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ONE STEP SYNTHESIS OF MIBK (METHYL ISOBUTYL KETONE) FROM ACETONE OVER CaO-SUPPORTED Ni CATALYST

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Abstract – One step synthesis of MIBK from acetone over Ni/CaO catalysts was studied. 10 wt% Ni/CaO catalysts were prepared by conventional impregnation method (catalyst I), and liquid phase oxidation method using NaOCl as an oxidant (catalyst L). Catalyst L showed much higher activity than catalyst I because of recovered CaO pore structure and high BET surface area. Catalyst C, prepared by coprecipitation method, showed 60 % of MIBK selectivity with a fairly high overall acetone conversion. Catalysts L and C had two CO_2 desorption states (α, β). Incorporated Ni enabled support precursor [$Ca(CO)_3$] to decompose easily into CaO and CO_2 even at low temperature and generated weak CO_2 desorption state (α) which was from active state.

Key words: MIBK, Ni/CaO, Liquid Phase Oxidation, NaOCl, CO_2 Desorption States

INTRODUCTION

Methyl isobutyl ketone (MIBK) is one of the most precious acetone-based synthetic materials. It is used as solvent for resins and pigments. And, so far, its commercial synthesis process consists of three steps; aldol addition of acetone to diacetone alcohol (DAA) over homogeneous catalyst in liquid phase, dehydration of DAA to mesityl oxide (MSO) over homogeneous acid catalyst, and selective hydrogenation of MSO to MIBK, the final product, over metal catalyst. But this three-step MIBK synthesis process has many problems such as complication of the process and difficulty in separating homogeneous catalysts. So, in recent years, much interest has been shown in the one-step synthesis of MIBK with an attempt to improve the commercial process [Gandia and Montes, 1993, 1994, 1995; Gandia et al., 1994; Higashio and Nakayama, 1996; Othmer, 1979]. High pressure one step synthesis of MIBK from acetone has been reported in several supported Pd catalyst systems giving high selectivity to MIBK in the temperature region of 80-160 °C with an overall acetone conversion of nearly 40 mol% [Othmer, 1979]. But, the operating pressure is between 10 and 100 atm. Gandia and Montes reported that one step formation of MIBK from acetone at atmospheric pressure over several supported Ni catalysts such as Ni/MgO [Gandia and Montes, 1993], Ni/ZnO [Gandia and Montes, 1994], Ni/Al_2O_3 [Gandia and Montes, 1994, 1995], and Ni/Aluminophosphate-oxynitrides [Gandia et al., 1994], showed relatively high MIBK selectivity and overall acetone conversion. 2-propanol, diisobutyl ketone (DIBK), and DAA were typical byproducts of this process. Generally, metal/basic metal oxide system has a problem that ready precipitation of metal salt during precipitation procedure due to high surface basic strength may lead to the blocking of pore mouth resulting in the decrease of BET surface area. In this work, we studied catalyst preparation methods to solve the problem mentioned above and the reaction conditions to increase both overall acetone conversion and MIBK selectivity in Ni/CaO catalyst system, and tapped the possibility of using such catalyst at atmospheric pressure to produce MIBK.

EXPERIMENTAL

10 wt% Ni/CaO catalyst was prepared by conventional impregnation method (catalyst I series), and liquid phase oxidation method (catalyst L series) using nickel nitrate and calcium hydroxide. After impregnation the solid was dried at 110 °C overnight (catalyst I), and then reduced at 500 °C for 1 hour (catalyst IR) before reaction. Catalyst L was prepared by oxidizing catalyst I with NaOCl or $K_2S_2O_8$ for half an hour. Catalyst LR was prepared by the same method mentioned above as catalyst IR in the catalyst I series. Because CaO could easily adsorb CO_2 to form $CaCO_3$ at 500 °C in air, we omitted calcination procedure. Catalyst C was prepared by coprecipitation method using nickel nitrate and calcium nitrate as precursors. To coprecipitate, the liquid phase oxidation (LPO) method was used and the solid was treated as the same sequences mentioned above. Acetone hydrogenation was carried out in a fixed bed reactor operating at 1 atm and 200 °C with a feed stream composition of 10 mol% acetone and 90 mol% H_2. About 50 mg of the catalyst was loaded in the quartz tube reactor and experiments were carried out at different acetone feed rate (AFR) of 6.22-300 $cc \cdot h^{-1} \cdot g_{cat}^{-1}$. The reaction mixture was analyzed by a gas chromatograph (HP 5890) with a HP Carbowax 20M capillary column. BET surface area and pore size distribution (PSD) of the catalyst were measured by nitrogen adsorption using a Micromeritics Pulse Chemisorption Unit (Model ASAP2000) to charac-

