



Influence of Catalyst Preparation Strategy on the Acid-Base Properties and Catalytic Performance of Metal-Modified NaX Catalysts in SATM Reaction

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Abstract

Achieving an appropriate balance between acid-base properties and dehydrogenation ability is essential for improving catalytic performance in the side-chain alkylation of toluene with methanol (SATM). In this work, a series of transition metal-modified NaX catalysts containing Cu, Ni, Co, Ag, and Ce were synthesized through an *in-situ* hydrothermal method using two different preparation strategies, denoted as M1 and M2. Subsequently, 17 wt% NaOH was introduced to regulate the surface acid-base properties. The effects of preparation sequence and metal incorporation on catalyst structure, acidity distribution, and catalytic performance were systematically investigated using XRD, BET, NH₃-TPD and FT-IR analyses. The results demonstrated that transition metal incorporation significantly enhanced catalytic activity compared with the parent PAI-NaX catalyst. All catalytic tests were conducted in triplicate per day, and the reported results represent the corresponding average values. Among the M1 catalysts, the Cu-modified sample exhibited the best catalytic performance, achieving a combined ethylbenzene and styrene yield of 71.9% with 99.7% methanol conversion, while the Ni-modified catalyst showed enhanced styrene formation with a total yield of 66.4%. The M2 preparation strategy further improved catalytic performance, with Cat-1Ni-17Na-M2 and Cat-

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1Cu-17Na-M2 achieving combined yields of 74.2% and 73.6%, respectively. The superior activity of the M2 catalysts is attributed to the introduction of NaX prior to metal incorporation, which promoted the formation of a larger proportion of weak acidic sites and a more favorable acid-base balance. These findings provide valuable insights into the rational design of highly efficient NaX-based catalysts for SATM reactions through controlled modulation of metal species and surface acidity.

Subject Areas

Chemical Engineering & Technolog

Keywords

Side-Chain Alkylation, PAI-NaX Zeolite, Transition-Metal Modification, Acid-Base Synergy, Overall Yield of SATM Products

1. Introduction

Styrene and ethylbenzene are important chemical intermediates widely used in polymer production, pharmaceuticals, agriculture, and fine chemical industries [1]. Industrially, these compounds are mainly produced through the Friedel-Crafts alkylation of benzene with ethylene. However, this conventional route suffers from several disadvantages, including high energy consumption, complicated multi-step processing, high production costs, and rapid catalyst deactivation [2] [3]. To overcome these limitations, side-chain alkylation of toluene with methanol (SATM), first proposed by Sidorenko in 1967, has attracted considerable attention as an alternative one-step route for styrene and ethylbenzene synthesis [4]-[6]. Compared with the traditional process, SATM offers several advantages, such as lower energy demand, simplified process conditions, reduced environmental impact, and lower raw material costs [4]-[6].

Initially, SATM was considered a purely base-catalyzed reaction [7] [8]. However, subsequent studies demonstrated that SATM is governed by an acid-base synergistic catalytic mechanism, in which the balance between acidity and basicity plays a decisive role in catalytic performance [2]-[4] [9]. In this mechanism, acid sites facilitate the adsorption and stabilization of toluene molecules, while base sites promote activation of the methyl group of toluene and catalyze methanol dehydrogenation to formaldehyde (HCHO), which acts as the effective alkylating agent in the reaction [10]-[12]. Therefore, rational regulation of acid-base properties is essential for improving catalytic activity and selectivity toward styrene and ethylbenzene.

Among various catalyst supports, NaX zeolite has been considered one of the most promising candidates due to its tunable acid-base properties, large pore structure, and excellent thermal stability [11]-[13]. Previous studies demonstrated that modification of X zeolite with alkali compounds could significantly promote

methanol dehydrogenation and toluene activation, thereby improving SATM performance [6] [10] [14]. Han *et al.* reported that introducing $\text{Na}_2\text{B}_4\text{O}_7$ and CuO into X zeolite effectively enhanced the catalytic activity for SATM reaction [11] [15]. Moreover, Cu species not only promote methanol dehydrogenation to formaldehyde but also regulate the acid-base properties of the catalyst, suppressing the undesired hydrogenation of styrene to ethylbenzene [16]. Our previous studies further confirmed that low-valence Cu species significantly improve methanol conversion and the selectivity of side-chain alkylation products [17].

Recently, increasing attention has been focused on optimizing the acid-base synergy and dehydrogenation ability of NaX-based catalysts through modification strategies and preparation methods [18]-[20]. In particular, the preparation sequence may strongly influence the distribution of active species, crystallinity, pore structure, and surface acid-base properties of the catalyst. Nevertheless, the influence of precursor addition sequence on the structural evolution and catalytic performance of phosphorus-modified Al-NaX catalysts has rarely been systematically investigated.

In this work, NaX catalysts containing different dehydrogenation metals, including Cu, Ni, Co, Ag, and Ce, were synthesized using an in-situ hydrothermal method combined with two different preparation sequences, denoted as M1 and M2. In the M1 route, phosphorus-aluminum precursors were first introduced before NaX addition, whereas in the M2 route NaX was initially dispersed in water before adding the precursor solution. Subsequently, 1 wt% metal species and 17 wt% NaOH were sequentially loaded onto the catalysts to optimize the acid-base properties and dehydrogenation performance. The effects of preparation sequence and metal loading on catalyst structure, acid-base characteristics, and catalytic performance for SATM reaction were systematically investigated using XRD, BET, and NH_3 -TPD analyses.

2. Experimental Section

2.1. Materials and Chemicals

NaX zeolite ($\text{Si}/\text{Al} = 2.7$) was purchased from the Catalyst Plant at Nankai University. Toluene, methanol, phosphoric acid (H_3PO_4), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were all supplied by Tianjin Kemiou Chemical Reagent Co., Ltd. Silver nitrate (AgNO_3), and sodium hydroxide (NaOH). We purchased diisopropylamine and aluminum isopropoxide from Shanghai Aladdin Reagent Co., Ltd. The aforementioned reagents were all analytical grade and didn't require any additional purification.

