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Modification of acidity in HZSM-5 zeolite for methane-methanol co-reaction

Key words:
methane conversion; methanol; co-reaction; acidity; HZSM-5

Background

- With high levels of CH_4 emission and the inevitable depletion of oil reserves, interest and demand are growing to find a direct method of converting methane to valuable products.
- Co-reaction, which creates more preferable converting conditions successfully, is one of the most efficient strategies to achieve methane conversion to olefins, alkanes, alcohols, etc.
- Methanol is inexpensive and is readily produced from various sources. The co-reaction of methane with methanol is reported to overcome the inertness of C–H bonds in methane, while heat neutralization is also reached.
- Previous research to study the effect of acidity on catalytic performance has involved the preparation of a series of catalysts with different Si/Al ratios. However, the influence of pore structure is not excluded.

Results

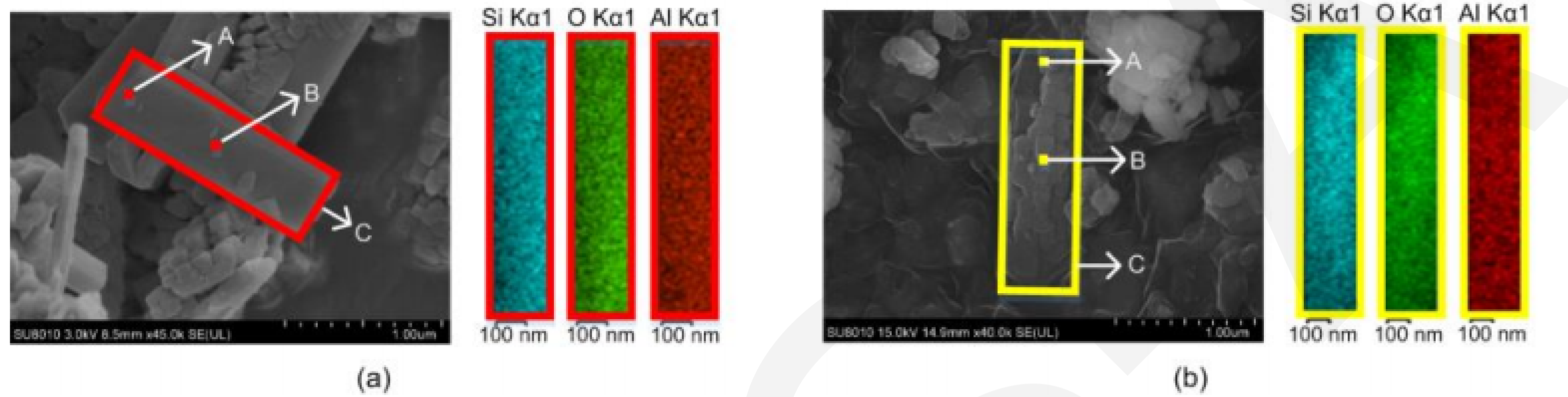

Fig. 3 EDS patterns of C-0 (a) and C-12 (b)

Table 2 Element contents of C-0 and C-12 tested by SEM-EDS (in weight)

Element	Element content (%)					
	C-0			C-12		
	Point A	Point B	Area C	Point A	Point B	Area C
O	65.47	67.96	67.75	70.10	69.18	69.01
Al	2.95	3.01	3.03	2.34	2.31	2.40
Si	31.58	29.03	29.21	27.56	28.51	28.59

Table 3 Textural properties of HZSM-5 and steam-treated catalysts

Catalyst	Surface area* (m^2/g)			Pore volume* (cm^3/g)			Pore diameter*	$D_{i,k}$**
	Total	Micro	External	Total	Micro	Meso	(nm)	($\times10^{-10}$ m^2/s)
C-0	418	308	110	0.34	0.13	0.21	3.27	1.04–4.18
C-1.5	387	281	106	0.32	0.12	0.20	3.32	1.39–5.54
C-3	389	274	115	0.34	0.12	0.22	3.48	0.77–3.10
C-6	381	270	111	0.33	0.12	0.21	3.43	0.91–3.66
C-12	386	274	112	0.36	0.12	0.24	3.74	0.71–2.84

Table 4 Acid concentrations and Al distributions in fresh and steam-treated ZSM-5 zeolites

Sample	Acid concentration* (mmol/g)	Mass fraction (%)	
		EFAL**	FAL***
C-0	1.166	11.28	88.72
C-1.5	0.992	12.12	87.88
C-3	0.692	15.05	84.95
C-6	0.597	21.31	78.69
C-12	0.474	21.85	78.15

