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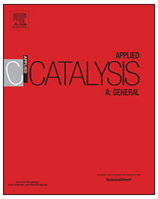

Deactivation mechanism and activity-recovery approach of composite ionic liquids for isobutane alkylation

Xuan Zhang[a], Rui Zhang[a], Xianghai Meng[a], Haiyan Liu[a], Zhichang Liu[a,*], Hao Ma[a], Chunming Xu[a], Peter A.A. Klusener[b]

[a] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, China*
[b] *Shell Global Solutions International B.V., Amsterdam, 1031 HW, The Netherlands*

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ABSTRACT

The deactivation mechanism and the activity recovery approach of composite ionic liquid (CIL), a kind of acidic chloroaluminate ionic liquids (ILs) modified with CuCl for the in 2013 successfully commercialized catalysis of isobutane alkylation are being discussed in this paper. CIL showed catalytic activity only in the presence of both Brønsted and Lewis acids. CIL deactivation was caused by the loss of Brønsted acidity and/or Lewis acidity. Brønsted acidity decreased by the loss of trace amount of formed chlorohydrocarbons with the outflowing alkylate. Lewis acidity was deactivated mainly due to the complexation of the formed acid soluble oil (ASO) with the CIL anions. Brønsted acidity was maintained by the continuous addition of hydrogen chloride (HCl) or *tert*-butyl chloride, and Lewis activity was recovered by $AlCl_3$ addition. However, Brønsted acidity could not be recovered when Lewis acidity was lost and was thus dependent on Lewis acidity. Furthermore, ASO interacted with active components of CIL, causing the loss of copper via precipitation of CuCl which is the major contributor to the high selectivity. Therefore, CuCl was added simultaneously with $AlCl_3$ to maintain the high selectivity of alkylate.

1. Introduction

Isobutane alkylation (C_4 alkylation) is a process that produces alkylate from isobutane and butenes in the presence of acidic catalysts. Alkylate is mainly composed of *iso*-paraffins, which have a high octane number, and it has low contents of sulfur, olefins, and aromatics, rendering an ideal blending component for motor gasoline.

Traditional commercial catalysts for isobutane alkylation are concentrated sulfuric acid (H_2SO_4) and hydrofluoric acid (HF). The alkylation processes catalyzed by H_2SO_4 and HF matured after several decades of development [1]. However, despite the high catalytic activity, C_8 selectivity, and long lifetime of these two catalysts, certain problems persist. The acid consumption of H_2SO_4 is large, and the treatment costs of waste H_2SO_4 are high, and there are environmental hazards requiring special treatment. Hydrofluoric acid is highly toxic and deleterious to the environment, and its leakage can form aerosols, which are lethal to human beings [2].

Facing the above problems, researchers have been exploring new environmentally friendly catalysts, such as solid acid catalysts and acidic ionic liquids (ILs) [3,4]. Acidic chloroaluminate ILs have attracted much attention on isobutane alkylation because of their unique features, such as low corrosion, low toxicity, environmental friendliness, and the presence of both Brønsted and Lewis acidity [5–10]. Our research group developed a composite ionic liquid (CIL), which is a kind of chloroaluminate IL modified by CuCl [6]. The first CIL-catalyzed isobutane alkylation plant with a scale of 100 kt/a was successfully started up in 2013, and it has been running for more than four years. Part of this process is the rejuvenation of the catalyst using continuous HCl or *tert*-butyl chloride addition to prevent rapid catalyst deactivation [11]. Nevertheless, the mechanism of this deactivation and rejuvenation was not well understood.

Without rejuvenation, chloroaluminate ILs will lose their catalytic activity for isobutane alkylation. Therefore, the deactivation mechanism and activity recovery method of chloroaluminate ILs were studied to support the commercial application of chloroaluminate ILs in catalytic areas.

Yoo et al. [12] reported that acidic chloroaluminate ILs, showing initially high catalytic activity, deactivated gradually mainly due to the moisture sensitivity of ILs. Moreover, they found that the butene conversion and TMP selectivity decreased because the Brønsted acid sites of C-2 proton were reduced by decomposition of imidazolium ions at high temperature. Bereblyum et al. [13] studied the catalytic activity of

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[*] Corresponding author.
E-mail address: lzch@cup.edu.cn (Z. Liu).

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chloroaluminate ILs in heptane isomerization and found the main cause for deactivation was HCl loss. Seddon et al. [14] reported that chloroaluminate ILs are sensitive to moisture under the release of HCl, resulting in a decreased catalytic performance. Liu et al. [11] pointed out that the lifetime of IL for isobutane alkylation could be prolonged significantly by adding HCl or halogenated hydrocarbons to the process. Chevron [15–17] suggested that conjunct polymers deactivate chloroaluminate ILs by weakening the acid strength through the formation of complexes of conjunct polymer and Lewis acids. In practice, conjunct polymers are also called acid soluble oil (ASO) because of their high miscibility in the catalysts. Other studies [13,18] showed that ASO molecules contain double bonds and/or conjugated double bonds with cyclic and/or acyclic skeletons or even several aromatic rings. Therefore, the interaction between ASO and the catalyst could occur through the donor/acceptor interaction, and consequently ASO is not simply to be removed by extraction using such solvents as hexane, toluene, or CH_2Cl_2. Although ASO can be isolated by means of hydrolysis, this method is destructive and would destroy the chloroaluminate ILs. Chevron [15,19–21] claims the use of hydrogenation to remove ASO from ILs by the saturation of double bonds, followed by the separation of the hydrogenated ASO with the reactivated ILs. Seddon et al. [22,23] reported the reduction of aromatics by a metal-acid combination in a chloroaluminate IL, providing a potential effective approach as alternative to high-pressure catalytic hydrogenation.