2.2. Catalyst Preparation

2.2.1. Preparation of M1

The PAI-NaX molecular sieve precursor (Method 1, M1) was synthesized via an in-situ hydrothermal route, followed by post-synthetic modification. In a typical

procedure, aluminum isopropoxide (17.11 g) was first hydrolyzed in distilled water under continuous stirring for 20 min. Subsequently, phosphoric acid (9.5 g) and diisopropylamine (3.5 mL), used to adjust the pH to approximately 5, were added dropwise under vigorous stirring to ensure homogeneous mixing. NaX zeolite (35 g, Si/Al = 2.7) was then introduced into the resulting solution, and the suspension was stirred for 3 h to obtain a uniform mixture. The obtained gel was transferred into a stainless-steel autoclave and subjected to hydrothermal treatment at 180°C for 72 h. After crystallization, the solid product was recovered by centrifugation, thoroughly washed with distilled water until neutral pH, and dried at 140°C for 2 h to obtain the PAI-NaX precursor. Following drying, metal species (1 wt%), including $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, were introduced via the incipient wetness impregnation method. The samples were subsequently treated with 17 wt% NaOH solution. The resulting catalysts were denoted as Cat-1Me-17Na-M1.

2.2.2. Preparation of M2

In Method 2 (M2), the same precursor concentrations, hydrothermal conditions, metal loading (1 wt%), and NaOH loading (17 wt%) were used. However, the preparation sequence was modified by first dispersing 35 g of NaX zeolite in de-ionized water before adding the phosphorus-aluminum precursor solution. The subsequent metal impregnation and NaOH loading procedures were identical to Method 1, and the catalysts were designated as Cat-1Me-17Na-M2.

2.3. Characterization

A LabXRD-6000 diffractometer (Shimadzu, Japan) using Cu K α radiation (40 kV, 30 mA) in 5° - 80° with a step size of 0.03° and a scanning rate of 8°·min⁻¹ was used to record powder X-ray diffraction (XRD) patterns.

A Micro Active for ASAP 2460 gas adsorption analyzer was used to evaluate the N₂ adsorption-desorption isotherms at 77 K. The samples were degassed in a vacuum for 6 hours at 573 K before the measurement. The BET (Brunauer-Emmett-Teller) method was utilized to determine the specific surface area, while the BJH (Barret-Joyner-Halenda) method was used to determine the pore volume and pore diameter.

Temperature-programmed desorption (TPD) characterization was performed on a TP-5080 to analyze the acidic property of the catalysts by using NH₃ as a probe molecules. Typically, the sample (0.1 g) was pretreated at 450°C for 1.5 h in a He stream and then cooled to the required temperature (50°C). After adsorbing pure NH₃ at 50°C for 30 min, the samples were purged with helium stream to desorb NH₃ for 30 min at 50°C. The samples were heated by He stream from 50°C to 810°C with a temperature ramp of 10°C·min⁻¹, and a thermal conductivity detector was used to detect the desorbed NH₃ simultaneously.

The FTIR was examined with a Bruker, USA, VERTEX 70 infrared spectrometer. A blank scan was carried out initially, and 0.1 g of KBr was combined with small amounts of the catalyst sample to grind the tablet. After that, the sheet sam-

ple was scanned between 4000 and 400 cm^{-1} .

The Escalab 250 was used for X-ray photoelectron spectroscopy (XPS) measurements. 2×10^{-7} Pa was the basal pressure. The X-ray source was monochromatized Al K α 1486.6 eV radiation. The binding energies were adjusted using the carbonaceous C1s signal at 284.6 eV as the energy reference.

2.4. Catalytic Testing

The SATM performance of synthesized catalysts was tested in a horizontal fixed-bed reactor at 1 atm of pressure. A fixed-bed reactor was typically filled with 1.2 g (40 - 60 mesh) of the catalyst sample. Before adding reactants, N_2 was used to purge the catalyst at approx 450 °C for two hours, and it was subsequently reduced to reaction temperature (425 °C). Over the catalysts, a 5:1 M toluene and methanol mixture was injected at a rate of 0.8 $\text{mL}\cdot\text{h}^{-1}$ while a nitrogen gas stream was flowing at a flow rate of 3 $\text{mL}\cdot\text{min}^{-1}$. The reaction products were found using a hydrogen flame ionization detector (FID) attached to a linear column (0.53 mm $\times$ 50 μm) in an online Haixin GC950 gas chromatograph. The following formulas were utilized when calculating yield (Y_X), product selectivity (S_X), and methanol conversion (C_{Meth}):

$$C_{\text{Meth}} = \left(1 - \frac{n_{\text{Meth outlet}}}{n_{\text{Meth inlet}}} \right) \times 100\%$$

$$S_X = \left(\frac{n_X}{n_{\text{Meth inlet}} - n_{\text{Meth outlet}} t} \right) \times 100\%$$

$$Y_X = S_X \times C_{\text{Meth}}$$

Styrene (ST), ethylbenzene (ET), formaldehyde (HCHO), methane (CH_4), and xylene (XY) are among the products that I am promoting here.

