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Supplementary Information

Rational design and fabrication of novel acid-resistant UZM-5 zeolite membrane for pervaporation dehydration processes

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Experimental details

1. Materials

All the chemicals and solvents were purchased from commercial suppliers and used as received. Aluminum sec-butoxide ($Al[O(s\text{-}Bu)]_3$, ≥95%), colloidal silica (Ludox AS-40, 40% SiO_2 in water), tetraethyl orthosilicate (TEOS, 98%), tetraethylammonium hydroxide (TEAOH, 35%), and tetramethylammonium chloride (TMACl, 97%) were purchased from Sigma-Aldrich. Sodium chloride (NaCl, AR), ethanol (EtOH, AR) was purchased from China national medicines Co. It is noteworthy that purified water (H_2O, Wahaha Co.) was used as solvent in this work. Asymmetric α-Al_2O_3 disc (Inocermic GmbH, Germany) with a diameter of 18 mm and a thickness of 1 mm was utilized as the substrate of UZM-5 zeolite membrane. The average pore size of the top layer of α-Al_2O_3 disc was 70 nm.

2. Synthesis and Characterizations

2.1 Synthesis of crystalline UZM-5 nanosheets

The uniform and discrete UZM-5 nanosheets were synthesized according to a modified protocol.[1] TEOS was used as silicon source for the seed preparation. Typically, $Al[O(s\text{-}Bu)]_3$ was first mixed with an aqueous solution of TEAOH and stirred at room temperature for 2 h. TEOS was then added into the solution and stirred for another 2 h to enable a thorough hydrolysis. The obtained aluminosilicate solution was kept at 353 K for 3 h to remove ethanol molecules generated from TEOS hydrolysis. After that, TMACl solution with NaCl was slowly added to the CDM aluminosilicate solution under vigorous stirring. The molar composition of the obtained solution was 8.0 SiO_2 : 0.5 Al_2O_3 : 8.0 TEAOH : 1.0 TMACl : 0.02 NaCl : 240 H_2O. This solution was stirred at room temperature for 1 day, and subsequently transferred into Teflon-lined stainless steel autoclaves, followed by crystallization at 423 K under rotation (30 rpm) for a total period of 5 days. The resultant white crystalline powder was recovered by centrifugation and washed with EtOH and H_2O thoroughly. Ultimately, the precipitate was re-dispersed in water using ultrasonic treatment, achieving a nanosheet suspension with a concentration of cal. 0.007 wt%. These UZM-5 nanosheets was used as seeds to fabricate subsequent membranes.

2.2 Fabrication of UZM-5 membranes

Following the protocol developed by our group previously,[2] typically, 15 mL of the UZM-5 nanosheet suspension was hot-drop coated on the surface of α-Al_2O_3 substrate at 423 K. The seed-coated substrate was de-templated in air at 723 K (heating at a rate of 0.5 K/min) for 5 h. For membrane growth, the reactant gel was prepared with SiO_2 served as silicon source rather than TEOS. In a typical process, $Al[O(s\text{-}Bu)]_3$ was added to the TEAOH (CDM SDA) under vigorous stirring to get a clear solution. SiO_2 and purified water were then added into this solution in succession. After stirring for 3 h, the obtained mixture was aged in an air-dry oven at 368 K for 18 h. And an aqueous solution containing the crystallization SDA, TMACl, was added into the mixture followed by vigorous stirring for 30 min, resulting in an obtained synthesis gel with a molar ratio of 8.3 SiO_2 : 0.5 Al_2O_3 : 8.3 TEAOH : 1.78 TMACl : 573 H_2O. Then, the resulting gel was transferred to a Teflon-lined stainless steel autoclave, which the seed-coated substrate was carefully immersed in. The autoclave was sealed and kept at 423 K for 5 days. Subsequently, the as-synthesized

membrane underwent a tertiary growth in order to obtain a dense UZM-5 zeolite membrane. The growth conditions were almost the same with those of the secondary growth. Noting that the alumina disc was placed vertically on a Teflon holder during the secondary growth while horizontally placed in the autoclave during the tertiary growth. And 8 μL EtOH added in the reactant solution was necessary for the tertiary growth, in order to ensure the reproducibility of UZM-5 membranes. Consequently, the obtained membrane was washed with deionized water and dried at 353 K overnight.