Most of the above studies focused only on the deactivation of chloroaluminate ILs by loss of Lewis acidity, while these ILs also consist of Brønsted acidity, which is as demonstrated in our current study to be essential for their activity as well. Moreover, the presence of copper is a further advantage of CIL in higher isobutane selectivity to C_8, especially trimethylpentane (TMP), than traditional chloroaluminate Ils [6,24–26]. Hence, this paper aims to study the deactivation mechanism of CIL by loss of Brønsted and/or Lewis acidity, and to develop an activity recovery method of CIL in isobutane alkylation, ensuring a long-term and stable operation of the industrial unit.

2. Experimental section

2.1. Materials

2.1.1. Materials for preparation of CIL

Triethylamine hydrochloride (Et_3NHCl), anhydrous aluminum chloride ($AlCl_3$), and cuprous chloride (CuCl) were obtained from Aladdin Industrial Corporation. Et_3NHCl was dehydrated with acetone. $AlCl_3$ was purified by sublimation at 180 °C. All reagents were stored in a glovebox or a dryer.

2.1.2. Raw materials for alkylation reaction

Isobutane and 2-butene were obtained from a refinery of China, t-butyl chloride (> 98%) was purchased from Alfa Aesar, and HCl was purchased from APK (Shanghai) Gas Co., Ltd. The C_4 feed composition is listed in Table 1, and the I/O ratio (molar ratio of isobutane to butene) was about 20:1. Water was removed from the C_4 feed by dried 4 Å molecular sieve while oxygen-containing compounds were removed by Selexsorb CD purchased from BASF according to different research needs.

2.2. Preparation of CIL (Et_3NHCl-$xAlCl_3$-$yCuCl$)

CIL was synthesized according to patent application US7285698 [27]. Et_3NHCl was first placed into a three-necked round bottom flask. Then, $AlCl_3$ was gradually added under N_2 protection while stirring and maintaining a temperature of 120 °C. After all solids became liquid, CuCl was introduced. The mixture was stirred at 150 °C for 4 h until complete homogenization was achieved.

Table 1
Composition of C_4 feed.

Component	Isobutane	n-Butane	trans-2-Butene	cis-2-Butene
Content (wt%)	94.48	0.79	2.75	1.98

Table 2
Pre-treatment of C_4 feed for isobutane alkylation experiments.

Entry	Items	C_4 feed pre-treatment
1	Isobutane alkylation experiment	Dried
2	Effect of water	None
3	Effect of oxygen-containing compounds	Dried and deoxygenated
4	Long-term alkylation (recovery of Brønsted acidity)	Dried and deoxygenated, with HCl or *t*-butyl chloride addition
5	Recovery of Lewis acidity	Dried and deoxygenated, with $AlCl_3$ and CuCl addition
6	Pilot test	Dried

2.3. Isobutane alkylation experiment

2.3.1. Isobutane alkylation experiment

The alkylation experiment was operated semicontinuously, and the apparatus, illustrated in Fig. S1, was as reported before [28]. CIL (200 g) was introduced into a 500 mL autoclave (reactor). While stirring at 1200 rpm, the C4 feed with an I/O ratio of 20:1 was pumped into the reactor at a flow rate of 750 mL/h. The pressure was maintained at 0.6 MPa, and the reaction temperature was 13 °C (Table 2, entry 1). Given the different densities of CIL and alkylate, the CIL phase remained in the bottom part of reactor, while phase separation took place in the top of the reactor. The hydrocarbon phase, including alkylate and excess of isobutane, flowed out from the top outlet of the reactor. Samples of the hydrocarbon phase were taken from the outlet to monitor the catalyst activity and selectivity. When the butene was detected, the run was stopped by stopping the stirrer and changing the C_4 feed to isobutane. The amount of C_4 feed introduced until butene breakthrough was recorded as measure for catalyst lifetime. The amount of alkylate was determined as the C_{5+} fraction in the collected hydrocarbon outlet.

Unless mentioned otherwise dried C_4 feed was used. In the study of the effect of impurities on C_4 alkylation, one experiment was done with undried C_4 feed (Table 2, entry 2) and another was done with deoxygenated dried C_4 feed (Table 2, entry 3).

2.3.2. Long-term alkylation experiments with chloride addition

Two long-term alkylation experiments were operated in the same apparatus and at the same experimental parameters as above except for the fact that HCl or *t*-butyl chloride were added to the dried and deoxygenated C_4 feed with a concentration of 47.7 or 95.4 mg/kg, respectively (Table 2, entry 4).

2.3.3. Pilot test alkylation experiment

Pilot test unit of isobutane alkylation catalyzed by CIL is shown in Fig. 10. C_4 feed with a molar ratio of isobutane to butene of 8:1 was prepared in E103 by mixing dried C_4 feed (Table 2, entry 6) from vessel V102 with an I/O ratio of 1:1 and isobutane from V101, wherein the circulated isobutane was collected. The C_4 feed from V102 was dried in a drier before being pumped into the mixer E103 (being a cooled static mixer). The reaction temperature was 13 °C, and the pressure was 1.0 MPa. The effluent from the reactor (being a static mixer) was separated in settler V104 from which the bottom layer (CIL phase) was circulated back to the reactor and the hydrocarbon phase (alkylate and excess isobutane) was partially fed via a second settler V105 into fractionator T101 and partially recycled to the reactor. The excess of isobutane was recovered via the top and fed back to V101 and alkylate