

Monochlorination of Methane over Pt/NaY-zeolite Catalysts with High Platinum Dispersion

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고분산도의 백금이 담지된 Pt/NaY 제올라이트 촉매상에서 메탄의 단일염소화 반응

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Abstract : Chlorination of methane was carried out over the Pt/NaY zeolite catalysts having different dispersion and location. On the finely dispersed platinum particles inside the zeolite methylchloride was the sole product, while on the large platinum ones outside surface of the zeolite all four chloromethanes were produced. Besides the role of highly dispersed platinum particles, the confined volume of the supercages in the support seems to have played another role on the exclusive production of methylchloride by restricting the further chlorination.

요 약

메탄의 염소화 반응을 여러 Pt/NaY 제올라이트 촉매상에서 수행하였고, 백금입자의 분산도 및 위치에 따른 반응의 특성변화를 관찰하였다. 큰 백금입자가 제올라이트의 외부표면에 주로 존재하는 촉매에서는 4 가지의 염화메탄이 모두 생성된 반면, 고도로 분산된 백금입자가 제올라이트내에 존재하는 촉매의 경우 유일하게 메틸염화물만이 생성되었다. 이는 고도로 분산된 백금입자의 역할뿐 아니라 한정된 공간을 지니는 담체내의 supercage에 의해 메틸염화물의 계속되는 염소화반응이 제한되었기 때문으로 생각된다.

1. INTRODUCTION

Methane, available for great quantities in natural gas, is used mainly as a fuel, but for strategic or economic reasons it may be more desirable to convert

methane into higher hydrocarbons. The first major advance in commercial production of higher hydrocarbons from methanol was achieved by the Mobil Corp. by developing the MTG process with the ZSM-5 catalyst[1]. The Mobil process requires steam reforming

of methane to produce synthesis gas, which is then converted to methanol. Methanol is reacted to form gasoline selectively over ZSM-5 catalyst. Recently many attempts for the direct methane conversion into higher hydrocarbons have been done to overcome the economic problem associated with the multistage conversion of the Mobil process. There are, however, many difficulties in the direct conversion, mainly due to the very high stability of the methane molecule and thermodynamic disadvantages. The thermodynamic disadvantage can be overcome somewhat by the oxidative condensation of methane (conventionally called the oxidative coupling of methane), but the oxidative coupling has some shortcomings [2,3]. The reaction requires high temperature, and the products are almost limited to C₂ hydrocarbons.

Monochlorination of methane is expected to show another promise for the production of higher hydrocarbons: $\text{CH}_4 \xrightarrow{-\text{Cl}} \text{CH}_3\text{Cl} \xrightarrow{-\text{HCl}} \text{CH}_2=\text{CH}_2$ higher hydrocarbons [4]. In the chlorination of methane all four chloromethanes are obtained. Methylchloride, the desired product of chlorination of methane, is chlorinated more readily than methane itself. Therefore it will become one of the key issues in the successful development of the above route to keep high selectivity of methylchloride.

During experiments platinum catalysts were proved to be active for chlorination of methane, and the formation of methylchloride was more favorable on the catalysts having higher platinum dispersions. So NaY zeolite was taken as the support for the encapsulation of the finely dispersed platinum clusters. In addition the confined volume of the supercages in NaY zeolite was thought to be able to restrict the further chlorination of methylchloride.

In this paper platinum catalysts supported on NaY zeolite were prepared through conventional ion exchange, and the changes in the dispersion and location of platinum particles with the temperatures of calcination and reduction were measured. The catalysts were then employed for chlorination of methane, and the catalytic properties of the catalysts were investigated.

2. EXPERIMENTAL

Alumina-supported catalysts having 2% platinum loading by weight were prepared to have different platinum dispersions. After filling the pores of $\gamma\text{-Al}_2\text{O}_3$ (Strem Chemicals) with aqueous solutions of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Strem Chemicals), the catalyst samples were dried for 24 h at 120 °C. The same impregnation procedure was repeated up to 4 times on the dried samples, and the prepared samples were reduced with hydrogen at 400 °C for 6 h. Subsequent to the reduction platinum dispersions were measured by dynamic pulse chemisorption of H₂. The dispersion varied from 68 to 82% with the repetition number of impregnation.

NaY zeolite with Si/Al ratio of 2.5 was provided from Strem Chemicals. The zeolite sample was heated *in vacuo* by raising the temperature from 25 to 400 °C for a period of 12 h and kept at 400 °C for another 24 h. The dehydrated NaY was then ion exchanged with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution at 80 °C for 12 h. After the ion exchanged the samples were filtered, washed and dried at 120 °C overnight. The platinum loading was 7.5% by weight.