2.3 Characterizations

Powder X-ray diffraction (XRD, Rigaku D/Max-2500, Cu Kα radiation, λ=0.154 nm at 40 kV and 200 mA) and grazing-incidence diffraction (SmartLab, Cu Kα radiation, λ=0.154 nm at 40 kV and 40 mA, angle of incidence α=1°) was used to determine the crystalline structures of the as-synthesized products in a 2θ range of 2-40° with a scan step width of 0.02°. The morphologies of the UZM-5 nanosheets and membranes were recorded on a scanning electron microscopy (SEM, Quanta 200 FEG, FEI Co.) operated at 20 kV and a field emission scanning electron microscopy (JSM-7900F) operated at 2-5 kV.

2.4 PV dehydration tests

The as-synthesized UZM-5 membranes were evaluated for EtOH (90 wt% EtOH/water) dehydration via a PV technique at different feed temperatures and concentrations, and underwent AcOH (90 wt% AcOH/water) dehydration capability evaluation at 338 K. Notably, the vapor penetrating through the UZM-5 membranes was collected after condensation by liquid nitrogen. The real-time component concentrations of the feed solution and the condensed permeate solution were investigated using a gas chromatograph (Agilent 7890A equipped with a thermal conductive detector and an Agilent 6Ft 1/8 2mm Porapak Q 80/100 SS stainless steel column). The PV performances of the UZM-5 membranes were determined by two factors, *i.e.* the total flux permeating to the downstream of the membrane and the separation factor of water against organics. The total flux (J) and separation factor ($\alpha_{w/o}$) of the membranes were calculated by equations listed as follows.

$$J = \frac{w}{A \times t} \tag{1}$$

$$\alpha_{W/O} = \frac{y_{w,F}x_{o,F}}{x_{w,F}y_{o,F}} \cdot \frac{y_{w,p}y_{o,F}}{y_{w,F}y_{o,p}} = \frac{x_{o,F}y_{w,p}}{x_{w,F}y_{o,p}} \tag{2}$$

Where w, A, and t denote the permeate mass (kg) penetrated through an effective membrane area (m^2), and condensed in the cooled trap over a period of testing time (h). $x_{w,F}$, $x_{o,F}$, $y_{w,F}$, $y_{o,F}$, $x_{w,P}$, $x_{o,P}$, $y_{w,P}$, and $y_{o,P}$ denote the mass fractions of the water and organics at the feed and permeate sides, respectively. The weight of permeate was calculated by measuring the mass increase of cold trap after collection.

3. Results and Discussions

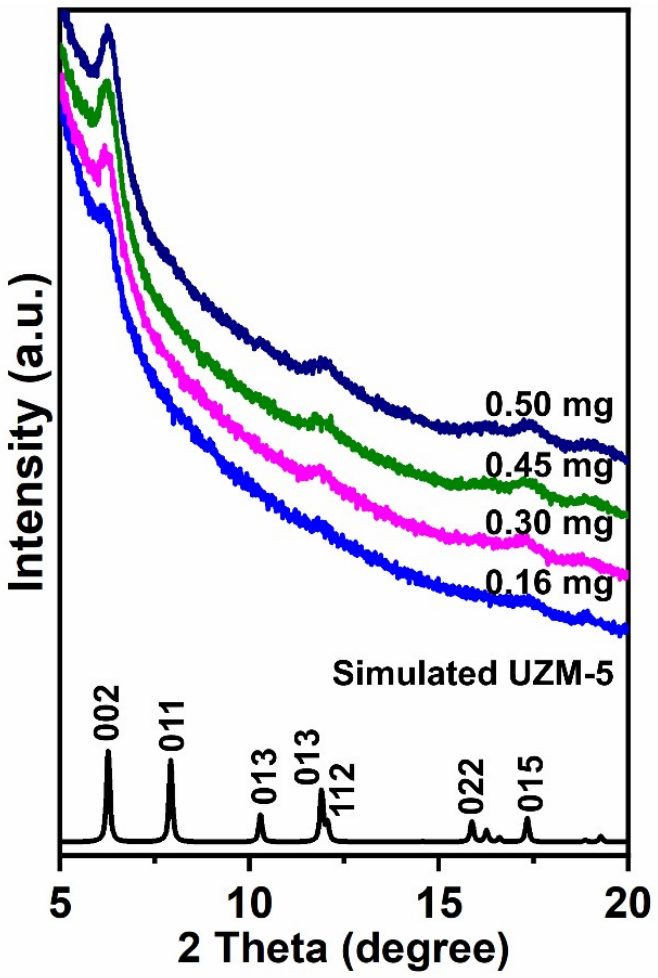

Fig. S1. XRD patterns of the UZM-5 seed layers coated on α-Al_2O_3 substrates at different loading weights.

