

An Investigation of Mo₂C/HY Zeolite Acidity for Selective Ring Opening Reactions

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Introduction

Transition metal carbides supported on solid acids are of interest in a number of hydrocarbon conversion reactions, including selective ring opening reactions (SRO), through which highly aromatic petroleum distillate (e.g. synthetic crude oil derived from Canadian oil sand) could be effectively processed [1]. Acidities of the bifunctional catalysts mentioned above play a crucial role in SRO. In this study, pulse adsorption (PA) and TPD of *n*-propylamine (nPA) were performed together with XRD, TEM and XPS to better understand the acidic properties of bifunctional Mo₂C/HY catalysts.

Materials and Methods

Catalysts with 4-15 wt% Mo₂C supported on HY zeolite (Zeolyst™ CBV720, SiO₂/Al₂O₃ ratio = 30) were prepared by wet impregnation of the zeolite using an ammonium heptamolybdate tetrahydrate (MoO₃ 81.0-83.0%, Sigma) aqueous solution containing the required amount of Mo. Following calcination, Temperature-Programmed Reaction in a CH₄/H₂ flow, was used to convert the MoO₃ precursor to Mo₂C [2]. PA of nPA was performed at room temperature and used to determine the total acidity by calculating the net uptake of amine in a series of nPA saturated vapor pulses. Following the PA experiment, TPD of nPA from room temperature to 700 °C at a ramp rate of 5 °C/min was done. In the TPD profiles, the peaks emerging before 300 °C, attributed to Lewis acid sites (undecomposed nPA), were deconvoluted from the envelope peaks and quantified. The amount of Brønsted acid sites, on which ammonia and propylene are generated by the decomposition of nPA above 300 °C [3], was achieved by subtracting the Lewis acidity from the total acidity. The effluent from the PA and TPD of nPA were monitored in-situ with a TCD detector and the amount of nPA adsorbed and desorbed was calibrated with a sample loop of known volume, filled with a vapour saturated with nPA.

Results and Discussion

TPD of nPA showed that Brønsted-acid sites dominate on HY zeolite (Figure 1 A) while bulk Mo₂C exhibits very weak acidity, although the Lewis acid strength is somewhat higher than that on HY zeolite (compare the desorption temperatures of the first peaks of Figure 1 A and C). When Mo₂C was added to HY zeolite, the acidity decreased and the relative proportion of Brønsted and Lewis acid sites was also significantly changed (Figure 1 B)

As indicated in Table 1, the total acidity of Mo₂C/HY catalysts decreases with increasing Mo content. Since the BET surface areas decreased significantly with increased Mo content, framework collapse of HY zeolite during the catalyst preparation seems likely. However, XRD of the Mo₂C/HY catalysts (not shown) proved that the crystallinity of HY zeolite was

maintained. TEM experiments (not shown) indicated that the Mo₂C particles were too large to enter the channels of HY zeolite and cover Brønsted acid sites. Therefore, ion-exchange between hydrogen and molybdenum ions appears to occur during catalyst preparation. Moreover, the increasing ratio of Mo/(Si+Al) with increased Mo loading (Table 1, XPS results) indicates that more molybdenum disperses over the surface of catalyst and covers some extra framework Lewis acid sites. This conclusion also follows from the change in percent of Lewis acid sites with Mo loading (Table 1, numbers in brackets).

Table 1. Physico-chemical properties of supported molybdenum carbide catalysts.

Catalyst	S _{BET} m ² /g	Acidity (mmol/g)			XPS	
		Lewis	Brønsted	Total	Mo/(Si+Al)	Si/Al
HY	711	0.19 (23) ^a	0.65 (78)	0.84	-	-
4 wt% Mo ₂ C/HY	606	0.12 (18)	0.55 (82)	0.67	0.03	26.6
7 wt% Mo ₂ C/HY	525	0.02 (3)	0.48 (97)	0.50	0.06	28.0
11 wt% Mo ₂ C/HY	417	0.05 (10)	0.42 (90)	0.47	0.10	21.9
15 wt% Mo ₂ C/HY	309	0.04 (13)	0.28 (87)	0.32	0.13	13.3
Bulk Mo ₂ C	6.8	0.007 (37)	0.013 (63)	0.02	-	-

^a The numbers in brackets are the percentage of certain kind of acid in total acid

Based on the results, introducing Mo₂C obviously decreased the acidity of Mo₂C/HY catalysts, especially the Brønsted acidity, which is crucial for SRO because SRO is favored over zeolites with a low density of Brønsted acid sites; strong and high density Brønsted acidity leads to extensive cracking and dealkylation [4]. Our own experimental data for naphthalene conversion will be presented to demonstrate these effects.

Significance

The present study illuminated the change in acidity of HY supported Mo₂C, which provides for a better understanding of the development of highly efficient SRO catalysts with desired acidity.

References

1. Du, H., Fairbridge, C., Yang H. and Ring, Z. *Appl. Catal. A: General* 294, 1 (2005).
2. Claridge, J.B., York, A.P.E., Brungs, A.J. and Green M.L.H. *Chem. Mater.* 12, 132 (2000).
3. Parillo, D.J., Adamo, A.T., Kokotailo, G.T. and Gorte, R.J. *Appl. Catal.* 67, 107 (1990).
4. Arribas, M.A. and Martinez A. *Appl. Catal. A: General* 164, 467 (1996).

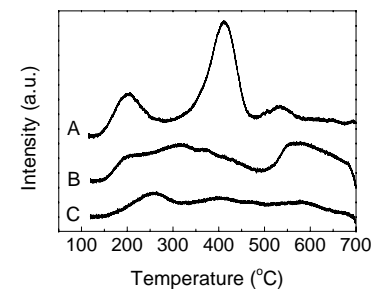


Figure 1. *n*-propylamine TPD profiles for various catalysts. A) HY zeolite, B) 11% Mo₂C/HY, C) bulk Mo₂C.