A New Active Catalyst for Single Step Synthesis of Methyl Isobutyl Ketone from Acetone

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(Received March 16, 1998; CL-980194)

2 wt% Ni-CaO catalyst prepared by sol-gel process showed 70-80% acetone conversion and 60% MIBK selectivity at 200 °C of reaction temperature. The incorporated Ni influenced $CaCO_3$, catalyst intermediate, to readily decompose into CaO, active basic component, and CO_2 at even 500 °C. Meanwhile, Co or Pd did not influence $CaCO_3$ decomposition at the same temperature of 500 °C and showed no catalytic activity. That is, Ni played a role as promoter for catalyst activation as well as active site of hydrogenation.

Methyl isobutyl ketone (MIBK) is one of the most precious acetone-based synthetic materials. It is used as a solvent for resins and pigments. Commercial MIBK synthesis process is operated under high pressure and 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 by using bifunctional catalyst composed of basic metal oxide for acetone dimerization and transition metal for hydrogenation.[1-7] However, CaO, despite its high basicity, has not been used for this reaction due to its strong CO_2 sorption ability and difficulty in impregnating or doping transition metal by rapid precipitation. Unlike MgO, CaO reacts easily with CO_2 to form $CaCO_3$, inactive material for this reaction. So, if we use CaO as a catalyst, heat treatment at about 700 °C - maybe a severe condition resulting in sintering - is inevitable.

In this study, Ni-CaO catalyst, which was never tried before as a catalyst for the present reaction, was used as a bifunctional catalyst and tapped the possibility of using such catalyst to produce MIBK at atmospheric pressure. CaO has two problems in using as a component of the catalyst as mentioned above. First, ready precipitation of metal salt in impregnating it onto CaO due to high surface basicity leads to the blocking of pore mouth resulting in the decrease of BET surface area.[8, 9] Second, in this reaction, metal-CaO catalyst shows relatively poor activity when treated thermally at high temperatures such as 700 °C, the decomposition temperature of $CaCO_3$. The first problem could be solved by treating the catalyst precursor with NaOCl solution,[8, 9] and also by sol-gel-processing the catalyst precursor adopted in this study.

2 wt% Ni-CaO (2NCA5r) catalyst was prepared by sol-gel process as follows: After dissolving nickel acetate and calcium acetate (catalyst precursor) together in water for 2 wt% Ni, evaporation was performed with stirring to form a gel state of nickel acetate-calcium acetate, so, ready precipitation mentioned above did not occur. The catalyst precursor (2NCA) obtained after drying the above gel at 200 °C overnight was then reduced at 500 °C for 1.5 h in a stream of 43% hydrogen and 57% nitrogen before reaction (2NCA5r). The reaction of MIBK synthesis was carried out in a fixed bed reactor operating at 1 atm and 200 °C with an acetone feed rate (AFR) of 14 $cc\cdot h^{-1}\cdot g_{cat}^{-1}$, and ca. 50 mg of the catalyst was loaded in a quartz tube reactor. The reaction mixture was analyzed by a gas chromatograph (HP5890) with a HP Carbowax 20M capillary column. Temperture-programmed reduction / temperature-programmed decomposition (TPR/TPD) experiments were carried out at a heating rate of 10 °C/min in 25 cc/min of total flow rate composed of 10% hydrogen and 90% nitrogen stream. Thermal gravimetric analysis (TGA) and BET measurement were also performed using a thermal gravimetric analyser (Rigaku, CN8078B2) and a pore size analyser (Micromeritics, ASAP 2010), respectively.

We could easily find out from TGA that pure calcium acetate (CA) was decomposed into $CaCO_3$ and acetone at about 400-450 °C, and $CaCO_3$ into CaO, active compound, and CO_2 at about 700 °C. In other words, the decomposition of calcium acetate consists of two steps as follows:

Step 1) calcium acetate (precursor) $\rightarrow$ $CaCO_3$ + acetone
(at about 450 °C)
Step 2) $CaCO_3$ (intermediate) $\rightarrow$ CaO +CO_2
(at about 700 °C)