3. Results and Discussion

3.1. Catalytic Performance

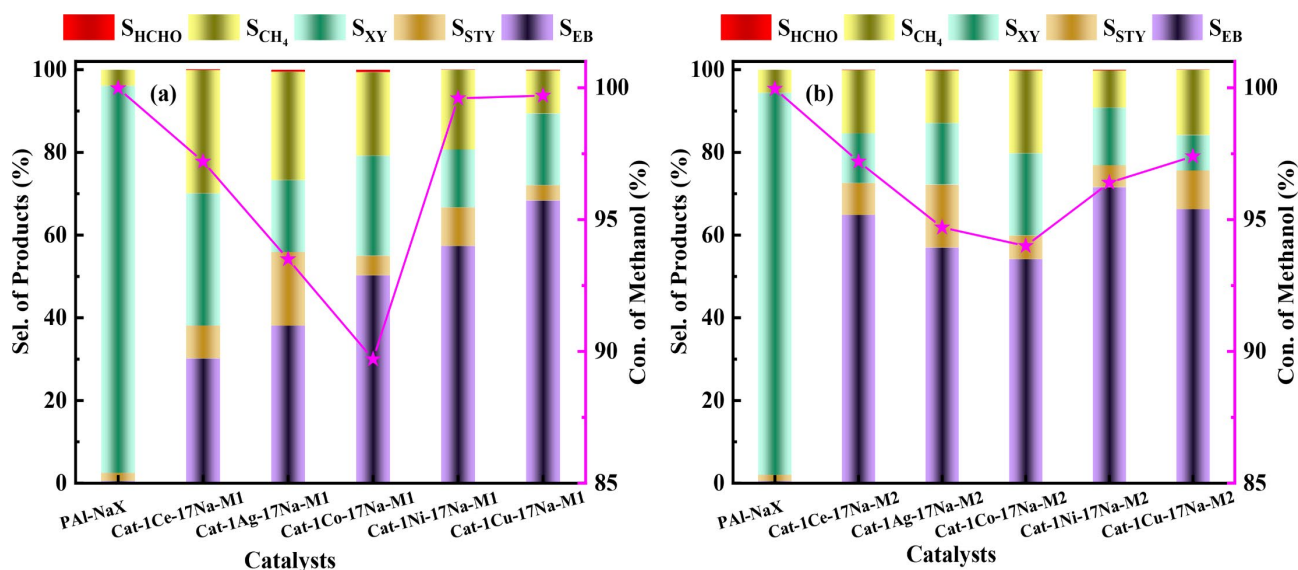
Table 1, **Table 2** and **Figure 1**, compare the catalytic performances of the Cat-1Me-17Na catalysts prepared by the M1 and M2 methods in the SATM reaction. For both preparation methods, the metal-modified catalysts exhibit significantly improved catalytic performance compared with the parent PAI-NaX catalyst. The parent catalyst mainly favors xylene formation and shows very low selectivity toward ethylbenzene and styrene due to the high proportion of medium and strong acid sites. Such stronger acid sites promote undesired side reactions and suppress the SATM pathway. After metal incorporation, both preparation methods substantially enhance the selectivity and yield of ethylbenzene and styrene. In the M1 series, the selectivity toward EB and ST increases from 0.55% over PAI-NaX to 30.2% - 68.4%, while the total yield increases from 2.47% to 37.1% - 71.9%. Similarly, the M2-prepared catalysts also exhibit remarkable improvements in catalytic activity, indicating that metal introduction effectively promotes methanol activation,

Table 1. Catalytic performances of Cat-1Me-17Na-M1 series catalysts for the SATM.

Catalyst	C_{MET} (%)	Selectivity (%)					Yield (%)		
		SEB	SST	SCH4	SXY	SHCHO	YEB	YST	Y (EB + ST)
PAI-NaX	99.98	0.55	1.92	3.85	93.65	0.00	0.55	1.92	2.47
Cat-1Ce-17Na-M1	97.2	30.2	7.9	29.8	32.0	0.2	29.4	7.6	37.1
Cat-1Ag-17Na-M1	93.5	38.1	17.8	26.2	17.4	0.5	35.7	16.6	52.3
Cat-1Co-17Na-M1	89.7	50.3	4.7	20.2	24.2	0.6	45.1	4.2	49.3
Cat-1Ni-17Na-M1	99.6	57.4	9.3	19.3	14.0	0.1	57.1	9.3	66.4
Cat-1Cu-17Na-M1	99.7	68.4	3.7	10.4	17.3	0.2	68.2	3.7	71.9

Table 2. Catalytic performances of Cat-1Me-17Na-M2 series catalysts for the SATM.

Catalyst	C_{MET} (%)	Selectivity (%)					Yield (%)		
		SEB	SST	SCH4	SXY	SHCHO	YEB	YST	Y (EB + ST)
PAI-NaX	99.96	0.52	1.52	5.58	92.36	0.00	0.52	1.52	2.04
Cat-1Ce-17Na-M2	97.2	64.9	7.7	15.3	12.0	0.1	63.0	7.5	70.6
Cat-1Ag-17Na-M2	94.7	57.0	15.2	12.7	14.9	0.2	54.0	14.4	68.4
Cat-1Co-17Na-M2	94.0	54.2	5.7	20.0	19.9	0.2	51.0	5.3	56.3
Cat-1Ni-17Na-M2	96.4	71.6	5.3	9.0	13.9	0.2	69.0	5.1	74.2
Cat-1Cu-17Na-M2	97.4	66.3	9.3	15.8	8.6	0.1	64.5	9.0	73.6

**Figure 1.** (a) Catalytic performance of Cat-1Me-17Na-M1 and (b) Catalytic performance of Cat-1Me-17Na-M2 catalysts.

toluene side-chain activation, and ethylbenzene dehydrogenation to styrene. The enhanced catalytic behavior is strongly associated with the modification of surface acidity after metal incorporation. Among all catalysts, the Ni- and Cu-modified samples exhibit the best catalytic performances for both preparation methods. In

the M1 series, Cat-1Ni-17Na-M1 achieves a high total yield of 66.4%, which is attributed to its high proportion of weak acid sites (78.1%) and low medium acidity (21.7%), providing a favorable acid environment for SATM. Cat-1Cu-17Na-M1 exhibits the highest overall catalytic performance, with 99.7% methanol conversion, 68.4% selectivity, and 71.9% total yield. The superior performance of the Cu-modified catalyst suggests that Cu species not only suppress undesirable acid-driven reactions but also actively promote C-H bond activation and the side-chain alkylation pathway. Similarly, in the M2 series, Cat-1Ni-17Na-M2 and Cat-1Cu-17Na-M2 exhibit the highest total yields of 74.2% and 73.6%, respectively, which are slightly higher than those obtained for the M1 catalysts. This result indicates that the M2 preparation strategy provides a more favorable catalyst structure and acid-base balance for SATM. The enhanced performance is attributed to the synergistic effect between the weak-acid-dominated surface and the dehydrogenation ability of Ni and Cu species, which promotes methanol activation and side-chain C-H bond activation of toluene. In addition, NaOH modification plays a crucial role in regulating acid strength by neutralizing strong Brønsted acid sites and optimizing the surface acid-base properties.