Results

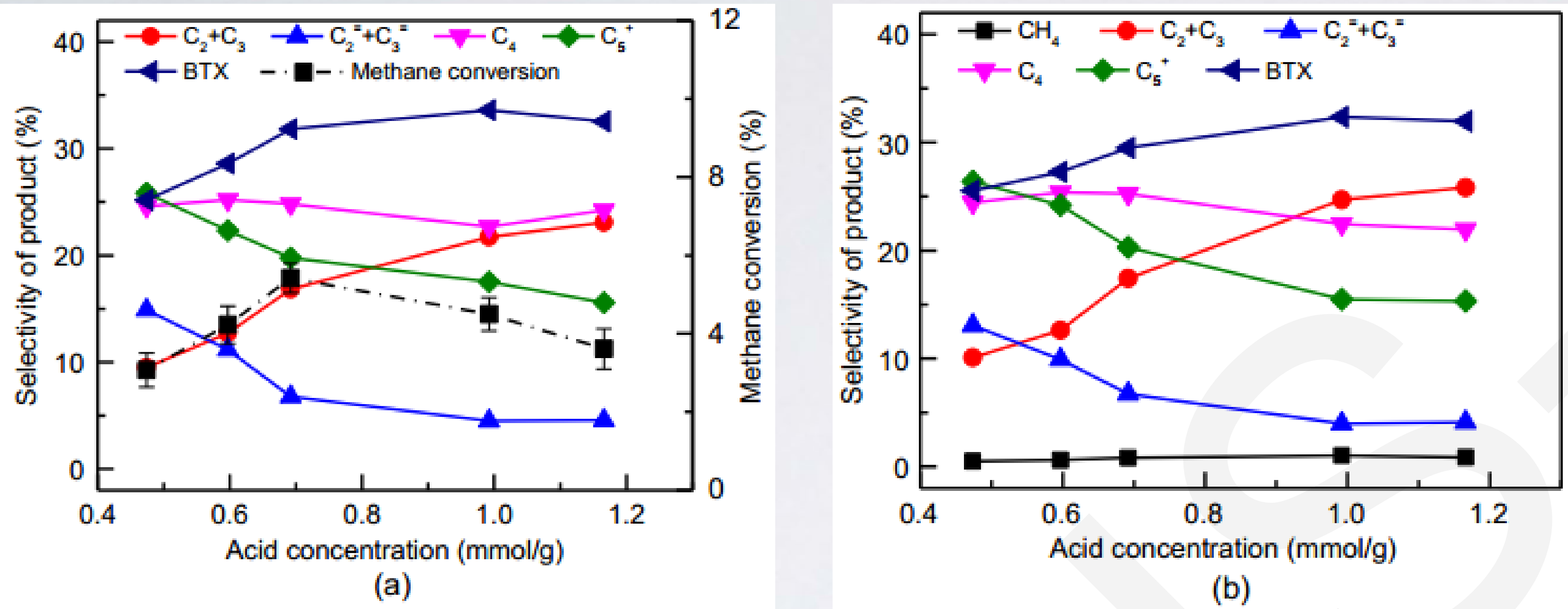

Fig. 7 Methane conversion and product distribution for the methane and methanol co-reaction (a) and the methanol reaction (b)