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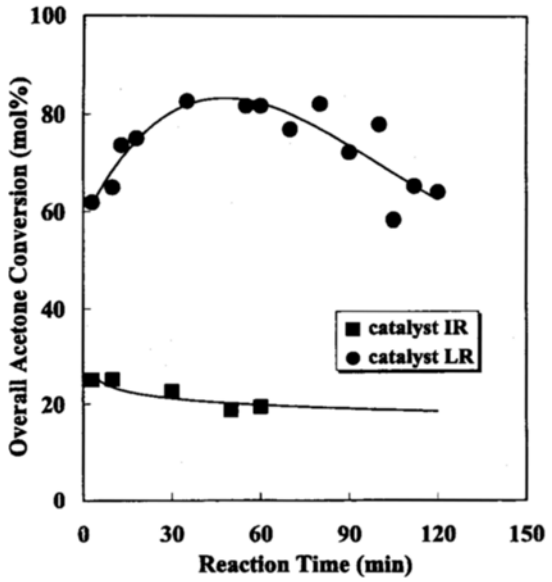

Fig. 1. Reaction time vs. overall acetone conversions over catalysts IR and LR.

terize physico-chemical properties of each catalyst. CO_2 TPD and XRD experiments were also performed. For TPD measurements, samples were treated at 500 °C for 1 hour in a flow system of 10 cc/min H_2 and 20 cc/min N_2, and then exposed to CO_2 for 30 min at room temperature. TPD was run at a heating rate of 10 °C/min. The gas desorbed was analyzed by a thermal conductivity detector.

RESULTS AND DISCUSSION

1. 10 wt% Ni/CaO by LPO Method

Fig. 1 shows overall acetone conversions over catalyst IR and LR, and Figs. 2 and 3, selectivities for several products in the selective hydrogenation of acetone over catalysts IR and LR, respectively. The feed rate of acetone was kept with 6.22 $cc \cdot h^{-1} \cdot g_{cat}^{-1}$. Catalyst LR showed very high overall acetone conversion relative to catalyst IR giving about 30 mol% of MIBK selectivity (Fig. 3). Furthermore, the BET surface area of catalyst L was 27 m^2/g which was about 7 times higher than that of catalyst I (4 m^2/g). The pore mouths of CaO were thought to be blocked by $Ni(OH)_2$ due to the ready precipitation of nickel nitrate to $Ni(OH)_2$ in basic CaO suspension. But CaO pore structure was easily recovered by oxidizing $Ni(OH)_2$ to NiOOH with NaOCl (Fig. 4). Because NiOOH, which has been used as an electrode material, has poor crystallinity, higher surface area than that of $Ni(OH)_2$, and Ni oxidation state of +3-most of Ni catalyst precursor has oxidation state of +2-resulting in a relatively strong metal-support interaction, it can be used effectively as a catalyst precursor. The increase of BET surface area could be explained in this sense. 2-Propanol formed at metal site and DIBK formed through successive aldolization of MSO and acetone at basic site (CaO site) were favoured over catalyst IR and LR, respectively, because CaO pore was blocked by metal salt resulting in the decrease of basic sites from CaO in catalyst IR and recovered in catalyst LR. When using $K_2S_2O_8$ as an oxidant, 10 mol% MIBK selectivity and 70 mol% 2-propanol selectivity were measured despite high overall acetone conversion due to CaO dissolution by $K_2S_2O_8$ resulting in high metal loading-about 60 mol% Ni-because the formation of 2-propanol occurs on metal site. However, this method using $K_2S_2O_8$ is convinced of being a novel preparation method for, especially, hydrogenation catalyst such as Ni/SiO_2 and Ni/Al_2O_3 because of no dissolution of the support.