3.2. Catalytic Stability

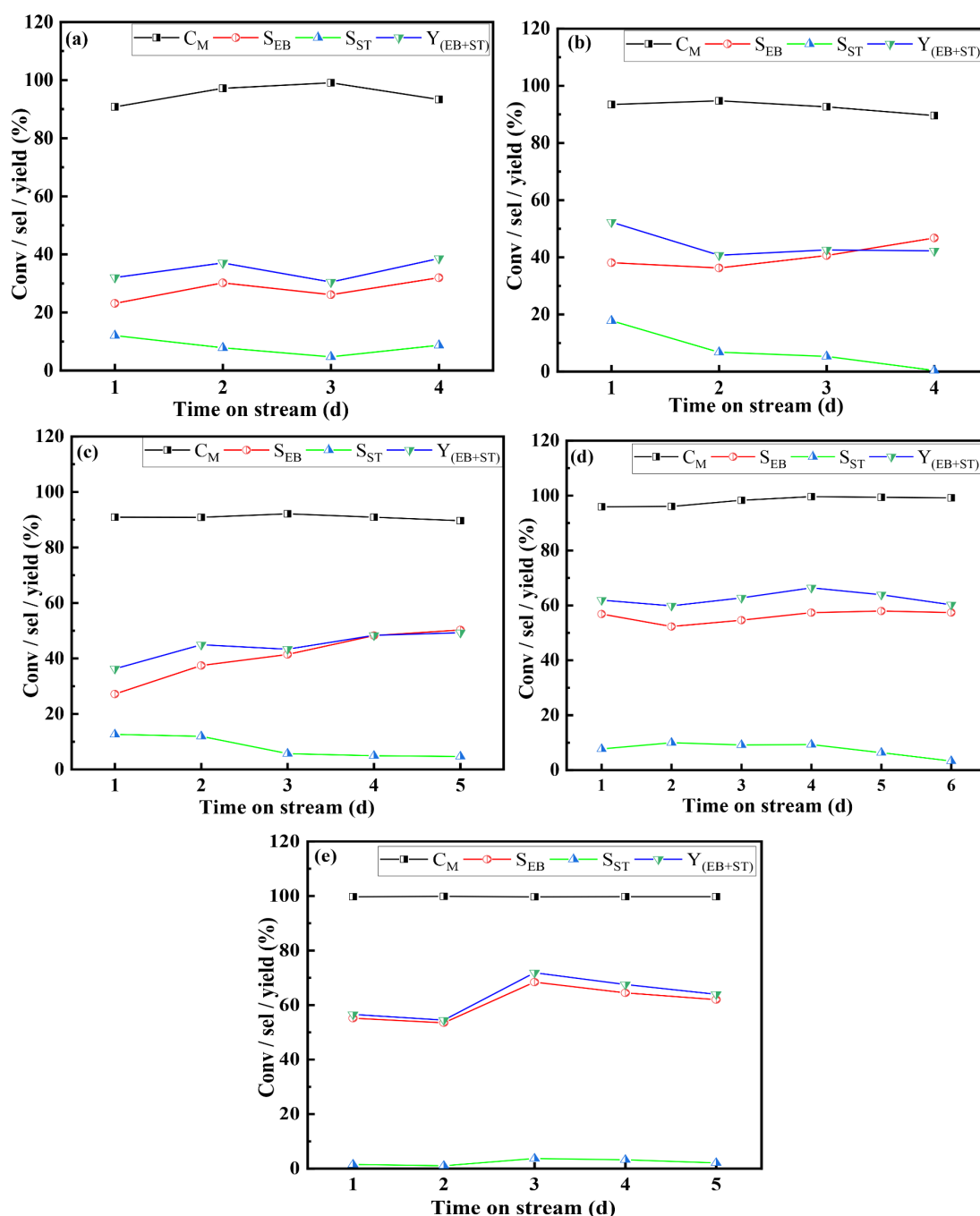
3.2.1. Catalytic Stability of M1

The stability of the Cat-1Me-17Na-M1 catalyst for SATM was evaluated. No significant deactivation was observed in any of the catalysts in this series during the evaluation period (4-6 days). **Figure 2** shows the evaluation of the Cat-1Ag-17Na-M1 catalyst after 4 days of continuous reaction. The figure clearly shows that the selectivity of the Cat-1Ag-17Na-M1 catalyst for styrene reached its highest point of 17.8% on the first day of reaction, which decreases continuously with time-on-stream. Cat-1Cu-17Na-M1 demonstrates the best overall stability and catalytic performance, maintaining nearly constant methanol conversion, with a high total yield around 71.9%. The temporary increase in yield around the third day, followed by only a slight decline, indicates that Cu-modified sites remain highly active during prolonged operation. This superior stability can be explained by the dual role of Cu species to favor C-H activation and side-chain alkylation, and provide an effective dehydrogenation Component, while preserving a stable catalytic surface under reaction conditions.