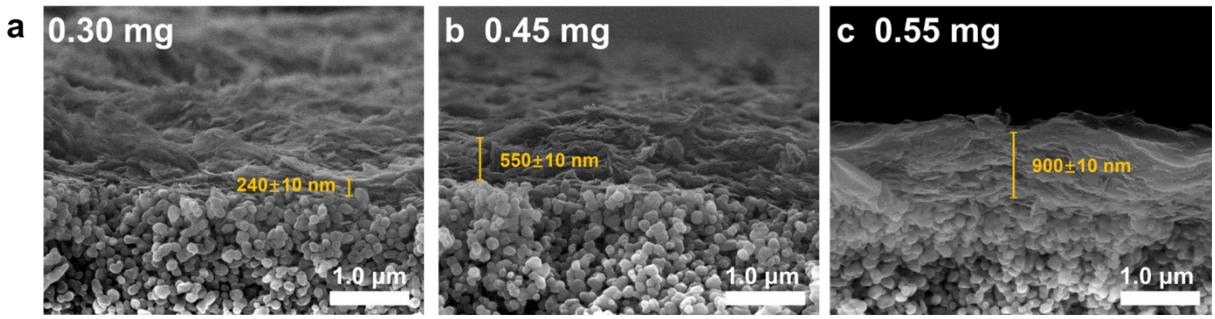

Fig. S2. SEM images of the cross-section view of UZM-5 seed layers at different loading weights.

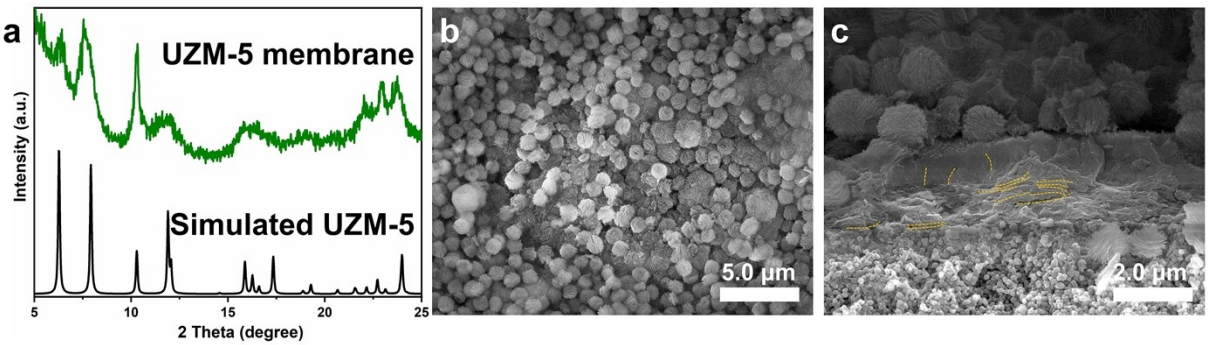

Fig. S3. (a) XRD patterns and SEM images of (b) the top view and (c) the cross-section view of the obtained UZM-5 membranes fabricated using 0.26 mg seeds. The yellow dashed lines depict intercrystalline defects and cracks within the membrane.

Notes: The obtained hydrophilic UZM-5 zeolite membrane fabricated using a seed layer of ~0.30 mg exhibited a quite large flux of 29.4 kg m^{-2} h^{-1} and a water/ethanol separation factor of only 1.2, during the PV dehydration test of a 90 wt% ethanol/water solution.