We could easily find out that the main by-products of this reaction were 2-propanol and DIBK, and MIBK selectivity could be increased up to 70 mol% giving a fairly high conversion of 40 mol% with increasing the feed rate of acetone to 56 $cc \cdot h^{-1} \cdot g_{cat}^{-1}$ because the formation of DIBK was not favored relatively than that of MIBK in an acetone-rich condition due to both lack of α-hydrogen and steric hindrance

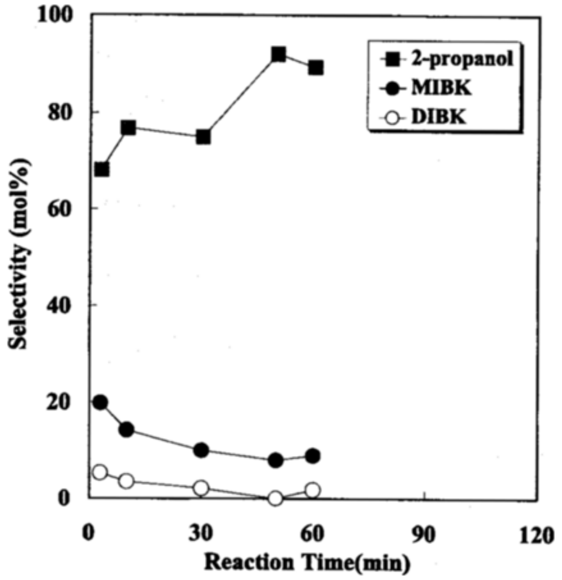

Fig. 2. Reaction time vs. selectivities for several products over catalyst IR.

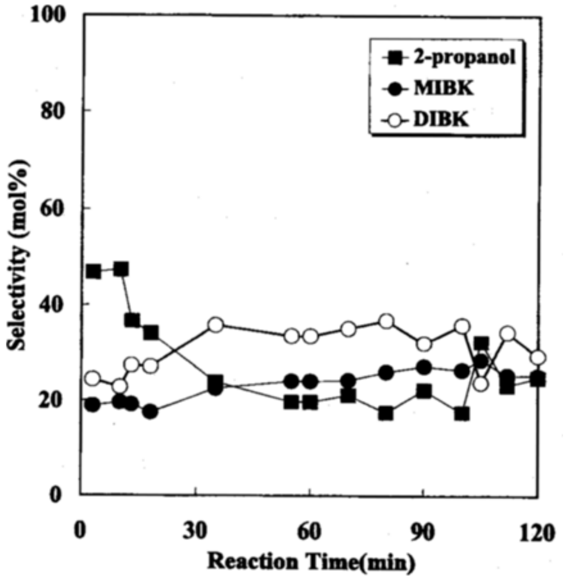

Fig. 3. Reaction time vs. selectivities for several products over catalyst LR.

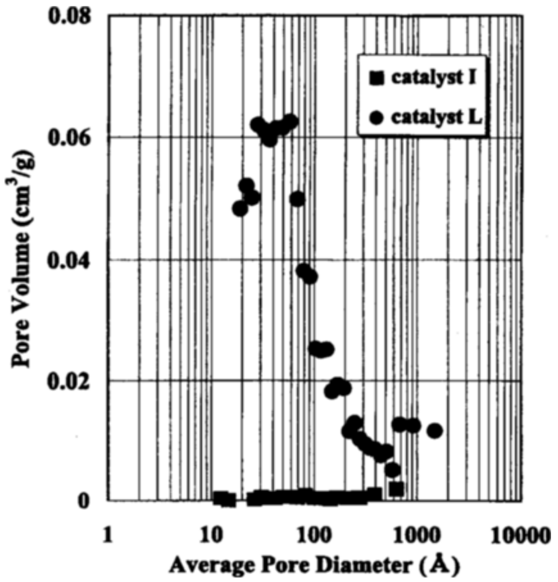

Fig. 4. Pore size distributions of catalysts I and L.