3.2.2. Catalytic Stability of M2

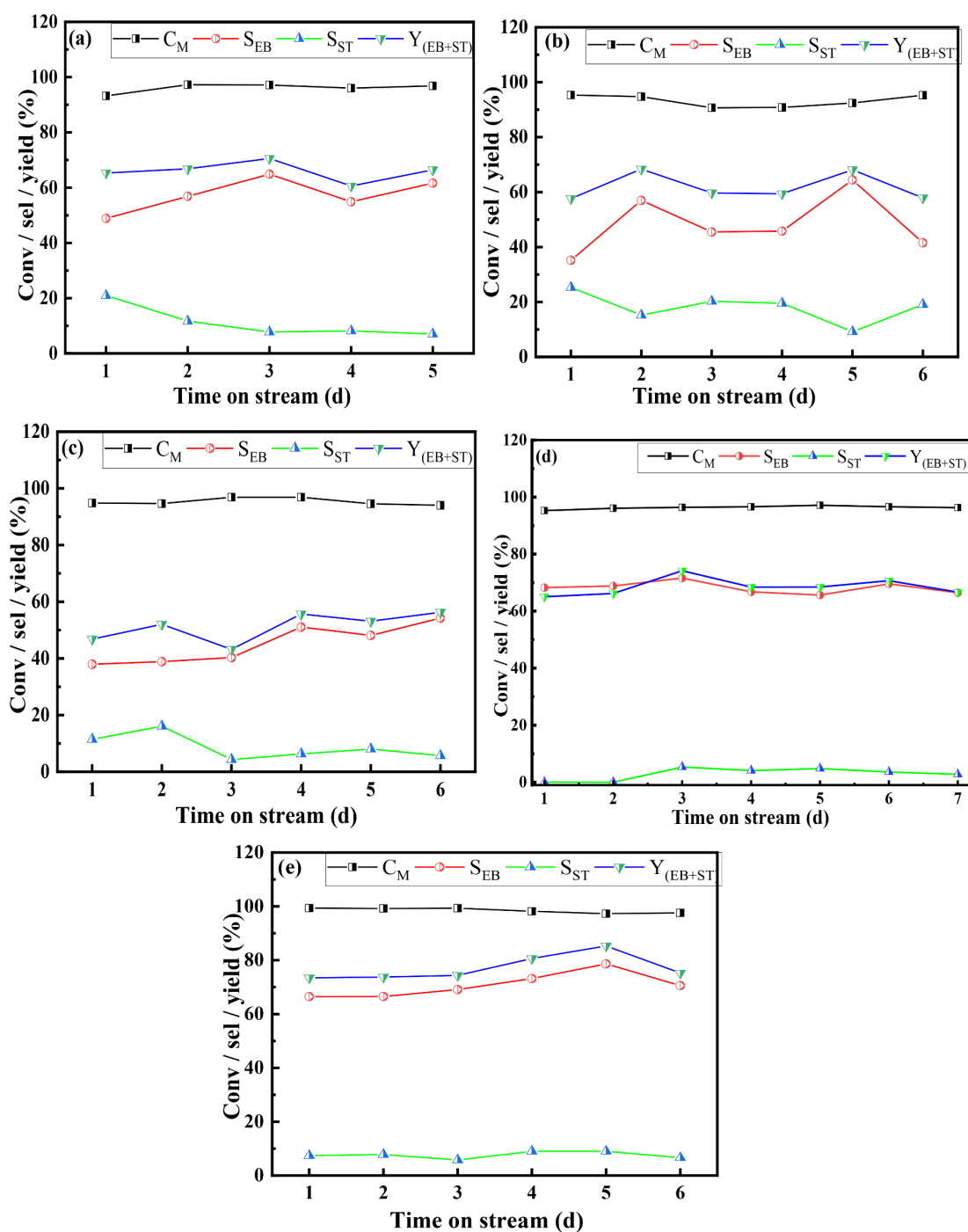
Figure 3 presents the stability evaluation of the Cat-1Me-17Na-M2 series catalysts (M = Ce, Ag, Co, Ni, and Cu). It can be seen that the selectivity of the products and the stability of the methanol conversion rate of each catalyst are good during the reaction, eventually stabilizing or decreasing slowly. This is because the catalyst structure of this series is well maintained (as determined by XRD), and the stable reactions are ensured since the structure is difficult to collapse during the reaction. Another reason could be that the catalysts made using this strategy are stable and have uniformly distributed active centers on their surface. Cat-1Ni-

17Na-M2 has the best performance over the catalysts evaluation. The catalysts including Ce, Ag, and Co, on the other hand, exhibit smaller changes and comparatively lower yields, suggesting a lack of cooperation between the metal component and the catalytic framework. Additionally, during the reaction process, a distinct opposing trend between the selectivity of styrene and ethylbenzene may



Reaction conditions: $T = 425^\circ\text{C}$, toluene/methanol ratio of 5/1; MET: methanol, EB: ethylbenzene, ST: styrene, XY: xylene.

Figure 2. Cat-1Ce-17Na-M1 (a); Cat-1Ag-17Na-M1 (b); Cat-1Co-17Na-M1 (c); Cat-1Ni-17Na-M1 (d); Cat-1Cu-17Na-M1 (e).



Reaction conditions: $T = 425^\circ\text{C}$, toluene/methanol ratio of 5/1; MET: methanol, EB: ethylbenzene, ST: styrene, XY: xylene

Figure 3. Cat-1Ce-17Na-M2 (a); Cat-1Ag-17Na-M2 (b); Cat-1Co-17Na-M2 (c); Cat-1Ni-17Na-M2 (d); Cat-1Cu-17Na-M2 (e).

be seen. Ethylbenzene's selectivity progressively improves with increasing during time, while styrene's selectivity correspondingly reduces. We can explain these phenomena by hydrogenation processes or secondary hydrogen transfer taking place on the catalyst surface, which over time gradually change styrene into

ethylbenzene.

3.2. Structural and Chemical Composition Modifications after Metal and NaOH Introduction

Figure 4(a) and **Figure 4(b)** present the XRD patterns of the Cat-1Me-17Na catalysts prepared by the M1 and M2 methods. All catalysts exhibit the characteristic diffraction peaks of the FAU-type NaX zeolite structure at $2\theta = 6.1^\circ$, 10.0° , 15.4° , 15.8° , 20.1° , 23.4° , 26.0° , 28.8° , 30.4° , and 31.1° , confirming the successful formation and preservation of the NaX crystalline framework after metal incorporation and NaOH treatment. No disappearance of the characteristic FAU reflections is observed, indicating that the overall zeolite structure remains stable during both preparation methods. However, variations in diffraction peak intensity are observed after metal modification, suggesting that the preparation method influences the crystallinity and local framework environment of the catalysts. In the M1 series, a slight decrease in the intensity of the characteristic diffraction peaks is observed after metal incorporation, particularly for the Cu-modified catalyst. This decrease may be associated with the combined effects of metal introduction and alkaline treatment, which can induce partial framework perturbation and local structural degradation. In the M2 series, changes in relative peak intensity are also detected, indicating that the modified preparation sequence affects the structural evolution of the catalysts. In particular, the diffraction peak near $2\theta \approx 15.8^\circ$ becomes more pronounced in the Ag- and Ce-modified catalysts, suggesting improved preservation or stabilization of specific framework domains through the M2 preparation route. In contrast, Co, Ni, and Cu-modified catalysts exhibit relatively weaker peak intensity, implying stronger interactions between these metal species and the zeolite framework.