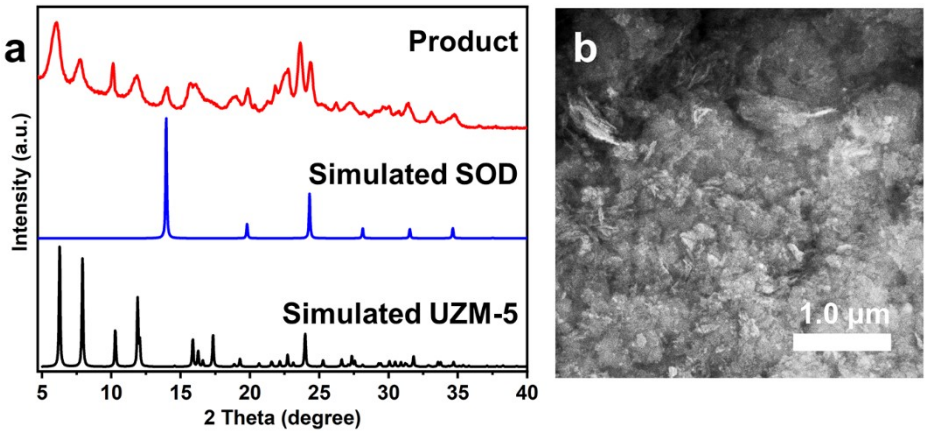

Fig. S4. (a) XRD pattern and (b) SEM image of the corresponding solid products synthesized using SiO_2 as silicon source.

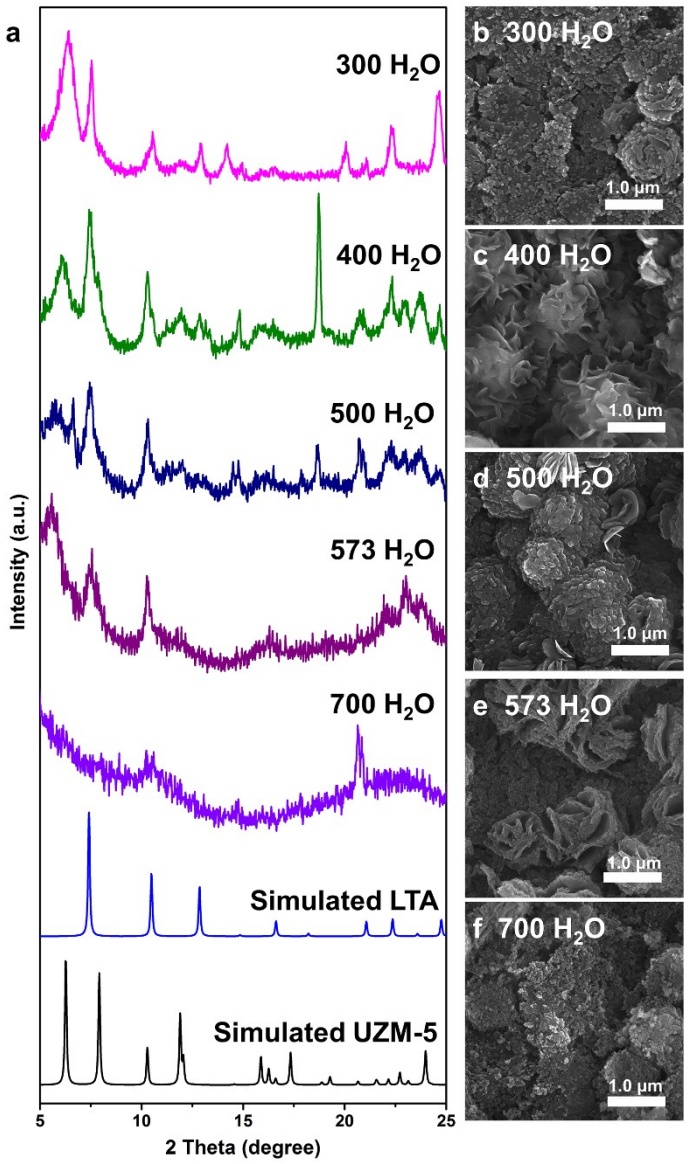

Fig. S5. (a) XRD patterns and (b-f) SEM images of the UZM-5 membranes prepared at different H_2O contents.

