Electronic Supplementary Material (ESI) for RSC Advances.

Photocatalysis Direct Amination of Benzene and ammonia over Ti-V-MCM-41

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Table S1. The raw materials and proportion of catalyst preparation

Catalyst sample	nSi:nTi	CTAB (g)	$VOSO_4$ (g)	TEOS (mL)	TBOT (mL)
MCM-41	∞	1.35	0	14.5	0
V-MCM-41	∞	1.35	0.422	14.5	0
Ti- MCM-41(60)	60	1.35	0	14.5	0.37
Ti-V-MCM-41(80)	80	1.35	0.422	14.5	0.28
Ti-V-MCM-41(60)	60	1.35	0.422	14.5	0.37
Ti-V-MCM-41(40)	40	1.35	0.422	14.5	0.55
Ti-V-MCM-41(20)	20	1.35	0.422	14.5	1.11

During the synthesis of Ti-V-MCM-41 catalyst, the pH of the mixed gel solution after the introduction of silicon source, titanium source and vanadium source has a certain influence on the activity of the catalyst. Five groups of parallel experiments were designed to investigate the effect of pH of mixed solution on catalyst activity. As shown in Figure S1, the yield and selectivity reach maximum at pH =10.0. Under this condition, the yield and selectivity are 6.11% and 90.7% respectively. However, when the pH of the solution was further increased, the catalytic activity started to decrease.

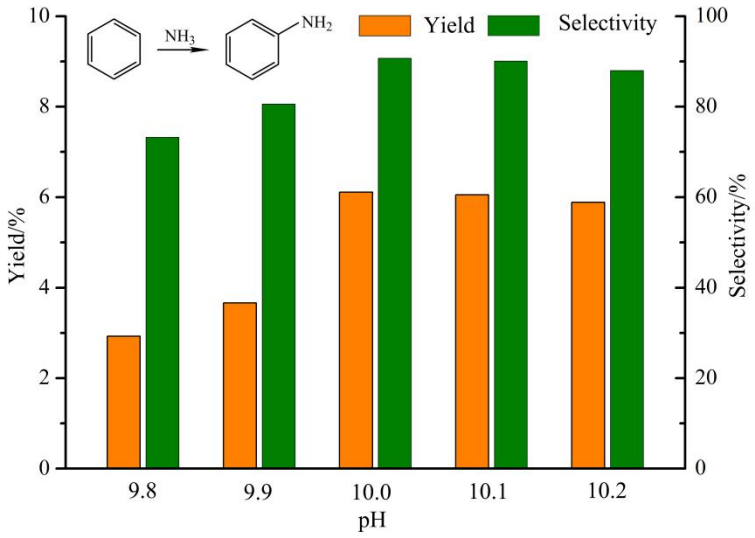

Figure S1. Yield and selectivity of aniline over Ti-V-MCM-41 catalysts

Furthermore, the operating temperature of the solution in the reactor during crystallization has a significant effect on the catalyst activity. Five groups of parallel experiments were designed to investigate the effect of crystallization temperature of mixed solution on catalyst activity. According to the experiment results, the best crystallization temperature is 110℃, as shown in Figure S2, and the yield and selectivity are 6.11% and 90.7% respectively.

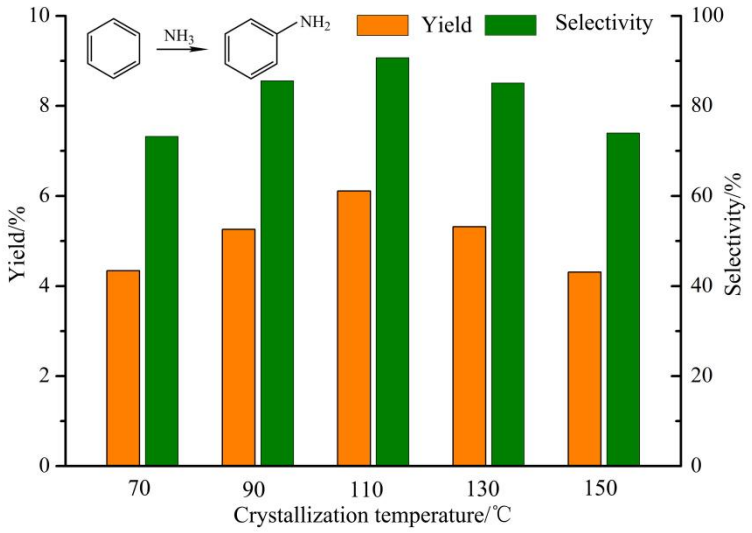

Figure S2. Yield and selectivity of aniline over Ti-V-MCM-41 catalysts prepared at different crystallization temperature.