A conventional apparatus (Fig. 1) was used for temperature programmed reduction (TPR) experiments. After the catalyst samples being calcined in O₂ at various temperatures, they were cooled slowly to -78 °C in Ar. In order to prevent autoreduction of Pt by decomposing NH₃ during calcination, a high O₂ flow rate of 1000 cc/min per gram catalyst was used, following the suggestions by Della Betta and Boudart [5], Gallezot et al. [6] and Tzou et al. [7]. Gas flow was then switched to 5% H₂/95% Ar, and the catalyst samples were heated from 0 °C to 500 °C linearly at 10 °C/min. The changes in H₂ concentration between the reference and sampling side of the TCD cell were detected and recorded. Separate runs with the NaY zeolite only were also done for the correction of base line drift due to gas temperature fluctuations. The dispersion of platinum was measured by dynamic pulse chemisorption of H₂. Transmission electron mi-

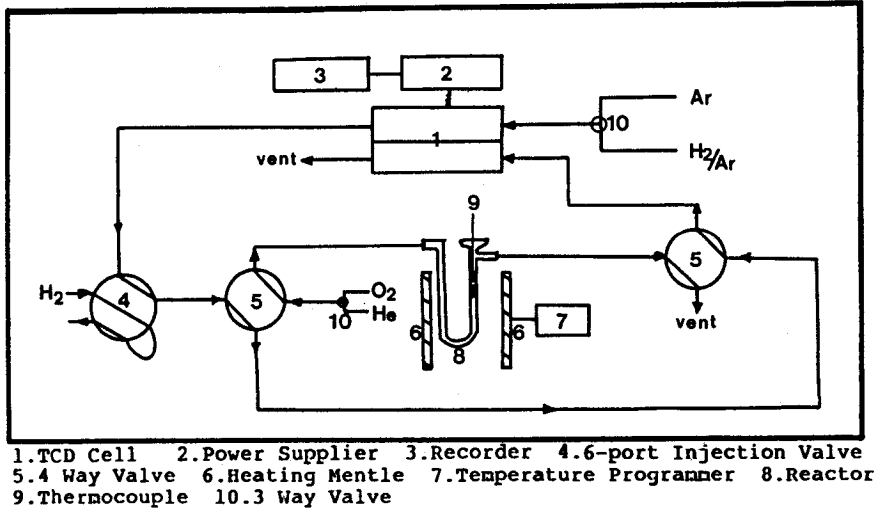


Fig. 1. Apparatus for TPR experiments.

croscopy (TEM) was done with JEOL 200CX microscope.

Chlorination of methane was carried out in a tubular microreactor operating at atmospheric pressure. All the stainless steel lines of the reaction apparatus were heated and purged sufficiently with helium prior to reaction. The molar ratios of CH_4/Cl_2 were adjusted to 3–9, because the methane-chlorine system is known to be explosive within the range from about 62 to 6% by volume methane and 38 to 94% by volume chlorine. The products were analyzed in an on-line GC (HP5890A) with FID detector and 60/80 Carbowax/1% SP-1000 column.

3. RESULTS AND DISCUSSION

Fig. 2 shows the changes in the activity and methylchloride selectivity with the dispersion of the γ -alumina-supported catalysts. From the outstanding increase of selectivity with dispersion the preparation of highly dispersed platinum catalysts is known to be a prerequisite for the selective production of methylchloride in the chlorination of methane.

3. 1. Pt/NaY catalysts

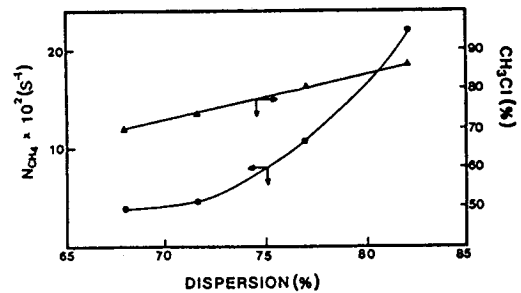


Fig. 2 Changes in the activity and methylchloride selectivity with the platinum dispersion of the γ -alumina-supported platinum catalysts. ($\text{CH}_4/\text{Cl}_2=3$, reaction temperature = 220 °C, conversion = 7.3 %)