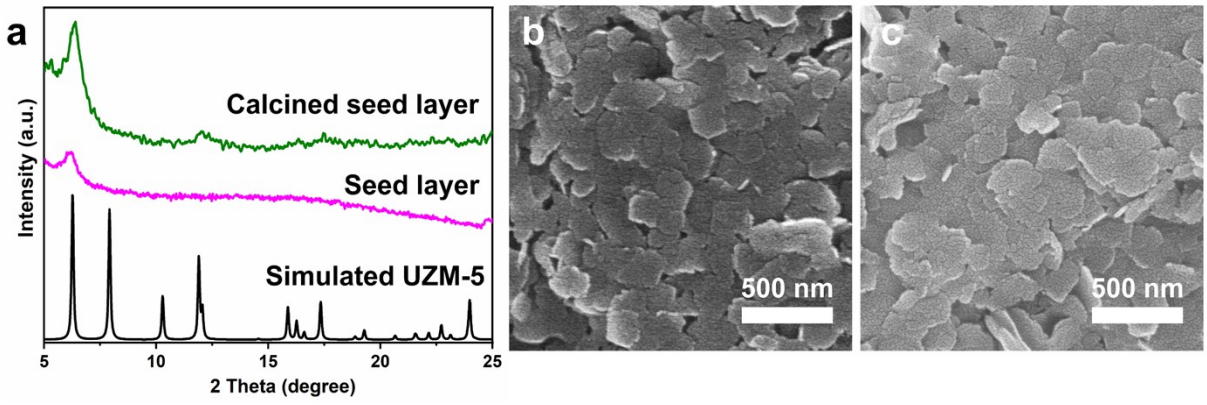

Fig. S6. (a) XRD patterns and (b-c) SEM images of the supported UZM-5 seed layer before and after calcination.

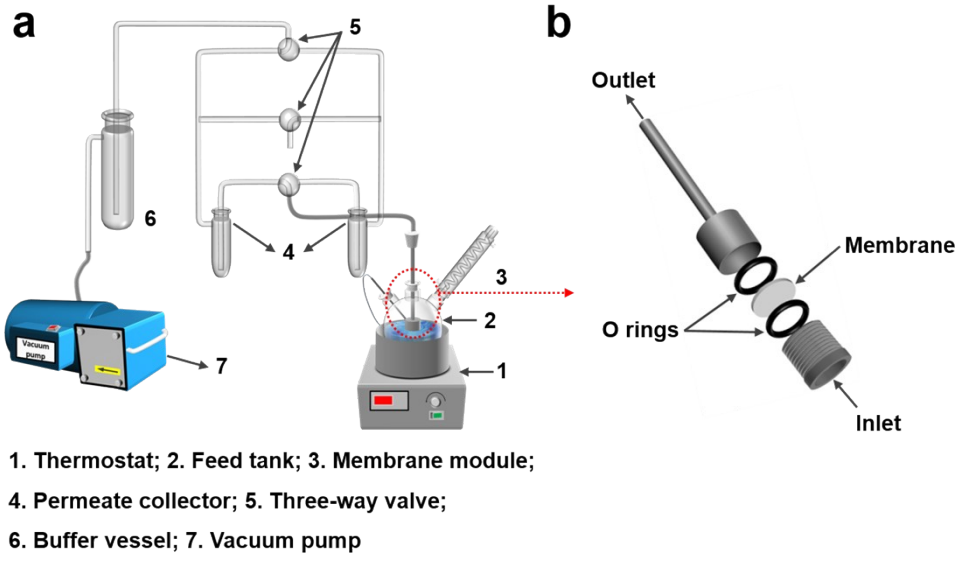

Fig. S7. Schematic diagrams of (a) the home-made pervaporation apparatus and (b) the membrane module.