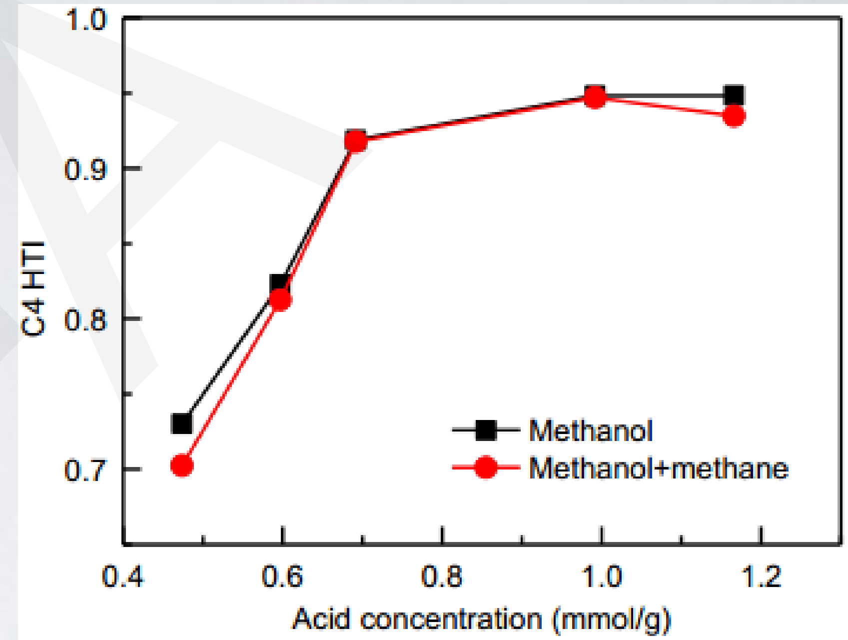

Fig. 8 C4 HTI index of the methanol reaction and the methane and methanol co-reaction

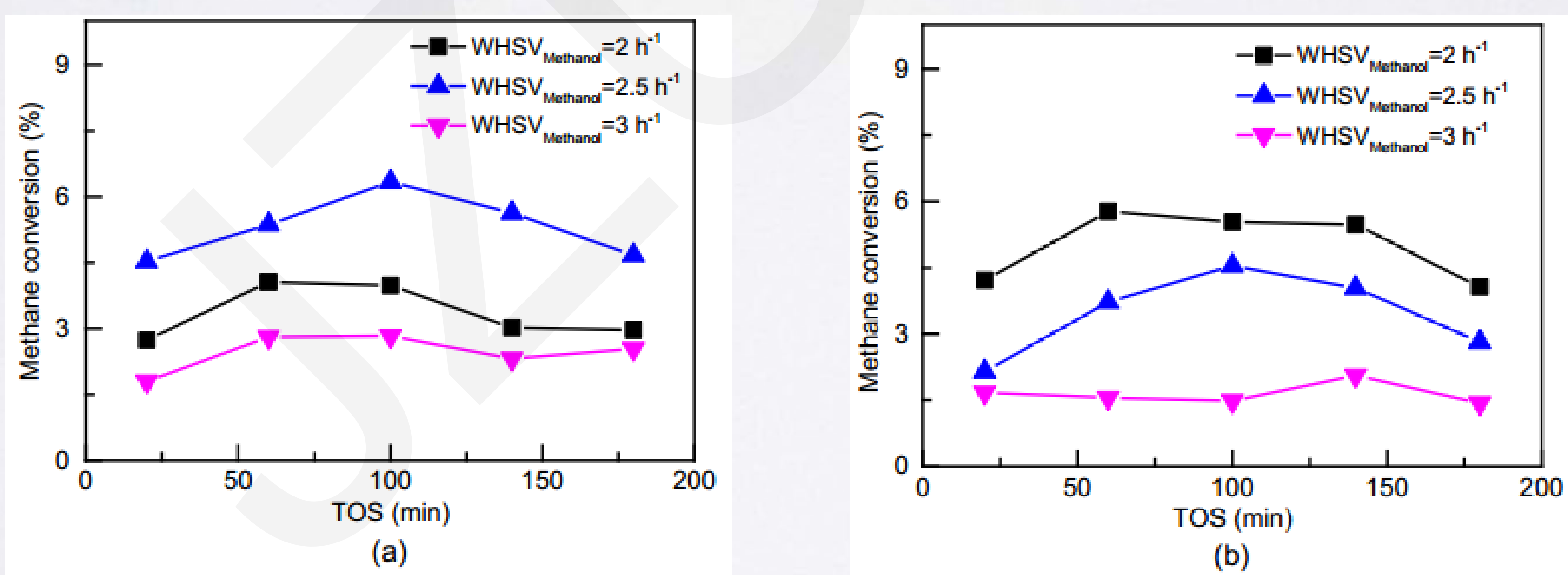

Fig. 9 Methane conversion in the methane and methanol co-reaction on catalyst C-0 (a) and catalyst C-3 (b)

Conclusions

- With an increasing duration of treatment, the acid concentration of the catalyst declines significantly regardless of crystal size, pore structure, or diffusion properties, which are similar or comparable among catalysts.
- As the acid concentration in zeolite increases, methane conversion reaches a maximum of 5.42% on zeolite C-3, which contains Brønsted acids at 0.262 mmol/g.
- On the basis of these results, it is proposed that methane is activated at acid sites of the zeolite that has methanol molecules adsorbed. Excessive amounts of catalyst acid or too many methanol molecules inhibit methane activation. This provides guidance for catalyst selection in the co-reaction of methane with methanol, aimed to achieve higher methane conversion rates under mild conditions.