Preparation of Pt/NaY catalysts usually consists of three steps ; ion exchange, calcination and reduction. Dispersion of the reduced platinum is known to be affected critically by both the calcination and reduction [8–10]. In Fig. 3 are shown the TPR profiles for Pt/NaY calcined with O_2 at different temperatures. Calcination is done to remove NH_3 ligands from Pt $(\text{NH}_3)_4/\text{NaY}$. When the Pt $(\text{NH}_3)_4/\text{NaY}$ is calcined at low temperature, the part of the ligands will be removed. In this case the majority of Pt^{2+} ions will be

in the supercages where Pt^{2+} ions are accessible to H_2 molecules and thereby will be easily reduced at low temperatures. If the $\text{Pt}(\text{NH}_3)_4/\text{NaY}$ is calcined at high temperatures enough for the total removal of the NH_3 ligands, most of the Pt^{2+} ions will migrate to sodalite cages, because the negative charge density in hexagonal prisms is higher than that at any other sites of the zeolite [11,12]. The high Coulomb interaction and the steric difficulty of admitting H_2 molecules (2.9 Å) through O_6 rings (2.2 Å) in sodalite cages require higher reduction temperature. The changes in reduction temperature in Fig. 3 seem to be due to the different extent of NH_3 ligand removal with calcination temperature, which resulted in different color of the sample; i.e., greenish-black at 350 °C, while light gray at 550 °C.

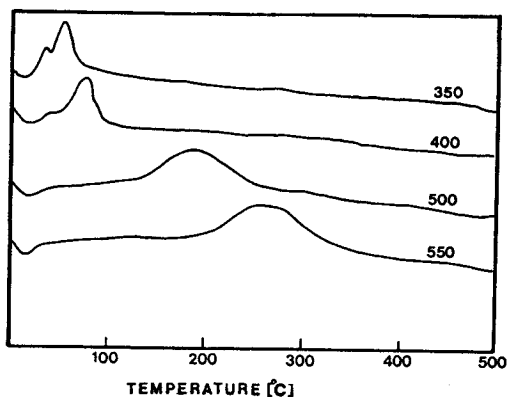


Fig. 3 TPR profiles of Pt/NaY catalysts calcined with O_2 at different temperatures.

After TPR experiments, the catalyst samples were treated with flowing He at 500 °C (the final temperature of TPR experiments) for 2 h and then cooled slowly to room temperature for the measurements of platinum dispersions with H_2 chemisorption. Fig. 4 shows the changes in the platinum dispersion with calcination temperature. High dispersion (about 85 %) can be obtained after calcination at 350 °C, but the dispersion becomes poorer with increasing calcination temperature.

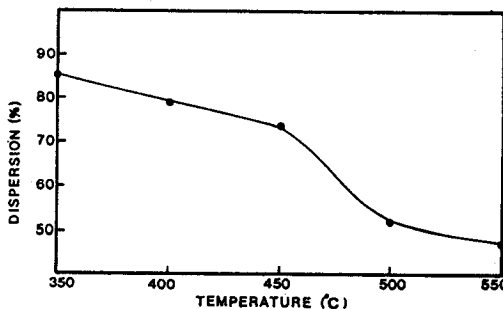


Fig. 4 Changes in the platinum dispersion of Pt/NaY with calcination temperatures.

Subsequent to calcination at the given temperatures, the catalyst samples were reduced with hydrogen at different temperatures (Fig. 5). As shown in Fig. 5-a (sample calcined at 350 °C) nearly 100 % dispersion could be obtained at the reduction temperature of 350 °C. As the reduction was carried out at higher temperatures, the dispersion decreased slightly probably due to the prolonged agglomerations of the primarily formed platinum atoms ($\text{Pt}^{2+}\text{-zeol.} + \text{H}_2 \rightarrow \text{Pt}^0 + 2\text{H}^+\text{-zeol.}$) to larger platinum particles. Comparing the catalyst samples calcined at 400 (b), 450 (c), 500 (d) and 550 °C (e), the drop of platinum dispersion with reduction temperature is known to be more drastic for the catalyst samples calcined at higher temperatures. This indicates that the reduced platinum atoms

