzene with 1-dodecene. At all pretreatment temperatures in Fig. 1A, conversion of 1-dodecene increases gradually at the early stage of time on stream. At the pretreatment temperature of 400, 450, or 500 °C, the conversion gets to a plateau with a same conversion level of about 100% after ca. 15 h of time on stream, by contrast, at 350 °C, the conversion reaches a maximum point of about 75% which is far lower than the other three catalysts, at a time on stream of ca. 20 h, after which, a rapid deactivation of the catalyst occurs. A slow deactivation is also observed for the other two catalysts pretreated at 400 or 450 °C, when time on stream is beyond 40 h. By contrast, for the catalyst pretreated at 500 °C, no deactivation is found during all time on stream employed. On the other hand, for all catalysts, Fig. 1B shows at the early stage of reaction a decrease of the

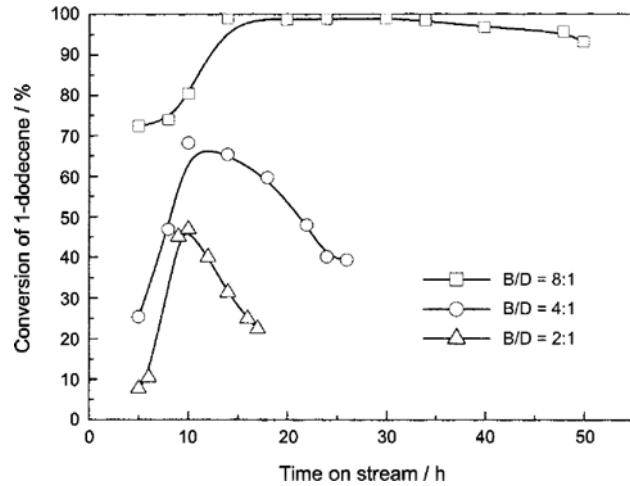


Fig. 2. Alkylation of benzene with 1-dodecene over USY zeolite catalyst: effect of ratio of benzene to 1-dodecene (Reaction temperature=120 °C, Pressure=3.0 MPa, WHSV=4 h⁻¹, Pre-treatment temperature=400 °C).

selectivity of 2-phenyldodecane (2-P), which is the most desired isomer among the reaction products because it gives detergent of better emulsibility and biodegradability. At the last half of the reaction time on stream, the selectivity is stable, except that an increase of selectivity of 2-P is observed on the catalyst pretreated at 350 °C.

2. Effect of the Molar Ratio of Benzene to 1-Dodecene

The experiment was performed at the typical reaction condition with the pretreatment temperature being 400 °C. The effect of B/D on the catalytic activity and stability of the USY catalyst is displayed in Fig. 2. It can be seen in Fig. 2 that the conversion of 1-dodecene increases obviously with the increase of benzene content in the reactant mixture, and moreover, at low B/D values, the catalyst is observed to deactivate quickly. It is also found in Fig. 2 that the higher the B/D is, the longer reaction time on stream is needed for the catalyst to reach its maximum activity.

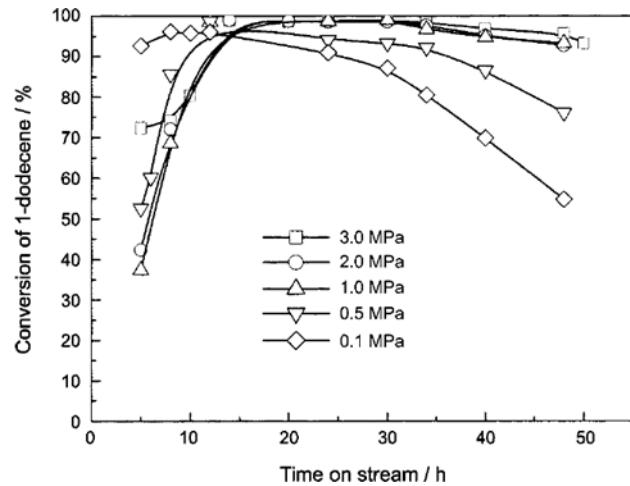


Fig. 3. Alkylation of benzene with 1-dodecene over USY zeolite catalyst: effect of reaction pressure (Reaction temperature=120 °C, WHSV=4 h⁻¹, B/D=8, Pre-treatment temperature=400 °C).