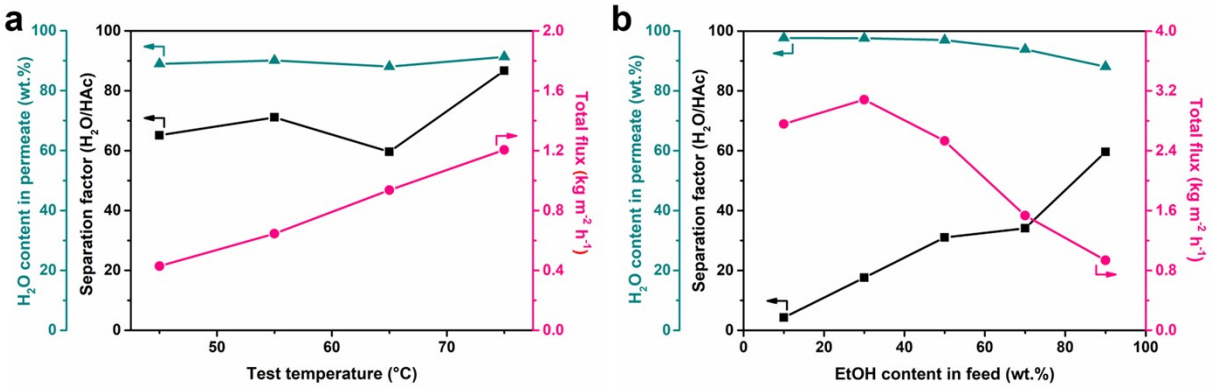

Fig. S8. Effects of (a) operating temperature and (b) feed concentration on the PV dehydration performance of UZM-5 membrane. Feed concentration in (a): 10/90 (w/w) H_2O/EtOH mixture. PV temperature in (b): 338 K.

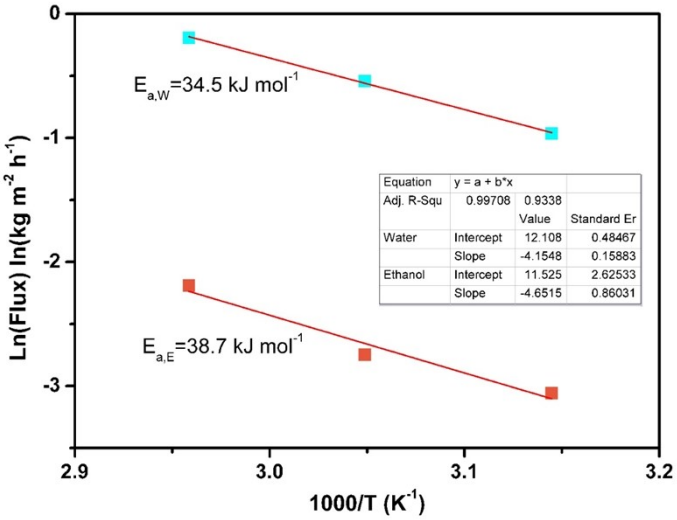

Fig. S9. Arrhenius temperature dependence of water and ethanol fluxes for a UZM-5 membrane.

Table S1. PV performances of the UZM-5 membranes. Feed: 90 wt% EtOH/water mixture; Temperature: 338 K.

Membrane	Total flux (kg/m^{-2} h^{-1})	$\alpha_{(w/Et)}$
M1	2.2	98
M2	1.5	58
M3	0.3	74
M4	3.3	41
M5	0.6	171
M6	2.5	4423.24*

* The feed solution used for PV test of M6 was 90 wt% isobutanol/water; Testing temperature was 338 K.

Table S2. PV performances of the UZM-5 membranes and typical acid-resistant zeolite membranes in AcOH dehydration process.

Membrane	Feed composition (wt% AcOH)	Temperature (K)	Total flux (kg/m^{-2} h^{-1})	$\alpha_{(w/Ac)}$	Ref.
PVA (Malic acid)	90	313	0.29	670	4
PVA (Sodium alginate)	90	306	0.05	22	5
PVA (SPEK-C)	90	323	0.49	59	6
PVA (Tartaric acid)	90	333	0.10	708	7
PVA (AN)	90	303	0.09	15	8
SPEK-C (STA/PVA)	90	323	0.59	91	9
NaAlg-6 (NH_2-MIL125(Ti))	90	303	0.20	328	10
NaAlg (Al rich zeolite)	90	303	0.05	612	11
NaAlg (4A zeolite)	90	303	0.19	991	12
Composite (GO/Psf)	90	303	0.29	131	13
HCl-BTESE	90	353	2.07	780	14

NP-h-WO_3	90	353	0.03	43	15
MOR	90	348	0.44	2300	16
MOR	90	348	0. 56	3010	17
MOR	90	348	0.87	>11400	18
MOR	90	353	0.44	627	19
MOR	90	348	0.97	1200	20
MOR	90	353	<0.05	50	21
MFI	90	348	0.25	165	22
MFI	50	343	0.78	381	23
DD3R	90	348	0.23	1700	24
M1	90	338	0.80	989	
M2	90	338	1.60	89	
M3	90	338	1.30	93	This
M5	90	338	0.20	90	work
M6	90	338	0.28	591	
M7	90	338	0.40	169814	

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