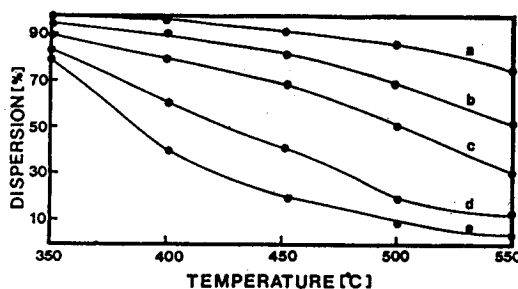


Fig. 5 Changes in the platinum dispersion of Pt/NaY with reduction temperature. (a: catalyst calcined at 350 °C, b: 400 °C, c: 450 °C, d: 500 °C, e: 550 °C)

from the Pt^{2+} ions locating at sodalite cages agglomerate more easily to larger particles than those from the Pt^{2+} ions locating at supercages. According to the suggestion by Tzou et al.[7], the small platinum particles in the supercages act as nucleation sites to trap the platinum atoms coming out of the sodalite cages. When the concentration of Pt clusters in the supercages is low, Pt atoms leaving the sodalite cages traverse the O_6 rings and then the channels and supercages. Eventually the platinum atoms will migrate all the

way to the exterior surface of the zeolite crystals to form large particles. Accordingly the platinum particles formed from the reduction of Pt^{2+} ions in supercages (samples calcined at lower temperature) will remain inside the zeolite, while the reduced platinum atoms from Pt^{2+} in sodalite cages will agglomerate to larger particles outside the zeolite. The existence of large particles at the exterior surface of zeolite crystals is evident from the TEM photograph of the catalyst calcined and reduced at 550 °C (Fig. 6).

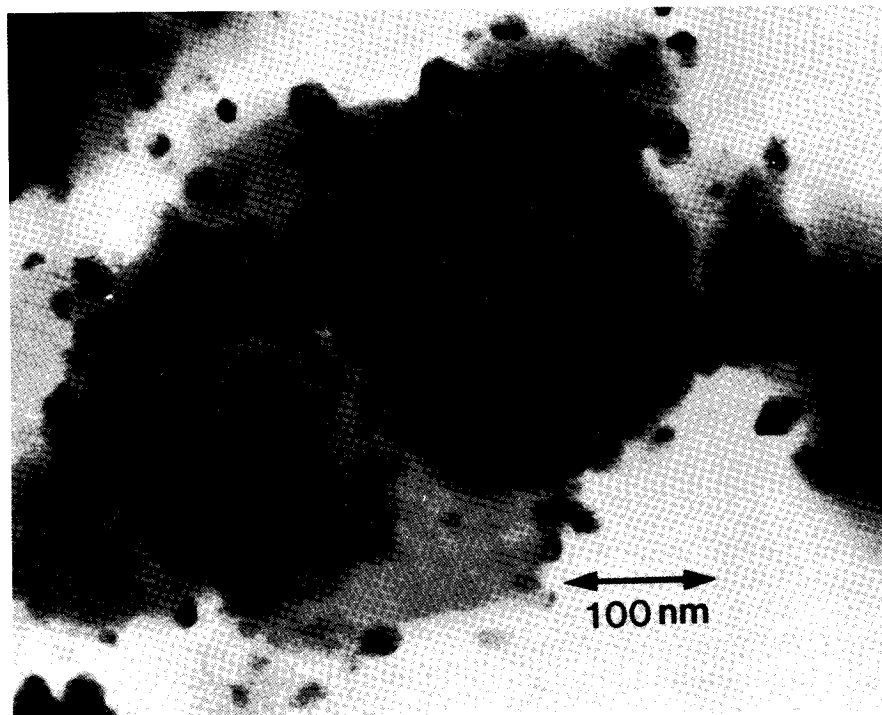


Fig. 6 TEM photograph of the Pt/NaY calcined and reduced at 500 °C.

3. 2. Chlorination of methane

Table 1 shows the summarized data for the chlorination of methane over the Pt/NaY catalysts. On the catalyst which was calcined and reduced at 350 °C methyl chloride is the sole product, while on the large platinum particles outside surface of the zeolite all

the four chloromethanes were produced (60 % methylchloride, 23 % methylenechloride, 14 % chloroform and 3 % carbon tetrachloride). In addition the activities on the finely dispersed platinum is somewhat greater than those on the large platinum particles, which is indicative of the more active lower coordina-

tion number sites. Therefore it can be said that the finely dispersed platinum particles inside the zeolites are suitable for the monochlorination of methane.