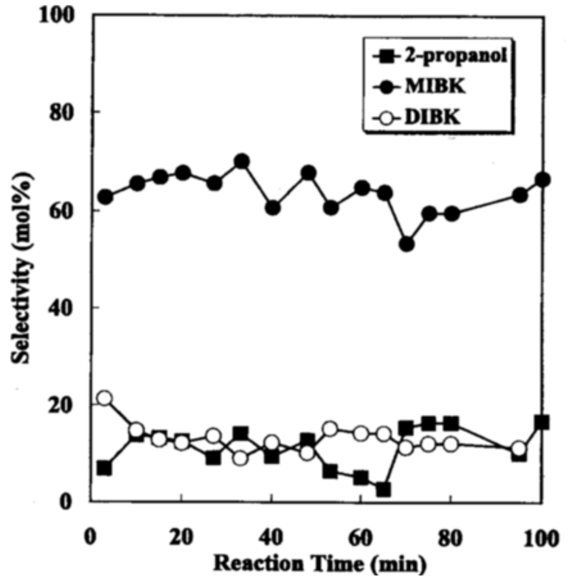

Fig. 5. Reaction time vs. selectivities for several products over catalyst LR at an acetone feed rate of 56 cc·h^{-1}·g$_{cat}$$^{-1}$.

of MSO (Fig. 5). Increasing the feed rate of acetone to 300 cc·h^{-1}·g$_{cat}$$^{-1}$ which is extremely severe condition to the catalyst, MIBK selectivity and overall acetone conversion was 75-80 mol% and 20 mol%, respectively. So, we concluded that very high activity could be obtained with the limitation of increase in MIBK selectivity to nearly 100 mol% by increasing the acetone feed rate using catalyst L series only. Therefore, the research on promoter is necessary and is now on doing.

In contrast to Ni/MgO [Gandia and Montes, 1993], Ni/CaO catalyst showed much higher catalytic activity and selectivity to DIBK, product of successive aldolization of MSO, due to higher basic strength of CaO than that of MgO.

When using the feed composed of 10 mol% DAA and 90 mol% H_2 instead of the feed composed of 10 mol% acetone and 90 mol% H_2, the main products were acetone and 2-propanol, whereas for the feed composed of 10 mol% MSO and 90 mol% H_2, MIBK and DIBK were mainly formed (Table 1). The result provides an evidence that MSO is firstly formed directly without the formation of DAA, and is in agreement with that of high pressure reaction over $Pd/Nb_2O_5 \cdot nH_2O$ [Higashio and Nakayama, 1996].

Table 1. Product composition by feeding DAA or MSO instead of acetone

Feed	Products					
	Acetone	2-Propanol	DAA	MSO	MIBK	DIBK
DAA	36 mol%	44 mol%	N.D.*	8 mol%	7 mol%	N.D.
MSO	N.D.	N.D.	1 mol%	N.D.	79 mol%	20 mol%

*not detectable.

2. Coprecipitated 0.5 wt% Ni-CaO

Generally, as mentioned above, metal/basic metal oxide system has a problem that ready precipitation of metal salt during precipitation procedure due to high surface basic strength may lead to the blocking of pore mouths resulting in reduction of BET surface area. We could solve this problem to some extent by oxidizing the catalyst precursor. However, coprecipitation method was more effective for solving the problem. It has been reported that 2-propanol is formed through the reaction of acetone and hydrogen which are adsorbed on Ni site [Gandia and Montes, 1994]. So, we prepared catalyst 0.5CR which had a very low metal loading of 0.5 wt% Ni by coprecipitation in order to suppress the formation of 2-propanol. The XRD pattern of Fig. 6 indicates that the structure of catalyst 0.5C is mainly calcium hydroxide. Ni is not detected in the pattern due to low loading. Selectivities to MIBK, DIBK, and 2-propanol over catalyst 0.5CR are shown in Fig. 7. About 70 mol% overall acetone conversion and 60 mol% MIBK selectivity which are much higher than those reported previously were measured at a feed rate of acetone kept