In order to investigate the effect of crystallization time on catalyst synthesis, five groups of parallel experiments were designed with different crystallization times ranging from 12 h to 36 h, and the results are shown in Figure S3. Before 24 h, the activity of the catalyst increased with time, and remained almost unchanged after 24 h. Therefore, we believe that the optimal crystallization time is 24 h. The maximum values of yield and selectivity were 6.11% and 90.7%, respectively.

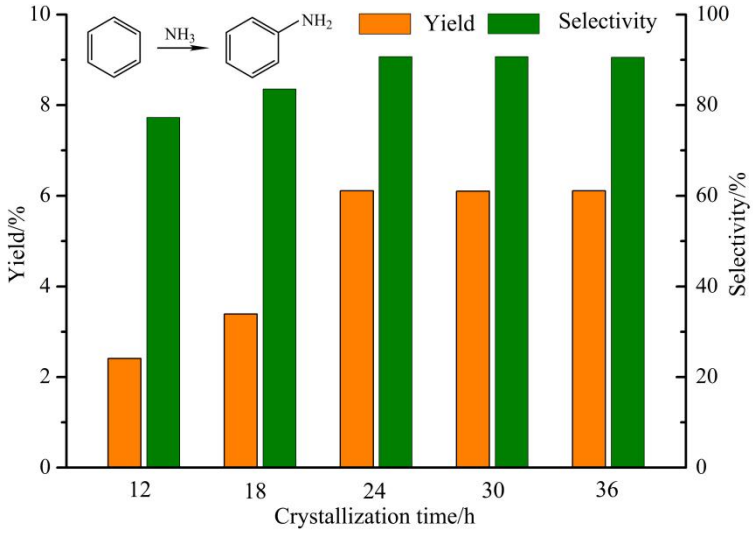

Figure S3. Yield and selectivity of aniline over Ti-V-MCM-41 catalysts prepared at different crystallization time.

Before finally obtaining the Ti-V-MCM-41 molecular sieve catalyst, the sample needs to be calcined. Likewise, different calcination temperatures will lead to different catalytic activities. The calcination temperature experiment results are shown in Figure S4, and when the temperature is 550℃, the molecular sieve exhibit the best yield and selectivity (6.11% and 90.7%, respectively).

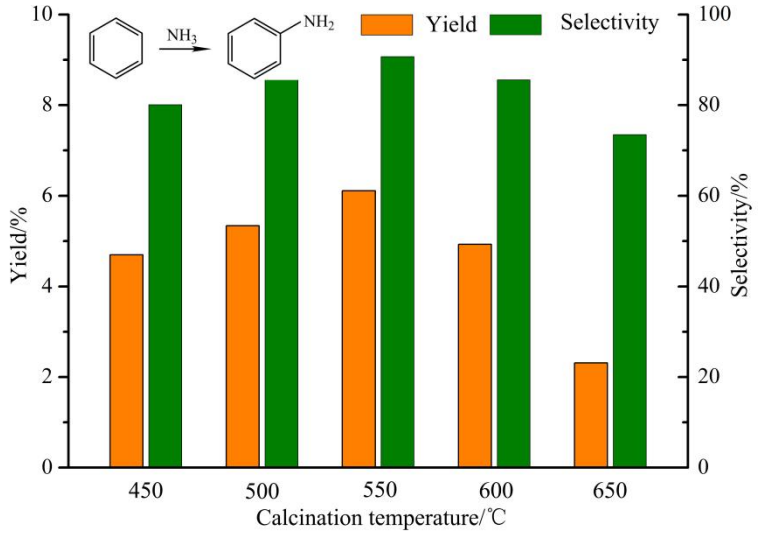

Figure S4. Yield and selectivity of aniline over Ti-V-MCM-41 catalysts prepared at different calcination temperature.

Five parallel experiments were designed to determine the catalyst best calcination time, and the results are given in Figure S5. It can be seen from the figure, the best calcination time is 6 h, the yield and selectivity are 6.11% and 90.7%, respectively.