Table 1. Data for Chlorination of Methane over the Pt/NaY Catalysts with Calcination and Reduction Temperatures (Reaction Temperature = 220 °C, CH₄/Cl₂ = 3, Conversion = 5–7 %)

calcination temperature(°C)	reduction temperature(°C)	CH ₃ Cl(%)	N _{CH₄} (sec ⁻¹)×10 ²
350	350	100	31
	400	94	28
	450	86	25
	500	78	20
	550	71	17
400	350	92	27
	400	79	20
	450	70	18
	500	68	18
	550	65	19
450	350	86	23
	400	69	18
	450	66	18
	500	64	19
	550	64	19
500	350	70	20
	400	65	17
	450	64	18
	500	62	15
	550	62	15
550	350	67	16
	400	62	14
	450	62	17
	500	61	14
	550	60	12

Fig. 7 shows the changes in methylchloride and methylenechloride selectivity with reaction temperature for the two representative catalysts; the one calcined and reduced at 350 °C, and the other at 550 °C. On the catalyst treated at 350 °C methylchloride

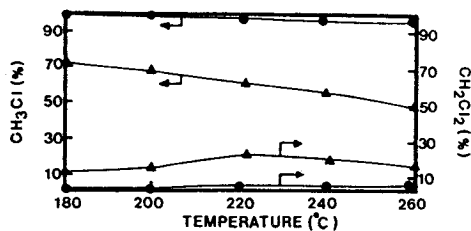


Fig. 7 Changes in the methylchloride and methylenechloride selectivity with reaction temperature. (CH₄/Cl₂ = 3, conversion = 5 %; ● : Pt/NaY calcined and reduced at 350 °C, ▲ : Pt/NaY calcined and reduced at 550 °C)

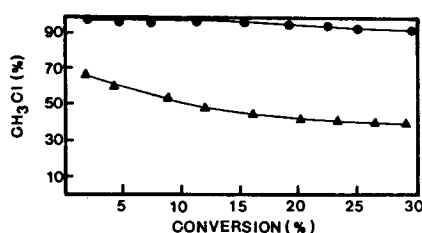


Fig. 8 Changes in the methylchloride selectivity with conversion. (reaction temperature = 220 °C, CH₄/Cl₂ = 3; ● : Pt/NaY calcined and reduced at 350 °C, ▲ : Pt/NaY calcined and reduced at 550 °C)

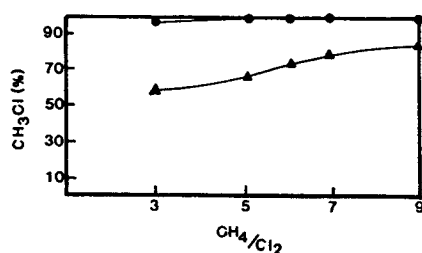


Fig. 9 Changes in the methylchloride selectivity with CH₄/Cl₂ ratio. (reaction temperature = 220 °C, conversion = 5 %, ● : Pt/NaY calcined and reduced at 350 °C, ▲ : Pt/NaY calcined and reduced at 550 °C)

is exclusively produced irrespective of the reaction temperature, but the fraction of methylchloride decreases and that of the methylenechloride increases

significantly with reaction temperatures(180–260 °C) on the catalyst treated at 550 °C. Measurements of selectivity were also done on the above two catalysts at various conversions(Fig. 8). Upto conversion of 30 % methylchloride is still the major product on the catalyst treated at 350 °C, while the methylchloride selectivity decreases greatly with conversion on the catalyst treated at 550 °C, which is thought to be due to the further chlorination of methylchloride by the longer residence on the surfaces of platinum particles. About 100 % selectivity of methylchloride is also maintained on the catalyst treated at 350 °C at various CH₄/Cl₂ ratios. But much poorer selectivity is observed at lower CH₄/Cl₂ ratio on the catalyst treated at 550 °C(Fig. 9).

Nearly exclusive production of methylchloride on the catalyst calcined and reduced at 350 °C respectively is in sharp contrast to the purely thermal chlorination of methane, typically giving about 11 % CH₃Cl, 35 % CH₂Cl₂, 45 % CHCl₃, and 9 % CCl₄[13,14]. Although the highly dispersed platinum particles must be essential for the formation of methylchloride, the restricted dimensions of the supercages are also believed to have played an important role on the limitation of the further chlorination of methylchloride, thereby resulting in the sole production of methylchloride irrespective of reaction conditions.

4. CONCLUSION

Chlorination of methane was carried out on the Pt/NaY catalysts which were calcined and reduced from 350 to 550 °C respectively. The dispersion and location of platinum particles in the catalysts were greatly affected by the calcination and reduction temperatures, and the selectivity of methylchloride varied significantly with the dispersion and location of platinum particles. On the large platinum particles outside surface of the zeolites all four chloromethanes were produced, while on the finely dispersed platinum ones inside the zeolites methylchloride was the sole product irrespective of reaction conditions. The exclusive

production of methylchloride assumed to have played not only the high dispersion of platinum particles but also the restriction of further chlorination of methylchloride by the confined volume of the supercages in the support.

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