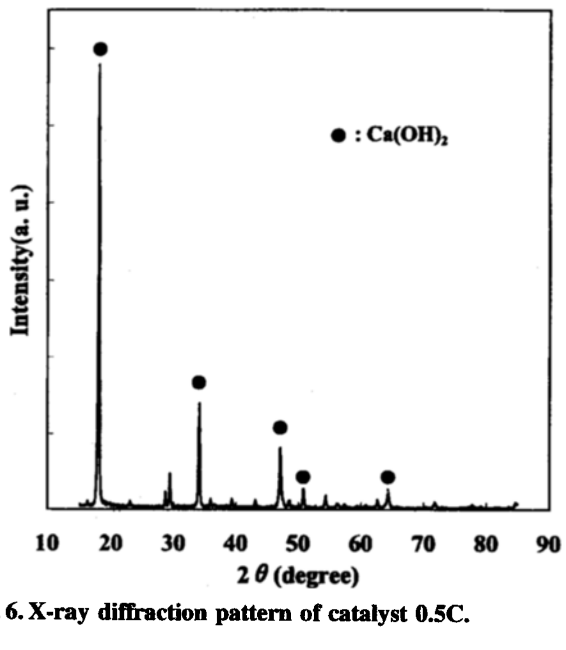

Fig. 6. X-ray diffraction pattern of catalyst 0.5C.

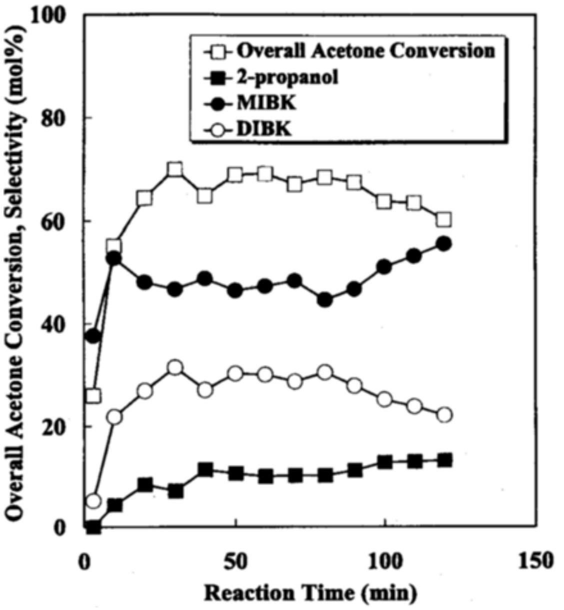

Fig. 7. Reaction time vs. overall acetone conversion and selectivities for several products over catalyst 0.5CR at an acetone feed rate of 6.22 cc·h^{-1}·g$_{cat}$$^{-1}$.

with 6.22 cc·h^{-1}·g$_{cat}$$^{-1}$. Owing to the very low amount of metal loading, 2-propanol formation was suppressed drastically as expected. Meanwhile, the catalyst 0.5LR which has 0.5 wt% Ni showed very low catalytic activity regardless of the same amount of Ni as catalyst 0.5CR.