Figure 1 shows TPR/TPD profiles of various materials. As mentioned above, the first peak appeared at about 450 °C was due to the decomposition of calcium acetate into $CaCO_3$ and acetone (Step 1), and whose position was overlapped to that of reduction of Ni^{2+} to Ni^0. As we used thermal conductivity detector (TCD) instead of mass spectrometer, the signal could go down below the baseline (2NCA in figure 1). This means that the generated molecules (cracked acetone in this case) during TPR/TPD experiment has higher thermal conductivity than that of reference stream (10% hydrogen and 90% nitrogen). The second peak at about 700 °C was attributed to the decomposition of $CaCO_3$ into CaO and CO_2 (Step 2). In order to use CaO as a component of the catalyst, decomposition of $CaCO_3$ which was formed already in air as mentioned above unlike MgO system is necessary before using it for the reaction, and the decomposition should be carried out at a relatively low temperature to minimize sintering of the metal particles. Comparing respectively the TPR/TPD profiles of 2NCA and 2NCA5r with those of CA and CA5r, the incorporated Ni was suggested to influence $CaCO_3$, catalyst intermediate, to decompose readily into CaO, active basic compound, and CO_2 at even 500 °C in this study resulting in high activity. So, the addition of Ni could solve the second problem by lowering the decomposition temperature of $CaCO_3$ from 700 °C to 500 °C. That is, the added Ni could play a role of decomposition promoter as well as active site of hydrogenation. The results were confirmed from BET measurements in Table 1. 2NCA5r showed a drastic increment of BET area due to the formation of CaO structure, but CA5r and 2NCA gave even a slight decrement of area by heating and by blocking,

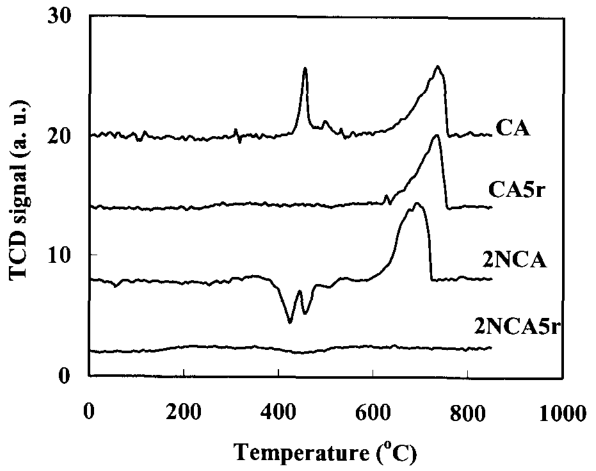

Figure 1. TPR/TPD profiles of two different catalysts and their precursors. (heating rate of 10 °C/min; stream of 2.5 cc/min hydrogen and 22.5 cc/min nitrogen).

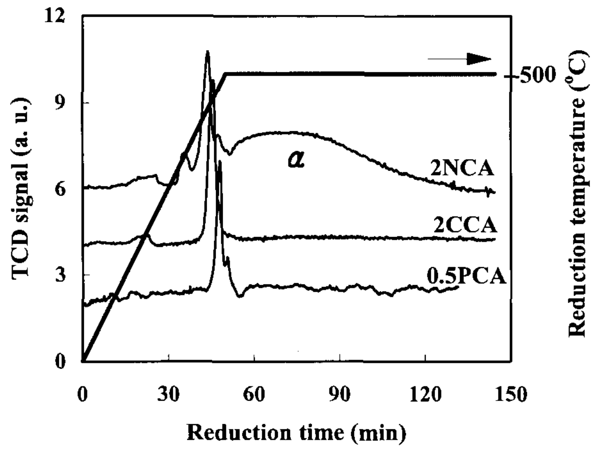

Figure 2. TPR/TPD profiles of various materials during reduction procedure (heating rate of 10 °C/min and holding at 500 °C for 1.5 h; stream of 15.2 cc/min hydrogen and 20 cc/min nitrogen).

Table 1. BET areas of two different catalysts and their precursors by nitrogen adsorption method

Catalyst	CA	CA5r	2NCA	2NCA5r
BET area (m^2/g)	19	14	16	43

respectively as well as no formation of CaO, being compared with CA. The role of the promoter of Ni was not necessary in the MgO system because of no carbonate formation of MgO due to little sorption of CO_2 in air. However, much lower activity was shown in the catalyst of MgO system. Meanwhile, when we used 2 wt% Co or 0.5 wt% Pd instead of 2 wt% Ni as hydrogenation site, namely, 2CCA5r or 0.5PCA5r catalysts, $CaCO_3$ did not decompose and showed no catalytic activity by the heat treatment at 500 °C. Figure 2 shows TPR/TPD profiles of various materials during reduction at 500 °C in a stream of 43% hydrogen and 57% nitrogen. As we can observe a broad peak assigned to α during holding time at 500 °C for 1.5 h, $CaCO_3$ decomposed in case of 2NCA, but no significant signal was obtained in both 2CCA and 0.5PCA.

Consequently, the 2NCA5r catalyst had much higher activity than those ever reported in the system of base metal/MgO[2], especially, whose hydrogenation site was Ni which is a base metal instead of precious metals. It showed 70-80 % of overall acetone conversion and 60 % of MIBK selectivity at an acetone feed rate of 14 $cc\,h^{-1}\,g_{cat}^{-1}$. Both 2CCA5r and 0.5PCA5r catalysts had no catalytic activity due to the remained catalyst intermediate, $CaCO_3$.

This work was supported by the Korea Science and Engineering Foundation (KOSEF) under Grant No. 971-1108-053-2.

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