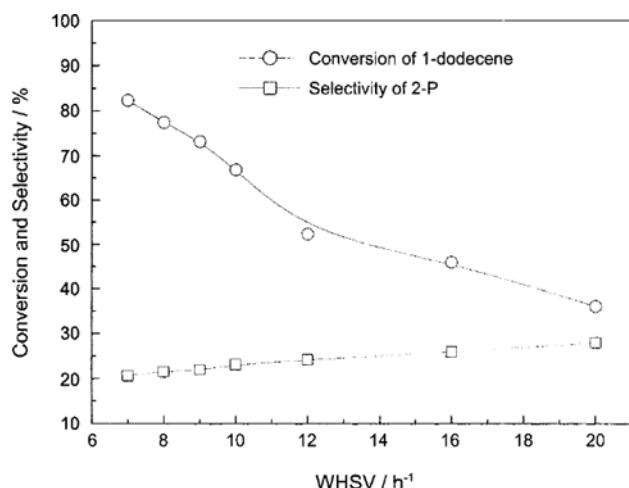


Fig. 4. Alkylation of benzene with 1-dodecene over USY zeolite catalyst: effect of weight hourly space velocity of the reactant (Reaction temperature=120 °C, Pressure=3.0 MPa, B/D=8, Pretreatment temperature=400 °C).

3. Effect of Reaction Pressure

Fig. 3 exhibits the effect of reaction pressure on the catalytic activity as a function of reaction time on stream. It is clearly observed that at the pressure lower than 1.0 MPa, no stabilized activity can be achieved, while at the high pressures, the catalyst gives similar results: after ca. 15 h of time on stream, stabilized conversion higher than 95% can be obtained.

4. Effect of the Space Velocity of Reactant Mixture

The experiment was measured at 100 °C and 3.0 MPa, with the pretreatment temperature of 400 °C and the B/D of 8. Fig. 4 indicates that the conversion of 1-dodecene decreases with the increase of WHSV, and meanwhile, the selectivity of 2-P gradually increases with the decrease of conversion.

5. Effect of Reaction Temperature

The effect of reaction temperature on the catalytic activity, stability and selectivity is shown in Table 1. It is found that at all employed temperatures very high conversion of 1-dodecene is obtained at the reaction time on stream of 20 h, however, the higher the reaction temperature is, the lower the final conversion is observed. As for the selectivity, whatever the reaction temperature and time on stream, no obvious discrepancy of selectivity of 2-P is observed.

Table 1. Conversion of 1-dodecene and selectivity of 2-P as a function of reaction temperature^a

Temperature / °C	Time on stream / h	Conversion / %	Selectivity / %
80	20	98.4	26.0
	50	96.7	23.2
120	20	98.6	22.0
	50	93.2	23.7
160	20	98.6	21.2
	50	79.2	22.6

^aReaction Pressure=3.0 MPa, B/D=8, Pretreatment temperature=400 °C

DISCUSSION

The alkylation of benzene with 1-dodecene takes place via a carbonium ion mechanism at the acid site of catalyst. Six carbonium ions possibly appear due to the double bond isomerization of 1-dodecene. According to the stabilities of them, one would expect the content of produced phenyldodecane isomer to increase with the carbon number (toward the center of the dodecane chain), and in fact, 1-phenyl isomer is not detected in the product, due to the very low stability of the primary ion. This is found to be so in case of HF, in which thermodynamic equilibrium is probably reached [Sivasanker and Thangaraj, 1992]. However, on the heterogeneous acidic catalyst with a pore structure like zeolite, it is expected that the catalytic activity, selectivity and stability would be influenced by catalyst acidity (acid density, acid strength and acid type), pore structure of zeolite and location of acid sites. For instance, polymers produced on acid sites in small pores through polymerization of dodecene will block the pores and lead to the deactivation of catalyst. It is proposed that there would be optimum performance with the most acid sites coupled with the most open mesoporosity in catalyst [Meriaudeau et al., 1997].