Figure 5(a), **Figure 5(b)** present the FTIR spectra of the Cat-1Me-17Na catalysts prepared by the M1 and M2 methods. All catalysts exhibit the characteristic absorption bands of the FAU-type NaX zeolite, confirming that the fundamental aluminosilicate framework is preserved after metal incorporation and NaOH

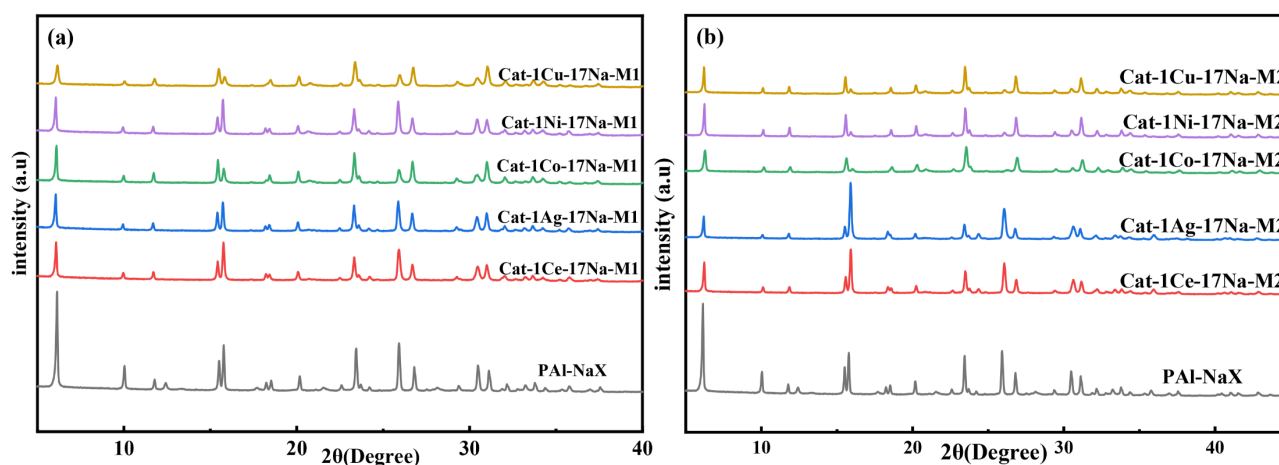


Figure 4. (a) XRD patterns of Cat-1Me-17Na-M1 series catalysts, (b) XRD patterns of Cat-1Me-17Na-M2 series catalysts.

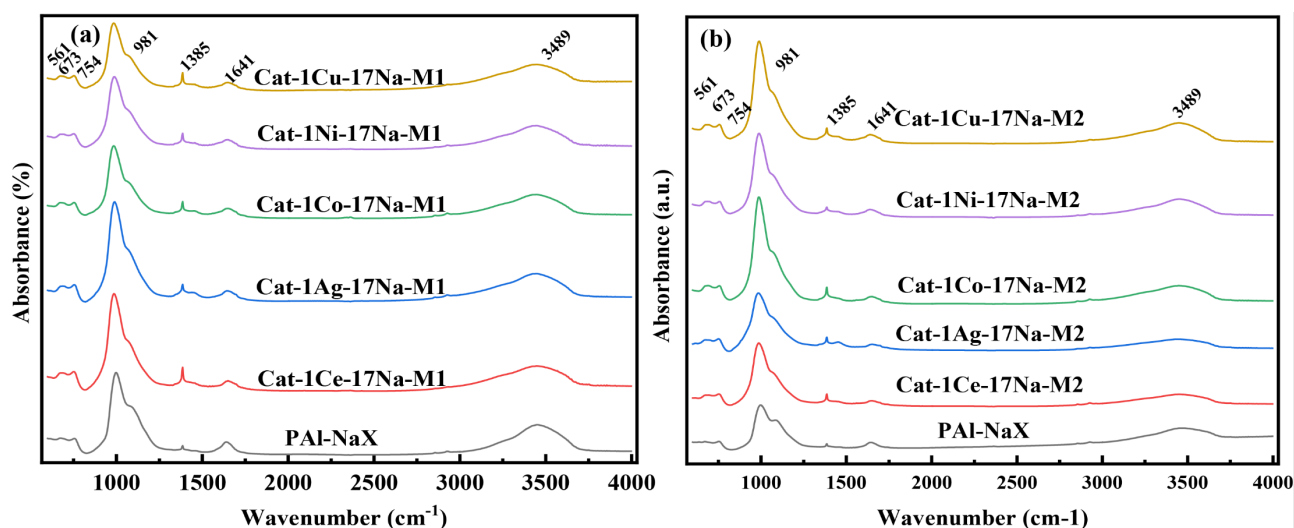


Figure 5. (a) FT-IR spectra of Cat-1Me-17Na-M1 series catalysts, (b) FT-IR spectra of Cat-1Me-17Na-M2 series catalysts.

treatment. The absorption bands at 3489 cm^{-1} and 1641 cm^{-1} are attributed to the O-H bending vibration of adsorbed water [21]. The band at 1385 cm^{-1} corresponds to the stretching vibration of $\text{P}=\text{O}$ groups, indicating the successful introduction and stabilization of phosphorus-containing species within the zeolite structure during hydrothermal treatment [22] [23]. In addition, the absorption bands located at 561 cm^{-1} are assigned to the vibrations of Si-O-Si and Si-O-Al bonds [24] [25], while the peaks at 673 cm^{-1} and 754 cm^{-1} are associated with tetrahedral symmetric stretching vibrations. The strong absorption band at 981 cm^{-1} is attributed to the asymmetric stretching vibration of aluminosilicate tetrahedral units and is commonly considered an important indicator for evaluating the structural integrity of the zeolite framework [26]. Compared with the parent PAI-NaX catalyst, both the M1 and M2 catalyst series exhibit variations in band intensity and thickness, indicating that metal incorporation and alkaline treatment induce local structural modifications within the zeolite framework. In particular, the absorption band at 981 cm^{-1} becomes more pronounced after modification, especially in the M2 series, suggesting enhanced exposure or rearrangement of framework tetrahedral units. These changes imply that the preparation sequence affects the local framework environment and metal-framework interactions without causing complete structural collapse. The preservation of the characteristic NaX absorption bands in both catalyst series is consistent with the XRD results, confirming that the overall FAU-type zeolite structure remains stable after catalyst modification.