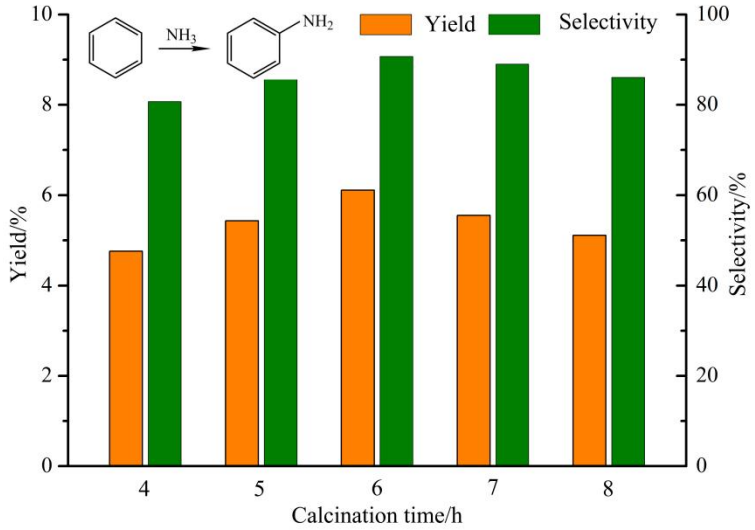

Figure S5. Yield and selectivity of aniline over Ti-V-MCM-41 catalysts prepared at different calcination time.

As shown in Figure S6, the N_2 adsorption-desorption isotherm of Ti-V-MCM-41 belonged to the IV isotherm according to IUPAC, which indicates preliminarily that the material is a mesoporous material with cylindrical canals[1,2]. It could be seen from Figure S6 that the adsorption capacity increases slowly in the lower pressure section. At this time, N_2 molecules are adsorbed on the inner surface of the mesoporous monolayer or multilayer. MCM-41 has a sudden increase in the adsorption capacity around P/P_0 = 0.5~0.8, while after the loaded of vanadium and titanium, the pressure of the sudden increase in the adsorption capacity increases to P/P_0 = 0.8~1.0. This phenomenon was caused by vanadium and titanium load, which led to the original pore structure of the molecular sieve was changed, the pore volume and specific surface area were both reduced.

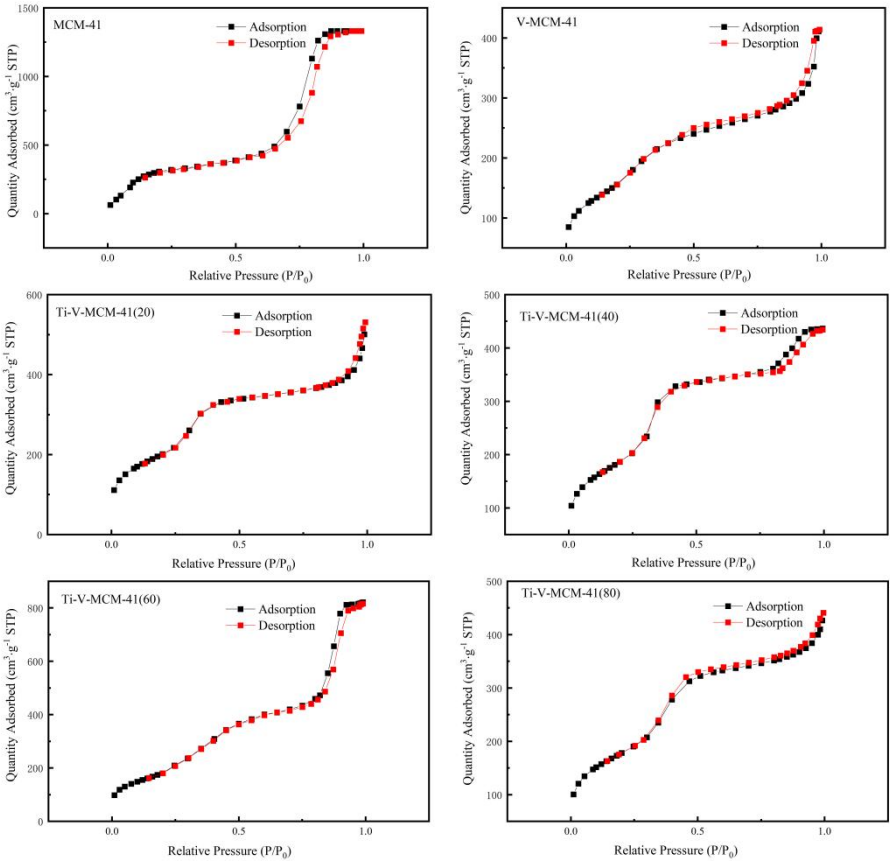

Figure S6. The N_2 adsorption-desorption isotherms of different catalysts

Figure S7 showed the pore size distribution curves of different catalysts. It could be seen from the figures that the pore size distribution of the molecular sieve was narrow, the most pore sizes are in the 2~5 nm range. It shows that the pore size is relatively uniform and belongs to the mesoporous molecular sieve material. On the one hand, the structure has a sufficiently large specific surface area, which can provide more active sites. On the other hand, the size of the reactant benzene and the product aniline are both less than 1 nm and can diffuse freely in the pores. This can improve the effective collision probability between the reactant and the active site of the catalyst, which is beneficial to improve the yield of aniline.