The acidity of zeolite relates closely to the pretreatment temperature. For USY, both acid strength and acid number increases with the calcination temperature, with the release of proton in zeolite crystal pore by dehydration. At very high calcination temperature, two Brønsted acid sites transform into one strong Lewis acid site, resulting in the decrease of acid density, and at the same time, slight dealumination occurs with the generation of more secondary mesopores [de Almeida et al., 1994]. Therefore, the observation in Fig. 1A that the catalysts pretreated at high temperatures (≥ 400 °C) display higher activities than the one at low temperature (350 °C) corresponds well with the enhancement of number of strong acid site produced at high pretreatment temperature. Through FT-IR characterization results of a series of modified H-mordenite zeolites, a recent literature [Wang et al., 2001] found the sum of the numbers of strong Brønsted and Lewis acid centers exhibits a most similar trend with the conversion of the benzene alkylation with 1-dodecene, and thus the authors indicated that both strong Brønsted and Lewis acid sites are responsible for this reaction. For the catalyst pretreated at 350 °C, there dominate weak and medium strong acid sites, which are supposed to be favorable to the polymerization of dodecene and the catalyst pores are clogged easily, and thus deactivation occurs quickly. Accompanying with the deactivation of the catalyst pretreated at 350 °C, the selectivity of 2-P is apparently increased (Fig. 1B). This is considered to arise from the shape selectivity of the more narrow pores formed by the part blockage of zeolite channel. For the catalyst pretreated at 500 °C, the acid density deceases, but the acid strength increases simultaneously, with the number of mesopores being enhanced. This may account for its always high activity and stable selectivity. On the other hand, at its stabilized stage, the selectivity of 2-P is around 22%, which is just slightly higher than that of HF [Sivasanker and Thangaraj, 1992], and shows no shape selectivity. This is because the wide-pore system of Y zeolite that is largely retained, together with plenty of mesopores that are favorable to mass transfer during the reaction.

Not only pretreatment temperature, but also reaction conditions drastically affect the reaction result. When B/D drops to a low value,

dodecene has more chance to polymerize into polyolefins, therefore the zeolite pore tends to be blocked easily in this case, which causes the short life of the catalyst (Fig. 2). In addition, high reaction temperature can also lead to the comparatively quick deactivation of catalyst. It could be expected that the tendency of the polymerization of dodecene would be raised by high reaction temperature, which might be the reason for the deactivation of catalyst in Table 1 at the high reaction temperature of 160 °C.

An important observation in this work is that for most of experiments, an increase of catalytic activity is found with time on stream at the early reaction stage (Figs. 1-3). In a batch reactor, a previous report revealed that the used HY zeolite could be regenerated by the hot benzene [Liang et al., 1996]. Thus, one could reasonably consider that benzene is not only a reactant, but also a solvent, which can partly refresh the deactivated acid sites by dissolving the polymers produced on acid sites locating in zeolite channel through dodecene polymerization. Based on the above consideration, it is deduced that at the very initial reaction time on stream, a large amount of polymers are generated and thus block the zeolite pores, however, this is partly compensated by the dissolution of polymers by benzene solvent at a comparatively low speed, with the release of a part of strong acid sites being active for alkylation. This could be the explanation for the increment of alkylation activity at the early stage of time on stream. The increment of B/D leads to the rapid dissolution of polyolefin and thus the catalyst can reach the maximum activity point at a short time on stream (Fig. 2). The only exception is found in Fig. 3 on the catalyst performed at 0.1 MPa, in which the reaction actually takes place in gas phase, and no solvent effect could be expected, as a result of which, the activity decreases from the very beginning of the reaction.

CONCLUSIONS

Through detailed experiments for benzene alkylation with 1-dodecene over a USY zeolite catalyst with a continuous high pressure fixed bed reactor, the following conclusions are obtained:

1. Pretreatment temperature and reaction conditions drastically influence the catalytic activity and stability, by contrast, slightly influence catalytic selectivity. Increase of pretreatment temperature can enhance the catalyst acid strength, decrease acid density, and create more mesopores [de Almeida et al., 1994; Sasaki et al., 1998], which is indispensable for the high catalytic activity and stability. High B/D value and reaction pressure are favorable to the enhancement of catalytic activity and stability, but high reaction temperature causes the deactivation of catalyst.

2. At the early reaction stage, an increase of alkylation activity is found in all experiments. This is supposed to originated from refreshment of a part of strong acid sites in zeolite pores by the competition between the quick polymerization of dodecene on acid sites

and the slow dissolution of a part of thus produced light polymers into benzene solvent.

3. It is found that USY catalyst pretreated at 500 °C in air flow for 4 h has a very high activity (near 100%) and stability (no deactivation being observed within the employed 50 h time on stream), and a slightly higher selectivity (23%) than that of HF, when the reaction was carried out at 120 °C, 3.0 MPa, with the WHSV and B/D being 4 h⁻¹ and 8, respectively.

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