Figure 6 presents the N_2 adsorption-desorption isotherms and pore size distributions of the Cat-1Me-17Na catalysts prepared by the M1 and M2 methods. All catalysts exhibit typical type I adsorption isotherms with a sharp adsorption increase at low relative pressure ($P/P_0 < 0.1$), confirming the preservation of the microporous NaX zeolite framework after metal incorporation and alkaline treatment. A slight adsorption increase at high relative pressure further indicates the

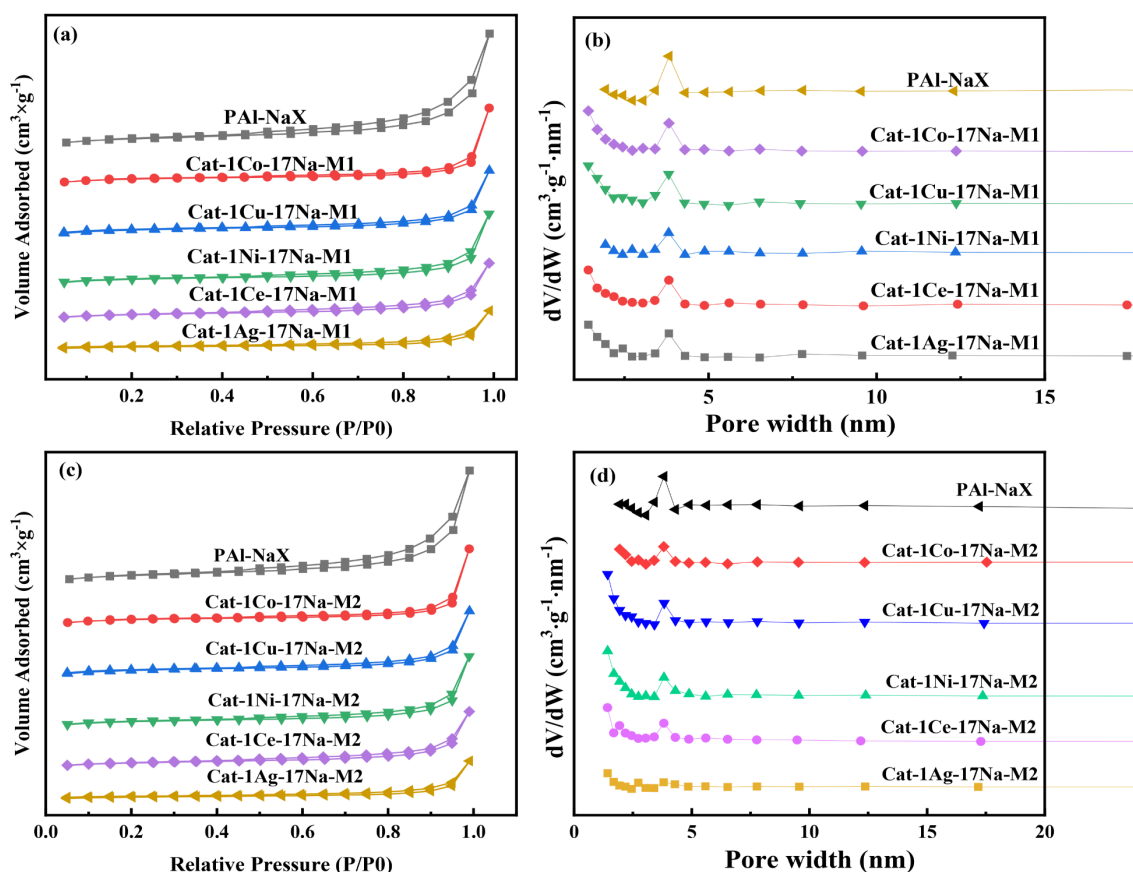


Figure 6. (a) N₂ adsorption-desorption isotherms, pore size distribution (b), of Cat-1Me-17Na-M1 series, (c) N₂ adsorption-desorption isotherms, pore size distribution (d), of Cat-1Me-17Na-M2 series.

presence of a small amount of mesoporosity. Compared with the parent PAL-NaX support, all modified catalysts show reduced adsorption capacity and surface area, suggesting partial pore occupation or blockage caused by the introduced metal species.

The preparation method significantly influences the textural properties and catalytic behavior of the catalysts. In the M1 series, metal incorporation leads to a pronounced decrease in BET surface area, particularly for the Cu- and Ni-modified catalysts, indicating stronger metal-support interactions and partial blockage of micropore entrances. Despite the reduced surface area, Cat-1Cu-17Na-M1 and Cat-1Ni-17Na-M1 exhibit excellent catalytic performance, suggesting that the nature of the active metal species plays a more important role than the total surface area in determining SATM activity. In contrast, the M2 catalysts retain relatively higher surface area and pore accessibility after modification. In particular, Cat-1Ni-17Na-M2 exhibits a comparatively high surface area and moderate pore volume, which favor the dispersion of active species and reactant diffusion within the porous structure, resulting in the highest catalytic yield among the M2 catalysts. Overall, both preparation methods preserve the microporous structure of the NaX framework, while the M2 method appears more favorable for maintaining textural properties and pore accessibility after metal incorporation. (See [Table 3](#) & [Table 4](#))

Table 3. Texture parameters of Cat-1Me-17Na-M1 series catalysts.

Catalyst	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{BJH} ($\text{cm}^3\cdot\text{g}^{-1}$)	D_{BJH} ($\text{cm}^3\cdot\text{g}^{-1}$)
PAI-NaX	230.6	0.070	3.82
Cat-1Co-17Na-M1	129.0	0.021	1.42
Cat-1Cu-17Na-M1	123.6	0.020	1.42
Cat-1Ni-17Na-M1	105.8	0.017	3.81
Cat-1Ce-17Na-M1	114.8	0.020	1.42
Cat-1Ag-17Na-M1	112.4	0.016	1.42

Table 4. Texture parameters of Cat-1Me-17Na-M2 series catalysts.