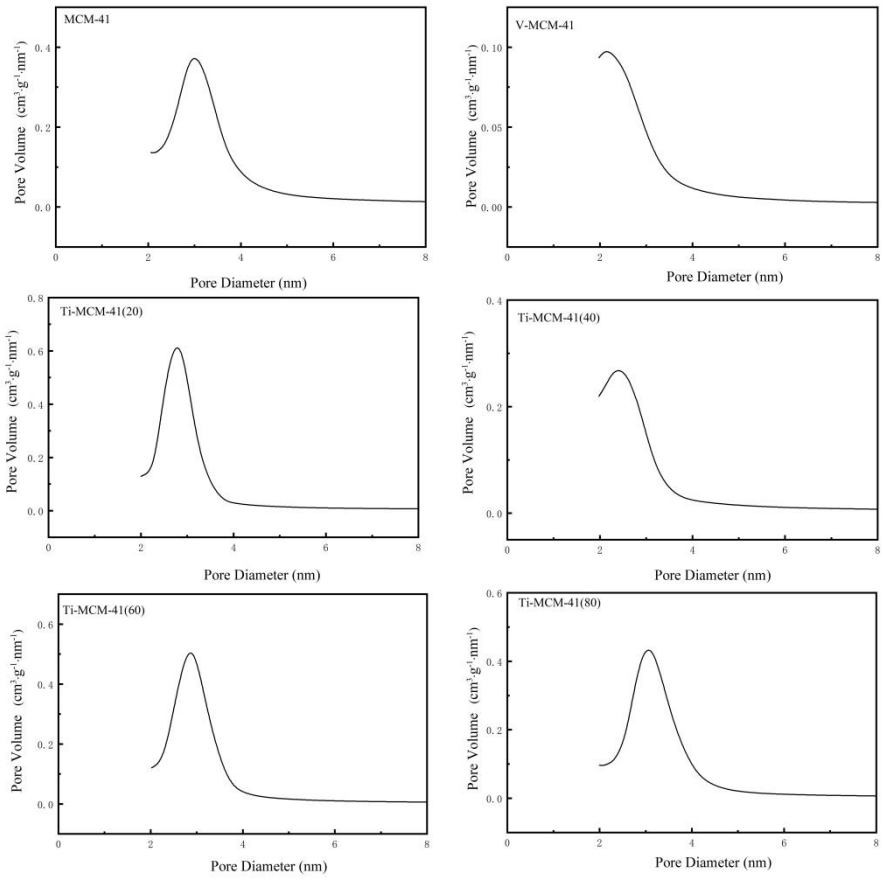

Figure S7. The pore size distribution curves of different catalysts

Specific surface area, average pore diameter, and average pore volume were measured by the BET method, and the data were listed in Table S2. The specific surface area of MCM-41 was 973 m^2g^{-1}. The average pore volume and average pore diameter decreased with the increase of titanium loading. When the nSi/nTi=20, the specific surface area was 442 m^2g^{-1}. The above analysis showed that titanium and vanadium occupied the pore space in the catalyst materials, which led to the reduction of pore specific surface area, average pore diameter, and average pore volume. The theoretical diameter of aniline is 0.57 nm, so the catalyst had a better catalytic effect when the average pore diameter was larger than 0.57 nm.

Table S2. The BET specific surface area, average pore diameter, and average pore volume of different catalysts

Catalyst sample	S_{BET}/m^2g^{-1}	D_p/nm	V_p/cm^3g^{-1}
MCM-41	973	6.12	0.86
V-MCM-41	871	5.61	0.77
Ti-V-MCM-41(80)	805	5.06	0.71
Ti-V-MCM-41(60)	755	4.76	0.69
Ti-V-MCM-41(40)	681	4.32	0.62
Ti-V-MCM-41(20)	442	3.93	0.37

According to the SEM images of each molecular sieve material (as shown in Figure S8), there were long and thin channels in MCM-41. However, the MCM-41 loaded with vanadium and titanium showed spherical or hexagonal shape, and the channel became shorter. The reason for this phenomenon was that vanadium and titanium replaced the silicon in the MCM-41 skeleton, which led to the transformation of original skeleton structure. And it led to the transformation of morphology, shortened the pore channel.