3. CO_2 Temperature Programmed Desorption (TPD)

There is a serious difficulty in characterizing base catalysts, that is, base materials can adsorb or absorb readily CO_2 and H_2O in air. CO_2 TPD is known to be one of the valuable methods to characterize the surface basic strength of base catalysts [Hattory, 1995; Zhang et al., 1988]. The strength and amount of basic sites are reflected in the desorption temperature and the peak area in a TPD spectrum, respectively. The results of CO_2 TPD of the catalysts 0.5CR and 0.5LR are shown in Fig. 8. Each catalyst had two CO_2 desorption states, weak (α) and strong (β) states. But, the decomposition temperature of $CaCO_3$ into CaO and CO_2, about 700 °C, is close to the position of β state. As mentioned above, basic materials like CaO can easily absorb CO_2 to form $CaCO_3$, suggesting that the β peak is not desorption peak but bulk decomposition one. What are the effect and the role of incorporated Ni? First, incorporated Ni made it ease to decompose bulk $CaCO_3$ into CaO and CO_2 weakening the basic strength. Second, it increases the amount of α state, the weak basic state. Kurokawa et al. [1990] reported that the base strength of MgO increased drastically with the addition of a metal ion with a radius slightly larger than that of Mg^{2+}, whereas it either decreased or remained unchanged when a metal ion with a radius smaller than that of Mg^{2+} was added to MgO. When a metal ion with a radius larger than that of Mg^{2+} is incorporated into MgO lattice, the lattice is distorted surrounding the added metal ion and the distortion may result in the localization of electrons on the oxygen atom of MgO [Kurokawa et al., 1990]. Consequently, the solid base property may increase. When the metal ion with a radius smaller than that of Mg^{2+} is incorporated, the effect of decreasing base strength can be explained in reverse sense [Kurokawa et al., 1990]. In the case of catalysts 0.5CR and 0.5LR, the added metal ion and basic material were Ni^{3+} and CaO, respectively. Because the radius of Ni^{3+} was smaller than that of Ca^{2+}, the base strength decreased resulting in the generation of weak basic states. The increase of the amount of α state-it thought to be surface basic state-in catalyst 0.5CR can be explained in the sense of well incorporation of Ni^{3+} into the lattice. Meanwhile, the α state of the catalyst 0.5LR hardly existed because Ni^{3+} could not be incorporated into the CaO structure due to the difference in preparation method from the catalyst 0.5CR. The former was prepared by impregnation, and the latter, coprecipitation. The β peak due to bulk $CaCO_3$ decomposition shifted to lower temperature in the catalyst 0.5CR than in the catalyst 0.5LR. This result can be also explained by the difference of base strength due to metal incorporation. In short, to the best of our knowledge, Ni incorporation was more effective in the catalyst 0.5CR than the catalyst 0.5LR prepared by impregnation and coprecipitation, respectively, and incorporated Ni generated α states and shifted β peak to lower temperature, as was the main factor of increasing catalytic activity.

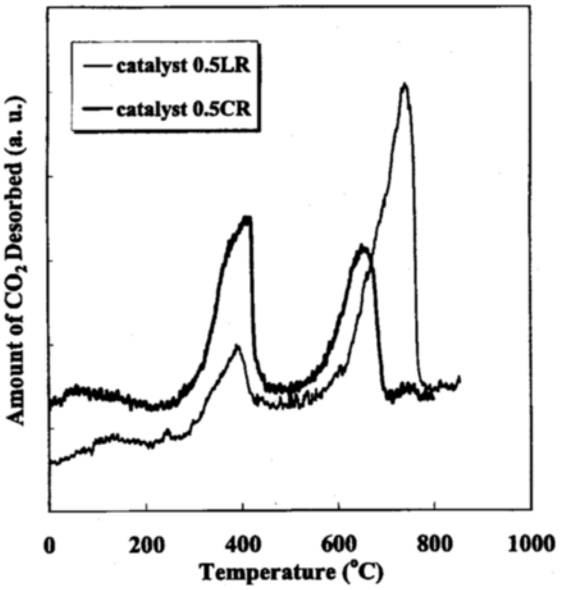

Fig. 8. CO_2 thermal desorption spectra over catalysts 0.5LR and 0.5CR.

CONCLUSIONS

Catalyst LR prepared by LPO method showed very high activity relative to the catalysts of I series due to recovery of CaO pore structure resulting in high BET surface area. The formation of main byproducts, 2-propanol and DIBK, was decreased by lowering the amount of metal loading and increasing the feed rate of acetone, respectively. Consequently, MIBK selectivity could be increased up to 70-80 mol% giving a fairly high conversion. Using 10 mol% DAA as a feed instead of acetone, the main products were acetone and

2-propanol, whereas for 10 mol% MSO, MIBK and DIBK were mainly formed, suggesting that MSO is firstly formed directly without the formation of DAA as a reaction intermediate. Catalyst 0.5CR prepared by coprecipitation showed 60 % of MIBK selectivity with a fairly high overall acetone con- version, and had two CO_2 desorption states (α, β). Incorporated Ni enabled β peak to shift easily to lower temperature and generated weak CO_2 desorption state (α state), which was the main factor of increasing catalytic activity.

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