Catalyst	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{BJH} ($\text{cm}^3\cdot\text{g}^{-1}$)	D_{BJH} ($\text{cm}^3\cdot\text{g}^{-1}$)
PAI-NaX	230.6	0.070	3.82
Cat-1Co-17Na-M2	161.0	0.020	3.81
Cat-1Cu-17Na-M2	151.9	0.026	1.42
Cat-1Ni-17Na-M2	152.3	0.029	1.42
Cat-1Ce-17Na-M2	113.2	0.025	1.42
Cat-1Ag-17Na-M2	44.2	0.014	1.42

3.3. The Synergetic Effect of Metal and NaOH on Acidity and Alkalinity

The conjunct effect of acidic and strong basic sites has been widely accepted to determine the SATM [6] [27]. The acidity properties of the metal-modified NaX catalysts prepared by the M1 and M2 methods were analyzed by NH_3 -TPD. The NH_3 desorption profiles were divided into three regions corresponding to weak (50°C - 200°C), medium (200°C - 400°C), and strong (400°C - 700°C) acid sites. As shown in **Figure 7(a)**, **Figure 7(b)** all catalysts exhibit NH_3 desorption peaks mainly in the 100°C - 300°C region, indicating that weak and medium acid sites dominate the surface acidity after modification. Compared with the M1 catalysts, the M2-prepared catalysts exhibit a more pronounced increase in weak acid sites and a further reduction in medium and strong acid sites, indicating that the M2 preparation strategy is more effective in improving weak acidity and regulating the acid strength distribution (See **Table 5**). This result suggests that the modified preparation sequence promotes a more uniform interaction between metal species and the zeolite framework, leading to more efficient neutralization of strong Brønsted acid sites. In addition, the total NH_3 desorption amount decreases significantly after metal loading compared with the parent PAI-NaX catalyst, confirming the suppression of excessive strong acidity after catalyst modification.

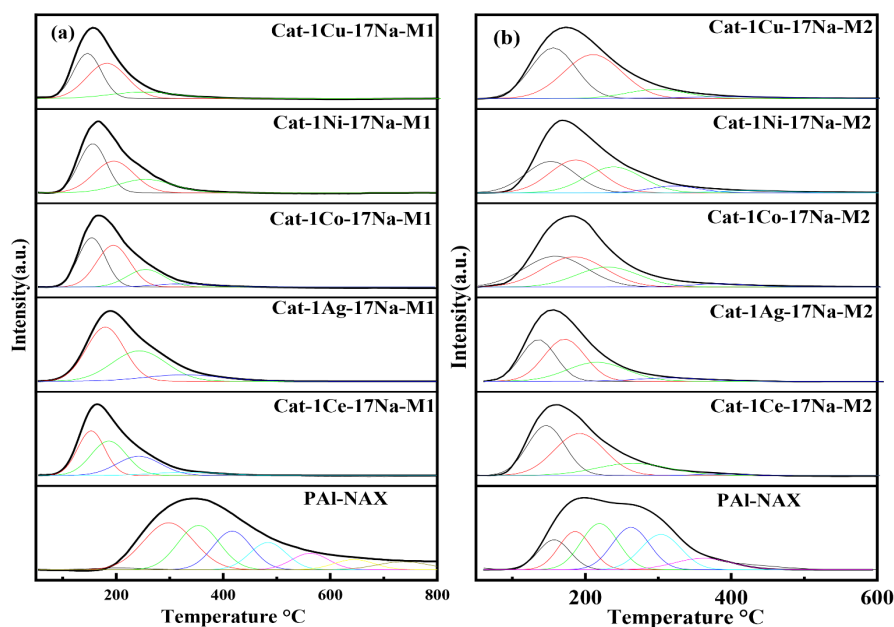


Figure 7. NH_3 -TPD (a) of Cat-1Me-17Na-M1 and (b) Cat-1Me-17Na-M2 catalyst.

Table 5. Acid sites distributions of Cat-1Me-17Na-M1 catalysts.

Catalysts	Distribution of acid sites ^a		
	Weak	Middle	Strong
Cat-1Ce-17Na-M1	68.8	30.2	0.0
Cat-1Ce-17Na-M2	80.8	19.0	0.2
Cat-1Ag-17Na-M1	49.1	50.05	0.0
Cat-1Ag-17Na-M2	70.1	29.8	0.1
Cat-1Co-17Na-M1	76.3	23.2	0.0
Cat-1Co-17Na-M2	77.5	22.3	0.2
Cat-1Ni-17Na-M1	78.1	21.7	0.0
Cat-1Ni-17Na-M2	78.5	21.3	0.0
Cat-1Cu-17Na-M1	85.7	14.2	0.0
Cat-1Cu-17Na-M2	89.8	10.1	0.1

4. Conclusion

By introducing different transition metal components, the SATM was effectively promoted over modified NaX-based catalysts, demonstrating that catalytic activity and product distribution can be regulated through the synergistic interaction between metal species and acid-base properties. Compared with the parent PAI-NaX catalyst, all metal-modified catalysts showed significantly enhanced production of ethylbenzene (EB) and styrene (ST), confirming the important role of transition metals in improving SATM performance. Among the investigated catalysts, Cu- and Ni-modified catalysts exhibited the best catalytic activities. In the M1

catalyst series, Cat-1Cu-17Na-M1 achieved the highest combined yield of EB and ST (71.9%) with a methanol conversion of 99.7%, while Cat-1Ni-17Na-M1 reached a combined yield of 66.4%. In the M2 series, catalytic performance was further improved, with Cat-1Ni-17Na-M2 exhibiting the highest combined EB and ST yield of 74.2%, followed by Cat-1Cu-17Na-M2 with 73.6%. The superior performance of the M2 catalysts is attributed to the preparation strategy, where NaX was introduced prior to metal incorporation, leading to the formation of a greater amount of weak acidic sites and a more favorable acid-base balance. This optimized surface environment effectively promoted methanol activation and enhanced selectivity toward the desired products while suppressing side reactions. Overall, this study demonstrates that rational modulation of transition metals and acid-base properties is an effective strategy for designing highly efficient NaX-based catalysts for SATM reactions.

Ethics and Consent to Participate

This study did not involve human participants or animals.

Consent for Publication

All authors have reviewed and approved the final version of the manuscript and consent to its publication.

Conflicts of Interest

The authors declare no conflicts of interest.

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