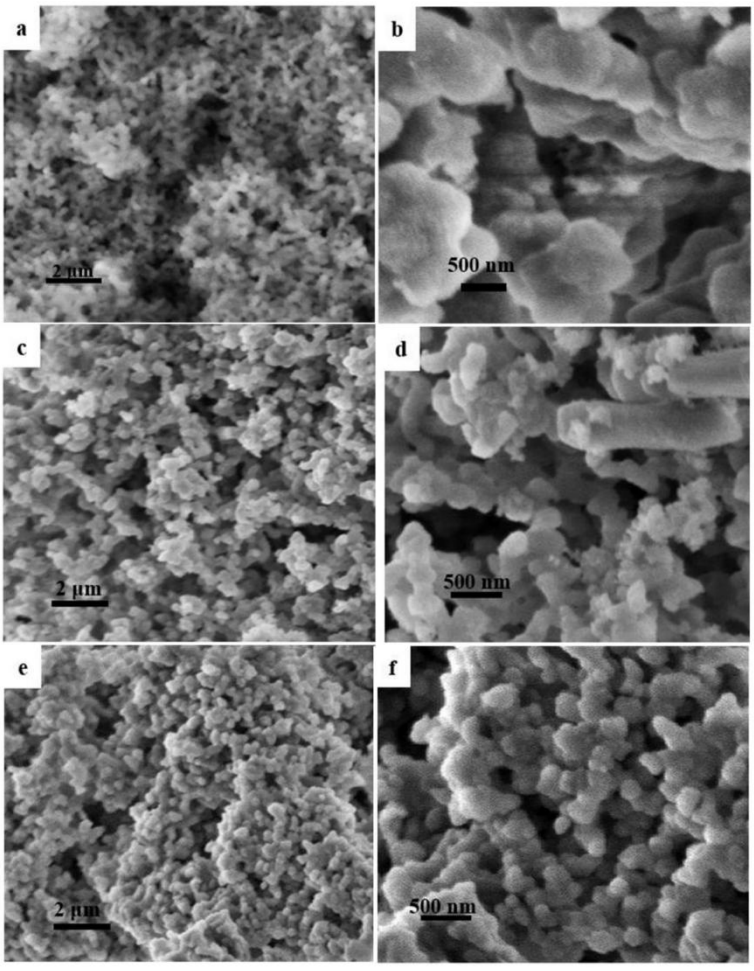

Figure S8. The SEM images of different catalysts. a, b: MCM-41; c, d: V-MCM-41; e, f: Ti-V-MCM-41(60)

Recyclability, reuse and stability are key parameters for evaluating catalysts. As shown in Figure S9, catalyst repeatability experiments were performed under optimal reaction conditions using Ti-V-MCM-41(60) catalyst. After the catalyst was used for 2 hours in each cycle, the catalyst is filtered, washed and dried. The recovered catalyst is used for the next reaction cycle. After five catalytic cycles, the yield and selectivity decreased from 6.11% to 5.05% and 90.7% to 86.5%, respectively. The recycling test indicated that Ti-V-MCM-41(60) had the good stability in direct amination reaction.

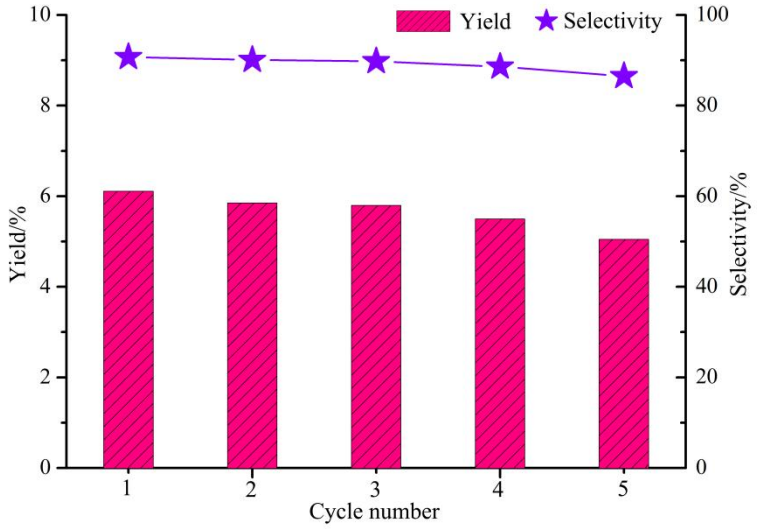

Figure S9. Ti-V-MCM-41(60) catalyst stability testing under optimal reaction conditions.

References

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2 Y. Tian and J. Z. Wu, AIChE J, 2018, **64**, 286-293.